Materials Issues for VCSEL Operation and Reliability

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Abstract

Significant advancements have been made in the characterization and understanding of the behavior of III-V semiconductor materials employed in Vertical Cavity Surface Emitting Laser (VCSEL) diodes. For the first time a technique has been developed whereby it is possible to view the entire active region of a solid state laser in a TEM using a novel plan-view sample geometry. This, in conjunction with cross-section samples enables a three-dimensional characterization of the degradation mechanisms that lead to laser failure. Additionally, proof of concept has been established for an in-situ TEM experiment in which electrical current is passed through a sectioned VCSEL diode and for which it is possible to correlate experimental parameters, such as electrical bias, current flow, and membrane temperature to diode degradation. Finally, due to the fact that layers of laterally grown Al$_x$Ga$_{1-x}$As oxide (which are commonly employed in VCSEL designs) are possible initiation sites for laser degradation, the oxidation behaviors of a range of III-V materials in the Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ and Al$_x$In$_{1-x}$As$_y$P$_{1-y}$ systems have been investigated.

For a subset of the studied degraded VCSELs that consists of a single, rapidly failing oxide-confined laser operated for different periods of time, the degradation proceeds as follows. There is an initial drop in laser power output due to the development of cracks in the upper mirror layers (leading to a loss of the resonance cavity) and also, possibly due to a mechanism whereby the resistivity of the active region increases. Subsequently, dislocations are punched out near the oxide aperture, some of which then extend over the active region leaving behind dislocation loops in the process. It is also found that the onset of these degradation mechanisms can be detected in the trace of the device’s optical power output as a function of time. Characterization of material degradation in other VCSELs designs demonstrates the role that preexisting defects play in laser failure. Specifically, complex three-dimensional dislocation arrays which exhibited dendritic-like growth and which covered the entire active region were observed to nucleate on a single defect, present from growth or mishandling of the device.

In order that material degradation in VCSEL devices can be observed in real-time, an electrical in-situ experiment has been designed whereby it is possible to pass electrical
current through a TEM-transparent, sectioned VCSEL. Methods have been designed to account for current losses from parallel current paths and for potential drops across series resistances, thereby determining the precise currents and potential drops experienced by the sectioned VCSEL diode. Furthermore, finite element modeling has been employed in order to determine the temperature rise in the membrane as a function of the driving conditions to facilitate separation of thermally assisted dislocation motion from recombination enhanced dislocation motion.

Finally, oxidation of III-V quaternary compounds in the $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ and $\text{In}_x\text{Al}_{1-x}\text{As}_y\text{P}_{1-y}$ systems was studied. The controlled parameters in these studies were composition and epitaxial strain, although it is found that pressures induced during the oxidation and the microstructure of the oxide also likely influence the oxidation. For lateral oxidation of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ ($y \approx 0.78$) it was found that increased phosphorous content led to slower oxidation rates and higher activation energies. The lateral oxidation of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ ($y \approx 0.20$) also exhibited a decreasing oxidation rate for increasing phosphorous concentration although the activation energy decreased, which is likely explained by a diffusion mechanism controlling the oxidation of these high P containing materials. For these compounds and for $\text{In}_{0.5}\text{Al}_{0.5}\text{P}$, $\text{In}_{0.47}\text{Al}_{0.53}\text{As}$, and $\text{Al}_x\text{Ga}_{1-x}\text{P}$ ($x \approx 0.80$) materials, it is shown that, in general, increasing the P concentration and decreasing the Al concentration led to lower oxidation rates.
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# Table of Contents

**ABSTRACT** ........................................................................................................................................................................... I

**ACKNOWLEDGMENTS** ......................................................................................................................................................... III

**LIST OF FIGURES** .............................................................................................................................................................. IX

**LIST OF TABLES** ................................................................................................................................................................. XVII

**LIST OF SYMBOLS** ............................................................................................................................................................... XVIII

1 **INTRODUCTION** ................................................................................................................................................................. 1

1.1 **REVIEW OF EXPERIMENTS** ....................................................................................................................................................... 1

1.1.1 *VCSEL degradation experiments* ........................................................................................................................................ 1

1.1.2 *In-Situ observation of degradation in VCSEL structures* .................................................................................................. 2

1.1.3 *Oxidation experiments* ..................................................................................................................................................... 2

2 **REVIEW OF UNDERLYING CONCEPTS AND EXISTING LITERATURE** ................................................................................................. 4

2.1 *VCSEL VS. EDGE EMITTING SOLID STATE LASERS* ............................................................................................................. 4

2.1.1 *The VCSEL structure* ....................................................................................................................................................... 6

2.2 *CLASSIFICATION OF FAILURE IN LASERS* ......................................................................................................................... 8

2.2.1 *Failure in edge emitting lasers* ........................................................................................................................................ 8

2.2.2 *Observation of failure in VCSELs* .................................................................................................................................... 10

2.3 *MATERIAL DEGRADATION IN III-V LASERS AND MATERIALS* ............................................................................................ 11

2.3.1 *Typical defect configurations in III-V semiconductors* .................................................................................................. 11

2.3.1.1 *III-V crystalline structure* ........................................................................................................................................... 11

2.3.1.2 *Point defects* .............................................................................................................................................................. 12

2.3.1.3 *Linear defects* ............................................................................................................................................................ 13

2.3.2 *Theory of Radiation Enhanced Defect Motion (REDM): The Phonon Kick Mechanism* ............................................................................ 15

2.3.3 *Material degradation of Al$_x$Ga$_{1-x}$As based edge-emitting lasers* .................................................................................. 18

2.3.3.1 *DLD spatial orientation* ............................................................................................................................................. 18

2.3.3.2 *DLD structure* ............................................................................................................................................................ 19
2.3.3.3 Nucleation and rate of DLD growth ............................................. 19
2.3.3.4 Temperature rise in the vicinity of DLDs .................................. 23
2.3.3.5 Role of residual stress ................................................................. 24
2.3.3.6 Catastrophic failure ..................................................................... 24
2.3.4 Laser degradation in other III-V material systems ........................... 25
2.3.5 Improvement to Laser stability ..................................................... 25
2.3.6 III-V material behavior under high injection conditions .............. 26
  2.3.6.1 Experimental observation of optically induced material defects 26
  2.3.6.2 Experimental observation of electrically induced material defects 29
  2.3.6.3 Experimental observation of electron beam induced material defects 29
2.4 III-V OXIDE MATERIALS .................................................................. 32
  2.4.1 Theoretical considerations .............................................................. 32
    2.4.1.1 Fundamental reactions .......................................................... 33
    2.4.1.2 Dominant mechanisms ........................................................... 34
    2.4.1.3 Chemical Parameters .............................................................. 36
    2.4.1.4 Electronic Processes ................................................................. 38
    2.4.1.5 Structural and geometrical parameters .................................... 39
3 EXPERIMENTAL METHODS USED IN THIS WORK.................. 41
  3.1 VCSEL DEGRADATION EXPERIMENTS ............................................ 41
    3.1.1 TEM analysis ........................................................................ 48
    3.1.2 Details of TEM use for this work ............................................. 49
    3.1.3 Stereographic Viewing ......................................................... 50
  3.2 OXIDATION EXPERIMENTS ............................................................ 51
    3.2.1 Measurement techniques ...................................................... 57
  3.3 TRANSMISSION ELECTRON MICROSCOPY ................................ 58
    3.3.1 TEM Instruments ................................................................. 59
    3.3.2 Elastic scattering. Diffraction pattern and Image formation ....... 60
      3.3.2.1 Electron-Sample interaction ............................................... 60
      3.3.2.2 The Diffraction Pattern .................................................... 63
6.1 MOTIVATION ............................................................................................................. 173

6.2 RESULTS OF OXIDATION EXPERIMENTS .............................................................. 174

6.2.1 Sample A, Al\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} (y \geq 0.78) on GaAs ................................................................. 174

6.2.2 Sample B, Al\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} (y < 0.2) on GaP ................................................................. 183

6.2.3 Sample C, In\textsubscript{0.5}Al\textsubscript{0.5}P on GaAs ................................................................. 189

6.2.4 Sample D, In\textsubscript{0.47}Al\textsubscript{0.53}As on InP ................................................................. 191

6.2.5 Sample E, Al\textsubscript{x}Ga\textsubscript{1-x}P on GaP ................................................................. 193

6.3 DISCUSSION ............................................................................................................. 196

6.4 CONCLUSIONS ....................................................................................................... 201

7 SUMMARY AND FUTURE WORK .............................................................................. 205

7.1 FUTURE WORK ..................................................................................................... 206

A OXIDATION FURNACE CONFIGURATION ............................................................... 208

B DETERMINATION OF STRAIN RELIEF IN OXIDE SAMPLES ..................................... 211

C GROWTH AND PROCESSING DATA FOR VCSEL V1 ........................................ 213

D COMPLEX PATTERNED GROWTH ......................................................................... 215

D.1 EXTENDED GROWTH PATTERNS IN OTHER BRANCHES OF SCIENCE ...... 215

D.1.1 Dendritic patterns ............................................................................................ 217

D.1.2 Dense branching morphology (DBM) .............................................................. 217

D.1.3 Diffusion-limited aggregation ......................................................................... 217

D.2 NATURE OF DISLOCATION PATTERNS SEEN IN DEGRADED VCSELS .... 218

E DATA ACQUISITION FOR ELECTRICAL IN-SITU WORK (CHAPTER 6) ...................... 221

E.1 ELECTRIC CIRCUITRY .......................................................................................... 221

E.2 DATA ACQUISITION MODULE USED IN ELECTRICAL IN-SITU STUDIES .... 225

F THERMAL TRANSPORT EQUATION (CHAPTER 6) ................................................. 230

G OPTICAL IN-SITU DEGRADATION ...................................................................... 233

G.1 OPTICAL IN-SITU EXPERIMENTAL DESIGN ......................................................... 234

G.1.1 Fiber insertion .................................................................................................. 235
G.1.2 Sample heating................................................................. 237
G.1.3 Preliminary results......................................................... 238
**List of Figures**

Figure 2-1. Schematic of coincidence of the laser gain curve and the longitudinal modes supported by the Fabry-Perot cavity

Figure 2-2. Two examples of edge emitting lasers. A (a) pn-junction laser, and a (b) heterojunction laser

Figure 2-3. The VCSEL structure

Figure 2-4. DLDs in InGaAsP imaged using CathodoLuminescence (CL)

Figure 2-5. Lifetime characteristics for various failure modes

Figure 2-6. Schematic of the zinc-blende structure with the two different size balls representing the two types of atoms

Figure 2-7. Schematic of zinc-blende structure looking down the <01-1> direction

Figure 2-8. Schematic of the types of perfect edge dislocations that occur in the zinc-blende structure

Figure 2-9. Possible configurations of partial dislocations in the zinc-blende structure. The lines of the hexagon represent dislocation line directions and the arrows indicate the respective Burger’s vector directions

Figure 2-10 Simplified energy band schematic for a semiconductor with a defect state

Figure 2-11. Typical dislocation dipole array found in failed lasers

Figure 2-12. Glide model that accounts for DLDs with <100> directions

Figure 2-13. Effect of electron beam injection on glide velocity of α and β dislocations

Figure 3-1. Example of power vs. time at a forward bias current of 23mA during degradation of VCSEL V1

Figure 3-2. Example of power vs. current traces before and after degradation

Figure 3-3. Schematic of finished planview sample geometry

Figure 3-4 Schematic of effect of Ga⁺ beam/heterointerface misorientation on surface composition of TEM membrane

Figure 3-5. Steps involved in planview sample preparation

Figure 3-6. Schematic of cross-section sample prior to membrane fabrication
Figure 3-7. Schematic of cross sectional sample geometry. White lines depict lateral oxide layers. .............................................................................................................. 48
Figure 3-8. Graph of strains and P concentrations used in the oxide experiments........ 54
Figure 3-9. Cross-section schematic of oxidation trench geometry. ............................. 56
Figure 3-10 Secondary electron image recorded in the FIB of sample A taken during measurement of oxide lengths in FIB. Compositions are given with reference to \( \text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y} \).......................................................................................................... 58
Figure 3-11. Schematic of JEOL 2010 F\(^+(\) ................................................................. 60
Figure 3-12. Ray diagram illustrating Bragg’s law. ...................................................... 63
Figure 3-13. Schematic of electron transitions responsible for X-ray spectra\(^{144} \) ........ 67
Figure 3-14 Schematic of FIB column.............................................................................. 68
Figure 4-1 00-4 bright field cross-section TEM image of undegraded VCSEL, V1-A.. 74
Figure 4-2. Planview TEM image of undegraded VCSEL V1-Ap.................................... 74
Figure 4-3. Power vs. current traces before and after degradation for V1-B.................... 76
Figure 4-4. Power vs. time for operation at 23 mA for V1-B........................................ 76
Figure 4-5. 004 bright field cross-section TEM image of V1-B...................................... 77
Figure 4-6. Power vs. current before and after degradation for V1-C.............................. 79
Figure 4-7. Power vs. time for operation at 23 mA for V1-C.......................................... 79
Figure 4-8 Planview TEM image of V1-C. ............................................................... 80
Figure 4-9. Anaglyph TEM image of V1-C (red lens - right eye). ................................. 81
Figure 4-10 Power vs. current before and after degradation for 60 seconds at 23 mA for V1-D................................................................................................................. 83
Figure 4-11. Power vs. time during degradation of V1-D at 23 mA. ............................ 83
Figure 4-12 Planview TEM image of V1-D, for which (a) is used to show the correlation between this TEM image and the following FIB image. ................................. 84
Figure 4-13 Plan-view secondary electron image of upper DBR of V1-D................. 85
Figure 4-14. Anaglyphic TEM image of V1-D (blue lens - right eye). ......................... 86
Figure 4-15. Power vs. current traces before and after degradation at 23mA for 120 seconds for V1-E................................................................................................. 88
Figure 4-16. Power vs. time during degradation of V1-E at 23mA............................... 88
Figure 4-17 Planview TEM image of degradation in V1-E............................................ 89
Figure 4-18. Anaglyph of V1-E (blue lens - right eye). The feature labeled (a) is due to dust on the membrane surface. 

Figure 4-19. Power vs. current traces before and after degradation at 23 mA for 120 seconds for V1-F. 

Figure 4-20. Power vs. time trace during degradation of V1-F at 23 mA. 

Figure 4-21. Cross section 00-4 bright field TEM image of V1-F. 

Figure 4-22. Cross-section 00-4 TEM bright field image of V1-F. 

Figure 4-23. Power vs. current traces before and after degradation of V1-G at 23mA for 240 seconds. 

Figure 4-24. Power vs. time during degradation of V1-G at 23mA. 

Figure 4-25. Cross-section –2-20 bright field TEM image of V1-G. 

Figure 4-26. Dark field TEM image showing regions of nanocrystalline oxide in a DBR crack. 

Figure 4-27. Diffraction pattern from the oxide contained in the crack, which has spacings consistent with $\gamma$-Al$_2$O$_3$. 

Figure 4-28. Secondary electron taken in the FIB during TEM membrane fabrication, showing a crack extending over a portion of the upper DBR. The lighter contrast regions correspond to oxide bridges. 

Figure 4-29. Power vs. current before and after degradation of V1-H at 23 mA for 800 seconds. 

Figure 4-30. Power vs. time during degradation of V1-H at 23 mA. 

Figure 4-31. Planview TEM image of degradation in V1-H. 

Figure 4-32. Anaglyphic TEM image of V1-H (blue lens - right eye). 

Figure 4-33. Planview section series through upper DBR of V1-H. 

Figure 4-34. Power vs. current traces before and after degradation of V1-I at 23 mA for 1000 seconds. 

Figure 4-35. Power vs. time during degradation of V1-I at 23 mA. 

Figure 4-36. Cross-section 220 bright field TEM image of degradation in V1-I. 

Figure 4-37. Power vs. current traces before and after degradation of V1-J for 1200 seconds at 23 mA. 

Figure 4-38. Power vs. time during degradation of V1-J at 23 mA.
Figure 4-39 Planview TEM image of degradation in V1-J................................. 109

Figure 4-40 Loop/dipole array in active region of V1-J. Labeled are, (a) a screw segment as determined by dislocation contrast analysis and, (b) a helical dislocation segment. ................................................................................................................................. 110

Figure 4-41 -400 bright field image of V1-J taken at the 001 zone axis. ............... 111

Figure 4-42. -311 bright field image of V1-J taken at the 112 zone axis. ............... 111

Figure 4-43 Power vs. current traces before and after degradation of V1-K at 23 mA for 1200 seconds. .................................................................................................................. 112

Figure 4-44. Power vs. time trace during degradation of V1-K at 23mA. ............... 113

Figure 4-45. Cross-section TEM image of material degradation in V1-K. .......... 113

Figure 4-46. Cross-sectional 220 bright field TEM image. ................................. 114

Figure 4-47. Dipole/loop configuration in active region of V1-K......................... 114

Figure 4-48. Power output and applied voltage as a function of time. ................. 115

Figure 4-49. Anaglyphic representation of the active region of V1-J. (red lens-right eye) ................................................................................................................................. 117

Figure 4-50. 220 bright field TEM image of active region of V1-J with primary dislocation front traced in red. The arrow indicates the approximate direction of motion. .................................................................................................................. 119

Figure 4-51. Schematic of five successive iterations in the dislocation behavior leading to development of “oxbow lake” loops. In the schematic, a dislocation (burger’s vector, $b = \frac{1}{2}a<110>$) exists on a [111] plane and is confined vertically (within the blue lines at the crests and valleys shown). Through a series of glide, g, climb, c, and cross-slip motions, s, segments of opposite sign can meet, forming the oxbow-lake loop. .................................................................................................................. 120

Figure 4-52. Defect free active region area as a function of time after the second power drop. The inset represents one of the P-t traces (from Figure 4-38) showing a secondary drop in optical power and the arrow indicates the relevant data point. 121

Figure 4-53. TEM cross-section image of V2-A. .................................................. 122

Figure 4-54 Planview TEM image of V2-B. ......................................................... 123

Figure 4-55.  TEM plan-view image of V2-B. ......................................................... 124

Figure 4-56 Forward biased EL image of surface of V2-B. ................................. 125
Figure 4-57. 220 bright field TEM image of the dislocation dipole array in VCSEL V3.

Figure 4-58. 220 planview TEM image of degradation in VCSEL V3. The array enclosed by the black line is from an earlier growth. The blue line demonstrates that the end of any dislocation arm can be traced back to a single nucleation site.

Figure 4-59. Nucleation of dipole array in VCSEL V3

Figure 4-60. TEM image of a dislocation dipole array before heating at 615°C

Figure 4-61. TEM image of the dislocation dipole array shown in Figure 4-60 after heating at 615°C for 20 minutes

Figure 4-62. 400 two beam TEM diffraction image showing residual contrast

Figure 4-63. -311 two beam diffraction contrast image showing residual contrast

Figure 4-64. Anaglyphic image of V3 (red lens - right eye)

Figure 4-65. Anaglyphic image of V3 (red lens - right eye). The mottled contrast in the upper left as well as the horizontal, jagged band of darker contrast are surface features and not related to degradation.

Figure 4-66. Mechanism of loop nucleation in VCSEL V4

Figure 4-67 Cross section TEM image of catastrophic damage in VCSEL V5

Figure 4-68. Catastrophic damage in V6

Figure 5-1. Schematic for dicing of sample bars

Figure 5-2 Schematic of pre-FIB sample preparation

Figure 5-3. Finished in-situ membrane

Figure 5-4. Schematic of apparatus used to test electrical continuity in in-situ samples

Figure 5-5. Trace of $I_T$ versus $V_T$ for an in-situ membrane

Figure 5-6. Progression of trench geometry in the fabrication of the in-situ membrane (a-before any milling occurs; b-after milling up to the edge of the VCSEL, c-after milling up to the edge of the oxide aperture, and d-after the membrane is complete)

Figure 5-7 Evolution of I-V trace during the membrane fabrication process

Figure 5-8. Forward bias I-V trace of the finished membrane shown with finer current and voltage scales than Figure 5-7
Figure 5-9. I-V trace of finished membrane for bias where series resistance dominates circuit behavior. ................................................................. 153

Figure 5-10. Schematic of relative dimensions of the VCSEL, oxide confinement layers (on a plane below the page), and the inter-device proton isolation (to a depth approximately equal to the upper DBR). ................................................. 154

Figure 5-11. Evolution of I-V traces during membrane fabrication process shown for low forward bias. ................................................................. 156

Figure 5-12. I-V trace of finished membrane for small forward bias after subtracting effect of series resistance. ................................................................. 157

Figure 5-13. I-V trace from isolated contact pad. .................................................. 158

Figure 5-14. Forward bias I-V characteristics of membrane before and after correcting for the effects of series and parallel resistances. ................................................................. 159

Figure 5-15. Membrane geometry with loads and constraints indicated (R-radiation, H-heat generation, C-conduction, T-temperature) ................................................................. 162

Figure 5-16. Sample bar geometry. ......................................................................... 162

Figure 5-17. Secondary electron image of finished membrane and, plot of temperature distribution in membrane for a heat generation rate of ~5mW (i.e. the product of a typical combination of membrane current, 5mA, and membrane bias, 1V). ......... 164

Figure 5-18. Highest membrane temperature due to resistive heating for a membrane 750nm thick, and 20µm wide, and 10µm deep. ................................................................. 165

Figure 5-19. Additional parameters affecting highest membrane temperature for 17mW of heat generation in the membrane. ................................................................. 166

Figure 5-20. (measured Rs for this day is 531ohms. Max conditions give 8.5mW) .... 168

Figure 5-21. Degradation induced during a membrane by electrical pumping. .......... 169

Figure 5-22. Time series of defect movement under electrical stress. .................... 170

Figure 5-23. Exponential dependence of dislocation velocity on membrane current.... 171

Figure 6-1 Oxide lengths as a function of time at 399ºC for Sample A. .................. 176

Figure 6-2 Oxide lengths as a function of square root of time at 482ºC for Sample A. 177

Figure 6-3 Arrhenius plot for layer A-5. $E_A = 0.92 \pm 0.07$eV. ................................. 180

Figure 6-4 Arrhenius plot for A-4. $E_A = 0.96 \pm 0.10$eV. ........................................ 180

Figure 6-5 Arrhenius plot for A-3. $E_A = 1.04 \pm 0.15$eV. ........................................ 181
Figure 6-6 Arrhenius plot for A-2. $E_A = 1.30 \pm 0.11 \text{eV}$. ................................................. 181
Figure 6-7 Arrhenius plot for A-1. $E_A = 1.83 \pm 0.17 \text{eV}$. ................................................. 182
Figure 6-8. Activation energy as a function of epitaxial strain and phosphorous composition for Sample A. .......................................................................................... 182
Figure 6-9 (004) dark field TEM image of Sample B oxidized at 643°C for 37 minutes. 1-y indicates phosphorus concentrations. The substrate and spacer material is GaP. ........................................................................................................................................ 184
Figure 6-10 (004) bright field TEM image of Sample B oxidized at 503°C for 4 hours. Substrate and spacer material is GaP. ................................................................................................................................. 185
Figure 6-11. Oxidation length versus time at 575°C for Sample B ......................... 186
Figure 6-12 Arrhenius plot for B-6. $E_A = 0.34 \pm 0.19 \text{eV}$. ................................................ 187
Figure 6-13 Arrhenius plot for B-7. $E_A = 0.38 \pm 0.16 \text{eV}$. ............................................... 187
Figure 6-14 Arrhenius plot for B-8. $E_A = 0.38 \pm 0.16 \text{eV}$. ............................................... 188
Figure 6-15 Arrhenius plot for B-9. $E_A = 0.49 \pm 0.14 \text{eV}$. .............................................. 188
Figure 6-16 Activation energies as a function of strain for Samples A and B ............... 189
Figure 6-17 Phase contrast image of Sample C after oxidation at 449°C for ~4 hours. 190
Figure 6-18 Phase contrast image of Sample C after oxidation at 505°C for 4 hours. The pinch-off of the lateral oxidation, $L$, by vertical oxidation, $V$, is indicated and represented in the inset schematic.......................................................... 191
Figure 6-19. Secondary electron images of the oxide fronts of Sample D for oxidation at (a) 530°C and (b) 448°C.......................................................... 192
Figure 6-20 Oxidation length versus time for Sample D.............................................. 192
Figure 6-21 Arrhenius plot for Sample D. $E_A = 1.36 \pm 0.18 \text{eV}$. ................................. 193
Figure 6-22 (004) bright field TEM image of Sample E ............................................... 194
Figure 6-23 Oxidation length vs. time for sample E-3 at 575°C................................. 195
Figure 6-24. Arrhenius plot for E-3. $E_A = 0.79 \pm 0.08 \text{eV}$. .............................................. 195
Figure 6-25. Activation energy (closed circles) of oxidation as a function of biaxial strain and of the P content (open circles) of the compounds. ................................. 197
Figure A-1. Oxidation furnace .................................................................................. 208
Figure A-2. Gas exhaust and sample insertion system ............................................. 209
Figure A-3. H$_2$O-N$_2$ mixing system......................................................................... 209
Figure A-4. H_2O-N_2 mixing system................................................................. 210

Figure D-1. Various extended pattern growth shapes. (DLA-diffusion limited
aggregation. DBM-dense branching morphology) ........................................... 216

Figure D-2. Dependence of pattern type on growth conditions (solute concentration, C,
and driving voltage, V)^242. The example given is for electrolytic growth of Zn from
a concentration, C(M), of ZnSO_4................................................................. 216

Figure D-3. Dependence of pattern type on growth conditions^243 .............. 217

Figure D-4. (a) Dislocation line (black line) with a point defect gradient (contour plot in
grey) on one side. (b) Dislocation line and point defect gradient after extension of
dislocation line. ....................................................................................... 220

Figure E-1. Schematic of setup for in-situ electrical degradation experiment ....... 222

Figure E-2. Wiring diagram for in situ electrical circuit. Pa represents the external power
supply and Pc represents the NiDAQ power supply................................. 223

Figure E-3. User interface of LabView data acquisition program. .................... 227

Figure E-4. Icon driven programming of LabView data acquisition program. ....... 228

Figure G-1. Optical TEM in-situ holder ......................................................... 235

Figure G-2. Schematic of how to hold the fiber when pulling it back through the feed-
though tube......................................................................................... 236

Figure G-3. Technique for determining optical density impinging on sample ........ 237
List of Tables

Table 2-1. A table of parameters relevant to oxidation for the III-V constituents used in this work\textsuperscript{131} ................................................................................................................ 37
Table 2-2. Heats of formation of the relevant III-V binary compounds\textsuperscript{131} ................. 37
Table 2-3. Properties of relevant III-V oxides\textsuperscript{131}. Melting or decomposition temperatures, which are inversely proportional to vapor pressures, are given here, as vapor pressures for some oxides listed are unknown................................................ 38
Table 3-1. Summary of oxide sample chemistries and strains. Compressive strains are given a positive sign. Unless otherwise noted, chemistry data is given based on $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$.......................................................................................................... 54
Table 4-1. Summary of devices used and their respective degradation histories. P or C refers to plan-view or cross-section characterization................................................ 72
Table B-1. Strain relief determination........................................................................................................ 212
Table C-1. Growth table for VCSEL V1. ................................................................................................. 214
Table E-1. Sample of data acquired in Labview.......................................................................................... 229
Table G-1. Examples of optical output intensities for various VCSEL designs.............. 234
## List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Crystal lattice parameter</td>
</tr>
<tr>
<td>b</td>
<td>Burger’s vector of a dislocation</td>
</tr>
<tr>
<td>be</td>
<td>Edge component of a Burger’s vector</td>
</tr>
<tr>
<td>d</td>
<td>Lateral oxide length</td>
</tr>
<tr>
<td>d</td>
<td>Lattice planar spacing</td>
</tr>
<tr>
<td>E</td>
<td>Electron energy</td>
</tr>
<tr>
<td>E</td>
<td>Elongation vector of dark line defect</td>
</tr>
<tr>
<td>E_A</td>
<td>Activation energy of oxidation</td>
</tr>
<tr>
<td>f(Θ)</td>
<td>Atomic scattering factor</td>
</tr>
<tr>
<td>F(Θ)</td>
<td>Structure factor</td>
</tr>
<tr>
<td>f_x</td>
<td>X-ray scattering factor</td>
</tr>
<tr>
<td>I</td>
<td>Electron irradiation</td>
</tr>
<tr>
<td>I_T</td>
<td>Membrane current</td>
</tr>
<tr>
<td>I_V</td>
<td>Junction current</td>
</tr>
<tr>
<td>k</td>
<td>Electron wave vector</td>
</tr>
<tr>
<td>K</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzman’s constant</td>
</tr>
<tr>
<td>k_l</td>
<td>Linear oxide growth rate constant</td>
</tr>
<tr>
<td>k_p</td>
<td>Parabolic oxide growth rate constant</td>
</tr>
<tr>
<td>Q</td>
<td>Activation energy for dislocation motion</td>
</tr>
<tr>
<td>q</td>
<td>Electron charge</td>
</tr>
<tr>
<td>Q_r</td>
<td>Recombination energy</td>
</tr>
<tr>
<td>R</td>
<td>Displacement field caused by a dislocation</td>
</tr>
<tr>
<td>r</td>
<td>Electron position vector</td>
</tr>
<tr>
<td>R_P</td>
<td>Parallel resistance</td>
</tr>
<tr>
<td>R_S</td>
<td>Series resistance</td>
</tr>
<tr>
<td>R_V</td>
<td>Junction resistance</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
</tbody>
</table>
\textbf{u} \quad \text{Dislocation line direction}

\textbf{V}_\text{D} \quad \text{Drive voltage}

\textbf{V}_\text{T} \quad \text{Membrane voltage}

\textbf{V}_\text{V} \quad \text{Junction voltage}

\textbf{Z} \quad \text{Atomic weight}

\textit{z} \quad \text{Distance traveled through a sample by an electron}

\textbf{\Phi}_\text{g} \quad \text{Scattered electron wave amplitude}

\textbf{\Phi}_\text{o} \quad \text{Incident electron wave amplitude}

\textbf{\Omega} \quad \text{Differential solid angle}

\textbf{\Psi} \quad \text{Electron wave amplitude}

\textbf{\varepsilon} \quad \text{Epitaxial biaxial strain}

\textbf{\lambda} \quad \text{Wavelength}

\textbf{\nu} \quad \text{Poisson’s ratio}

\textbf{\theta} \quad \text{Bragg angle}

\textbf{\rho} \quad \text{Resistivity}

\textbf{\sigma} \quad \text{Electron scattering cross-section}

\textbf{\tau} \quad \text{Resolved shear stress}

\textbf{\upsilon} \quad \text{Dislocation velocity}

\textbf{\xi} \quad \text{Extinction distance}
1 Introduction

Vertical Cavity Surface Emitting Lasers (VCSELs) offer numerous advantages over previous laser designs and have thus become a crucial component in the advancement of telecommunications and other laser-based technologies. However, to fully enable this technology, it is necessary to understand the fundamental materials science of the degradation processes that hinder the realization of long lifetimes for the arbitrary VCSEL design. This dissertation describes work done to discover and understand the prevalent material failure mechanisms that are responsible for VCSEL failure.

The VCSEL presents a unique materials science setting in which to study the behavior of III-V materials under extreme stresses. During operation, successful VCSEL designs must be able to support extreme optical fluxes (e.g. $\sim$100kW/cm$^2$) and electrical fluxes (e.g. $\sim$2kA/cm$^2$) without material or structural failure. Such failure has been studied in conventional edge-emitting stripe lasers (for a recent review of this research refer to Ueda$^1$), but little known work has been published on the materials aspects of degradation phenomena in VCSEL devices.

Furthermore, the need in VCSEL designs for current confining material has spurred the interest in native oxides of III-V semiconductors, specifically oxides of Al$_x$Ga$_{1-x}$As. A number of previous studies have made it possible to predict the oxidation growth kinetics of these materials depending on parameters such as column-III chemistry and oxide thickness (for laterally grown buried oxides). However, two oxidation parameters which have received little attention in the literature thus far, but which likely impact oxidation growth kinetics, are epitaxial strain and column-V chemistry.

1.1 Review of experiments

1.1.1 VCSEL degradation experiments

Several novel experiments have been developed in this thesis in order to elucidate the nature of VCSEL degradation. Of interest are, the locations of nucleation sites for
defects, the final defect configuration within the VCSEL, and the effect of the VCSEL architecture on defect behavior.

In order to explore material degradation in a failed VCSEL, a series of VCSELs have been operated to various levels of failure (i.e. one current is chosen for a given device, and that device is then operated for various times at this current). To enable characterization of this sample set, a sample preparation technique was devised for which the use of a Focussed Ion Beam (FIB) was crucial. Of primary interest is the defect microstructure in the active region of the VCSEL. For this reason, a novel FIB technique is used, whereby, for the first time, it is possible to view the entire active region of a solid state laser in the TEM. Previous studies in this field have relied upon thinning small volumes of the structure to electron transparency, raising extensive questions about the statistical significance of such small sample regions, and the conclusions drawn therefrom.

1.1.2 In-Situ observation of degradation in VCSEL structures

An in-situ experiment will also be described which was designed to further elucidate the nature of VCSEL degradation and, more fundamentally, investigate the behavior of Al$_x$Ga$_{1-x}$As subjected to extreme electrical stresses. For this electrical pumping experiment, cross sections (~750nm thick) through the center of an undegraded VCSEL were subjected to current densities equal and greater than the current densities seen to cause degradation in VCSELs.

1.1.3 Oxidation experiments

Finally, to increase our understanding of the oxidation behavior of III-V materials, an experiment has been devised in which the activation energy for oxidation of a wide range of AlGaAsP and InAlAsP compounds has been determined. The lattice parameter over this range of compositions varies significantly (relative to the ~0.1% change in lattice parameter over the entire range of Al$_x$Ga$_{1-x}$As compositions) so that the experiment simultaneously measures the effect of the column V chemistry and lattice mismatch strain.
The overall goal of these experiments is to further understand the behavior of those materials that are fundamental to the VCSEL structure. Degraded VCSELS have been used to investigate those defects responsible for VCSEL failure. The in-situ experiment described above was designed to study material behavior under extreme conditions and can provide further avenues for investigating mechanisms responsible for VCSEL failure. The oxide studies described above have provided an understanding of the effects of additional oxidation parameters.
2 Review of Underlying Concepts and Existing Literature

Included in this chapter is a description of the VCSEL architecture and a comparison to edge emitting lasers (several texts were used as background for this treatment \(^2\)–\(^6\)). Also given is a summary of the degradation mechanisms that were observed for edge emitting lasers and for III-V materials in general. Finally, a brief summary of the current understanding of the oxidation of III-V materials is given.

2.1 VCSEL vs. edge emitting solid state lasers

The main components of any semiconductor laser are a p-n-junction gain region\(^i\) and a means of optical feedback\(^ii\). The function of the former is to supply the laser’s optical flux via photon emission through stimulated radiative recombination of electrically or optically injected carriers. The latter reflects a portion of the generated photons back to the gain region for continued stimulated emission and also partially controls the laser output wavelength that is determined by the length of the Fabry-Perot resonance cavity established between the mirrors. The number and spectral density of wavelengths supported by the cavity increases with cavity length and the actual laser output is determined by the coincidence of the wavelengths (in near-monochromatic peaks) supported by the Fabry-Perot cavity, and the wavelength distribution associated with the electron-energy band structure of the gain region as shown in Figure 2-1. The lasing wavelength(s), or mode(s), is that for which the respective photon population experiences the least amount of loss in the gain region. This mode will then grow at the expense of the other modes leading to the single wavelength output. However, it is possible in edge emitting lasers (and some larger VCSELs) for more than one mode to become strong enough to contribute to the laser output.

---

\(^i\) The p-n junction may be in the form of a homojunction, heterojunction, multiple quantum well stack, or most recently, a stack of quantum dot layers.

\(^ii\) The reflectivity of the optical feedback structure can be provided by cleaved crystal facets or by multiple epitaxially grown layers of \(\frac{1}{4}\) laser-wavelength thickness.
For edge emitting lasers (Figure 2-2), control of the emission spectra is relatively
difficult due to the comparatively long cavity lengths used (~10^-4-10^-3 m, as compared to
VCSELs with cavity lengths on the order of ~10^-5 m). Specifically, due to the large cavity
length, the density of supported wavelengths may be sufficiently high such that multiple
wavelength peaks coinciding with the gain distribution may experience low loss,
resulting in multiple output wavelengths. Furthermore, the cleaved-facet mirrors
typically used in edge emitting lasers provide a relatively low reflectance of ~30%iii for
optical feedback. Thus, lasers employing cleaved-facet mirrors typically have relatively
high threshold current requirements (>10^3-10^2 A, roughly an order of magnitude greater
than a VCSELiv) to begin and sustain lasing. However, despite these limitations, the
longer gain region (e.g. longer path over which stimulated emission may occur) of an
edge emitting laser allows for high power outputs on the order of 1 Watt.

iii The degree of reflectivity of a cleaved facet semiconductor-air interface is controlled by the indices of
refraction of the semiconductor (n ~ 3.6) and air (n = 1.0) (e.g. as described by the Fresnel equations)².
iv Though threshold current is typically reported in the literature for a particular device design, these
threshold currents correspond to current densities of order one kAcm⁻².
2.1.1 The VCSEL structure

The hallmark of the VCSEL is its mirror configuration located above and below its light-producing gain, or “active” region (Figure 2-3), and the fact that light propagation is parallel to the epitaxial growth direction whereas in edge emitting lasers light propagation is perpendicular to the growth direction. The mirror ‘stacks’, or Distributed Bragg Reflectors (DBRs), for structures considered here are comprised of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers of $\frac{1}{4}$ wavelength ($\lambda$) thickness through which, any variation in $x$ repeats every $\frac{1}{2}\lambda$. Due to an index of refraction change at each interface (and a corresponding reflection every $\frac{1}{2}\lambda$), a stack of these mirrors (consisting typically of 20 to 40 layers) can reflect 99% of the light output back to the active region. This high reflectance enables lower threshold currents on the order of $10^{-5}$A (~0.1kAcm$^{-2}$). Furthermore, the relatively short cavity length of the VCSEL, on the order of $10^{-5}$m, produces a ‘purer’ laser mode than is typically possible in an edge-emitting laser (i.e., a single wavelength supported by the Fabry-Perot cavity is coincident with the low loss region of the gain distribution).
A second feature common to solid state laser designs is the incorporation of a method of concentrating electrical carriers to the active region. VCSELs with both lateral-oxide carrier confinement and proton-implant carrier confinement will be investigated in this work. Figure 2-3 depicts a typical lateral oxide configuration. For proton implant confinement, protons are implanted into the upper mirror stack of a VCSEL except in the center of the device. Thus, a current path (~10µm in diameter) remains in the center of the device, producing a current-path geometry similar to that in Figure 2-3.

The third important component of the VCSEL structure is its photon-generating active region as shown in Figure 2-3. A quantum well structure is generally used in this capacity. The function of the quantum well is to further enhance carrier confinement and to allow for laser wavelength selection via the correlation between well dimensions and electron-hole recombination energies.

In addition to lower threshold currents and better output control, the smaller lateral dimensions of a VCSEL (10² – 10³ µm²) mean that this architecture lends itself readily to fabrication into dense, two dimensional laser arrays. Such arrays have applications in telecommunications and in computing as optical interconnects, for which the VCSEL’s low-divergence, circular output beam and ease of on-wafer testing are
advantageous. However, the disadvantage of the smaller dimensions of the VCSEL is its relatively short gain region, and hence relatively lower power output (~10^-2 W).

Thus, as mentioned above, the VCSEL structure is more complex than most edge emitting laser designs. In particular, greater complexity in the VCSEL arises from the use of several mirror layers (i.e. > 100 interfaces, many of which are graded) and the use of post growth processes such as oxidation or ion implantation that may alter the stress state of the device. In comparison, the simplest edge emitting lasers may contain only three epitaxial interfaces (although much more complex schemes exist).

2.2 Classification of failure in lasers

2.2.1 Failure in edge emitting lasers

Failed, or partially failed light emitting devices often exhibit Dark Line Defects (DLDs) or Dark Spot Defects (DSDs) from which no light generation occurs as shown in Figure 2-4. These defects can be directly observed by several techniques that rely on the radiative carrier recombination process that occurs in the direct bandgap semiconductors (e.g. GaAs and InP) used in optical devices. For example, the CathodoLuminescence (CL) (e.g. Yonezu et al.) and Photoluminescence (PL) (e.g. Ito et al.) techniques employ monochromatic electrons and photons respectively that are rastered across the sample to excite carriers in the sample that subsequently recombine, generating measurable photon intensities. In these techniques regions of zero or low intensity indicate that carriers excited with the incident beam in that region are relaxing via non-radiative paths. The Electron Beam Induced Current (EBIC) (e.g. Yonezu et al.) technique also employs a rastered electron beam to excite carriers in the depletion region of a diode which are then collected through electrical circuitry (driven by the built-in voltage of the device) and used to generate a spatially-resolved image. Defects in the depletion region will show up as dark regions due to the carrier trapping behavior of the defect. Finally, Electroluminescence (EL) (e.g. Zschauer and Petroff et al.) uses a

\footnote{In contrast, electrons in the conduction band of indirect bandgap semiconductors must interact with a lattice phonon in order to recombine with a hole in the valance band. The average time for a phonon and electron to meet is great enough so that recombination via non-radiative paths is more likely and thus the material does not luminesce efficiently.}
small current (sub-threshold for laser diodes) to generate measurable spontaneous emission in the laser material. Again the non-radiative trap nature of defects causes them to appear dark in the EL image. Whereas the EBIC and EL techniques generate images of the depletion region of the device (i.e. active region), the PL and CL techniques can generate an image from the entire device and are thus capable of detecting defects throughout the structure.

As the underlying operating principle of a solid state laser involves the generation of light via recombination of excited carriers, it follows that non-radiative defect regions detrimentally affect laser output. Furthermore, carrier absorption at DLDs can eventually become great enough to counteract the gain produced by the un-damaged material thus ceasing the lasing action of the device\textsuperscript{13}. Thus, given similar densities of DLDs, a laser with high levels of loss (other than via absorption at dislocations) is more susceptible to complete failure than a laser with low loss levels.

![DLDs in InGaAsP imaged using CathodoLuminescence (CL)\textsuperscript{1}.](image)

Figure 2-4. DLDs in InGaAsP imaged using CathodoLuminescence (CL)\textsuperscript{1}.

Figure 2-5 depicts typical output characteristics for different modes of laser degradation during lifetime studies under constant-current or constant-output-power configurations. “Rapid degradation” of laser output is often associated with DLDs, and occurs within a time interval of a few minutes to a few hours. In this regime, growth rates of DLDs can be as high as $10^{-6}$ cm/sec\textsuperscript{14,15}. DSDs are associated with a more “gradual degradation” occurring over thousands of hours and are the ultimate cause of
laser failure even if rapid degradation can be avoided. A third degradation mode, catastrophic failure, results from unintentional current surges and leads to almost instantaneous laser failure. In edge emitting lasers, this severe form of degradation is associated with gross damage to the mirror and active region (e.g. high-density dislocation networks, cracking, and melting).

Figure 2-5. Lifetime characteristics for various failure modes¹.

The three failure mechanisms mentioned above have been linked to a minority carrier injection-assisted defect growth mechanism referred to as Radiation Enhanced Defect Motion (REDM). This effect is discussed in Section 2.3.2.

2.2.2 Observation of failure in VCSELs

VCSEL power output characteristics show failure modes similar to those observed in edge emitting lasers (i.e. there occurs, gradual, rapid and catastrophic failure). Whereas there have been a limited number of published studies of failure in VCSELs¹⁶¹-¹⁶⁶, the means of study is typically one of the techniques mentioned above (i.e. EL, CL, EBIC or PL) or the failures are simply classified into the gradual, rapid or catastrophic type based on changes in power vs. current or current vs. voltage traces¹⁶. Thus, a thorough analysis of the material aspects of VCSEL failure has not been conducted prior to this work.
2.3 Material degradation in III-V Lasers and materials

2.3.1 Typical defect configurations in III-V semiconductors

The most commonly observed material defects in the III-V system are described below following a brief description of the III-V crystalline structure.

2.3.1.1 III-V crystalline structure

III-V semiconductors assume the zinc-blende\textsuperscript{vi, vii} configuration as shown in Figure 2-6\textsuperscript{17,18}. This configuration is composed of a face centered cubic lattice (FCC) of column V constituents offset by $\frac{1}{4}a[111]$ from an FCC lattice of the column III constituents (where $a$ is the lattice parameter of the material). In this configuration, each column III element is tetrahedrally bonded to four column V nearest-neighbor atoms and visa-versa. In unordered ternary or quaternary materials, the column III or column V atoms are randomly distributed on their respective column III or column V FCC lattice.

![Zinc-blende structure](image)

\textbf{Figure 2-6. Schematic of the zinc-blende structure with the two different size balls representing the two types of atoms}\textsuperscript{17.}

In the zinc-blende structure, the \{111\} planes are close-packed and in the [111] direction occur in pairs consisting of a plane of column III and a plane of column V

\textsuperscript{vi} The zinc-blende structure is also known as the sphalerite structure.

\textsuperscript{vii} Space group F-43m
atoms. These planes have the stacking sequence of \( \ldots a\alpha b\beta c\gamma a\alpha b\beta c\gamma \ldots \) where Roman characters represent the first FCC lattice and Greek characters represent the second FCC lattice. The \( a\alpha \) planes are separated by three times the distance that the \( \alpha b \) planes are as shown in Figure 2-7.

![Figure 2-7. Schematic of zinc-blende structure looking down the <01-1> direction\(^7\).](image)

### 2.3.1.2 Point defects

Point defects in III-V semiconductors include vacancies and multiple vacancy groups, interstitials and “antisite” atoms. Vacancy formation (i.e. removal of an atom from its lattice point) leaves four dangling electrons which form covalent bonds among the atoms neighboring the defect\(^7\). Interstitials (atoms not on lattice points) can occupy the large free volume at the center of the zinc-blende unit cell in an un-bonded state. The un-bonded nature of the interstitial leads to higher migration rates when compared to the migration rate of the single vacancy\(^7\).

Antisite defects are unique to compound crystalline semiconductors and occur where a column V element occupies a column III lattice point or visa-versa.
2.3.1.3 Linear defects

In III-V compound semiconductors, the most common dislocations are of the type $\frac{1}{2}\mathbf{a}<110>$ and $\mathbf{a}<100>$, although the latter occurs much less frequently due to its higher dislocation energy. Concentrating then on the $\frac{1}{2}\mathbf{a}<110>$ dislocations, which occur on the close-packed $\{111\}$ slip planes, there are several possible dislocation configurations that might occur that are dependent on crystallographic orientation and the type of atom at the core. Perfect edge dislocations ($\mathbf{b} = \frac{1}{2}\mathbf{a}<110>$) can terminate leaving either a core of column III atoms (termed a $\beta$ dislocation) or a core of column V atoms (termed an $\alpha$ dislocation). In Figure 2-8, removing half planes 1 or 4 generates $\beta$ dislocations whereas removing half planes 2 or 3 generates $\alpha$ dislocations. Furthermore, the extra half-plane of the dislocation can terminate between a set of $\alpha\alpha$ planes (called a shuffle set) or between the more closely spaced $\alpha\beta$ planes (a glide set). In Figure 2-8, removing half planes 1 or 2 generate shuffle dislocations whereas removing half planes 3 or 4 generate glide dislocations. However, experimental observation indicates that the glide set is the favored configuration.

![Figure 2-8. Schematic of the types of perfect edge dislocations that occur in the zinc-blende structure.](image)

---

\textit{viii} Dislocation energy is proportional to the square of the Burger’s vector.
Perfect dislocations in III-V semiconductors do disassociate into partial dislocations (e.g. $\mathbf{b} = \frac{1}{2} [110] \pm \frac{1}{6} [211] + \frac{1}{6} [12-1]$), of which, there are six possible partial configurations as depicted in Figure 2-9. However, the equilibrium separation of the partials for most zinc blende semiconductors (and the diamond cubic semiconductors, Si and Ge) has been reported as less than 10nm for screw and edge dislocations in both $\alpha$ and $\beta$ configurations. Thus, in the rather thick TEM samples (typically greater than 500nm) used in this work, separation of dislocations may not be readily observed.

Figure 2-9. Possible configurations of partial dislocations in the zinc-blende structure. The lines of the hexagon represent dislocation line directions and the arrows indicate the respective Burger’s vector directions.

Glide of dislocations in III-V semiconductors is expected to be by nucleation and migration of double kinks. Several reports have indicated that in III-V materials the velocity of $\alpha$ type dislocations differs from the velocity of $\beta$ type dislocations and that there is a strong dependence of dislocation velocity on doping (e.g. according to Choi et al. $\alpha$ dislocations are ~100 times faster than $\beta$ dislocations in n-type GaAs while $\beta$ dislocations are ~10 times faster than $\alpha$ dislocations in p-type GaAs).

Dislocation velocity in III-V semiconductors typically is a function of mechanical stress, $\tau$, and an exponential function of temperature such that it obeys the relationship.
given in Equation 2-1 (which is a simple form of the equation that models thermal activation of defect growth in many crystal systems).

\[
\nu = \nu_0 \left( \frac{\tau}{\tau_0} \right)^m e^{-\frac{Q}{k_BT}}
\]

Equation 2-1

Here, Q is the activation energy for dislocation glide to occur and \( \nu_0, \tau_0 \) and m are empirically determined constants.

In the Al_\textsubscript{x}Ga_{1-x}As system most relevant to the lasers studied in this work the lattice mismatch between the end-point binaries (i.e. AlAs and GaAs) is 0.13\% at room temperature. This relatively small lattice mismatch may not readily cause the formation of misfit dislocations for heteroepitaxial layers of device dimension (10^{-9} – 10^{-7} m thickness). However, there have been reports that layer interdiffusion occurs preferentially at dislocations\textsuperscript{37}. Therefore, since the interdiffusion lowers the interface energy, this acts as a strong driving force for dislocation kinetics in addition to misfit stress\textsuperscript{38}.

2.3.2 Theory of Radiation Enhanced Defect Motion (REDM): The Phonon Kick Mechanism.

The electronic band structure of a semiconductor is a direct consequence of the periodicity of its crystalline lattice. Hence, where crystalline defects disturb this periodicity, there will be a disturbance in the electronic band structure in the vicinity of the defect. Specifically, this disturbance often manifests itself as an available energy state within the bandgap as shown in Figure 2-10\textsuperscript{19,39-45}. 


Figure 2-10 Simplified energy band schematic for a semiconductor with a defect state\textsuperscript{56}.

In defect free, lasing semiconductors, electrons in the conduction band directly recombine with holes from the valance band to produce photons. If there exists an available energy state within the bandgap due to a defect, a charge carrier may be captured at the defect where it is then likely to relax via phonon production\textsuperscript{46,47} (i.e. non-radiatively) instead of by photon production. A collection of these phonons can couple their energy into vibrational modes at the defect (i.e. the “phonon kick”) and thus enhance defect motion beyond thermally activated defect migration rates\textsuperscript{48-51}. In a competing mechanism, for a small fraction of recombination events, the energy dissipated may excite other carriers via the Auger mechanism whereby the energy released from an electron-hole recombination event drives a carrier deeper into its respective band (and this carrier then thermally relaxes)\textsuperscript{52}.

Existing models predict that for a line dislocation, there is a greater chance that kinks will form and migrate under conditions of minority carrier injection via REDM\textsuperscript{53}. If there is a high density of point defects, the non-radiative recombination of charge carriers assists in additional formation and migration of these defects, and consequently increases the probability of non-conservative climb for segments of line dislocations (e.g. dipoles)\textsuperscript{54,55}.
In simplest terms, dislocation velocity is inversely proportional to the activation energy, \( E \), such that,

\[
\nu \sim e^{-\frac{Q}{k_B T}}
\]

**Equation 2-2**

According to the theory of REDM\(^{107}\), upon non-radiative recombination, the activation energy for dislocation motion is lower by the amount of energy, \( Q_r \), given by the non-radiative recombination event to the defect such that,

\[
\nu \sim e^{-\frac{Q}{k_B T}} + \eta \Re \nu e^{-\frac{(Q-Q_r)}{k_B T}}
\]

**Equation 2-3**

The probability of the non-radiative energy being coupled into the defect is accounted for in the term, \( \eta \). The rate of non-radiative recombination, \( R \), is dependent on minority carrier injection and hence, the velocity is expected to be linearly dependent on injection levels\(^{107}\).

Several factors\(^{56}\) affect the strength of the REDM effect: (i) the defect site must exhibit strong electron-phonon coupling (e.g., ionic and covalently bonded materials, in which electrons are strongly localized to crystalline bonds), (ii) the phonon energy must be significant relative to energy barriers for defect growth implying that larger bandgap materials (with a greater recombination energy) will exhibit a stronger REDM effect (which has been confirmed by Lang et al.\(^{57}\)), (iii) the recombination rate must be large compared to the thermal carrier generation rate.

In sum, these radiation-enhanced processes are capable of increasing the defect density present, leading to a greater percentage of material that cannot produce light; eventually rendering the laser inoperable. As is discussed in the following sections, it is thus extremely important to minimize the occurrence of any defect in the as-grown laser.
It is similarly important to minimize built-in epitaxial stress in the device that would magnify this process.

2.3.3 Material degradation of Al\textsubscript{x}Ga\textsubscript{1-x}As based edge-emitting lasers

The recombination enhanced defect motion mechanism discussed above has been linked to the growth of complex three-dimensional dislocation configurations, similar to that shown in Figure 2-11, which have been shown to directly correspond to DLDs in laser diode materials\textsuperscript{12,55,58-60}.

![Figure 2-11. Typical dislocation dipole array found in failed lasers\textsuperscript{55}.](image)

2.3.3.1 DLD spatial orientation

DLDs typically have an orientation along the $<$100$>$ directions and less frequently along the $<$110$>$ directions in the (001) junction plane\textsuperscript{9,55,61}. Models for the growth of DLDs in both of these directions are given in a following section. Furthermore, these defects are typically found to be localized to the lasing region of the laser diodes\textsuperscript{9,55,62}. Presumably, this spatial confinement is due to the presence of the epitaxial strain
difference at the interface between the active region and the cladding layers adjacent to the active region (cladding layers are generally under compressive strain relative to the active region) which may not be conducive to dislocation growth beyond that interface. A second factor, likely acting in conjunction with the one just mentioned, that limits dislocation growth into the DBRs is the confinement of carrier recombination (that is required for REDM to operate) to the active region.

2.3.3.2 DLD structure

TEM studies have revealed that the DLDs are composed of complex configurations of helical dislocations, loops and large dipole arrays extending in the <100> and <210> directions and less frequently in the <110> directions. The high density ($10^8$-$10^9$/cm$^2$) dislocation dipole arrays associated with DLDs typically have a Burger’s vector of $\frac{1}{2}a<011>$ type, inclined 45º to the plane of the laser substrate, although dipole arrays with Burger’s vectors of $\frac{1}{2}a<110>$ in the substrate plane and of $a<001>$ type perpendicular to the substrate are more rarely found (it was suggested that the latter was possibly due to the interaction of two $\frac{1}{2}a<110>$ type arrays; e.g. $\frac{1}{2}a[0-11]$ + $\frac{1}{2}a[011]$ a[001]). The helical nature of the dislocations and the presence of loops and dipoles, suggests the operation of a nonconservative dislocation climb process, although glide is also likely operative as is discussed later. A majority of observed loops are unfaulted (>90%).

These complex dislocation arrays are typically found to originate on other dislocations such as vertical threading dislocations. The originating dislocations are typically positioned at the edge of a dislocation array (instead of within the array) which has led some to suggest that the preferred growth direction may be associated with the polarity of the III-V crystal.

2.3.3.3 Nucleation and rate of DLD growth

Typical current densities required to initiate DLD growth in laser devices have been found to be on the order of $10^3$A/cm$^2$, although laser configuration (e.g. material and architecture) and the level of preexisting defects determines the exact threshold for
DLD growth. Furthermore, DLD growth is strongly dependent on the driving condition such that reducing the current “slightly” reduces DLD growth significantly\(^{65}\). Growth of the DLD’s displays erratic behavior\(^{66}\), starting after various times of aging and stopping after different periods of growth.

It was found that subjecting a fresh, normally-rapidly-failing laser diode to high temperatures (as high as 800°C) in the absence of current did not induce growth of DLDs, thereby confirming the role of a failure mechanism reliant on minority carrier injection such as REDM and precluding residual stress as the sole factor in causing DLDs to occur\(^{65}\). Finally, DLD growth rates have been found to be similar between lasing and non-lasing structures provided that electrical excitation is similar\(^{65}\) suggesting that electrical current is a contributing factor in the formation of DLDs (it is later described in this thesis how any method of carrier excitation can be sufficient to activate REDM).

Dislocation velocities in DLDs have been reported by Petroff et al\(^{12}\) to be greater than \(10^{-7}\) cm/s and by Nannichi et al to be between \(10^{-4}\) and \(10^{-6}\) cm/s for current injection of order \(10^3\) Acm\(^{-2}\)\(^{ix}\). That these velocities occur under typical active region temperatures of not more that 50°C again suggests the operation of an injection assisted mechanism such as REDM\(^{x,67}\).

Sources of the point defect densities required for the observed loop and dipole area have been considered by several groups. O’Hara et al.\(^{59}\) determined that native point defect densities typically occurring in GaAs are not sufficient to account for the observed loop and dipole area observed in DLDs suggesting a source associated with the architecture of the device or that some mechanism is operative which generates the extra point defects. Dopant atoms do not seem to be a viable source for the required point defects as DLDs have been detected in undoped GaAs\(^{68}\). Furthermore, proton implantation (commonly used to isolate the lasing region) is not considered as a critical point defect source as laser diodes employing\(^{55}\) and not employing\(^{69}\) implantation both exhibit DLDs.

\(^{ix}\) There are few reports in the literature of dislocation velocity as observed in devices that failed during operation. However, as described in the following sections, several researchers have measured dislocation velocities in controlled optical or electron injection experiments in laser materials.

\(^{x}\) In bulk GaAs under no injection, similar dislocation velocity requires a temperature greater than 200°C and a stress greater than \(10^7\) Pa.
Many researchers have speculated that compositional irregularities in the vicinity of heterointerfaces are a likely source of point defects\textsuperscript{12,68,70-72}. Other proposed point defect sources include inhomogeneities and precipitates in the substrate wafer\textsuperscript{73}, inclusions left during some growth methods (e.g. Liquid Phase Epitaxy (LPE))\textsuperscript{74}, non-stoichiometric III-V growth ratios\textsuperscript{75-78} and electromigration from the device surface via pipe diffusion along threading dislocations\textsuperscript{79}. It has also been suggested\textsuperscript{59} that point defects are generated at the site of the dislocation via the REDM mechanism (i.e. by a phonon kick as discussed in Section 2.3.2) and that vacancies migrate away while interstitials remain (i.e. to form extrinsic loops) due to stronger interaction between interstitials and dislocations (the cited authors give as an example the interaction of interstitial carbon with dislocations in iron\textsuperscript{80}). Actual diffusion of point defects to the growing dislocation front may be facilitated by residual stresses (e.g from lattice mismatch) and electric fields present during laser operation that act on the vacancies (a fraction of the vacancies will be charged) to constitute a drift force to drive vacancies toward climbing dislocation segments\textsuperscript{68}. 

Hutchinson et al.\textsuperscript{64} propose a simple nonconservative climb model to explain the observed direction of dipole elongation due to REDM where the originating dislocation has a Burger’s vector of type $\frac{1}{2}a<110>$, and where the dipoles and loops have pure edge character; i.e. a Burger’s vector normal to the dipole or loop. They propose that for a dislocation, such as a threading dislocation with a given Burger’s vector, a dipole will typically begin to grow outward in a plane perpendicular to the Burger’s vector. If this plane is tilted with respect to the substrate, elongation (along the axis of the projection of the device normal onto the plane) will cease when the edges of the dipole reach the upper and lower boundaries of the active region. However, the dipole is still free to elongate along the orthogonal in-plane directions. Mathematically, this elongation can be represented by

$$\vec{E} = \vec{b} \times [001]$$

\textbf{Equation 2-4}
where \( \mathbf{E} \) is the elongation direction projected on the [001] substrate plane and \( \mathbf{b} \) is the burgers vector of the originating dislocation. Thus, considering the six possible \(<110>\) axes, Equation 2-4 gives two elongations in a \(<110>\)-type direction and four elongations in a \(<100>\)-type direction, which is in accordance with the higher occurrence of DLDs along \(<100>\) directions.

Matsui et al.\(^{58,81}\), and Nannichi et al.\(^{65}\) propose a model that relies on a combination of conservative glide and nonconservative climb model to explain the observed dislocation extension. They cite as a concern regarding solely-climb models, the lack of a verifiable drive force that would concentrate point defects at the tips of dipoles and the fact that dislocations extend in different crystallographic directions at different rates (e.g. \(10^{-6}\) in \(<100>\) directions and up to \(10^{-2}\) cm/s in \(<110>\) directions\(^{82}\)). The authors assume a short (~ of order nanometers) screw segment with Burger’s vector \(\frac{1}{2}\mathbf{a}<110>\) that cross-slips alternatively onto two other \{111\} planes containing the Burger’s vector (i.e. double cross-slips\(^{83}\)), such that the 60° dislocations traced out at the edge of the gliding screw segment give rise to the appearance of a jagged sided dipole as is seen in TEM images. This glide model is shown in Figure 2-12 for a screw segment with Burger’s vector \(\frac{1}{2}\mathbf{a}[011]\), in which the general direction of the “dipole” is in the (-100) direction. As a driving force for glide, they reason that the faster recombination at the originating defect, and subsequently at the leading edge of the dipole, causes a thermal stress of order \(10^8\) Pa (in addition to residual stresses, e.g. from lattice mismatch) that drives the elongation of the dipole. Whereas regularly occurring double cross-slip produces a dipole with an overall \(<100>\) direction, the authors conclude that a preexisting anisotropy in residual stress can favor glide on only one \{111\} plane and thus give rise to a dipole in a \(<110>\) direction. They do use the climb model to explain the widening of the dipoles after initial extension.
2.3.3.4 Temperature rise in the vicinity of DLDs

Kobayashi et al.\textsuperscript{84,85} measured the temperature rise associated with dark line defects in laser diodes to be between 10 and 30ºC and attribute this effect to non-radiative current\textsuperscript{62,86} in the vicinity of the DLD. Nannachi et al.\textsuperscript{65} found the temperature of the active region to be ~10ºC hotter than ambient (based on laser output characteristics) although they stress that this is the average temperature and that temperatures at defects are likely higher. Thus, accounting for more efficient recombination and photon absorption at DLDs\textsuperscript{62,87}, Nannichi et al.\textsuperscript{65} use a simple model to compute that the temperature rise at a DLD may be as high as 100ºC. Furthermore, they report sudden irreversible loss of current rectification (resulting in ohmic behavior) that is associated with relative temperature rise at only one of many DLDs in a laser device suggesting the role of DLDs in a circuit shorting mechanism.
2.3.3.5 Role of residual stress

Although not the sole cause of DLD growth, residual, built-in stress in the laser diode has been associated with the appearance of DLDs. Kamejima et al. have systematically investigated the growth of DLDs under the influence of applied stress and current injection and have found that the growth direction of the DLD reflects the resolved shear stress on available \{111\} slip planes. For example, uniaxial compressive stress applied in the [110] and [-1-10] directions promotes DLD growth in the [-110] and [1-10] directions which are the projected directions on the (001) plane that a dislocation with a Burger’s vector component in the [110] or [-1-10] direction will move. Furthermore, DLD growth is not observed for laser diodes under stresses close to the limit of structural failure (e.g. $3 \times 10^8 \text{Pa}$) if there is no current injection. In contrast, they observe no defect generation under high current injection (e.g. $\sim 2 \text{kA/cm}^2$) if no stress is applied. Under application of both stress and current injection, they observe a set of threshold conditions above which the degradation rate dependence on the stress and current significantly increases. Thus, they conclude that both injection (i.e. source of non-radiative recombination energy) and stress are necessary for rapid defect growth. They further note that application of current injection reduces the stress threshold for dislocation glide by one order of magnitude.

2.3.3.6 Catastrophic failure

Immediate, or catastrophic, failure occurs when output intensities of the laser exceed $\sim 3 \times 10^6 \text{W/cm}^2$, due largely to unintentional current surges. Rapidly moving DLDs (200-400cm/sec) associated with catastrophic failure consist of arrays of high density dislocation tangles and recrystallized material. The DLDs appear to be due to recrystallization of highly non-radiative regions after the propagation of molten laser material within the active and mirror regions. Initial melting is likely due to intense non-radiative recombination at the laser surface or at an active region defect. Redistribution of Al in Al$_x$Ga$_{1-x}$As alloys is also observed upon recrystallization.

\[\text{For this experiment, the authors chose diodes that show very little aging under typical operating conditions; i.e. lasers with little residual stress as mentioned earlier.}\]
2.3.4 Laser degradation in other III-V material systems

While the above discussion has been concerned with degradation in Al\textsubscript{x}Ga\textsubscript{1-x}As/GaAs lasers, degradation in lasers fabricated from other III-V compounds have also been reported. Briefly, lasers employing GaInAsP on InP substrates have been reported to exhibit different degradation behavior (e.g. rate and orientation of DLD growth)\textsuperscript{1,92,93}. Lasers fabricated from InGaAsP/InGaP on GaAs substrates exhibit degradation traits similar to those of the Al\textsubscript{x}Ga\textsubscript{1-x}As/GaAs system\textsuperscript{60}. Lasers of InGaAs/Al\textsubscript{x}Ga\textsubscript{1-x}As on GaAs exhibit similar degradation rates for <110> DLDs but growth of <100> defects is suppressed, possibly due to the stress state of the InGaAs layer not being conducive to dislocation climb\textsuperscript{94}.

2.3.5 Improvement to Laser stability

Much can be done to improve the lifetime of Al\textsubscript{x}Ga\textsubscript{1-x}As edge emitting lasers. Yonezu et al.\textsuperscript{95} stress that careful substrate preparation to minimize dislocations threading through the active region removes the “seed” for nucleation of DLDs. Others\textsuperscript{96-98} have found that coating the mirror facets with a dielectric material (e.g. Al\textsubscript{2}O\textsubscript{3}) suppresses degradation that may originate at the mirror (although the lifetime improvement is most noticeable only for Al\textsubscript{x}Ga\textsubscript{1-x}As active regions with x 0.08 due to the fact that Al\textsubscript{x}Ga\textsubscript{1-x}As with lower Al concentrations are more stable against atmospheric oxidation which can be an important source of defects at the surface)\textsuperscript{99}. Still others have found that detrimental electron trap (e.g. As\textsubscript{Ga}) densities can be reduced by increased doping\textsuperscript{100}. Furthermore, increased concentrations of various dopants decreases the growth rate of DLDs due to pinning interaction between the impurities and defects involved\textsuperscript{54,101}. It has also been found that donor dopants increase the yield stress\textsuperscript{102} (i.e. decrease the mobility of dislocations) of III-V materials and that acceptor dopants decrease the yield stress\textsuperscript{103,104} (while the opposite is true for Si and Ge crystals).

Thus, as early as the late 1970’s (less than a decade after initial investigations of laser failure) there were reports of extrapolated (i.e. from accelerated lifetime testing), commercially feasible, edge-emitting-laser lifetimes of order 10\textsuperscript{6} h (i.e. > 100 years)\textsuperscript{105,106}. 
More recently, there have been reports of extrapolated VCSEL lifetimes of the same order.\textsuperscript{163}

2.3.6 III-V material behavior under high injection conditions

Prompted by observations of degradation in III-V semiconductor lasers, there have been a number of experiments designed to understand the behavior of III-V materials under extreme injection conditions. Following are summaries of the literature that is concerned with the effect that optical, electrical and e-beam injection have on III-V materials. It is found that several features of material degradation under these injection fluxes are similar to those observed in failed lasers and that the different injection types can produce similar effects. However, in some cases, specific properties of the material degradation have only been extensively studied for one type of injection so that only by considering all of these results together is a more complete understanding attained.

2.3.6.1 Experimental observation of optically induced material defects

Several researchers have subjected Al\textsubscript{x}Ga\textsubscript{1-x}As structures to optical pumping over the intensity range from \(\sim 5 \times 10^3\) W/cm\(^2\) to \(\sim 7 \times 10^5\) W/cm\(^2\) and with light both above and below the bandgap of the specific alloy of Al\textsubscript{x}Ga\textsubscript{1-x}As studied.

In one study\textsuperscript{107}, above bandgap light of wavelength 653nm, over the range of intensities, 6-660kW/cm\(^2\), caused DLD growth in the velocity range of \(\sim 5 \times 10^{-7}\) cm/s to \(5 \times 10^{-4}\) cm/s. Over this range of intensity, it was found that the velocity obeyed the super-linear relationship,

\[
\nu = CI^{1.8}
\]

Equation 2-5

where I is the optical injection intensity and C is a constant\textsuperscript{107}. Thus, as the REDM mechanism is expected to yield a linear dependence of dislocation motion on injection intensity, some other mechanism, possibly thermal excitation, was also operative\textsuperscript{107}. At
high temperatures (e.g. >~300ºC) and high stresses (e.g. >~20MPa) the effect of optical injection was not discernable from the effect of either the temperature or stress parameters\textsuperscript{108}.

Optical pumping at relatively lower intensities (~10\textsuperscript{3}W/cm\textsuperscript{2}) with above bandgap light (\(\lambda\)=616.4 & 647.1nm from a Kr-ion laser) produces climb defect structures identical to those observed in failed lasers\textsuperscript{68,109}, although only after some incubation period that may be dependent on strain conditions\textsuperscript{110} (e.g >16hr for 5x10\textsuperscript{3}W/cm\textsuperscript{2})\textsuperscript{68}.

At higher optical intensities (>1.5x10\textsuperscript{5}W/cm\textsuperscript{2}) the dislocation motion changes from the climb type as mentioned above, to a rapid but variable velocity\textsuperscript{107} glide type, at three orders magnitude greater rate (~10\textsuperscript{2}\textmu m/sec)\textsuperscript{111,112}. The change from climb to glide is reversible such that reducing the injection intensity below this level stops glide and again causes climb\textsuperscript{113}. As the sharp increase in dislocation motion does not obey the nearly linear dependence of dislocation motion on injection as is expected from the REDM mechanism, it is suggested\textsuperscript{113} that the affect is due to lower lattice “frictional” forces\textsuperscript{xii} (i.e. shear strength) in the presence of excited carriers\textsuperscript{114-117} or due to increased thermal excitation\textsuperscript{107}.

Climb is found to be favored on threading dislocation segments rather than on misfit dislocations\textsuperscript{113}. Furthermore, enhanced glide only occurs in “fresh” dislocations (e.g. from surface scratches) whereas only climb occurs on grown-in dislocations (presumably because strain compensation has already occurred near the grown-in dislocations)\textsuperscript{113}. DLD’s could not be generated in homoepitaxial junctions after ~250 hours suggesting the importance of heterointerfaces as point defect sources for dislocation climb\textsuperscript{68}.

In order to determine the nature of the climb mechanism, be it by vacancy emission or interstitial absorption, Hutchinson et al.\textsuperscript{118} optically pumped (15-20kW/cm\textsuperscript{2} for 1-80min) tellurium doped (4.4x10\textsuperscript{18}/cm\textsuperscript{3}) GaAs. Prior to pumping, samples were annealed for 5hr at 880ºC after which time, dislocation loops that had formed as a result of the condensation of the interstitial point defects ceased to grow, presumably because

\textsuperscript{xii} A simple interpretation of the theoretical work done by the referenced authors (namely Van Vechten et al.) is that the generation of an electrical carrier in a semiconductor is at the expense of a crystal bond within a diffusion length of that carrier. Thus, after the carrier generation, there is one less bond to break during the incremental glide of that atomic segment of a dislocation line where the missing bond exists.
no excess interstitials remain in solution. However, during optical pumping, it was observed that segments of these loops (only in the pumped regions) expanded into long dipoles with a defect structure identical to that observed in failed laser material. Due to the fact that no interstitials remained in solution, this growth suggests that the climb proceeds by vacancy emission, enhanced by non-radiative electron-hole recombination. Furthermore, this result suggests that continued growth by vacancy emission would eventually lead to a concentration of vacancies in the region of the defect (defined by the pumped region, outside of which vacancy migration is not enhanced) that will constitute a chemical force against further climb (in the form of a increasing concentration gradient away from the defect).

The precise structure of the dislocation under excitation determines its responsiveness to the excitation presumably due to the energy level that it introduces in the bandgap. For example, $\alpha$-dislocations react strongly to optical excitation whereas $\beta$-dislocations are not affected to the same extent\textsuperscript{119} suggesting that the energy level of the $\beta$-dislocation is sufficiently close to the valence band that non-radiative recombination from that energy level is insufficient to cause as great a measurable effect of REDM. Furthermore, electrically neutral edge dislocations (i.e. causing no midgap states presumably due to extensive reconstruction of bonds along the core) do not behave as strong non-radiative recombination centers and thus are unresponsive to injection conditions\textsuperscript{120}.

The operation of an injection-assisted mechanism (such as REDM) is further demonstrated by pumping $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with photons of energy greater and lesser than the bandgap of the material\textsuperscript{121}. For above bandgap photon energies, dislocation glide and climb occur for optical intensities of $10\text{kW/cm}^2$ (at ~646nm) while for the below bandgap photon energies (800 nm), no materials degradation is detected. More generally, light with a wavelength close to the bandgap of the material causes the greatest effect, while light of wavelength far above or below the bandgap (e.g. by 300nm) is observed to have less or no effect\textsuperscript{108}. 
2.3.6.2 Experimental observation of electrically induced material defects

There are few reports of dislocation dynamics in bulk III-V semiconductors under application of electrical current. However, there is a well-known effect of current injection on the bulk plasticity on other semiconductor materials (e.g. Si and Ge) and other materials (e.g. metals) known as the electromechanical or electroplastic effect. For example, in germanium, application of 0.2A/cm\(^2\) leads to a softening of the material by 30\%\(^{122}\). The effect, in general, saturates at high current densities and is most obvious at low temperatures. Since hardness is fundamentally linked to the mobility of dislocations, a possible explanation for the effect is that application of current decreases the interaction between point defects and dislocations\(^{122}\).

For Si, Makara et al.\(^{123}\) find a decrease in activation energy for dislocation motion of >50\% for a current density of ~1A/cm\(^2\). Furthermore, the authors find that dislocation velocity increases as the square of current density.

2.3.6.3 Experimental observation of electron beam induced material defects

Several researchers have found electron beam injection to cause long range dislocation motion similar to that observed by optical injection, as well as rapid dislocation oscillations (i.e. repetitive motion between two positions)\(^ {124}\). Misfit dislocations in Al\(_x\)Ga\(_{1-x}\)As\(_y\)P\(_{1-y}\)/GaAs heterostructures containing point defects due to 1-MeV electron irradiation exhibit climb when subsequently subjected to 200keV electrons with beam densities of ~10\(^{-2}\)A/cm\(^2\)\(^{54\text{xi}}\). As was seen with optical excitation, climb begins after an incubation period, then proceeds at a constant rate for a given beam density and finally ceases\(^ {54}\). The length of incubation and dislocation climb rate were functions of the beam current density. The rate of point defects arriving at the climbing dislocation, (presumably due to REDM), was estimated\(^ {\text{xiv}}\) to be 3x10\(^3\) defects/sec for a

\(^{\text{xiii}}\) While beam current densities approaching this value were employed in the work described in the thesis, no dislocation motion was observed. Presumably, the lack of observable dislocation motion was due to the fact that the samples employed in this work were not subjected to 1 MeV electron irradiation prior to imaging.

\(^{\text{xiv}}\) The author estimates the number of point defects involved as N ~ (area swept out by the climbing dislocation)/(average radius of a lattice site) and the rate of point defect arrival as ~N/(observation time).
50µA (~10^{-2}A/cm^2) beam and 7x10^2 defects/sec for a 25µA beam^{54}. In similar samples that did not undergo the 1MeV treatment, dislocation climb did not occur suggesting the lack of a critical density of the relevant point defect in the structure.

Under injection of 30keV electron radiation (in the range of 0.3 to 3.0 A/m^2) dislocations introduced from a surface scratch in a piece of GaAs glided in the [1-10] direction and were determined to have a Burger’s vector of type \( \frac{1}{2}a<110> \)\(^{125-128} \). As shown in the Arrhenius type plot for \( \alpha \) and \( \beta \) dislocations in Figure 2-13 irradiation can enhance dislocation motion by up to a factor of 10^5 (For purposes of later discussion, let \( T_C \) for curves such as shown in Figure 2-13 be the temperature above which the defect velocities in darkness and under irradiation are indistinguishable.)

![Figure 2-13. Effect of electron beam injection on glide velocity of \( \alpha \) and \( \beta \) dislocations\(^{126} \).]

Reductions in activation energy for dislocation motion are ~0.7eV (from 1.0 eV in the absence of irradiation) for \( \alpha \) dislocations and ~1.1eV (from 1.7eV in the absence of irradiation) for \( \beta \) dislocations for the irradiation levels indicated in Figure 2-13,
suggesting again that the energy levels in the bandgap for the two dislocation types are different. Varying irradiation levels does not affect the activation energy beyond the initial reduction mentioned above, but instead influences the prefactor \( \eta \), from Equation 2-3) such that dislocation velocity depends nearly linearly on irradiation intensity. Furthermore, the dependence of dislocation velocity under constant irradiation as a function of stress was similar to the dependence on stress in the absence of irradiation. Thus Maeda et al.\(^{126}\) model the velocity of the dislocations as shown in Equation 2-6.

\[
\nu(I) = \nu(\tau) \exp\left(-\frac{Q}{k_B T}\right) + \nu_t \left(\frac{I}{I_0}\right)^{0.84} \exp\left\{-\frac{(Q - Q_r)}{k_B T}\right\}
\]

\textit{Equation 2-6}

Here, the first term represents the typical stress and temperature dependent velocity of the dislocation in absence of irradiation (i.e. the Peierls model, where \( \nu(\tau) \) contains stress dependence) and the second term represents the increase in velocity due to irradiation. The irradiation prefactors, \( \nu_t \) and \( I/I_0 \), represent the efficiency and strength of the injection effect and can be changed to reflect other methods of injection (e.g. electrical current or optical irradiation).

The REDM effect is not observed for temperatures higher than \( T_C \), for low injection levels, or for low stress levels \((<10^7\sim10^8 \text{ Pa})\)\(^{89}\). The effect was completely reversible such that stopping the irradiation brought the dislocation velocity back to thermal equilibrium values. Similar dependencies of dislocation motion on electron beam injection were found for InP\(^{129}\).

Finally, it was mentioned previously that the various dislocations that occur in the III-V system behave differently under different doping conditions, i.e. that the mobility of dislocations depends strongly on the Fermi level of the material. To distinguish between this affect and the radiation enhanced glide motion discussed in the previous paragraph, it should be stressed that while \( \alpha \) dislocations are little effected by the Fermi level, (whereas \( \beta \) dislocations are strongly dependent on the Fermi level)\(^{25,28}\) under injection conditions, both \( \alpha \) and \( \beta \) dislocations experience measurable increases in mobility\(^{128}\).
2.4 III-V oxide materials

The need for current confinement in the VCSEL structure and other (opto)electronic device applications has spurred the development of the thermal oxide of $\text{Al}_x\text{Ga}_{1-x}\text{As}$. This oxide, along with the oxides grown from other III-V compounds (e.g. $\text{Al}_{1.49}\text{In}_{0.51}\text{P}$ and $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$), also has potential applications in electronic devices, such as Metal-Oxide-Semiconductor-Field-Effect-Transistors (MOSFETs), as an insulating material.

After their usefulness was realized about a decade ago, the understanding of these oxides has rapidly progressed (reference $^{130}$ and the citations therein), and although the growth kinetics can now be modeled empirically, an understanding of all the underlying materials issues which control the growth of the oxide does not exist. To date, studies have provided information about the dependence of oxide growth on oxidation conditions (e.g. temperature, gas environment), column III chemistry (e.g. Al to Ga ratio), and to some extent about the dependence on epitaxial architecture (e.g. buried lateral oxide layer thickness). Briefly, the oxidation process is thermally activated and the rate of oxidation increases exponentially with temperature. The use of a “wet” furnace environment (i.e. N$_2$ bubbled through 90°C water) produces the most robust oxide. The oxide retains the crystal’s Al to Ga ratio so that $\text{Al}_x\text{Ga}_{1-x}\text{As}$ oxidizes to become $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$, with As segregating to the interfaces and being desorbed as arsine. Decreasing the thickness of a laterally oxidizing layer below 200Å decreased the oxidation rate exponentially.

2.4.1 Theoretical considerations

Here we give a brief review of the fundamental mechanistic considerations underlying the oxidation of III-V semiconductor materials. Like the often-cited theoretical work on III-V oxidation by Wilmsen$^{131}$, much of that which follows borrows from our understanding of metal oxide growth, and the detailed work on the oxidation of silicon by Deal and Grove$^{132}$.

In the following discussion on the mechanics of oxidation, we consider a sample situated at some time after oxidation begins; that is, a portion of the material has already
been oxidized and possible initial transients in oxidation rate are no longer operative. Additionally, this discussion is largely limited to high temperature (>350ºC) steam oxidation due to its relevance to our experimental work.

### 2.4.1.1 Fundamental reactions

The oxidation reaction most relevant to this work is given in its simplest form in Equation 2-7, where M is the atom to be oxidized.

$$M + 0.5O_2 + H_2O \rightarrow M(OH)_2$$

**Equation 2-7**

Oxygen molecules are directly supplied via dissociation of water molecules or are produced as byproducts of secondary reactions (e.g. breakdown of intermediate oxide compounds). Other oxide molecules (e.g. M$_2$O$_3$) can be formed depending on the amount and valency of the reactants.

This reaction can be broken into two separate, equally important reactions given as an anodic reaction (Equation 2-8) and a cathodic reaction (Equation 2-9)$^{133}$.

$$M \rightarrow M^{++} + 2e^-$$

**Equation 2-8**

$$0.5O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$

**Equation 2-9**

As discussed below, for oxidation to occur, both of these reactions must take place, although there likely exist other reactions that both influence and depend on the products and reactants in Equation 2-7 through Equation 2-9 (e.g. the reactions controlling the availability of H ions$^{135}$). Furthermore, the slower of the anodic and cathodic reactions will be most influential in determining the measured oxidation rate. It
is important to note that it is necessary for electrons to be transported from the location of the anodic reaction to that of the cathodic reaction should these occur at separate locations along the oxide length.

### 2.4.1.2 Dominant mechanisms

Most generally, the oxidation of materials is controlled by two main mechanisms. These are, (i), the chemical reactions given above, between the oxygen containing species and the material to be oxidized (i.e. III-V constituents), and (ii), the transport mechanisms that bring these reactants together. Transport can occur via, (a) the diffusion of oxygen containing species through the previously formed oxide layer to the oxide/crystal interface, (b) the diffusion of III-V ions through the previously formed oxide to the steam/oxide interface, or (c) a combination of both of these. It is relevant to note that the oxidation of metallic Al occurs via transport mechanism (a) whereas the oxidation of metallic In occurs via transport mechanism (b)\(^\text{131}\).

The dominant transport mechanism and the overall chemical reaction rate will depend heavily upon chemistry, among other parameters, as is discussed below. The rate of the overall oxidation process is controlled by the slower of either the transport rate or chemical reaction rate. That is, if the chemical reaction consumes reactants faster than they diffuse to the reaction front, the oxidation rate will decrease as the length increases (i.e. it takes longer to replace the reactants at the front) and hence, the oxidation rate will be diffusion limited and often parabolic with time as is described mathematically below. If, on the other hand, the transport mechanism always supplies more than enough reactants to the oxidation front, the oxidation rate will be constant with oxide length and will be limited by the chemical reaction rate and hence, linear with time. Often, an initially linear oxide layer will gradually become parabolic at longer times. Thus, a combination of parabolic and linear growth dependencies most accurately reflects measured oxidation kinetics\(^\text{134}\) as is given in
\[
\frac{d^2}{k_p} + \frac{d}{k_i} = t + t'
\]

**Equation 2-10**

where \(d\) is the oxide length, \(k_p\) and \(k_i\) are parabolic and linear rate constants respectively, \(t\) is the oxidation time and \(t'\) is a constant that incorporates the length of pre-existing oxide, a nucleation time for oxidation to begin, or an initial transient in oxidation rate as observed in the oxidation of Si\(^{32}\).

The rate constants, \(k_i\) and \(k_p\), incorporate activation energies and diffusion properties. Assuming for the moment linear oxidation, the rate of oxidation can be modeled as,

\[
d = k_i t = k e^{-E_A/k_B T t}
\]

**Equation 2-11**

Similarly, in the purely parabolic regime,

\[
d^2 = k_p t = k e^{-E_p/k_B T t}
\]

**Equation 2-12**

Here, the thermally dependent exponential term containing the activation energy represents the probability of the complete oxidation reaction occurring (i.e. one column III or column V atom reacting to become one \(\text{M}_2\text{O}_3\) molecule) and depends on the energy exchanges (e.g. heats of formation) and energy barriers involved (e.g. ion migration barriers). The prefactor, \(k\), represents attempt frequencies (e.g. as for ion migration). Thus, measurements of activation energy, \(E_A\), are common in characterizing oxidation and will be employed in the results section of this chapter. However, single-valued activation energies and prefactors alone will not always accurately predict oxidation rates...
as the actual rate may be heavily influenced by additional factors such as electric fields or structural changes (e.g. microscopic pore development).

### 2.4.1.3 Chemical Parameters

It is likely that all constituents of the III-V compound will react to some extent with oxygen to form oxide compounds\(^{131,135}\). However, there is evidence that some III-V oxide materials contain a small volume fraction of unoxidized III-V or metallic nanoparticles\(^{130,221}\). Various factors, such as heat of formation of crystal constituents, oxidation potentials\(^{xv}\) of individual III-V constituents, vapor pressures of III-V constituents and their respective oxides, and heat of formation\(^{xvi}\) of these oxides, determine the final structure of the overall oxide. Values of these parameters for the elements and compounds relevant to the work are listed in Table 2-1, Table 2-2, and Table 2-3.

For instance, column III elements have higher oxidation potentials than column V elements and thus will be oxidized more readily once unbonded. This coupled with the fact that the oxidation potential differs for each element means that it is possible to form chemically segregated oxides (especially at the oxide reaction front) from III-V compounds. The degree of this segregation also depends on the mutual solubility of the different oxides. Another well known phenomenon is that the oxidation rate increases rapidly for Al\(_x\)Ga\(_{1-x}\)As as \(x\) increases, which is a reflection of the higher oxidation potential of Al and higher heat of formation of Al\(_2\)O\(_3\).

Furthermore, the relatively low vapor pressures for As and its oxide, As\(_2\)O\(_3\), coupled with a relatively low heat of formation for As\(_2\)O\(_3\) mean that As and its oxide are likely to evaporate from the oxide more readily than will column III elements and oxides. However, the most probable oxide of P, P\(_2\)O\(_5\), has a heat of formation similar to that of

---

\(^{xv}\) The oxidation potential is a relative measure of the tendency for the removal the valance electrons from an atom (as in Equation 2-8) relative to the same tendency in hydrogen. A positive sign indicates that the atom is more reactive than the hydrogen oxidation. (The term potential refers to a measured voltage in the technique used to determine this quantity).

\(^{xvi}\) The heat of formation (for the compound or oxide) is the energy exchanged with the environment when forming a compound from its constituents. A negative value indicates that the reaction to form the compound releases energy to the environment. Thus a more negative heat of formation means that the reaction will occur more readily.
the column III oxides as well as a relatively high melting point (compared to $\text{As}_2\text{O}_3$) and thus it is expected to remain in the oxide to a greater degree than $\text{As}_2\text{O}_3$. Both the absence of As and $\text{As}_2\text{O}_3$ and the presence of a P oxide in oxides of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_{0.5}\text{Al}_{0.5}\text{P}$ respectively have been confirmed in my previous work\textsuperscript{130}. Additionally, a chemically segregated oxide is formed from the surface oxidation of $\text{In}_{0.5}\text{Al}_{0.5}\text{P}$,\textsuperscript{221} which likely reflects on the discrepancies in oxidation potential of Al, In and P as well as in heats of formation of $\text{Al}_2\text{O}_3$, $\text{In}_2\text{O}_3$ and $\text{P}_2\text{O}_5$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation Potential$^{\text{xv,136}}$</th>
<th>Vapor Pressure$^{\text{137}}$ at 450ºC (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>+0.40</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Ga</td>
<td>+0.65</td>
<td>$10^{-11}$</td>
</tr>
<tr>
<td>Al</td>
<td>+1.67</td>
<td>$10^{-11}$</td>
</tr>
<tr>
<td>As</td>
<td>-0.25</td>
<td>$10^{1}$</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>$10^{3}$</td>
</tr>
</tbody>
</table>

Table 2-1. A table of parameters relevant to oxidation for the III-V constituents used in this work\textsuperscript{131}.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of formation$^{\text{138}}$ (eV/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs</td>
<td>-0.61</td>
</tr>
<tr>
<td>InP</td>
<td>-0.92</td>
</tr>
<tr>
<td>GaAs</td>
<td>-0.73</td>
</tr>
<tr>
<td>GaP</td>
<td>-1.06</td>
</tr>
<tr>
<td>AlAs</td>
<td>-1.21</td>
</tr>
<tr>
<td>AlP</td>
<td>-1.73</td>
</tr>
</tbody>
</table>

Table 2-2. Heats of formation of the relevant III-V binary compounds\textsuperscript{131}.
<table>
<thead>
<tr>
<th>Oxide</th>
<th>Heat of formation (eV/molecule)</th>
<th>Melting or decomposition temperature (°C)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>-7.59</td>
<td>1565</td>
<td>3.1</td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>-9.28</td>
<td>1725</td>
<td>4.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-15.39</td>
<td>2045</td>
<td>8-10</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>-6.55</td>
<td>315</td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>-14.00</td>
<td>580</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-3. Properties of relevant III-V oxides$^{131}$. Melting or decomposition temperatures, which are inversely proportional to vapor pressures, are given here, as vapor pressures for some oxides listed are unknown.

2.4.1.4 Electronic Processes

An additional mechanism influencing the oxidation rate is the transport of electrons and the possible buildup of a non-uniform charge distribution leading to an electric field along the oxide layer. For example, after a III-V element is unbonded from the crystal, and before it can bond to an oxygen containing molecule (e.g. O$^-$, or (OH)$^-$), it must give up valence electrons (with an ease proportional to its oxidation potential). Three possible scenarios then occur. (i) If electrically neutral H$_2$O molecules readily diffuse to the oxidation front via a concentration gradient, they will dissociate there, and form an oxide plus electron (and possibly H) byproducts. However, (ii) if H$_2$O molecules do not readily diffuse through the oxide, they must disassociate at the sample surface, and then O$^-$ will diffuse into the oxide while electrons from III-V constituents and previous products of the oxidation reaction diffuse out to maintain charge balance. (iii) Finally metal ions and electrons may diffuse to the oxide/steam interface where oxidation will occur. However, if the transport of electrons is limited, the oxidation can be stalled due to electron charge build up at the oxidation front and hence: reduced availability of electron energy states for III-V constituent ionization or electron transport which slows (i) and (iii), or through the development of the electric field which slows (ii). Some oxides that are good insulators (i.e. with very high bandgaps such as Al$_2$O$_3$ with $E_g = 8-10$eV) have limited transport of electrons and thus fall under this scenario. Oxidation with time for these
oxides and others where electron transport is limited has been reported as asymptotic or logarithmic in nature for longer oxidation times.

Furthermore, electrically active defects sites (e.g. oxygen vacancies or III-V constituent vacancies) constitute the primary path by which ion and electron diffusion through the oxide occurs. The number of electrically active defects, and thus Fermi level of, the oxidized material will influence oxidation rates. The Fermi level of the oxide is strongly influenced by the Fermi level of the crystal through band alignment, and thus may vary as the bandgap of the crystal varies.

2.4.1.5 Structural and geometrical parameters.

There are only a few reports dealing with the effect that structural parameters (e.g. applied strain or pressure) and geometrical parameters (e.g. lateral versus surface oxidation, thickness of lateral oxide layers) have on the oxidation of semiconductors. For the lateral oxidation of Al$_x$Ga$_{1-x}$As, it is known that as the oxide layer thickness decreases below ~50nm, the oxidation rate decreases exponentially and that this effect, which includes an increase in activation energy, may be explained by the surface energy increase due to the increasing oxide front curvature (i.e. the Gibbs-Thompson effect). It has also been shown that decreasing the spacing of laterally oxidizing layers to below ~12nm increases the lateral oxidation rate as reactants and products from the neighboring oxidizing layers interact. Furthermore, it has been shown that the activation energy of the lateral oxidation of Al$_x$Ga$_{1-x}$As (1.2eV to 1.9eV for the range of x = 1.0 to 0.92) is generally higher than the activation energy for surface oxidation (1.1eV to 1.8eV for the range of x = 0.78 to 0.48). Finally, it has been proposed that the removal of As (in the form of AsH$_3$) from the oxide causes the oxide to become porous. This porosity, reportedly, facilitates H$_2$O transport through the oxide leading to the observed rapid linear lateral oxidation rates.

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xvii Although similar to logarithmic growth, asymptotic growth of an oxide never extends past some critical length.

xviii Although the composition ranges for the surface and lateral oxides referenced do not overlap, the fact that the activation decreases with increasing x suggests that the surface oxidation of higher x material would be lower than the reported activation energy for the lateral oxidation of AlAs.
Additionally, though not mentioned in the literature regarding oxidation of III-V materials, it is known\textsuperscript{230-232} that there can be an effect on the activation energy for oxidation (e.g. of Si) due to the development of internal stresses during oxidation. The effect can be twofold, resulting in an increase in the activation energy for diffusion of reactants (e.g. as extra work which the diffusing reactants must do against the pressure field) and in an increase in the activation energy of the reaction (e.g. as extra work which must be done against the pressure field if there is an increase in volume upon formation of the oxide).

Finally, there are no known articles that report on the effect that epitaxial strain (one of the main parameters of the oxidation studies herein) has on the activation energy for oxidation. However, for oxidation of strained materials, the release of strain energy during the conversion of the III-V crystal to amorphous oxide may provide additional excitation for oxidation, thereby lowering the activation energy. The magnitudes of these factors are discussed in Section 6.3.
3 Experimental Methods used in this work

Transmission Electron Microscopy (TEM) diffraction contrast imaging has been used to characterize material degradation in failed VCSEL devices (e.g. dislocation patterns or fractures). Energy Dispersive X-ray Spectroscopy (EDXS) performed in the TEM has been used to check the composition of the compounds used for the oxidation experiments described in this work. Focused Ion Beam (FIB) milling has been used for sample preparation of thin film foils for TEM imaging and for in-situ electrical experiments. The first two sections of this chapter describe the experimental procedures employed in the study of degraded VCSELs and of the oxidation of III-V compounds while the remaining sections describe the operations of the TEM and FIB which are relevant to the experiments in this work.

3.1 VCSEL degradation experiments

Several experimental methods have been developed in this work in order to elucidate the nature of VCSEL degradation. Of interest are, the locations of nucleation sites for defects, the final defect configuration within the VCSEL, the effect of the various components of the VCSEL (e.g. mirror layers or current confinement strategies) on defect generation, and the nature of the defect growth with respect to current injection conditions.

In order to determine typical defect nucleation sites and final defect arrangements in failed oxide confined VCSELs, a series of devices have been operated to various levels of failure (i.e. one current was chosen for a given device, and that device was then operated for various times at that current). The operating conditions for the VCSELs used were chosen so that failure readily occurred on the time scale of minutes to hours (so that an extensive data set could be developed) but for which catastrophic failure did not occur. In addition, even for the accelerated degradation conditions, it was necessary to choose device sets from within a single processed batch that exhibited uncharacteristically short lifetimes. The extent of the failure was characterized by a P-t
(i.e. power output versus time at constant current) chart, an example of which is depicted in Figure 3-1. The time series shown is indicative of a loss of lasing capability although the device is still capable of emitting a small level of spontaneous emission. Indication of output power after degradation relative to output power prior to degradation is given in P-I (i.e. power vs. current) charts like that shown in Figure 3-2. In such charts, lasing is typically indicated by a relatively steep rise in output intensity after the threshold current is reached (although the precise threshold current is that for which spontaneous emission levels equal stimulated emission levels, for purposes of discussion, the threshold current of the laser for which the P-I curve is shown in Figure 3-2 is \(~18\text{mA}\)).

Many other devices were investigated in order to add breadth to understanding of the failure mechanism operative in VCSELs. These include a number of commercially available VCSELs (oxide and proton implant confined) that have undergone failure in the field and two oxide confined VCSELs that have catastrophically failed.

Figure 3-1. Example of power vs. time at a forward bias current of 23mA during degradation of VCSEL V1.
Figure 3-2. Example of power vs. current traces before and after degradation.

To enable characterization of these samples, a sample preparation technique was devised for which the use of a Focussed Ion Beam (FIB) was crucial. Of primary interest is the defect microstructure in the active region of the VCSEL. For this reason, a novel FIB technique is used, whereby, for the first time it is possible to reliably and consistently view the entire active region of a solid state laser in the TEM. Previous studies in this field have typically relied upon thinning small volumes of the structure to electron transparency, raising extensive questions about the statistical significance of such small sample regions, and the conclusions drawn there from. Using the present technique, the active region is isolated with the FIB\textsuperscript{xix} in a planview configuration as depicted in Figure 3-3 and Figure 3-4. It should be noted that a few mirror layers are left intact on either side of the membrane in order to prevent damage to the active region. Furthermore, as is seen in some of the planview data, a slight unintentional angle between the Ga\textsuperscript{+} beam and the heteroepitaxial planes of the VCSEL causes the membrane surface to intersect several DBR layers as is seen in Figure 3-4. Planview samples manufactured under slight tilt.

\textsuperscript{xix} In this work, a FEI FIB200 employing a 30keV gallium ion source.
will thus exhibit bands of contrast associated with the intersection of different DBR layers with the membrane surface. The bands may be in the form of bars perpendicular to the beam direction, or if the membrane is slightly bent, there may instead be non-uniform regions of contrast variation. For example, for a DBR structure with 100nm layers, and a 10µm long membrane, 1º of misorientation will result in at least one change on surface composition according to,

\[ n = \frac{w \sin(\Theta)}{l} \]

**Equation 3-1**

where \( n \) is the number of DBR interfaces intersected, \( w \) is the length of the membrane, \( h \) is the angle of misorientation and \( l \) is the width of the individual DBR layers.

![Figure 3-3. Schematic of finished planview sample geometry.](image)
The following steps are taken to prepare a planview TEM sample of a VCSEL active region. The itemized steps below correspond to those shown in Figure 3-5.

Step 1 in Figure 3-5 shows a planview schematic (i.e. parallel to the VCSEL output direction and perpendicular to the interfacial planes of the VCSEL) of a sample bar containing a VCSEL. In order to limit the amount of milling in the FIB, 6µm grit diamond lapping paper is used to grind that edge of the sample bar that will eventually be at the top of the membrane to within 20µm of the edge of the VCSEL.

Step 2 requires a TEM support grid (grids with small holes in the center are usable) that has been cut in half. The sample bar is mounted surface side down on the Cu grid with the VCSEL overhanging the edge of the grid as depicted. Hardman quickset epoxy is applied with a sharpened stylus to the area of the grid that will receive the sample bar. Once cured, this epoxy conveniently softens after a 30 second soak in acetone so that epoxy which has been accidentally applied over the VCSEL can be scraped off with a soft wooden stylus (this quick soak in acetone does not cause the sample bar to fall off).

In step 3 the bulk of the VCSEL substrate is removed. Leaving 50-100µm is sufficient to prevent fracturing.

Step 4 is performed in the FIB. Most of the remaining material next to the desired placement of the top of the membrane is removed with an 11nA Ga ion beam (a few µm
are left next to the VCSEL to allow for finer milling with an 1nA Ga ion beam so that the DBR layers can be imaged in the FIB).

In step 5, first the majority of the remaining substrate is removed with an 11nA Ga ion beam. A 2.7nA beam is used to mill to within 500nm of the active region (which is now visible after the 1nA polishing mill described in step 4). A 1nA beam is used to mill the membrane to its final thickness. (While it is common to use a smaller beam current (e.g. 70pA-150pA) in the final stages of membrane fabrication, the relatively large area of the plan-view membranes (approaching 5000µm² relative to ~150µm² for a cross-section membrane) made it convenient to use a larger beam current. Furthermore, TEM images of membranes finished with a 1nA beam did not show significantly increased levels of surface damage relative to membranes fabricated with smaller beam currents.)

![Diagram of sample preparation steps](image)

**Figure 3-5. Steps involved in planview sample preparation.**

Cross-section samples have also been important in characterizing degraded structures. As in the planview samples, use of the FIB makes possible the isolation of a membrane in the center of the degraded VCSEL as depicted in Figure 3-7.

Preparation of cross-section samples is as follows. A sample bar is placed on a Cu TEM support grid with Hardman epoxy as is depicted in Figure 3-6. The thickness of...
the bar should be 100μm or less to limit FIB milling time. The sample is placed in the FIB such that the beam direction is perpendicular to the VCSEL surface. A protective Pt layer can be laid down over the desired membrane location. (Briefly, this is accomplished in the FIB by reaction of the gallium ion beam with a Pt-containing metal-organic compound introduced in the immediate vicinity of the desired deposition area\textsuperscript{142}). A 11nA Ga ion beam is used to mill trenches on either side of the VCSEL though which the TEM beam will pass. A 2.7nA beam is used to mill up to within ~500nm of the membrane location. A 1nA beam is used to finish the membrane to 500nm thickness. The final membrane is as depicted in Figure 3-7.

Thus, the use of the planview and cross section techniques together (e.g. one membrane of each type for two similarly degraded VCSELs) provides a clearer three-dimensional picture of any material degradation present.

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Figure 3-6. Schematic of cross-section sample prior to membrane fabrication.
3.1.1 TEM analysis

TEM analysis is critical for structural investigations of material failure in VCSELs. However, it was noted in a previous work on VCSEL degradation that, TEM “…sample preparation for VCSELs is nearly impossible, and so the investment per sample is enormous... thus conclusions drawn from TEM results usually are based on a couple of ‘lucky samples’.“\textsuperscript{162} Fortunately, with the new FIB techniques described above this author was able to obtain better than 90% sample preparation success.

As discussed in Section 3.3.2.3.1, it is the property of crystal dislocations and planar crystalline defects that they give rise to a local strain field in an otherwise perfect crystal which permits their detection by TEM\textsuperscript{xx}. Other defects such as cracks or large-scale voids are also detected in the thin TEM samples by the simple fact that their corresponding vacuum regions do not interact with the electron beam and thus give rise to zero diffracted intensity.

As discussed previously, crystal dislocations are largely responsible for DLD’s, those regions of the laser material that are incapable of generating light. The properties of these dislocations, such as Burger’s vector and crystallographic orientation are also discernable by TEM.

Several texts give detailed explanations of the precise physics underlying electron beam/dislocation interaction and imaging\textsuperscript{143,144,145} while a brief summary of relevant TEM physics is given in the later sections of this chapter.

\textsuperscript{xx} In this work, a JEOL 2000FX employing 200keV electrons.
3.1.2 Details of TEM use for this work

The large area of the FIB prepared samples used in this work, and the fact that the membrane was the only large thin region on the entire sample bar, typically made it straightforward to locate the sample area in the TEM. In cases where the membrane location was not immediately obvious (e.g. in cases where the sample was tilted significantly with respect to the electron beam), the TEM was operated in scanning mode, and a secondary electron image collected, allowing for quick determination of the membrane location. Ideally, objective astigmatism was corrected at the upper edge of the membrane, on a thin region having a high radius of curvature\textsuperscript{xxi} by making the first Fresnel fringe (present upon slight defocusing) have uniform thickness. Alternatively, an amorphous region (sometimes present at the upper edge of the membrane due to FIB damage, or a region of carbon buildup) was checked for streaking, which if present was minimized by adjusting the objective stigmator settings. Focusing was performed by obtaining the sharpest (i.e. narrowest) dislocation images or in samples that lacked dislocations, by obtaining the sharpest oxide edge image (using the more conventional focusing procedure whereby the defocus is set to \(\sim100\)nm below minimum contrast, obtained at a thin edge, had somewhat ambiguous results for the plan-view samples due to the fact that the features of interest, for example the dislocations, were bounded by several hundred nanometers of material on either side).

The thickness of the samples (>1\(\mu\)m in some instances) made it difficult to observe features on the TEM screen. In this case, turning the TEM console lights off helped. Due to the thickness of the samples it was often necessary to acquire images with exposure times exceeding 1 minute (up to 3 minutes for low contrast diffraction conditions).

For this work, two beam conditions along the \(<110>, <001>\) and \(<112>\) zone axis are used for imaging and Burger’s vector analysis. Characterization of the degraded lasers generally did not require magnifications above 10,000x. A condenser aperture of

\textsuperscript{xxi} These regions typically occur at the upper two corners of the membrane due to milling by the tails of the gallium ion beam.
intermediate diameter (120um) was employed (per the trade off between being able to view sample features on the TEM screen for these very thick membranes, and minimizing the interaction between the sample and the electron beam). For two-beam imaging, an objective aperture of intermediate diameter (50um) was used (per the trade off between being able to view sample features on the TEM screen for these very thick membranes, and being able to select only one beam for imaging). Subsequently, beam currents of order $10^{-3}-10^{-2}$Acm$^{-2}$ were incident on the sample.

### 3.1.3 Stereographic Viewing

Stereographic viewing is an important aid in understanding the three dimensional spatial distribution of features contributing to the contrast in a two dimensional TEM image. Briefly, two images are taken using the same diffracting conditions (typically, the 220 two beam condition oriented approximately along the $y$ tilt axis, which gives strong dislocation contrast and which, in the JEOL 2000FX allows for easily controllable tilt via the manual $x$-axis goniometer), and at the same magnification (10,000) but separated by 5-15 degrees of tilt. When viewed with appropriate lenses (e.g. with one image for each eye) the brain is able to perceive the effect of the tilt (e.g. a parallax shift) as three-dimensional information.

In this thesis, anaglyphic images (the backbone of 3D movies) are used to represent stereo image pairs. Instead of using separate images for each eye, two images are superimposed in an RGB color image, one through the red spectrum and the other through the blue and green spectrums. When viewed with the appropriate glasses (one eye covered by a blue filter and the other by a red filter), the three-dimensional effect is produced.

Briefly, the anaglyphs are made as follows. In Adobe Photoshop, the scanned, grayscale images are copied into the same grayscale image file, each on its own layer. The transparency of the top layer is set at 50% so that the two images can be aligned and then the transparency of the top layer is returned to 100%. A new RGB color file is

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$^{xxii}$ It is important to make focus adjustments with the z-height control and not the objective lens current as adjusting the latter changes the magnification slightly.
created and one image is pasted into the red palette and the other image is pasted into the blue and green palettes. To insure the correct perception of orientations, if the right eye is to be covered with a blue lens (i.e. red will be blocked from that eye) the image taken from the right-hand tilt must be placed in the blue and green channel.

This form of 3D representation seems most appropriate for use in a printed thesis. Furthermore, whereas with a stereo viewer the user is typically restricted to the viewing direction perpendicular to the plane of the image, with a printed anaglyph, the user can tilt and to some degree rotate the paper to obtain a better feel for the three dimensional nature of the sample features. To our knowledge, this is the first recorded use of anaglyphs to analyze dislocation structures in materials.

In this thesis, the proper eye-lens combination is given in the caption of each anaglyphic image. Some individuals may not be able to perceive the effect. Finally, it has been found that viewing the images in natural light produces the strongest threedimensional effect.

### 3.2 Oxidation Experiments

We employ a range of undoped III-V compositions (Table 3-1), on multiple III-V substrate types, to investigate the role of epitaxial strain and column V chemistry on the growth kinetics of III-V thermal oxides (and as a corollary, to assess the suitability of these substrates for lateral oxidation under various oxidation conditions). These materials have been supplied by Prof. Russell Dupuis’ group from the Micro Electronics Research Center at the University of Texas at Austin.

The principal experiments in the study of these oxides have involved two structures (A and B) each comprised of multiple heteroepitaxial layers of various compositions of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, which are given in Table 3-1. The thickness (~100nm) of each of the layers used in these structures (as well as in further samples C, D and E) is such that strain relaxation via interfacial dislocations is suppressed and thus the strain in these layers is primarily defined by the inter-atomic spacing of the epilayer being constrained to the lattice parameter of the substrate (i.e. misfit strain).

Epilayer strains were measured by x-ray diffraction by Prof. Dupuis’ group. Planview TEM samples of each of the oxide layers were checked (at The University of
Virginia) for strain relief by the counting of misfit dislocations as explained in Appendix-B. (This has implications in the subsequent determination of composition as is described below). For all but one sample, the strain relief is less than 10% of the fully strained value.

Compositions of the samples were determined by XRD at the University of Texas (as described below), and were checked by energy dispersive x-ray spectroscopy (EDXS) at the University of Virginia. The compositions obtained by EDXS agreed within experimental uncertainties (generally 7% error in the Al or As fraction (i.e. x or y) as determined from x-ray counting statistics) with the x-ray diffraction results. However, layers grown with small percentages of P (e.g. <5% of the entire compound) were difficult to verify due to poor counting statistics yielded from the relatively week P x-ray signal. Furthermore, for one sample (sample D) dependable spectra were not obtainable via EDXS due to preferential milling during sample preparation. Finally, the compositions determined by XRD had less uncertainty (as described below) so that the compositions determined therefrom are used in this thesis.

Briefly, the composition of an epilayer was determined by x-ray diffraction as follows. An x-ray rocking curve was obtained that gave the angular distribution of reflected x-ray intensities for a small range (~2°) of incident angles about a main reflected x-ray beam; e.g. 004. The strain perpendicular to the plane of the substrate, ε, was determined by the degree of separation of the substrate peak and the epilayer peak (the peaks correspond to conditions satisfying the Bragg condition). The biaxial, in-plane strain was then determined from the strain perpendicular to the plane of the substrate via elasticity theory (i.e. ε=(1-ν)/(1+ν)ε 17). From the in-plane strain states, the strain-free lattice parameter of the epilayer, a, was determined (i.e. a = a + a, where a is the lattice parameter of the substrate). Finally, the composition was found from the known dependence of the lattice parameter on composition.

The accuracy of this measurement and the composition determined thereby depends on the accuracy of the peak separation determination. The layers in this work having the lowest strain (e.g. A-5) have the highest uncertainty from peak-separation determination of approximately ±0.05x10^-3 (~5% of the total strain value). The accuracy of the composition determination by this method is further affected by the degree of
strain relaxation (the above method assumes no relaxation). However, due to the significant dependence of lattice parameter on chemistry for the quaternaries employed, a strain relaxation, for example of $0.22 \times 10^{-3}$ in layer A-4 (the layer having the greatest relative strain relaxation) corresponds to an error in column V chemistry (i.e. y) of $\pm 0.5\%$.

The chart in Figure 3-8 depicts the strain and column V chemistry in samples A and B. By growing $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ ($y>0.75$) on GaAs, the amount of tensile strain can be increased, via lattice mismatch, by increasing the P concentration. Thus, in Figure 3-8 layer 1, composed of $\text{Al}_{0.93}\text{Ga}_{0.07}\text{As}_{0.80}\text{P}_{0.20}$, has the highest level of tensile strain. By growing $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ ($y<0.25$) on a GaP substrate, the level of compressive strain can be increased by decreasing the P concentration. Thus, layer 9, composed of $\text{Al}_{0.97}\text{Ga}_{0.03}\text{As}_{0.20}\text{P}_{0.80}$, has the highest compressive strain. The use of the two different substrate types is necessitated by the need to limit the mismatch strain of the compositions grown to less than 1% (which roughly corresponds to the level above which substantial strain relief via dislocations occurs for the employed layer thicknesses of $\sim 100\text{nm}$). For the same reason, and because of the strain dependence on column V chemistry, the range of usable P concentrations is limited.

The sample sets A and B are devised with the intent of making it possible to deconvolute the effect of lattice strain from column V chemistry. Although strain in these experiments is linearly dependent on column V chemistry, is it probable that these two parameters affect oxidation kinetics through different mechanisms as discussed above. As displayed in Figure 3-8, the strain steadily increases over the sample set while the P concentration steadily decreases apart from a distinct discontinuity between the layers on GaAs and those on GaP. Trends in oxidation kinetics are compared to these strain and chemistry values.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemistry</th>
<th>Nominal Strain (x10^{-3})</th>
<th>Strain Relief (x10^{-3})</th>
<th>Substrate &amp; spacers</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1(3827)</td>
<td>0.98 0.78</td>
<td>-6.3</td>
<td>0.31</td>
<td>GaAs</td>
</tr>
<tr>
<td>A-2</td>
<td>0.98 0.82</td>
<td>-5.0</td>
<td>0.27</td>
<td>GaAs</td>
</tr>
<tr>
<td>A-3</td>
<td>0.98 0.87</td>
<td>-3.3</td>
<td>0.19</td>
<td>GaAs</td>
</tr>
<tr>
<td>A-4</td>
<td>0.98 0.93</td>
<td>-1.2</td>
<td>0.22</td>
<td>GaAs</td>
</tr>
<tr>
<td>A-5</td>
<td>0.98 1.00</td>
<td>1.2</td>
<td>-0.07</td>
<td>GaAs</td>
</tr>
<tr>
<td>B-6(4040)</td>
<td>0.97 0.00</td>
<td>2.8</td>
<td>-0.04</td>
<td>GaP</td>
</tr>
<tr>
<td>B-7</td>
<td>0.97 0.06</td>
<td>4.9</td>
<td>-0.06</td>
<td>GaP</td>
</tr>
<tr>
<td>B-8</td>
<td>0.97 0.13</td>
<td>7.4</td>
<td>-0.04</td>
<td>GaP</td>
</tr>
<tr>
<td>B-9</td>
<td>0.97 0.20</td>
<td>9.9</td>
<td>-0.02</td>
<td>GaP</td>
</tr>
<tr>
<td>C(4065)</td>
<td>In_{0.50}Al_{0.50}P</td>
<td>-1.2</td>
<td>&lt;0.02</td>
<td>GaAs</td>
</tr>
<tr>
<td>D(4338)</td>
<td>In_{0.47}Al_{0.53}As</td>
<td>-4.3</td>
<td>0.24</td>
<td>InP</td>
</tr>
<tr>
<td>E(4039)-1</td>
<td>0.97 0.00</td>
<td>2.8</td>
<td>&lt;0.02</td>
<td>GaP</td>
</tr>
<tr>
<td>E-2</td>
<td>0.90 0.00</td>
<td>2.6</td>
<td>&lt;0.02</td>
<td>GaP</td>
</tr>
<tr>
<td>E-3</td>
<td>0.80 0.00</td>
<td>2.3</td>
<td>&lt;0.02</td>
<td>GaP</td>
</tr>
</tbody>
</table>

Table 3-1. Summary of oxide sample chemistries and strains. Compressive strains are given a positive sign. Unless otherwise noted, chemistry data is given based on $Al_{x}Ga_{1-x}As_{y}P_{1-y}$.

Figure 3-8. Graph of strains and P concentrations used in the oxide experiments.
Sample C is comprised of In\textsubscript{5}Al\textsubscript{5}P layers grown on a GaAs substrate and Sample D is comprised of In\textsubscript{47}Al\textsubscript{53}As grown on an InP substrate. Oxides formed from In\textsubscript{5}Al\textsubscript{5}As have been used in optical and electrical devices as reported in the literature\textsuperscript{147-150}. Oxides of InAlP have been investigated\textsuperscript{130,151,152,214,221} but use of this material as a dielectric layer in an electronic device is limited due to the presence of metal nano-particles\textsuperscript{153}. The oxidation kinetics of these two samples are measured and correlated to strain and chemistry.

Sample E is comprised of Al\textsubscript{x}Ga\textsubscript{1-x}P grown on GaP. The oxidation kinetics of this sample are compared to the oxidation kinetics of Al\textsubscript{0.98}Ga\textsubscript{0.02}As as in Sample A-1. Furthermore, sample E makes it possible to investigate the role of column III chemistry in the oxidation of the Al(Ga)P system.

All oxidation layers are 100 nm thick unless otherwise noted. Samples are prepared prior to oxidation in the FIB such that trenches 10x100\textmu m are sputtered through the epilayers as depicted in Figure 3-9. The width of these trenches is similar to those used for oxidation trenches in some VCSEL designs. Two orthogonal trenches oriented along the <110> directions are sputtered in order to check for dependencies of oxidation kinetics on sample orientation relative to the furnace tube axis (i.e. the length of one trench is parallel to steam flow while the other is perpendicular to it). Enhanced etch gas (iodine) is used in the FIB to increase the sputter rate and to facilitate straighter trench walls (the enhanced etch process also greatly reduces the amount of gallium redeposition onto to the trench walls, thus minimizing the influence of redeposited gallium on the measured oxidation kinetics). Neither the enhancement gas nor the residual implanted Ga\textsuperscript{+} appears to affect oxidation kinetics as test samples using this method of the frequently measured oxidation of Al\textsubscript{x}Ga\textsubscript{1-x}As and Al\textsubscript{0.47}In\textsubscript{0.53}As give similar results to those reported in the literature.
The oxidation runs are carried out in the furnace configuration designed for this work as described in Appendix-Furnace. Oxides are grown in a steam environment under atmospheric pressure \(^{xxiii}\) at temperatures ranging from \(~350^\circ C\) to \(~630^\circ C\). As is standard\(^{154}\) for this type of oxidation, dry N\(_2\) is bubbled through \(~1.5\) liters of distilled water (at 90\(^\circ\)C) at a rate of 2.9 liters/minute generating a H\(_2\)O-N\(_2\) vapor that is passed through quartz tubing into the furnace\(^{xxiv}\). All tubing between the distilled water vessel and the furnace is held at slightly greater than 100\(^\circ\)C to prevent condensation of the water vapor before it enters the furnace. Although others have indicated that this is not necessary\(^{151}\), we find it an essential precaution to prevent severe temperature fluctuations due to the introduction of condensation droplets into the furnace during oxidation for the furnace configuration used in this work.

Two types of oxidation rate measurements are taken. For the first type several samples are oxidized at the same temperature but for different times in order to determine whether the oxidation is rate limited or reaction limited (i.e. parabolic, logarithmic or linear). For the second type, several samples are oxidized at different temperatures in order to determine the activation energy of the oxidation process.

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\(^{xxiii}\) Pressure was measured explicitly at 14.4PSI (1.02 atmosphere) for typical furnace conditions (300-500\(^\circ\)C, 90\(^\circ\) water). If flow rate was increased to \(~4\)lpm or the water temperature increased to 100\(^\circ\), the furnace pressure increased by 0.1PSI.

\(^{xxiv}\) Although the water content of the N\(_2\)/steam mixture has not been explicitly measured, it has been shown for similar furnace configurations that above an N\(_2\) flow rate of \(~2\) splm there is no significant change in oxidation kinetics with respect to the flow rate\(^{154}\).
3.2.1 Measurement techniques

Oxide lengths greater than ~500nm were measured in the FIB by milling square patterns over portions of, or over the entire, oxidation trench as depicted in Figure 3-10. Oxide lengths were easily determined (as the distance from the trench edge to the oxide edge at the positions labeled “oxidation front” in Figure 3-10) as the oxide had relatively dark contrast (Figure 3-10, compared to unoxidized $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$) when it was exposed to the ion beam (i.e. after the crystal above it had been sputtered away). Instances where the FIB technique was not practical involved oxide samples whose variation in length for various oxidation conditions (e.g. varying time or temperature) were too small to be easily detected in the FIB. Use of the FIB technique is advantageous over measurements taken at a single point along the length of the oxidation trench as it gives an indication of roughness or bumps in the oxide front (e.g. the bump in the lower right hand corner of Figure 3-10). Apart from the “bump” in the lower right hand quadrant of the sample shown in Figure 3-10 the oxidation front is smooth. Such uneven areas (which maybe due to regions of compositional irregularity) are avoided in measuring the oxide length. In samples for which the FIB measurement technique was not feasible, cross-section TEM samples were prepared in the FIB using the process described earlier as used for cross-section VCSEL samples.
3.3 Transmission Electron Microscopy

TEM yields several signals that can be used for characterization of specimens. These signals originate from the different interactions of the incident electron beam with the specimen and, analysis of these signals leads to nano-scale information about the sample's structure and chemistry.

Briefly, as an electron passes through the sample, it can interact elastically, inelastically, or not at all. With the use of appropriate magnetic lenses elastically scattered (i.e. their trajectory is changed but they have experienced no significant energy loss; $\Delta E \ll 1 \text{ eV}$), or diffracted, electrons can be used to form electron diffraction patterns and images. One of the signals generated by inelastically scattered electrons is a collection of x-ray photons having an energy distribution that is specific to the material through which the electron beam has passed. Following is a description of the manner in which the TEM and its supporting equipment utilize the interactions experienced by incident electrons to provide structural and chemical information about the specimen.
3.3.1 TEM Instruments

The microscopes used in this work were a JEOL 2000 FX and a JEOL 2010 F. The JEOL 2000 FX uses a thermionic LaB$_6$ filament and has a point resolution of 0.32nm. The JEOL 2010 uses a field emission zirconated tungsten filament and, due to a lower aberration objective lens has a point resolution of 0.23nm$^{xxv}$. In addition, the JEOL 2010 F is equipped with an Oxford x-ray energy dispersive spectrometer.

Due to its greater total electron current, the bulk of sample imaging and diffraction analysis was performed on the JEOL 2000 FX. For analytical work the JEOL 2010 F was used.

Figure 3-11 shows a schematic of the JEOL 2010 F. In short, electrons are extracted by field emission from a source, roughly focused by a Wehnelt cup, and finely focused by the first set of magnetic lenses, the condenser lenses, onto a specimen. From here, another magnetic lens, the objective lens, focuses electrons of equal diffraction angle to the same point at the back focal plane of the lens thus forming a diffraction pattern. The first image plane of the TEM, formed by the objective lens, is formed below the back focal plane. A final set of magnetic lenses, the intermediate lenses and the projector lens, use as their object either the back focal plane (i.e. the diffraction pattern) or the first image plane of the objective lens. These final lenses form a diffraction pattern or a highly magnified image of the sample on the viewing screen, TV camera, or slow scan CCD array. A more detailed description of the electron-beam sample-interaction signals used for this work is now given.

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$^{xxv}$ Although the 2010 is capable of greater point resolution (0.19nm) use of a high-tilt lens geometry (pole piece) limits the resolution.
3.3.2 Elastic scattering. Diffraction pattern and Image formation.

The formation of electron diffraction patterns and image contrast depend primarily on the manner in which the specimen elastically scatters incident electrons. Understanding of the mechanisms involved in the formation of diffraction patterns gives detailed insight into the crystal structure of a specimen. For imaging, there are three different types of image contrast. Understanding the mechanisms involved in the electron scattering and the subsequent interaction between the main beam and the diffracted beam(s) is critical to imaging analysis of the specimen.

3.3.2.1 Electron-Sample interaction

Fundamental to electron scattering theory is the principle of atomic scattering amplitude, \( f(\Theta) \). Every possible interaction between the incident electron and the sample
has a probability of occurring, governed by its scattering cross section, $\sigma$. The differential, $d\sigma/d\Omega$, indicates the differential probability, $d\sigma$, that an electron is scattered into the differential solid angle, $d\Omega$. The atomic scattering amplitude is related to the scattering cross section by

$$\left| f(\Theta) \right|^2 = \frac{d\sigma(\Theta)}{d\Omega}$$

Equation 3-2

Thus, $f(\Theta)$ gives the scattered amplitude of the electron wave as a function of scattering angle, and $|f(\Theta)|^2$ is proportional to the scattered intensity. As such, the atomic scattering amplitude relates the incident electron plane wave to the spherical scattered wave for an electron scattering from a single atom in the sample by

$$\Psi_{\text{scattered}} = \Psi_{\text{incident}} f(\Theta) \frac{e^{2\pi i kr}}{r}$$

Equation 3-3

Here $\Psi$ is the electron wave, $k$ is the wave vector and $r$ is the distance traveled by the electron after scattering. The actual value of the atomic scattering factor $f(\Theta)$ is dependent on incident beam conditions and the atom in the sample and is given by:

$$f(\Theta) = \frac{1 + \frac{E}{E_o} \left( \frac{\lambda}{2\sin\Theta} \right)^2 (Z - f_x)}{8\pi 2a_o}$$

Equation 3-4

where $E$ is the electron energy after scattering, $E_o$ is the initial electron energy, $a_o$ is the Bohr radius, $\Theta$ is the scattering angle, $Z$ is the atomic number and $f_x$ is the scattering
factor for x-rays\textsuperscript{xxvi}. To describe the way by which an assembly of atoms in a crystal contributes to the outgoing wave function, individual atomic scattering amplitudes must be summed into a structure factor, $F(\Theta)$:

$$F(\Theta) = \sum_i 2\pi i (hx_i + ky_i + lz_i)$$

\textbf{Equation 3-5}

Here $x_i, y_i, z_i$ are the components (fractions of the lattice parameters) of any basis vector (a basis vector describes all possible, unique positions in a crystal unit cell), and $h,k,l$ are the Miller indices for the planes containing these atoms. A non-zero $F(\Theta)$ indicates intensity in the diffracted beam for the $(hkl)$ plane in question. Therefore the above equation predicts the possibility of diffraction from a set of planes in a crystal and thus will be useful in understanding diffraction contrast.

Also fundamental to electron diffraction theory is Bragg’s law. Bragg’s law describes the total constructive interference between waves that are $n\lambda$ ($n=0,1,2,3...$) out of phase and destructive interference between waves that are not $n\lambda$ out of phase. This phase relationship is applied to waves that are diffracted by a set of planes such that there is a finite path length difference between the electron waves scattered from one plane relative to those scattered from the parallel planes above or below. This is shown in Figure 3-11. Accordingly, when

$$2d\sin \Theta = n\lambda$$

\textbf{Equation 3-6}

there will be constructive interference and hence, strong diffracted intensity from that set of planes with spacing $d$ and incident angle $\Theta$.

\textsuperscript{xxvi} Physically, the term, $f_x$, accounts for elastic scattering from the electron cloud associated with an atom\textsuperscript{157}. 
3.3.2.2 The Diffraction Pattern

Bragg's law is used to describe the spatial distribution of elastically scattered electrons at the objective lens back focal plane. Mathematically, it can be shown that the diffraction pattern is a Fourier transform of the sample. This Fourier transform gives an indication of the atomic periodicities present in the sample. Any inverse length in this Fourier transform space, or 'reciprocal space', corresponds to a physical length in real space. In the TEM, since the diffraction pattern occurs below the sample at the back focal plane of the objective lens, specific spots can be selected there with the objective aperture to create images containing information about one specific set of diffracting planes.

3.3.2.3 Electron images

3.3.2.3.1 Diffraction contrast

As a consequence of electron scattering, image contrast can be obtained in three ways (described in these three subsections). Dynamic diffraction contrast images are based on multiple elastic interaction of incident electrons with the sample (there is a special case of diffraction contrast known as 'kinematic diffraction' which occurs in thin crystals where there is a maximum of one scattering event per incident electron.). High contrast images can be made by tilting the sample such that only one set of planes satisfies the Bragg condition giving rise to a 'two-beam' condition in which only the direct beam and one diffracted beam contain intensity and either the resultant diffracted
beam (dark field imaging) or the straight-through beam (bright field imaging) is used to
generate an image. It is diffraction contrast that typically makes imaging of crystal defects possible, as these defects cause local perturbations in the crystal uniformity and thus affect a set of planes’ ability to cause constructive interference. How this applies to dislocations is discussed later in this chapter.

Contrast arises due to the coupled transfer of intensities between the single diffracted beam and the direct beam. Mathematically, the amplitude, $\Phi_g$, of the scattered beam and amplitude, $\Phi_o$, of the direct beam as a function of distance, $z$, traveled through the sample are described by the Howie-Whelan equations,

$$\frac{d\Phi_g}{dz} = \frac{\pi i \Phi_o e^{-2\pi i s z - 2\pi \vec{n} \cdot \vec{R}}}{\xi_g} + \frac{\pi i \Phi_g}{\xi_o}$$

Equation 3-7

$$\frac{d\Phi_o}{dz} = \frac{\pi i \Phi_o}{\xi_o} + \frac{\pi i \Phi_g e^{2\pi i s z + 2\pi \vec{n} \cdot \vec{R}}}{\xi_g}$$

Equation 3-8

via the extinction distance $\xi$, and the excitation error, $s$. In these equations, $\vec{g}$ represents the diffraction vector (in reciprocal space the vector from the direct beam to the single diffracted beam) and $\vec{R}$ represents any crystal displacement that might be present, for example due to a dislocation. The extinction distance $\xi$, is the characteristic length through the thickness of the sample over which the intensity of the diffracted or undiffracted beam goes through one period of oscillation. This parameter depends on the structure factor of the material and thus couples composition to diffraction contrast. The excitation error, or deviation parameter, $s$, corresponds to the deviation from the exact Bragg condition.

Two-beam bright-field diffraction-contrast imaging is a method by which the objective aperture is used to allow only the direct beam to form the image. Similarly,
two-beam dark-field diffraction-contrast imaging is a method by which the objective aperture is used to select only the diffracted beam. The exact two-beam condition can be chosen to elucidate a particular feature of the sample (e.g. strain or compositional variation).

The degree to which a defect is visible in a diffraction contrast image depends on the specific imaging conditions (i.e. $g$). For example, in a crystal the displacement vector, $R$, caused by a general dislocation is given as

\[
\vec{R} = \frac{1}{2\pi} \left( \vec{b} \beta + \frac{\vec{b}_e \sin 2\beta}{4(1-\nu)} \right) + \vec{b} \times \vec{u} \left[ \ln r + \frac{2\nu}{2(1-\nu)} \right]
\]

Equation 3-9

where $b$ is the burgers vector of the dislocation (i.e. a vector describing the deviation in the perfect lattice spacing of the crystal caused by the dislocation), $b_e$ is the edge (i.e. perpendicular) component of the burgers vector, $u$ is the line direction of the dislocation (or dislocation segment), $\beta$ and $r$ define the location of the point relative to the dislocation and $\nu$ is Poisson’s ratio. Thus when $g \cdot R = 0$ neither the diffracted or direct beam amplitudes will be affected by the dislocation (Equation 3-7 and Equation 3-8) and the dislocation will be invisible. Thus, the fact that a certain $g$ will cause $g \cdot R = 0$ can be used to determine the burgers vector of the dislocation. Specifically, if for a certain two beam condition the dislocation is completely invisible, the condition is satisfied that $g \cdot b = 0$, $g \cdot b_e = 0$, and $g \cdot (b \times u) = 0$ (note that the latter two conditions are automatically met for a pure screw dislocation if the first condition is met). In theory, two of the vectors, $u$ and $g$, are known from the image and diffraction pattern so that the third, $b$ can be determined. In practice, $u$ can be difficult to determine precisely without the use of stereomicroscopy or prior knowledge of the dislocation behavior of a sample (i.e. misfit dislocation direction). However, knowledge of two two-beam conditions, $g_1$ and $g_2$, which give residual contrast only leads directly to determination of the Burger’s vector by $g_1 \times g_2$. 

3.3.2.3.2 Absorption contrast

The term absorption contrast refers to electrons that are scattered outside the image collection system (e.g. out of the objective aperture), and thus “absorbed” by the TEM. Absorption contrast generally arises from mass and density differences. Hence, higher mass atoms elastically scatter incident electrons more efficiently and to higher angles so that there is less intensity on the viewing screen for heavier, denser regions. Along the same lines, thicker regions will have a higher probability of causing an electron to scatter outside of the image collection system and thus appear darker.

3.3.2.3.3 Phase contrast

Phase contrast makes it possible to image atomic planes in crystals. The mechanism here is the interference between the direct and diffracted beams where the electron beams have gone through different phase changes during diffraction from different atomic columns in a crystal. Thus, unlike diffraction contrast imaging, where it is necessary to image with either the direct or single diffracted beam alone, phase contrast imaging involves the interaction of one or more diffracted beams along with the direct beam. A detailed development of the theory is given in many TEM texts\textsuperscript{143,157}.

The contrast mechanisms discussed above may be competing mechanisms for a particular image. For example, a darker band in the image that is due to diffraction contrast can be confused with mass or thickness contrast. Knowing which mechanism is dominant is critical to image interpretation. Re-imaging under different diffraction conditions typically enables the contrast mechanisms to be differentiated.

3.3.3 Energy Dispersive Xray Spectroscopy, Inelastic scattering

The previous discussion applies to electrons that have been elastically scattered by the sample. Spectral analysis of the signals generated by the inelastically scattered electrons (and of the electrons themselves) leads to valuable chemical information about the sample. EDXS has been employed in this work to quantitatively investigate elemental concentrations of the compounds that were oxidized in this work.
When an electron from the TEM source inelastically interacts with an atom in the sample, it may eject an electron from one of the tightly bound energy states of the atom as depicted in Figure 3-13. When an electron falls back into this empty state, it releases an x-ray photon whose energy equals the difference in energy between the empty energy state and the state from whence the relaxing electron originated. Due to the fact that every element has a characteristic set of electron energy levels, the x-rays given off can be used to identify the element with which the source electron interacted. Furthermore, for given TEM conditions (e.g. beam size, specimen tilt, etc.), elements will have a characteristic ratio of photons generated per incident electron and hence, through use of appropriate compositional standards, the chemistry of the unknown sample can be determined quantitatively.

![Figure 3-13. Schematic of electron transitions responsible for X-ray spectra](image)

3.4 Focused Ion Beam column

A Focused Ion Beam instrument is used in sample preparation and characterization of oxide samples and for sample preparation of ex-situ and in-situ VCSEL samples as described in the relevant chapters. Following is a brief description of the FIB. An FIB column schematic is shown in Figure 3-14. The LMIS (Liquid Metal

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xxvii Note that the tightly bound inner shell electron energy levels are not significantly affected by the chemistry of the compound that the element may be part of.
Ion Source) is composed of a resistively heated reservoir that contains a low melting point metal. This liquid metal then wets a sharp tungsten tip. In this work, gallium was the LMIS source used. The metal is periodically heated to keep a small amount on the tip of the source. A positive bias of ~7 kV is placed on a nearby extracting anode and this causes the metal to form a "Taylor cone" which has its shape determined by the balance of electrostatic forces and the surface tension of the metal. This cone has a tip diameter of ~5nm and thus, a modest potential will produce a substantial electric field which is capable of extracting the metal ions with a current density of ~1A/cm$^2$ for an emission current of 1pA. Larger current densities of ~10A/cm$^2$ are typical for emission currents above 10pA.

Figure 3-14 Schematic of FIB column.

The source is brought up to a positive potential of 30kV and the sample held at ground. Extracted ions are accelerated towards the sample and focused into a 10nm-
1000nm beam at the sample by way of a series of apertures and electrostatic lenses and deflection coils.

The ion beam is rastered over the region of interest on the sample and sputtering of ions and neutral species occurs. Secondary electron emission also occurs. The secondary electrons were used in this work to take images of the sample. Secondary ions can also be used as the image signal when samples (generally insulators) charge and it is necessary to flood the sample region with extra electrons. The sputtering yield depends on the ion beam energy and target material and is roughly 5 atoms per incident Ga ion for GaAs at 30keV. Relatively high beam currents of 11 nA were used to do rough scale milling but beam currents of 1nA were used to mill the final faces of the TEM membrane due to the lower damage from the lower current and the higher milling resolution due to the finer beam diameter.

An additional capability of the FIB is metal and insulator deposition with a resolution close to that of the beam diameter. These have potential uses in the microelectronics industry, for device repair either by circuit wiring or insulation. Platinum metal deposition has been useful in this work as a protective coating against unwanted surface damage. For the deposition, an organic compound containing platinum, \((\text{CH}_3\text{C}_5\text{H}_4)(\text{CH}_3)_3\text{Pt}\), is concentrated near the region where it will be deposited via a small diameter tube held \(\sim 100\mu\text{m}\) above the sample. An ion beam current density of 4-8pA/\(\mu\text{m}^2\) will disassociate the organic compound and cause metal buildup in the region defined by the beam scan area.
4 Study of degraded VCSELs

The working Vertical Cavity Surface Emitting Laser (VCSEL) presents a unique materials system in which to study the behavior of III-V materials under extreme electrical and optical stresses. For example, successful VCSEL designs must be able to support extreme optical fluxes (~100kW/cm$^2$) and electrical fluxes (~kA/cm$^2$) without material or structural failure. Cases of such failure have been widely studied in conventional edge-emitting stripe lasers (for recent reviews of this research refer to Ueda$^{1,158-160}$), but limited work$^{161-166}$ has been published on the materials aspects of degradation phenomena in VCSEL devices.

The necessity to study failure in VCSELs, rather than rely on previous failure analysis of edge emitting lasers, stems from the differences in these laser designs and the overall greater complexity of the VCSEL design as described in Section 2.1. Hence, it is possible that fundamentally different failure mechanisms may occur in VCSELs that will need to be addressed in order to facilitate fabrication of commercially viable devices.

Accordingly, by employing Focused Ion Beam (FIB) and Transmission Electron Microscopy (TEM) techniques we are able to identify and explain several degradation mechanisms responsible for failure in various VCSEL designs. A systematic study of the dependence of degradation on duration of laser operation has been conducted for one VCSEL design employing lateral oxidation layers for current confinement. To add breadth to our understanding, laser failures in four commercially available VCSEL designs (three employing proton implantation and one employing lateral oxidation for current confinement) are also investigated. Finally, severe material degradation (i.e. catastrophic failure) in two oxide confined VCSELs is explored.

4.1 Results and Discussion

A list of the devices used in this work is given in Table 4-1. The main body of this work is concerned with an extensive study of the failure mechanisms operative in one oxide confined VCSEL device, V1 (grown by Metal Organic Chemical Vapor Deposition
(MOCVD). Additional growth and processing details are given in Appendix-C). Many
lasers of this configuration were operated for various durations at close to the roll over
current (23mA)\textsuperscript{xxviii}. (Some variation was observed in the lasing characteristics of this
device, possibly due to the variations (e.g. structural or chemical) on the length scale of
the inner-device spacing). Device V1 was chosen due to it tendency to rapidly fail (i.e.
cease to lase on the time scale of seconds to minutes) under these operating conditions
and so to provide an extensive set of degraded structures. The alternative was to choose a
commercially feasible device that rapidly failed only after a considerable stable lifetime,
or to subject long-lived lasers to accelerated lifetime conditions (e.g. high temperature).
Time constraints (i.e. the half-life of this graduate student) and lack of access to lifetime
accelerating equipment precluded these latter two options. However, a few devices have
been made available for this work, which failed after operation in the field for thousands
of hours (V3 and V4) or which were failed under accelerated conditions (V2 A & B).
These devices help to add breadth to the results obtained from the main sample set V1,
and enabled us to extrapolate damage mechanisms to devices that degraded with more
characteristic life times. Finally, catastrophic degradation in two oxide confined
VCSELs (V5 and V6) was examined.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\lambda) (nm)</th>
<th>Confinement technique (aperture dimension)</th>
<th>Active region configuration</th>
<th>Constant I and J or constant P</th>
<th>Time of operation</th>
<th>TEM type</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1-A</td>
<td>955</td>
<td>7.5 (\mu)m oxide aperture</td>
<td>GaAs/ 3 In\textsubscript{0.14}Ga\textsubscript{0.86}As Quantum wells (Qws)</td>
<td>Undegraded</td>
<td>0</td>
<td>C</td>
</tr>
<tr>
<td>V1-Ap</td>
<td>955</td>
<td>7.5 (\mu)m oxide aperture</td>
<td>GaAs/ 3 In\textsubscript{0.14}Ga\textsubscript{0.86}As Qws</td>
<td>Undegraded</td>
<td>0</td>
<td>P</td>
</tr>
<tr>
<td>V1-B</td>
<td>955</td>
<td>7.5 (\mu)m oxide aperture</td>
<td>GaAs/ 3 In\textsubscript{0.14}Ga\textsubscript{0.86}As Qws</td>
<td>23 mA 41 kAcm\textsuperscript{-2}</td>
<td>16 sec</td>
<td>C</td>
</tr>
<tr>
<td>V1-C</td>
<td>955</td>
<td>7.5 (\mu)m oxide aperture</td>
<td>GaAs/ 3 In\textsubscript{0.14}Ga\textsubscript{0.86}As Qws</td>
<td>23 mA 41 kAcm\textsuperscript{-2}</td>
<td>31 sec</td>
<td>P</td>
</tr>
<tr>
<td>V1-D</td>
<td>955</td>
<td>7.5 (\mu)m oxide aperture</td>
<td>GaAs/ 3 In\textsubscript{0.14}Ga\textsubscript{0.86}As Qws</td>
<td>23 mA 41 kAcm\textsuperscript{-2}</td>
<td>61 sec</td>
<td>P</td>
</tr>
<tr>
<td>V1-E</td>
<td>955</td>
<td>7.5 (\mu)m oxide aperture</td>
<td>GaAs/ 3 In\textsubscript{0.14}Ga\textsubscript{0.86}As Qws</td>
<td>23 mA 41 kAcm\textsuperscript{-2}</td>
<td>120 sec</td>
<td>P</td>
</tr>
</tbody>
</table>

\textsuperscript{xxviii} Power output increases with applied voltage until the roll-over current is reached at which point device heating causes the gain wavelength to shift away from the cavity resonance wavelength. Briefly, this is due to temperature effects on the bandgap and mirror reflectivity.
<p>| | | | | | |</p>
<table>
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<tbody>
<tr>
<td>V1-F</td>
<td>955</td>
<td>7.5 µm oxide aperture</td>
<td>GaAs/3 In₀.₁₄Ga₀.₈₆As Qws</td>
<td>23 mA/41 kAcm⁻²</td>
<td>120 sec/C</td>
</tr>
<tr>
<td>V1-G</td>
<td>955</td>
<td>7.5 µm oxide aperture</td>
<td>GaAs/3 In₀.₁₄Ga₀.₈₆As Qws</td>
<td>23 mA/41 kAcm⁻²</td>
<td>240 sec/C</td>
</tr>
<tr>
<td>V1-H</td>
<td>955</td>
<td>7.5 µm oxide aperture</td>
<td>GaAs/3 In₀.₁₄Ga₀.₈₆As Qws</td>
<td>23 mA/41 kAcm⁻²</td>
<td>800 sec/P</td>
</tr>
<tr>
<td>V1-I</td>
<td>955</td>
<td>7.5 µm oxide aperture</td>
<td>GaAs/3 In₀.₁₄Ga₀.₈₆As Qws</td>
<td>23 mA/41 kAcm⁻²</td>
<td>1000 sec/C</td>
</tr>
<tr>
<td>V1-J</td>
<td>955</td>
<td>7.5 µm oxide aperture</td>
<td>GaAs/3 In₀.₁₄Ga₀.₈₆As Qws</td>
<td>23 mA/41 kAcm⁻²</td>
<td>1200 sec/P</td>
</tr>
<tr>
<td>V1-K</td>
<td>955</td>
<td>7.5 µm oxide aperture</td>
<td>GaAs/3 In₀.₁₄Ga₀.₈₆As Qws</td>
<td>23 mA/41 kAcm⁻²</td>
<td>1200 sec/C</td>
</tr>
<tr>
<td>V2-A</td>
<td>850</td>
<td>15 µm oxide aperture</td>
<td>Al₀.₈₅Ga₀.₁₅As/Al₀.₁₅Ga₀.₈₅As</td>
<td>30 mA/4.2 kAcm⁻²</td>
<td>96 hr/C</td>
</tr>
<tr>
<td>V2-B</td>
<td>850</td>
<td>15 µm oxide aperture</td>
<td>Al₀.₈₅Ga₀.₁₅As/Al₀.₁₅Ga₀.₈₅As</td>
<td>30 mA/4.2 kAcm⁻²</td>
<td>96 hr/P</td>
</tr>
<tr>
<td>V3</td>
<td>850</td>
<td>~30 µm proton implant aperture</td>
<td>GaAs/Al₀.₁₅Ga₀.₈₅As</td>
<td>&lt;15mA/0.5 kAcm⁻²</td>
<td>Field failure after years of usexxix.</td>
</tr>
<tr>
<td>V4</td>
<td>850</td>
<td>~30 µm proton implant aperture</td>
<td>GaAs/Al₀.₂₅Ga₀.₇₅As</td>
<td>&lt;15mA/0.5 kAcm⁻²</td>
<td>Field failure after years of use.</td>
</tr>
<tr>
<td>V5</td>
<td>840</td>
<td>9 µm oxide aperture</td>
<td>GaAs/Al₀.₂₀Ga₀.₈₀As</td>
<td>0.5mW (constant power)</td>
<td>55 days/C</td>
</tr>
<tr>
<td>V6</td>
<td>850</td>
<td>10.5 µm oxide aperture</td>
<td>GaAs/Al₀.₂₀Ga₀.₈₀As</td>
<td>5 current scans to 20mA (18kAcm⁻²) scan rate was ~+1mA/sec</td>
<td>P</td>
</tr>
</tbody>
</table>

Table 4-1. Summary of devices used and their respective degradation histories. P or C refers to plan-view or cross-section characterization.

4.1.1 Degradation in Oxide confined VCSELS

Figure 4-1 shows a cross section TEM image of an undegraded (i.e. as fabricated) sample of VCSEL V1-A. No dislocations are evident in the active region or in the upper and lower DBRs apart from small dislocation loops that occur only in the lower part of the bottom DBR. As shall be shown, these dislocations are visible in all cross-section samples of differently degraded V1 VCSELS in the same concentrations and configuration. Therefore, they apparently do not participate in the degradation of this laser type, although they may by an indication of less than ideal material quality (e.g a

xxix These devices were customer returns to a VCSEL manufacturer who supplied them for this work. The company wishes to remain anonymous.
super saturation of grown in point defects). These loops are immediately visible when beginning TEM characterization and thus are not caused by the electron beam. It should also be pointed out that a short-range (~100nm) strain field exists in the vicinity of the oxide layers, as evidenced by the darker contrast immediately above and below these layers. Previous TEM studies\textsuperscript{216} have shown a possibly detrimental strain field\textsuperscript{167} surrounding the oxide layers (due to volume contraction upon oxidization), the magnitude of which increases in proportion to the amount of Al in the Al\textsubscript{x}Ga\textsubscript{1-x}As layer that is oxidized. For example, oxide layers grown from AlAs have even been shown to promote severe structural failure upon annealing treatments (e.g. the upper DRB separates from the lower DBR)\textsuperscript{154,215}. Theoretically, this stress is as high as 80GPa according to one source\textsuperscript{215}, although in practice, this must\textsuperscript{xxx} be reduced due to partial separation of the oxide/crystal interface. Thus, even by TEM examination of the undegraded laser, it is possible to anticipate to some degree the inherent structural “weaknesses” that may lead to degradation and failure. For example, in the case of VCSEL V1 the strain surrounding the oxide layers and a possible high point defect density in the lower DBR may be warnings of rapid failure.

For comparison to planview TEM images of degraded V1 VCSELs, an undegraded VCSEL, V1-A is shown in Figure 4-2. With the exception of the feature marked “a”, no defects are observed in the active region of the device and the contrast variations visible through the oxidized region (darker contrast at the periphery of the image) are due to interaction of the electron beam with the oxide\textsuperscript{xxxi}. The feature marked “a” is within the volume of the membrane (rethinning the membrane did not remove it) and is possibly a grown-in defect such as a precipitate or particulate.

\textsuperscript{xxx} Stresses of this magnitude are physically unreasonable and thus unattainable in light of the fact that the bulk modulus of Al\textsubscript{2}O\textsubscript{3} is ~100GPa.

\textsuperscript{xxxi} Briefly, it was shown earlier that oxides formed from III-V materials were initially amorphous but were nano-crystalline after exposure to the high energy electrons (200keV) of the TEM\textsuperscript{130}. 
Figure 4-1  00-4 bright field cross-section TEM image of undegraded VCSEL, V1-A.

Figure 4-2. Planview TEM image of undegraded VCSEL V1-Ap.
VCSEL V1-B, which was degraded for 16 seconds, is shown in cross-section in Figure 4-5 and relevant P-I and P-t traces are given in Figure 4-3 and Figure 4-4 respectively. Prior to degradation, this particular device did not exhibit an increase in optical power at ~20mA which would have indicated lasing for the device. However, the observed spontaneous emission decreased during the 16 seconds, indicating the operation of a degradation mechanism, and suggesting the importance of the injected current in the degradation process. Specifically, even for the short operation time of 16 seconds, there occurs a greater than 50% decrease in output power as is seen in Figure 4-4. However, no degradation features were detected in the active region or DBR apart from the pre-existing dislocation loops in the lower DBR previously mentioned. It is thus possible that the degradation feature responsible for the decrease in output power does not exist within the TEM cross-section membrane, or that some other degradation mechanism not readily observed by TEM is operative at these short degradation times. One such degradation mechanism is current-shunting whereby current is forced to the periphery of the active area (due to the passivation of dopants by mobile point defects\textsuperscript{168} in the p-n junction immediately adjacent to the active region\textsuperscript{162,169}) thereby decreasing the light output (spontaneous or stimulated) from the active area.

Finally, while the measurement rate shown in Figure 4-4 (and the following charts of the same type) is low, giving a data point every one or two seconds, the smooth nature of the curve suggests a smoothly decreasing power output (i.e. it seems less likely that the power output fluctuates between the given data points). Thus, despite the fact that the measurement rate is initially lower, the power output likely decreases smoothly in those first two seconds, presumably due to the operation of some process such as the current-shunting mechanism.
Figure 4-3. Power vs. current traces before and after degradation for V1-B

Figure 4-4. Power vs. time for operation at 23 mA for V1-B
V1-C, degraded for 30 seconds at 23mA is shown in the planview TEM image in Figure 4-8 and relevant P-I and P-t curves are shown in Figure 4-6 and Figure 4-7 respectively. Both oxide apertures (above and below the active region) are clearly seen in this image as squares surrounding the center of the device; i.e. the active region. (As was seen in the cross section images for V1-A and V1-B, the oxide aperture above the QW active region extends further toward the center of the device than the oxide aperture below the QW region. Thus, the bottom oxide aperture is visible near the outer edge of the image).

The large area of different contrast to the right of the feature labeled ‘sample prep artifact’ is due to sample/Ga⁺ beam misorientation as described in Section 3.1. Further evidence that this feature type is an artifact of sample preparation rather than a signature of material degradation induced during device operation is the fact that similar features are also detected in planview samples of undegraded VCSELs.

At this stage of degradation, additional types of structural features appear, (although only to a relatively small extent compared to data shown later for longer degradation times). A region of DBR disruption is visible in the upper right hand and left hand corners of the oxide aperture. Additional insight into this degradation feature will be shown via comparison of the cross-section and plan-view samples that follow. That the contrast features labeled “DBR disruption” are structural and not TEM related (e.g. not bend contours) is established by the fact that they remain stationary during specimen
tilting. Additionally, a small punched-out\textsuperscript{xxxii} dislocation half-loop appears in the lower left hand corner of the oxide aperture. This loop is likely related to the small segment of DBR disruption visible in that corner of the device as is supported by additional evidence below.

Finally, a long-range modulation feature with ~120nm periodicity is detected running horizontally in the active region. Due to the relatively high thickness of the planview samples used in the work (typically $> 500$nm), and thus high levels of diffuse scattering, clear diffraction patterns that might further elucidate the nature of this periodic feature were impossible to acquire. The fact that this feature runs perpendicular to the ion beam direction precludes its origin as a sample preparation artifact. It is noted that in some ternary III-V alloys, including the InGaAs alloy system used in the active region of V1 (and more generally for the InGaAsP alloy system), compositional ordering or phase-separation is possible depending on the growth conditions\textsuperscript{170 - 173} and that these compositional fluctuations may contribute midgap electrical states that contribute to non-radiative recombination\textsuperscript{174} or affect the optical properties of the material through spectral broadening of the luminescence of the material\textsuperscript{172}. (In some cases, the phase separation mechanism inherent in these materials is used to intentionally grow quantum dot layers for use as laser active regions\textsuperscript{175,176}). However, the anaglyph shown in Figure 4-9 indicates that the image modulation occurs on the upper membrane surface (especially in the region that was labeled ‘sample preparation artifact’ in Figure 4-8). Furthermore, Treacy et al.\textsuperscript{177} and others\textsuperscript{178,179} have shown how strain present in a TEM membrane can give rise to periodic bending of near-surface lattice planes, thus giving the impression of phase separation. These features are experimentally and theoretically seen for sample thicknesses of up to ten times the extinction distance of the electron beam in the sample. Therefore, the long-range periodicity visible in the plan view TEM image may be more likely indicative of strain in the membrane and not a reflection of compositional modulation in the active region of the laser.

\textsuperscript{xxxii} The term “punch-out” dislocation refers to dislocations which are apparently caused due to stresses associated with the oxide layers (i.e. in contrast to misfit or threading dislocations). Hull and Bacon (reference 83, p. 165) use the term in describing dislocation punched out around an inclusion.
Figure 4-6. Power vs. current before and after degradation for V1-C.

Figure 4-7. Power vs. time for operation at 23 mA for V1-C
Figure 4-8 Planview TEM image of V1-C.
VCSEL V1-D that has been degraded for 60 seconds at 23mA is shown in Figure 4-12 and the relevant P-I and P-t traces are given in Figure 4-10 and Figure 4-11 respectively. The features labeled, oxide/e-beam interaction, are bend contours resulting from an e-beam induced volume change due to recrystallization of the oxide. Although no dislocations were detected in the TEM membrane, it is evident that the DBR layers at the peripheries of the narrower aperture have been disrupted. This disruption is made clearer by the FIB secondary electron image given in Figure 4-13. (There is a 180º rotation between the TEM image in Figure 4-12 and the FIB image Figure 4-13. It is easiest to see the correlation between the two images by matching up the feature labeled
(a). In Figure 4-13, the membrane surface is tilted 45° with respect to the plane of the image. Furthermore, the stripes in Figure 4-13 are classic examples of the effect of misorientation between the Ga⁺ beam and the heterointerfaces of the sample. Apparently, part of the upper DBR has shifted vertically, as is seen in the relative positions of the stripes (due to misorientation between the Ga ion beam and the interfaces of the device) in the area of the active region in Figure 4-13, and the origination of the shift is near the periphery of the narrower oxide aperture. That this feature is not related to the FIB sample prep technique is precluded by the fact that similar features have not been detected in undegraded planview samples. Furthermore, it is shown later that this feature does not arise due to strain effects on the thin membrane as similar features are seen for serial FIB sectioning of degraded VCSELs for which a thin foil is not fabricated.

One additional degradation feature in Figure 4-12 (it is also faintly detected in the plan-view image of V1-C) are the diagonal streaks in the vicinity of the DBR disruption region. These streaks extend over the entire active region although the strength of the image contrast due to these features is apparently linked to the composition of DBR layer that is at the membrane surface. Furthermore, as is seen in the anaglyph in Figure 4-14, these features are at the surfaces of the membrane. The precise origin of these features is not understood at this time.
Figure 4-10 Power vs. current before and after degradation for 60 seconds at 23 mA for V1-D^{xxxiii}.

Figure 4-11. Power vs. time during degradation of V1-D at 23 mA.

^{xxxiii} The appearance of two traces on the low drive-current side of the power output peak is likely due to “self-pulsations” of the laser output, a little understood phenomenon that has been linked to laser degradation^2.
Figure 4-12 Planview TEM image of V1-D, for which (a) is used to show the correlation between this TEM image and the following FIB image.
Figure 4-13 Plan-view secondary electron image of upper DBR of V1-D.
The results of the degradation of VCSEL V1-E for 120 seconds at 23mA, are shown in Figure 4-17 and relevant P-I ad P-t traces are given in Figure 4-15 and Figure 4-16 respectively. The mirror damage that is present is marked as ‘DBR disruption’ and represents areas where the crystal has likely started to crack at the oxide interface, as is shown in the cross-section samples that follow. Further confirmation that this contrast feature is due to disruption of the DBR is shown later via serial FIB sectioning of the upper DBR of V1-H. Surprisingly, it appears that the mirror damage is not as severe in the vicinity of the active region of this sample, despite the longer operation time with
respect to VCSEL V1-D. However, it is expected that some variation should exist in
degradation behavior among devices from the same wafer (e.g. devices will fail at
different times during lifetime testing). This particular device seems to be relatively free
of damage in the vicinity of the active region, although some mechanism, possibly the
current shunting mechanism has caused the significant decrease in output power.

Finally, the anaglyphic TEM image in Figure 4-18 is used as further evidence that
features attributed to sample preparation artifacts are on the surface of the membrane.
Namely, a large patch of rough contrast due to ion beam and interface misalignment is
seen to be on the bottom membrane while a narrower stripe of rough contrast is seen to
be on the top of the membrane. The dark line across the image is also seen to be on the
upper surface and is due to a ledge on the membrane surface.
Figure 4-15. Power vs. current traces before and after degradation at 23mA for 120 seconds for V1-E.

Figure 4-16. Power vs. time during degradation of V1-E at 23mA.
Figure 4-17 Planview TEM image of degradation in V1-E.
VCSEL V1-F, which has also been degraded at 23mA for 120 seconds, is shown in Figure 4-21 and relevant P-I and P-t curves are given in Figure 4-19 and Figure 4-20 respectively. This cross-section image and the image at higher magnification in Figure 4-22 show more clearly the nature of the DBR disruption that was shown in previous plan-view images. Specifically, much of the upper DBR has separated from the oxide layer. Associated with this oxide/crystal separation is a crack extending into the upper DBR region that covers a significant portion of the active region (the actual three-
dimensional nature of this feature is shown later). Despite the fact that a significant portion of the crack does not exhibit a clear void in the TEM image, further evidence that this contrast feature type is a crack is shown for VCSEL V1-G. Briefly, the normal to the inside surfaces of the crack for that portion which does not exhibit a void is not parallel to the plane of the membrane, so that the TEM image consists of the projection through the inside surfaces of the crack.

It should be noted that no defects in the form of glide or climb dislocations are detected in this cross-section slice, or in the plan-view slice shown for VCSEL V1-E, both of which were degraded for 120 seconds. Furthermore, while the large defect in the upper DBR likely would cause serious loss of lasing (e.g. by loss of the resonance cavity), the decrease in spontaneous emission (which should still be present regardless of the cavity structure and which is inferred by the gradual decrease in the P-t trace in Figure 4-20) is likely due to some other degradation mechanism, such as current shunting.162

![Graph](image)

**Figure 4-19** Power vs. current traces before and after degradation at 23 mA for 120 seconds for V1-F
Figure 4-20. Power vs. time trace during degradation of V1-F at 23 mA.

Figure 4-21. Cross section 00-4 bright field TEM image of V1-F
A greater extent of damage is observed in VCSEL V1-G, which has been degraded at 23mA for 240 seconds. As the cross section image shows in Figure 4-25 (relevant P-I and P-t curves are given in Figure 4-23 and Figure 4-24 respectively), there is more severe cracking (i.e. two cracks labeled (a) and (b)) in the upper DBR with respect to the previous VCSELs degraded only for 120 seconds. The nature of the crack is less certain for segments of the defect such as the area in Figure 4-25 marked (c) which do not exhibit void regions under the sample tilt used for the image shown. However, tilts can be found for which all segments of the defect do exhibit a separation of the DBR crystal (i.e. the plane of the crack is not constant over its length in the TEM membrane).
Figure 4-23 Power vs. current traces before and after degradation of V1-G at 23mA for 240 seconds.

Figure 4-24 Power vs. time during degradation of V1-G at 23mA.
Furthermore, as seen in Figure 4-26, portions of the crack contain a nanocrystalline material (evidenced by the white speckle contrast in the crack). Electron diffraction analysis of this material has yielded a ring pattern with spacings consistent with the planer spacings of $\gamma$-Al$_2$O$_3$ as is shown in Figure 4-27. These oxide bridges were also seen during TEM sample preparation in the FIB as seen in Figure 4-28, thus the oxidation does not occur as a result of exposing the thin membrane to air (the FIB chamber is under a vacuum of $10^{-7}$ Torr). Undegraded devices did not exhibit cracks indicating that device processing (e.g. oxidation of current confinement layers or rapid thermal annealing) did not directly result in these features. Thus, it appears that the cracking and development of the oxide bridges occurred during the degradation of the device\textsuperscript{xxxiv}. The source of oxygen for the oxide bridges to occur is possibly the oxide confinement layer, as all of the DBR cracks (for samples discussed later as well) are seen to terminate on the oxide layer. (An excess H$_2$O concentration is likely present in the oxide layer due to the fact that the oxidation process is terminated by removing the

\textsuperscript{xxxiv} Similar crack-like features have been observed by researchers at SUNY Albany (unpublished results).
sample from the oxidation furnace. Thus, $\text{H}_2\text{O}$ molecules in transport through the oxide layer when the sample is removed from the furnace are quenched in). It is not likely that the development of the oxide bridges acts to separate the surfaces of the crack as the oxide of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ contains a smaller volume than the crystal it consumes. Thus, it is likely that the cracks developed because of stresses associated with the oxide layer and that as the cracks formed, the high Al content layers of the DBR experienced conditions favorable to oxidation (e.g. heat from the operating device and a source of water molecules. Regarding the former, active region temperatures in good devices can reach $\sim100^\circ\text{C}$ when operated near the roll-over current$^{180}$. Poor heat sinking in this device may have contributed to yet higher temperatures).

Finally, at this level of degradation, a second reduction$^{xxxv}$ occurs in the P-t trace (Figure 4-24). It is also at this level of degradation that a dislocation dipole/loop array exists in the active region of the VCSEL. Furthermore, there is a small segment of dislocation in the lower DBR (labeled “mirror dislocation”), which likely is associated with the oxide aperture tip. (The location of coincidence of this mirror dislocation and the oxide aperture presumably occurs in a portion of the VCSEL that was removed in fabricating the TEM membrane). Although the correlation between the oxide aperture tip, the mirror dislocation, and the dislocation array in the active region is shown more clearly in the following data, it seems likely that this second decrease in power output is linked with the existence of the dislocation array in the active region which occurs only after this level of degradation. This correlation is further clarified with the data shown below.

$^{xxxv}$ That is, although the power output was steadily decreasing with time, after roughly 200 seconds, the power begins to decrease more rapidly.
Figure 4-26. Dark field TEM image showing regions of nanocrystalline oxide in a DBR crack.

Figure 4-27. Diffraction pattern from the oxide contained in the crack, which has spacings consistent with $\gamma$-$\text{Al}_2\text{O}_3$. 
Figure 4-28. Secondary electron taken in the FIB during TEM membrane fabrication, showing a crack extending over a portion of the upper DBR. The lighter contrast regions correspond to oxide bridges.

VCSEL V1-H, degraded at 23mA for 800 seconds is shown in Figure 4-31 and relevant P-I and P-t traces are given in Figure 4-29 and Figure 4-30 respectively. For this device, the initial laser output is not as strong as for the bulk of the devices studied here, although extensive degradation has occurred again suggesting that the electrical current is a significant factor in the degradation process.

This VCSEL exhibits punched-out dislocations and a dislocation array. These features are shown in three dimensions in the anaglyph in Figure 4-32. The light stripe that transverses the image horizontally and the ribbon of speckle contrast are due to the FIB and are not features of degradation. That these are surface features from the membrane fabrication process is more clearly seen in the anaglyph in Figure 4-32. An additional feature of interest in the anaglyph is the fact that the punched out dislocations appear to extend from the lower to upper membrane surface while the dislocation array is confined to one plane of the membrane (presumably the active region as is shown later for VCSEL V1-J).

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Sample preparation artifacts similar to the light line (i.e. ~perpendicular to the Ga-beam direction in the FIB) occur when a ledge or valley is formed on the side of the membrane due to prematurely advancing the sample into the path of the Ga-beam. Ideally, the membrane is only advanced after the membrane region previously under the beam is milled to the desired depth. The ribbon of speckle contrast is due to the exposure of a differing Al-content layer as the sample bowed slightly into the path of the Ga-beam front.
A more detailed description of the types of damage at this level of degradation is deferred until the entire set of results of the characterization of oxide-confined VCSELs is discussed in Section 4.1.1.1. Still, it should be noted that the second serious reduction in output power occurs at ~700 seconds, whereas in the previously described sample, it occurred near 200 seconds. However, despite the later occurrence of this second drop, the coverage of the dislocation dipole array is still relatively small (< ½ of the active region), compared with samples degraded longer (that are discussed later) suggesting that this type of failure mechanism has operative for a relatively short time. Thus, it is likely that the nucleation of the threading dislocations and dipole/loops was as recent as 700 seconds. Further proof of this is given after the remaining V1 VCSELs are discussed.
Figure 4-29. Power vs. current before and after degradation of V1-H at 23 mA for 800 seconds.

Figure 4-30. Power vs. time during degradation of V1-H at 23 mA.
Figure 4-31 Planview TEM image of degradation in V1-H
Figure 4-32 Anaglyphic TEM image of V1-H (blue lens - right eye).

VCSEL V1-H is also used to show the three-dimensional nature of the upper DBR damage. Figure 4-33 shows a series of secondary electron images taken in the FIB after successive milling steps through the upper DBR (starting at (1)). Here, a technique is used whereby the sample can be imaged in the FIB along the normal to the device and then milled with the beam parallel to the device heterojunctions\textsuperscript{xxxvii}. Thus, after milling roughly ~0.5\(\mu\)m off the top of the VCSEL, the sample is imaged, then another ~0.5\(\mu\)m is

\textsuperscript{xxxvii} Normally, because the stage in the FIB only allows for 45° of tilt, secondary electron images are taken at a 45° angle with respect to the surface normal. However, by mounting the sample on a 45° stub, viewing angles 0°-90° with respect to the surface normal can be achieved.
milled off the top of the sample, and so on. As can be seen, the crack (or DBR disruption) extends close to the top of the VCSEL (consistent with the cross section and planview images already shown). At the level of the active region (image segment (6)), the crack coincides with the oxide layer over nearly 2/3 of the oxide aperture. Two square edges where the crack ends on the oxide aperture are seen in the last image in the series. Further clarification of the three dimensional nature of the crack is possible by comparison of the serial sectioning in Figure 4-33 and the cross-section sample shown in Figure 4-21.
Figure 4-33 Planview section series through upper DBR of V1-H
Further evidence that a second decrease in output power occurs only after the nucleation of punched-out dislocations and a dipole/loop array is seen in VCSEL V1-I. This sample, shown in Figure 4-36 (relevant P-I and P-t curves are given in Figure 4-34 and Figure 4-35 respectively), exhibits oxide/crystal separation and two cracks but no punched-out dislocations or a dipole/loop array. The absence of these linear defects is thus likely attributed to the lack of a secondary power decrease in the P-t trace for this sample.

![Figure 4-34 Power vs. current traces before and after degradation of V1-I at 23 mA for 1000 seconds.](image-url)
Figure 4-35. Power vs. time during degradation of V1-I at 23 mA.

VCSEL V1-J, which has been degraded at 23mA for 1200 seconds, is shown in Figure 4-39 and relevant P-I and P-t curves are shown in Figure 4-37 and Figure 4-38 respectively. This sample exhibits disruption of the DBR layer, punched-out dislocations
associated with the oxide aperture and coverage of the entire active region by a dislocation dipole/loop configuration. Accordingly, the P-t curve exhibits a second drop at ~500 seconds and presumably, the remaining ~700 seconds of degradation were sufficient to generate the defect density seen throughout the active region.
Figure 4-37. Power vs. current traces before and after degradation of V1-J for 1200 seconds at 23 mA.

Figure 4-38. Power vs. time during degradation of V1-J at 23 mA.
Figure 4-39 Planview TEM image of degradation in V1-J.

The corner of the active region containing the high density of punched-out dislocations is shown at higher magnification in Figure 4-40. Segments of some of the punched-out dislocations undergo climb as evidenced by helical shaped dislocation segments\(^8\) (marked (b) in image Figure 4-40). Furthermore, the loops seen in Figure 4-39 and Figure 4-40 appear to be “self standing”; that is, without an apparent association to the punched-out dislocations. The fact that the observable loops do not exhibit stacking fault contrast for low index diffraction conditions of the <110> zone axis (the cross section images) or the <001> zone axis (the majority of the planview images) indicates that they are perfect dislocation loops.
The Burgers vector of the dislocations present in VCSEL V1-J is determined by standard contrast techniques. Of the low index diffraction conditions checked (±400, ±040, ±220, ±-220 at the [001] zone axis and ±111, ±-31-1, and ±1-3-1 at the [112] zone axis) only the ±400 and ±-311 two beam conditions gives residual contrast as shown in Figure 4-41 and Figure 4-42. Thus, the Burger’s vector is perpendicular to the −400 and -311 directions (i.e. there should be residual contrast only for the two beam condition \( g \) such that \( g.b = 0 \)) and dislocation segments should be completely invisible if they satisfy the full invisibility criteria, \( g.b_x=0, g.b_z=0 \) (where \( b_z \) is the edge component of a mixed dislocation) and \( g.b = 0 \). Thus, the cross product of [−400] and [-31-1] gives the burgers vector ±½a[0-11] which is inclined 45° from the plane of the active region. While there will be residual contrast if not all three invisibility criteria are met, screw dislocations automatically meet all the criteria if \( g.b = 0 \). Thus the segment marked a in the figures below (and Figure 4-40) is a screw segment.

Discussion regarding the nature of dislocation growth across the active region is reserved until after the remaining V1 sample is described.

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**Figure 4-40 Loop/dipole array in active region of V1-J. Labeled are, (a) a screw segment as determined by dislocation contrast analysis and, (b) a helical dislocation segment.**
VCSEL V1-K which was also degraded for 1200 seconds at 23mA is shown in Figure 4-45 through Figure 4-47 and relevant P-I and P-t traces are given in Figure 4-43 and Figure 4-44 respectively. This sample exhibits the degradation features already seen (e.g. oxide/crystal separation, DBR disruption in the form of cracking, punched-out dislocations extending into the upper and lower DBRs and a dislocation dipole/loop array in the active region). Again, the complete coverage of the active region by the dipole/loop array is consistent with continued degradation for a significant time (~700 seconds) after the initial introduction of the punched-out dislocations and the dipole/loop array presumably after only ~500 seconds of degradation, as is seen in the P-t trace for this sample.
Figure 4-46 shows more clearly the association of the threading dislocations with the oxide aperture tip (i.e. they only occur in the vicinity of the oxide aperture). In Figure 4-47 the vertical extent of the dislocation dipole/loop is seen to be limited to the active region. As discussed in the background material for this work (Section 2.3.3.1), this spatial confinement could be related to the fact that carrier recombination is largely limited to the active region of the device, or due to the fact that the stress state of the DBR layers is not conducive to climb of the dislocations (which is consistent with the higher compressive stress of the $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ DBR layer above the GaAs active region if the climb is extrinsic in nature\textsuperscript{xxxix}). Two different dislocation geometries are observed in the active region (marked as a and b) which will be discussed shortly.

![Graph showing Power vs. Current traces before and after degradation of V1-K at 23 mA for 1200 seconds.](image)

\textsuperscript{xxxix} At room temperature, the $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ layer is under a compressive stress of ~0.14%.
Figure 4-44. Power vs. time trace during degradation of V1-K at 23mA.

Figure 4-45. Cross-section TEM image of material degradation in V1-K.
4.1.1.1 Discussion of microstructural degradation features in VCSEL V1

Consideration of the results just presented (especially those for V1-J and V1-K) provides a clearer understanding of the mechanisms operable in the failure of VCSEL V1. The power output and applied voltage are plotted as a function of time for VCSEL V1-J in Figure 4-48. Due to the fact that the driving current is held constant (at 23 mA), an increase in applied voltage represents an increase in device resistance. Thus the initial increase in voltage is consistent with a mechanism that increases the resistance of the VCSEL, possibly the current shunting mechanism. The more severe fluctuations in the voltage trace after ~100 seconds may be associated with the development of the cracks in the upper DBR (it has already been shown that cracks form during the time before the second power drop in spontaneous emission). Finally, after ~400 seconds, the resistance
of the device appears to decrease at the same time that the secondary drop in spontaneous emission occurs. Thus, it is likely that a low resistance current path develops such that current flows again through the active region (i.e. negating the current-shunting mechanism), which provides the energy source (i.e. by non-radiative recombination) for the development of the dislocation array that grows across the active region.

![Figure 4-48. Power output and applied voltage as a function of time.](image)

The 3D positioning of the various features of degradation is shown in the active region of V1-J in the anaglyph in Figure 4-49. Several of the punched-out dislocations have segments that thread to the upper membrane surface. There are at least two segments of the dislocation loop array (marked by arrows) that rise out of the image and thus do not resemble to rest of the array. Furthermore, the anaglyph suggests that the arrowed segment on the right extends on the (-111) plane while the segment on the left extends on the (1-11) plane. Thus these two segments are likely relatively long glide and climb segments respectively based on the previous determination of the burgers vector of these dislocations. An occurrence of this relatively longer dislocation geometry was seen
in V1-K in Figure 4-47 (marked a). These longer climb or glide segments only occur in the thicker clad layers; i.e. in a region free of interfaces. Thus, there is a strong indication that the multiple interfaces of the active region act to contain a significant portion of the dislocation length within that region (i.e. dislocation segments having relatively long vertical components are not seen in the quantum well region which contains relatively close-spaced interfaces).

The greater part of the dislocation loop array has its average normal direction perpendicular to the plane of the active region, shown in Figure 4-47 (dislocation geometry b) and shown as relatively flat in-plane loops in Figure 4-49. That entire loops are confined to the thin active region (having a [001] normal) and the fact that the Burger’s vector is oriented 45° from the plane of the active region indicates that the dislocations propagate by continually “reflecting” back to the quantum well region (likely through a combination of climb, glide, and multiple cross slip events as is discussed shortly). Continuous glide or climb motion of the ±½a[0-11] dislocation (i.e. without cross-slip to motion on another allowed {111} plane) would not produce a dislocation pattern having an average normal in the [001] direction (i.e. perpendicular to the plane of the active region). (For example, the pattern produced by continuous glide motion would have an average normal perpendicular to the ±½a[0-11] direction). This confining behavior suggests that the dislocation propagation is dependent on the available energy due to non-radiative recombination occurring in the quantum well region and that the dislocation segments preferentially propagate within a region where this source of activating energy exists.
The spatial arrangement of dislocations in VCSEL V1-J in the plane of the substrate is also significant. As shown in Figure 4-50, there appears to be a primary dislocation (traced in red) that has moved through the active region, leaving dislocation loops in its wake. The apparent origin of the primary dislocation was a punched-out dislocation in the upper left corner of the image of the active region presumably caused by stresses related to the oxide aperture (other punched-out dislocations have also begun to exhibit a jagged nature). There are other documented cases whereby a primary dislocation gives rise to dislocation loops as it moves through material (e.g. the Orowan...
mechanism\textsuperscript{83,181,182}). The basic mechanism is one in which a dislocation bows around an obstacle to the extent that the separated fronts meet and form a new dislocation front as well as a loop. While there are no obvious obstacles from TEM imaging in the active region of V1-J, it appears that as fingers of the primary dislocation develop, some of them meet, forming a new dislocation front and leaving “oxbow-lake” loops behind. Thus, a model is proposed, as explained below, whereby the only obstacles leading to the development of the oxbow-lake loops are the heteroepitaxial interfaces bounding (and possibly within) the active region of the device. As was seen previously, the dislocations are generally contained within the quantum well region (although they sometimes extend as far as the inner edges of the DBRs). Thus the upper and lower bounds of the active region acting as obstacles to the dislocation, may lead to the development of the oxbow-lake dislocations. A possible scenario in which this might occur is depicted in Figure 4-51. The schematic shows five successive snapshots of a growing dislocation loop, although the model works equally well for a long dislocation segment passing through the region depicted. The terrain shown is a set of \{111\} planes, which are the sets of planes that dislocations in zinc-blende semiconductors glide on. In the model, the dislocation is prohibited from moving above or below region depicted (the boundaries of which are marked by blue lines in the crests and valleys) similar to the manner in which the dislocations under discussion are confined to the active region. As the loop expands, screw portions of the loop may cross slip onto other \{111\} planes containing the $\frac{1}{2}\mathbf{a}<110>$ type burgers vector (i.e. similar to the model in which multiple cross-slip occurs under conditions of REDM as proposed by Matsui et. al.\textsuperscript{58} as discussed in Section 2.3.3.3). Upon reaching the upper or lower boundary of the region, edge or mixed character segments may be induced to switch from glide motion to climb motion (on a \{111\} plane not containing the burgers vector) or vice versa. Thus, as depicted, a series of these actions can produce a dislocation front with a jagged nature, some fingers of which can meet, annihilate and form oxbow-lake dislocation loops. While the residual stress state present in the VCSEL is initially complex and further complicated by the introduction of the dislocation array into the active region, it must be assumed in applying this model to VCSEL V1-J that the average stress state is one which favors the
occurrence of repeated cross-slip and glide-to-climb orientations such that the net dislocation motion is in the direction shown in Figure 4-50.

Figure 4-50. 220 bright field TEM image of active region of V1-J with primary dislocation front traced in red. The arrow indicates the approximate direction of motion.
Figure 4-51. Schematic of five successive iterations in the dislocation behavior leading to development of “oxbow lake” loops. In the schematic, a dislocation (burger’s vector, $b = \frac{1}{2}a<110>$) exists on a $\{111\}$ plane and is confined vertically (within the blue lines at the crests and valleys shown). Through a series of glide, g, climb, c, and cross-slip motions, s, segments of opposite sign can meet, forming the oxbow-lake loop.

Finally, Figure 4-52 shows a plot of the fraction of defect free active region of the V1 samples as a function of time after the secondary power drop (e.g. as occurred at ~400 seconds for V1-K as shown in Figure 4-45). Here, the defect free active region is the area of the active region in which no dislocations exist. In areas where dislocations do exist the dislocation spacing is typically less than 1um (approximately the minority carrier diffusion length for III-V materials$^{183-194}$). Thus, luminescence from these areas will be significantly decreased as carriers migrate to and non-radiatively recombine at the dislocations. This graph lends support to the argument that the secondary drop in power indicates the onset of dislocation propagation throughout the active region. Specifically, the two data points with a dislocation free active region area of ~37$\mu$m$^2$ are from samples V1-G and V1-H operated for a total time of 240 seconds and 800 seconds respectively, thus illustrating a much stronger correlation between the dislocation free active region
and the time after the second power drop than there is between the dislocation free active region and the total operating time. Furthermore, as further evidence of this relationship, for V1 samples showing no secondary power drop, the active region remains free of dislocations.

Figure 4-52. Defect free active region area as a function of time after the second power drop. The inset represents one of the P-t traces (from Figure 4-38) showing a secondary drop in optical power and the arrow indicates the relevant data point.

4.1.1.2 Commercial oxide confined devices

As is seen in the cross-section and plan-view images of a severely degraded oxide confined VCSEL V2 (Figure 4-53 and Figure 4-54 respectively), a dislocation dipole array extends well past the edge of the oxide aperture tip. It is generally accepted that both optical and electrical fluxes exist outside the oxide aperture within a few microns due to lateral carrier diffusion (proportional to the carrier concentration gradient) or due to the active region having a resistance greater than the mirror layers (i.e. leading to a lower resistance current path parallel to and above the active region instead of through
The extent of the first effect is controlled to some extent by the carrier population, carrier diffusion length and device architecture. Because the second effect occurs when the resistance of the current path through the active region diode is greater than the resistance of the VCSEL layers between the active region and oxide layer, the extent of the current spreading may also be controlled by the level of degradation in the active region. Specifically, in forward bias, dislocations will act to restore the equilibrium concentration of carriers (i.e. as would be present in the absence of an applied bias) by acting as recombination sites. Compared to undegraded areas, the degraded area of the active region has a higher resistivity due to lower carrier concentrations. Thus, carriers will flow laterally, around the high resistivity degraded region. Eventually, as the defect array fills the active region within the aperture, carriers will flow under the oxide layer, ultimately contributing to the extension of the dislocation array beyond the edges of the oxide aperture.

Figure 4-53. TEM cross-section image of V2-A.
Figure 4-54 Planview TEM image of V2-B.
In VCSEL V2 the radial arrangement of dislocation dipole array (as seen viewed along the device normal in the planview image in Figure 4-54) is markedly different from the overall linear arrangement of dislocation dipole arrays (i.e. as in DLDs; discussed in Sections 2.1.1 and 2.3.3) seen for edge emitting lasers as reported in the literature. Furthermore, when VCSEL V2-B was viewed using the EL technique (EL data was provided with the degraded VCSEL), as shown in Figure 4-56, the non-luminescent region corresponding to the radial dislocation array was two-dimensional, resembling a dark-area defect which is normally attributed to heavy concentrations of point defects. In previous reports on degradation in VCSELs\textsuperscript{163,164}, there has not been a successful correlation of similar two dimensional non-luminescent regions to a fundamental
degradation feature. However, this correlation between a dark area defect as seen in the EL image in Figure 4-56 and a radial dislocation dipole array as seen in the TEM image in Figure 4-54 has been shown clearly for the first time in this work with the use of the planview sample preparation technique. Fundamental mechanisms responsible for the radial nature of the dislocation arrays are discussed at the end of this chapter.

![Image of EL image](image.png)

**Figure 4-56** Forward biased EL image of surface of V2-B.

4.1.2 Degradation in Proton Implanted devices

All devices shown in this section were completely failed so that observation of incremental failure was not possible. However, analysis of these completely failed VCSELs is still informative.

One such example of degradation in a proton-implant confined VCSEL is shown in Figure 4-57. A large dipole array has apparently nucleated from a short segment (~6µm) of a linear dislocation that runs through the active region. The majority of the arms of the dipole array can be traced back to the nucleation of a single dipole as is
demonstrated by the blue line in Figure 4-58. Other segments of the dipole array cross the linear dislocation but do not appear to have interacted with it, which suggests that the dislocations exist at different depths in the active region (further evidence of this is given shortly). The circular confinement of the dense array of dislocations is apparently associated with the circular proton implant aperture used. Again, it is likely that beyond the implant aperture (through which no current flows), the level of carrier recombination is sufficiently low to prevent the REDM mechanism from operating. Segments of the dipoles are approximately aligned along <100> directions in the plane of the active region which is consistent with the preferred orientation of the climb based DLDs as seen in edge emitting lasers.

A portion of the dipole array (the upper ~5µm of the region enclosed by the black line in Figure 4-58 and shown at higher magnification in Figure 4-59) exhibits an array of stand-alone dislocation loops in an arrangement similar to the characteristic pattern of dislocation arms in the remainder of the array as is shown at higher magnification in Figure 4-59. To elucidate the equilibrium state of these dipoles, a proton implanted device containing a similar dipole pattern was heated for 20 minutes at >600ºC. TEM images before and after this treatment are shown in Figure 4-60 and Figure 4-61 respectively. It is evident that provided this thermal energy, the dislocation dipole arms form loops indicating that the loops represent a trend toward an equilibrium distribution of dislocations. While it is thus likely that these loops in device V3 were once connected to form dipoles in a pattern similar to that seen in the remainder of the loop, it appears that the formation of loops represents a trend towards equilibrium (implying that the dipole configuration represents a non-equilibrium condition) and/or that some of the point defects involved in the formation of the original dipoles may have been drawn to the tips of the other, more recently grown dipoles leading to the formation of these loops. Similar behavior was reported in the literature in a TEM sample containing a DLD type dislocation array whereupon by heating the sample to 440ºC for longer times, some loops and dipoles grew at the expense of others.51

Several parallels can be made between the dislocation patterns seen in V3 and the complex extended patterns seen in other branches of science (e.g. dendritic growth or diffusion limited aggregation). While rigorous modeling would be necessary to assign
the operation of physical mechanisms which lead to complex-extended patterns (e.g. the Mullins-Sekerka instability\textsuperscript{245}) to the dislocation patterns seen in degraded laser material, such parallels are tentatively discussed in Appendix-D.

Figure 4-57. 220 bright field TEM image of the dislocation dipole array in VCSEL V3.
Figure 4-58. 220 planview TEM image of degradation in VCSEL V3. The array enclosed by the black line is from an earlier growth. The blue line demonstrates that the end of any dislocation arm can be traced back to a single nucleation site.
Figure 4-59. Nucleation of dipole array in VCSEL V3

Figure 4-60. TEM image of a dislocation dipole array before heating at 615°C.
The Burgers vector of the dislocation array in VCSEL V3 was determined using standard invisibility criteria. The plan view images in Figure 4-62 and Figure 4-63 show the dislocation array in residual contrast only for the [-400] and [-311] two beam conditions. As discussed in the footnote on page 110, loop segments that do not satisfy the full set of invisibility criteria will exhibit image contrast. Furthermore, for the set of diffraction conditions (i.e. \( \mathbf{g} \)'s) which satisfy the \( \mathbf{g} \cdot \mathbf{b} = 0 \) criteria, the level of residual dislocation contrast is effected by the value of \( \mathbf{g} \cdot \mathbf{b} \mathbf{u} \). Thus, it is expected that the level of dislocation contrast in Figure 4-62 and Figure 4-63 will be different. Finally, though the contrast appears strong in Figure 4-62, the exposure time is several times the exposure time for images taken under \( \mathbf{g} \cdot \mathbf{b} \neq 0 \) (e.g. Figure 4-59), indicating a condition of residual contrast. Thus as discussed for the Burger’s vector analysis of V1-J, the Burger’s vector is the cross product of these two diffraction vectors, \( \pm \left\frac{1}{2} \mathbf{a}[0\text{-}11] \right\).
Figure 4-62. 400 two beam TEM diffraction image showing residual contrast.

Figure 4-63. -311 two beam diffraction contrast image showing residual contrast.
Anaglyphic TEM images of V3 are given in Figure 4-64 and Figure 4-65. In contrast to the dislocation array seen in VCSEL V1, the arms of dislocations in VCSEL V3 appear to have a component in the vertical direction (with respect to the plane of the anaglyph). While it is difficult using this qualitative form of stereomicroscopy to ascertain the precise plane on which the dislocation dipole array exists, it is evident that the normal to this plane is in the vicinity of the [101] direction (i.e. towards the upper right hand corner of the image and out of the page). The fact that the direction of the Burger’s vector (±½a[0-11], i.e. towards the lower right hand corner of the image and out of the page) is not perpendicular to any {111} plane-normals in this vicinity is consistent with those claims in the literature (as discussed in Section 2.3.3) that the extension of the dislocation arms is by climb. Finally, as was suggested earlier, apart from the region of initial growth, the dislocation does not interact with the seed dislocation. Rather, in these stereograms, the dislocation array appears to have grown on a plane under the seed dislocation.
Figure 4-64. Anaglyphic image of V3 (red lens - right eye).
A second possible mechanism by which dislocation patterns form via REDM is depicted in Figure 4-66. In this sample a dense cluster of linear dislocations extends from lower to upper DBR (and likely from the substrate to the surface of the VCSEL although this is not verifiable in light of the fact that this portion of the device is removed in sample preparation). The vertical cluster of dislocation loops appears to have generated a
set of glide\textsuperscript{a1} dislocation half-loops that extend perpendicular to the cluster. On several of these glide dislocations, dipoles have formed that extend approximately in the [010] direction. A fortunate consequence of the growth of the defects in this sample is that it elucidates, in a series of snapshots, a mechanism of formation of dipoles and subsequent loops off of glide dislocations. Specifically, on the smallest glide dislocation, labeled (a), there is a small rise in the upper left leading edge of the dislocation, which presumably is the start of a dipole. On the second and third glide dislocations, (b) and (c), the dipole is increasingly extended while the base is increasingly pinched off. Finally, on the fourth glide dislocation, (d), the dipole is completely pinched off leaving a dislocation loop behind. It is also likely that the glide dislocations continued to move after the loop pinched off as is seen in the fact that while dipoles (a)-(c) occur on the leading upper edge of the glide dislocation, in dislocation (d), the upper leading edge has progressed past the bottom of the loop. Thus, dislocation loops may be formed in the active region by a gliding dislocation. Subsequently, the glide dislocation may continue to move leaving freestanding dislocation loops. The source of the point defects necessary to create the dislocation loops may be generated at the gliding dislocation from non-radiative recombination\textsuperscript{59} (e.g. from the phonon kick mechanism as discussed in Section 2.3.3.3) or from possible compositional irregularities at the numerous heterointerfaces in the active region, both of which are point defect sources that have been reported in the literature\textsuperscript{12,68,70-72}.

Finally, there are no obvious crystalline defects that would indicate a clear reason for dipole growth to occur in the orientation seen (e.g. akin to a drag point or other obstacle that one would expect to influence a gliding dislocation). However, as discussed in the background section, dipole extension is favored in <100> directions. Thus, the combination of, (i) a source of point defects, (ii) minority carriers from the operation of the laser, (iii) a dislocation upon which to nucleate (and where non-radiative recombination likely occurs), (iv) the preferred crystallographic growth orientation and,

\textsuperscript{a1} The assignment of glide nature to the dislocations seen here is due to the fact that glide dislocations are typically relatively straight. Conversely, climb dislocations typically exhibit extensions with a relatively high radius of curvature (e.g. dipoles) or a wavy nature (e.g. from the two-dimensional projection of a helical dislocation).
(v) a stress field capable of driving the growth, are believed to be sufficient to cause the
growth of the dipoles in the manner seen in this sample.

![Figure 4-66. Mechanism of loop nucleation in VCSEL V4.](image)

4.1.3 Catastrophic failure

Devices subjected to unintentional high current pulses such that output powers
reach $10^6 \text{W/cm}^2$ typically degrade catastrophically due to the extreme optical density.
Alternatively, if a device is operated under constant power conditions (i.e. such that
current varies to keep the output power constant), current densities near the end of the
VCSEL lifetime increase sharply as the efficiency decreases, and the VCSEL can fail due
to electrical overstress$^{200,201}$.

A case of catastrophic failure is shown in cross section for VCSEL V5 in Figure
4-67. Whereas catastrophic failure often occurs at the mirror surface in an edge-emitting
laser, the focal point of damage in V5 appears to be the active region. Features of the
catastrophic damage include melting and void formation at the active region and a high density of dislocation tangles and stacking faults that appear to have grown semi-radially from the active region.

Figure 4-67 Cross section TEM image of catastrophic damage in VCSEL V5.

Catastrophic damage in V6 is shown in planview in Figure 4-68. Voiding has occurred which is apparently associated with melted portions of the active region. Arms of darker contrast are apparently radial extensions of molten zones from the center of the active region. Finally, a network of dislocation tangles also exists around the catastrophic damage in the center of the active region presumably due to stresses generated during melting and recrystallization.
Thus, catastrophic failure in VCSELs appears to proceed differently than is typical for edge emitting lasers, presumably due to the very different device geometries. Specifically, catastrophic failure in edge emitting lasers usually begins on the mirror surface or at an inclusion in the active region of the laser. For the two VCSELs just shown, it is evident that failure has begun in the center of the device and propagated outward. Furthermore, catastrophic failure in part relies on thermal run away from intense non-radiative recombination (i.e. a self-feeding mechanism in which the defect created generates more heat via non-radiative recombination which propagates the defect further). That the failure begins at the center of the VCSEL is consistent with the confinement of carrier recombination to the active region (in the pre-degraded VCSEL). Lastly, the fact that the optical and electrical field intensities are greatest at the center of
the device (due to the high reflectivity of the DBR mirrors and to current confinement
techniques respectively) are further reasons for catastrophic failure to begin at the center
of the device. Therefore, following the models given for catastrophic failure in edge
emitting lasers, the catastrophic failure of these VCSELs likely proceeds as follows. A
preexisting defect or a defect such as a dislocation array occurs in the active region.
Intense non-radiative recombination (due to greater than normal driving conditions such
as a current spike or due to a rise in the drive current as the laser degrades under constant
power operation) occurs at this defect leading to the melting of the nearby material.
Intense non-radiative recombination continues on the molten material further propagating
the molten arm. A tangle of dislocations is formed to compensate for the stresses
involved in the melting and solidification of these arms.
4.2 Conclusions

Several new and important results have been discussed in this chapter. For the first time a technique has been developed whereby it is possible to view the entire active region of a solid state laser in a TEM and thereby conclusively identify the degradation mechanisms that lead to laser failure. Also (for the first time), a characterization technique is demonstrated whereby anaglyphic images are used to elucidate three-dimensional defect distributions in failed devices. These techniques have been systematically applied to the characterization of a single, rapidly failing VCSEL device structure thus showing the evolution of material failure in the device and ultimately linking the material failure to the output characteristics of the device. Additional examples of degraded VCSELS, drawn from a wider set of failure conditions, were examined to give breadth to our understanding of VCSEL failure mechanisms.

In VCSEL V1, the degradation proceeds as follows. There is an initial drop in laser output due to the development of cracks in the upper DBR layers (leading to a loss of the resonance cavity) and also, possibly due to a mechanism such as current shunting. Although this latter mechanism is not readily detected by TEM, it appears to be a likely cause of degradation in the absence of damage to the DBR or a dislocation network in the active region. The force driving the crack propagation is not fully understood at this time. However, the oxide layers do seem to be involved in the crack formation (all of the observed cracks ended on the oxide layers).

The damage to the DBR is typically connected with separation of the upper DBR from the oxide layers and in some instances extends over the entire active region. In some cases, dislocations are punched out near the oxide aperture presumably due to stresses associated with damage to the DBR layers. That these dislocations are a result of the damage to the DBR layers (as opposed to the cause of it) is seen by the fact that several of the V1 devices (e.g. V1-D, V1-E, and V1-I) exhibited cracking but no dislocations while the opposite scenario (i.e. dislocations without cracking) was not observed. Some of these punched-out dislocations then extend over the active region, presumably by a combined process of climb and glide that keeps them largely confined to the active region. The controlling parameter is likely non-radiative recombination in the active region that supplies energy for the evolution of the dislocation array. The burgers
vector of the dislocations in VCSEL V1 is $\frac{1}{4}[0\,-1\,-1]$, which is inclined 45° to the plane of the laser substrate and the type of which is consistent with the burgers vector for dislocations in III-V semiconductors. Freestanding dislocation loops which are left in the active region are explained by a process in which segments of the jagged dislocation front meet and form a new front leaving a loop behind. The jagged nature of the dislocation front can be explained by a combination of cross-slip and fluctuation between climb and glide due to confinement of the dislocation motion to the active region. Furthermore, it has been shown how the beginning and extent of active region coverage by the dislocation array can be determined by the onset and duration of time after a secondary drop in the power versus time curve.

Also, explicit materials defects in VCSELs have been linked to luminescence patterns seen with techniques such as electroluminescence (EL). Specifically, the two-dimensional dark area seen in the EL pattern for VCSEL V2 was associated with a high-density dislocation array which covered the active region.

Two additional mechanisms for the formation of stand alone dislocation loops seen in the active regions of failed lasers are also described. In the first, the individual extended arms of a complex patterned dislocation array pinch off to form loops. In the second, a gliding dislocation grows a dislocation dipole that eventually pinches off to form a free standing loop. The loops formed from these two mechanisms, as well as those seen in VCSEL V1 do not exhibit stacking faults as evidenced by the lack of stacking fault image contrast for all of the several diffraction conditions employed.

Some of the VCSELs studied (especially V3 and V4) demonstrate the role that preexisting defects play in laser failure. Specifically, in these devices, complex dislocation arrays were shown to nucleate on a single grown in defect. Thus, while the complex dislocation patterns lead to the loss of laser output, the initial preexisting defect was ultimately responsible for the laser failure.

Finally, the study of catastrophically failed VCSEL shown in this chapter demonstrates that several of the degradation mechanisms that occur during the catastrophic failure of edge emitting lasers are also operative in VCSELs. Namely, laser material is melted and resolidified causing the formation of a tangle of dislocations. However, catastrophic failure in VCSELs is seen to originate at the active region in the
center of the device while it was reported to occur on mirror faces in edge emitting lasers. Presumably the cause for this difference is the carrier recombination that occurs at the active region in the center of the VCSEL.

In sum, these results are of immediate interest to the VCSEL industry for the development of long-lifetime devices and more generally, they are of importance in the advancement of our understanding of material degradation mechanisms in III-V semiconductor materials.
5 In-situ degradation

This chapter describes the development of a novel in-situ TEM experiment that makes it possible to observe nano-scale level material degradation in VCSEL devices in real time. Prior to this work, there were no reports of an in-situ TEM experiment in which current was passed through a TEM-transparent sectioned device and for which it was possible to correlate the current density through, potential drop across, and temperature of the membrane to the experimental observations. The feasibility and usefulness of this electric in-situ TEM experimentation is demonstrated and discussed in the following text.

Ex-situ examination of degraded lasers provides a solid foundation upon which to deduce the process by which laser failure mechanisms occur. However, important characteristics of the degradation process such as the relative rates and sequences by which individual degradation mechanisms occur may be better understood by observing material degradation during real time laser operation. Unfortunately, no existing characterization technique is capable of observing the entire three-dimensional volume of a laser during operation with high spatial resolution. However, it is possible to observe material and laser-architecture response to driving conditions similar to those present in operating lasers by applying in-situ TEM stressing techniques to representative sectioned lasers. As discussed in the previous chapter, several groups have exposed laser material to stresses such as high electrical and optical fluxes, but examination of the degraded material was always performed ex-situ so that the characteristics of the degradation could never be completely understood. Thus, for this work, an in-situ TEM experiment has been developed to further investigate the nature of degradation in III-V laser materials. Specifically, material behavior was studied in the VCSEL system under injection conditions of electrical current densities as high as 100kA/cm$^2$. 
5.1 Experimental setup for electrical in situ degradation\textsuperscript{xli}

The goal in sample preparation for the electrical in-situ experiment was to create a cross section TEM membrane in the center of an undegraded VCSEL such that the current path was maintained through the active region of the device and only through that region (i.e. such that substantial leakage current paths, for example over the surface of the membrane, were minimized). The following sections explain the techniques used to accomplish this and discuss the electrical behavior of the sectioned-laser TEM sample with respect to the electrical behavior of whole device. The VCSEL structure used for this experiment was a reliable\textsuperscript{xlii} oxide-confined device with an aperture width of 15\textmu m. The emission wavelength was 850nm.

5.1.1 Preparation of FIB sample

Preparation of the in-situ sample was as follows. Prior to dicing, the backside of a section of wafer containing finished VCSELs was attached to a piece of scrap wafer with wax. Individual VCSEL devices were then diced from the host wafer with a diamond saw (~100\textmu m kerf) such that the device was centered on a 2.5mm x 150\textmu m bar as depicted in Figure 5-1. The wax prevented the diced bars from moving. Next, ~10mm lengths of 25\textmu m diameter AuSi wire were attached to the bonding pads of the VCSELs using a thermal compression ultrasonic gold ball bonding machine (~1% Si is added to Au to achieve desired melt characteristics\textsuperscript{202}). The VCSEL and scrap wafer combination were next soaked in acetone until the VCSEL-containing bars were easily freed from the wax. Individual VCSEL bars were then attached with epoxy to a Cu TEM half-grid in a manner that allowed for both FIB milling and TEM analysis as shown in Figure 5-2.

\textsuperscript{xli}These techniques are discussed here rather than in the Chapter 3 due to the fact that the development of these techniques was central to the realization of a working electrical in-situ experimental apparatus.
\textsuperscript{xlii}This reliable (relatively long-lived) device was used for these experiments due to its robust metal contact (rapidly failing devices generally are not processed to this extent).
5.1.2 Membrane fabrication and testing

TEM membrane fabrication was performed using the conventional FIB cross-sectioning technique described in Chapter 3. However, in order to limit membrane resistance (and hence resistive heating), to minimize membrane surface effects, and to provide for a greater volume for observing degradation mechanisms, the membrane
thickness was finished at ~750µm (membrane thickness greater than this made it difficult to record useful images with exposures on the time scale of a standard video frame, the primary image recording technique employed).

Figure 5-3 shows a secondary electron image taken in the FIB of a VCSEL device after membrane fabrication. In preliminary experiments, Pt lines were deposited with the FIB over the intended membrane location with the intention of protecting the membrane from damage and to insure electrical conductivity. However, in later samples, Pt strips were not employed as it was found that membranes were thick enough so that damage due to the outer tails of the ion beam was of little consequence\textsuperscript{xliii}. Furthermore, test runs showed that the as-grown gold contacts provided sufficient current paths even after being narrowed during membrane fabrication. Moreover, not using the Pt strip removed a possible source of extraneous rectifying behavior (e.g. as a metal-semiconductor Schottky diode) that may have complicated interpretation of I-V traces.

The contact metalization does not contribute significant rectifying behavior (such that it might be confused for the diode behavior of the membrane). For the device used in this experiment, the contact structure is 200 nm Au / 20 nm Pt / 20 nm Ti / 14 nm GaAs (carbon doped to $2 \times 10^{19} \text{cm}^{-3}$). The contact was annealed for 15 minutes at 440ºC (i.e. during the oxidation step). For contact designs where the semiconductor side is doped above $10^{18} \text{cm}^{-3}$ (as is the case for this structure), the electron current between the metal and semiconductor is dominated by tunneling across the contact barrier (regardless of the barrier height of the metal) leading to ohmic rather than rectifying behavior\textsuperscript{203}. Several specific examples of ohmic behavior for Au/Ti based contact structures to p-type GaAs are reported in the literature\textsuperscript{204-208}. Additional reports of ohmic behavior have been reported for highly p-doped contact structures but for other contact compositions, for example Pt/Ti\textsuperscript{209}.

\textsuperscript{xliii} For thinner membranes (~ 100nm) milling from the tails of the ion beam (i.e. the ion beam does not have a uniform current density across its entire area) on each side of the membrane overlaps and thus removes material from the top of the membrane.
After membrane completion and prior to placement in the in-situ TEM holder, the I-V characteristics could be tested on the apparatus shown in Figure 5-4. (This apparatus was connected to the acquisition hardware (described in Appendix-E) in the same manner as the in-situ TEM holder was). The I-V characteristics of the whole device prior to membrane fabrication in the FIB could be determined on this apparatus for comparison to the I-V characteristics of the finished membrane as will be shown later.

If the completed in-situ sample exhibited a diode-like I-V trace, a ~3mm length of 125 µm diameter AlSi wire\textsuperscript{xlv} was attached with non-conducting epoxy to the copper grid to serve as the backside contact of the device (known to be ohmic). To facilitate bonding between the wire and stub and the minimize the overall height of the wire/stub configuration, the end of the wire was crushed in a small vice as depicted in Figure 5-2.

\textsuperscript{xlv} AlSi is also employed as a connector material in the semiconductor industry with the addition of ~1% Si lowering the melting temperature of the wire. Its relatively low cost (compared to the AuSi wire used at Sandia National Labs) made it attractive for use in this experiment.
Silver paint was used to provide a conductive path between the backside contact wire and the VCSEL substrate. Once this sample was placed in the TEM electrical in-situ holder\textsuperscript{xlv} the AuSi wire was attached with silver paint to that electrical post that represented the positive side of the circuit. Likewise, the AlSi wire was attached with silver paint to the post on the TEM holder that represented the negative side of the circuit.

![Figure 5-4. Schematic of apparatus used to test electrical continuity in in-situ samples.](image)

Additional details of the external electrical circuitry and data analysis techniques are given in Appendix E.

### 5.2 Analysis of current path

A great deal of information concerning the current flow through the membrane can be deduced from the trace of $I_T$ versus $V_T$ for a particular membrane; an example of which is shown in Figure 5-5. (Henceforth, $I_T$ and $V_T$ will refer to the current and voltage passing through the in-situ electrical circuit which includes the diode membrane and any additional parallel or series resistances). Briefly, rectification in the trace confirms that current was passing through the diode membrane but does not rule out the possibility that a portion of the total current may have flowed along some other path (e.g. the membrane surfaces) or that a portion of the potential drop occurred over series resistances. The treatment of $I_T-V_T$ behavior below \textsuperscript{xlv} for traces measured on the test pad (Figure 5-4).

\textsuperscript{xlv} The holder was made by Gatan Inc, Warrendale, Pennsylvania.
Series and parallel resistances for the sample after placing it in the in-situ holder are given in the results section.

Several steps in the fabrication of the in-situ membrane are depicted in Figure 5-6 and the corresponding I-V characteristics are shown in Figure 5-7\textsuperscript{xlv}. The determination of the extent of any parallel or series resistances that develop during the membrane fabrication process is described in the following sections. Generally, series resistances dominate the I-V characteristics at higher voltages in contrast to parallel resistances that dominate at lower applied potentials as is shown below mathematically. The development of both series and parallel resistances during the membrane fabrication process is detected in Figure 5-7 as follows. An increase in series resistance is seen as a decrease in the slope of the I-V trace for relatively high forward bias (>1V; recall that $R=V/I$ so that the inverse of the slope of the curve in Figure 5-7 represents resistance). Likewise, the development of parallel current paths is seen as an increased slope of the I-V trace for the finished membrane relative to the entire device for small forward biases (<1V).

For reference during the treatment of the effects of series and parallel resistances, the forward bias I-V trace of the finished membrane is given in Figure 5-8.

\textsuperscript{xlv} The significant level of current flow seen in the device before thinning for applied biases below ~1.46 V (which corresponds to the emission wavelength of the device) is possibly indicative of significant levels of electrically active defect states on the perimeter or in the active region of the device (i.e. for devices with a minimum level of these defect states, appreciable current is typically only observed for biases above that which corresponds approximately to the wavelength of the device). An alternative possibility, that current does not flow through the VCSEL but through some other path, can be ruled out due to that fact that the I-V characteristics change significantly as portions of the VCSEL are milled away. Finally, for the finished in-situ membrane, for which knowledge of the parallel current paths is important, the effect of parallel current paths are largely accounted for as demonstrated in Section 5.2.2.
Figure 5-5. Trace of $I_T$ versus $V_T$ for an in-situ membrane.

Figure 5-6. Progression of trench geometry in the fabrication of the in-situ membrane (a-before any milling occurs; b-after milling up to the edge of the VCSEL, c-after milling up to the edge of the oxide aperture, and d-after the membrane is complete).
Figure 5-7 Evolution of I-V trace during the membrane fabrication process.

Figure 5-8. Forward bias I-V trace of the finished membrane shown with finer current and voltage scales than Figure 5-7.
5.2.1 Additional series resistance

Circuit elements (e.g. the numerous silver paint contacts, lengths of AuSi and AlSi wire, etc.) in addition to the VCSEL’s metal contacts and mirror layers add a small amount of series resistance not yet accounted for. Furthermore, the series resistance of the membrane should increase as the cross-sectional area decreases per $R = \rho l / A$ (where $\rho$ is the resistivity, $l$ is the membrane length, and $A$ the cross-sectional area of the membrane). The evolution of these additional series resistances is evident in comparing the I-V characteristics of the whole device and membrane in Figure 5-7 as previously mentioned.

A quantitative determination of the series resistance can be made as follows. The total potential drop measured via the Labview interface (see Appendix E), $V_T$, can be written as the sum of the potential drop across the membrane p-n junction, $V_V$, and the potential drop across any series resistances, $R_s$, as given below,

$$V_T = V_V + I_T R_s = \frac{k_B T}{q} \ln\left(\frac{I_T}{I_o}\right) + I_T R_s$$

Equation 5-1

where $I_T$ is the current measured by the Labview interface, $k$ is Boltzman’s constant, $T$ is the junction temperature, and $I_o$ is a parameter of the ideal diode equation (which depends on the carrier properties of the device). Therefore, as $I_T$ increases, the logarithmic component increases more slowly than the linear component ($I_T R_s$) so that eventually, the I-V trace for higher driving conditions will be dominated by ohmic behavior. Such behavior is evident in Figure 5-8 for biases greater than ~1.5V. Thus, the slope of the I-V curve for biases greater than 1.5V is used to determine the series resistance as is depicted in Figure 5-9. The series resistance in the in-situ circuit is thus 967\(\Omega\) and the potential drop across the diode portion of the membrane is thus,
\[ V_r = V_t - I_t (967\Omega) \]

\textbf{Equation 5-2}

The effect of this correction is shown in the next section, after discussion of parallel resistances.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5-9.png}
\caption{I-V trace of finished membrane for bias where series resistance dominates circuit behavior.}
\end{figure}

5.2.2 Parallel current paths

For the devices employed in this work, the portion of the wafer surface that is not occupied by the VCSEL structure is proton implanted (as is shown in Figure 5-10) to raise the resistance of that area to a level much higher (\(\sim 20M\Omega^{210}\)) than the resistance of the current path through the VCSEL. Thus, an insignificant amount of current is drawn off through paths other than through the VCSEL. However, once a VCSEL is fabricated into a membrane, the resistance of the current path through the VCSEL membrane is increased due to the decreased area of the current path. Hence, it is possible that current
paths through other parts of the wafer, for example, directly under the contact pad, may be of comparable resistance to the membrane and hence, drain a significant portion of the total circuit current. Furthermore, the introduction of milled surface areas on the edges of the current path may introduce low resistance current paths (e.g. due to electrically conductive surface states). Finally, the effect of parallel current paths is likely to be most significant for relatively small biases, due to the property of a diode that the resistance initially decreases as the forward bias is increased and due to the fact that current flow will be favored on the parallel current path having the smallest resistance (the form of this behavior corresponds to a current divider circuit as is shown below).

**Figure 5-10. Schematic of relative dimensions of the VCSEL, oxide confinement layers (on a plane below the page), and the inter-device proton isolation (to a depth approximately equal to the upper DBR).**

During the development of this experiment, two early findings were thought to indicate the existence of parallel current paths in the in-situ circuit. The fact that subjecting the membrane to high current densities (>50kAcm$^{-2}$; which is one or two orders of magnitude greater than typical operating conditions for a VCSEL, and sufficient to cause degradation in many VCSEL architectures as shown in Table 4-1) did not cause degradation suggested the possibility that a significant portion of the current, $I_V$, was
diverted through some paths other than through the membrane, such as over the membrane surfaces via surface states created by ion beam damage, or through other portions of the sample bar. Secondly, the fact that the reverse bias current for the membrane was greater than for the whole device (shown in Figure 5-7) further suggested that some other parallel current path was active.

The quantitative determination of the parallel resistances is as follows. As can be seen by Equation 5-3 (an application of Kirkoff’s laws), which gives the total current flow through a diode and resistor in parallel, the exponentially dependent diode current increasingly dominates as the forward biases increases (until series resistance dominates as discussed in Section 5.2.1). Thus, for forward biases, current contributions from parallel paths will only be significant at lower applied biases, provided that the parallel resistance is sufficiently large as is shown below to be the case for the membrane geometry employed in this work\textsuperscript{xlvii}. Furthermore, adding additional parallel current paths (e.g. increasing the area of the side walls which may contain electrically conductive surface states) will reduce the total parallel resistance, leading to a greater contribution of current from parallel current paths.

\[ I_T = I_o \left( e^{\frac{qV_o}{kT}} - 1 \right) + \frac{V_a}{R_p} \]

\textbf{Equation 5-3.} $R_p$ is the resistance of the parallel path.

Thus, according to Equation 5-3, a smaller parallel resistance will lead to a greater initial slope of the I-V trace for the diode. The evolution of the parallel resistances during the membrane fabrication is illustrated in Figure 5-11. The increase in slope for the I-V trace measured after milling step (B) (Figure 5-6) relative to the pre-milled diode (step (A)) indicates that the process of milling up to the sides of the diode introduces parallel current paths or that the resistance of the diode current path increases relative to the pre-existing high resistance current paths in other parts of the sample bar. Additional current paths are introduced as the trench wall area increases during further thinning of

\textsuperscript{xlvii} For a current divider, a parallel resistance will draw a fraction of the total circuit current proportional to the corresponding ratio of that parallel resistance to the sum of all resistors in parallel.
the membrane as is evidenced by the further increase in the initial slope of the I-V trace for milling steps (C) and (D).

Figure 5-12 shows the I-V trace of the thinned membrane only. Series resistance has already been accounted for (though the effect is small for the range of biases shown) by subtracting the term $I_T R_S$ from the measured voltage, $V_T$. While diode-like behavior is evident for these small biases, the initial slope of the I-V trace corresponds approximately to $6 \times 10^4 \Omega$. Thus, when the resistance of the diode membrane is comparable to this parallel resistance (at low forward biases), there will be significant diversion of the total measured current through the parallel resistance. However, as is shown below, for higher currents, the effect of the parallel resistance is minimal.

Figure 5-11. Evolution of I-V traces during membrane fabrication process shown for low forward bias.
An additional check of the parallel resistance is made by measuring the I-V characteristic of the sample circuit after removing the membrane (so that the only possible current paths are via surface states over the trench walls or through the high resistance material under the contact pad). The I-V trace thus measured is given in Figure 5-13. Measurement of the inverse slope of the ohmic portion of this trace (bias > 5V) yields a resistance of $5 \times 10^5$ ohms. Thus, the parallel resistances through the sample bar (i.e. not including the membrane) account for ~10% of the current lost to parallel current paths.
Quantitative determination of the effect of parallel resistances is as follows. For a circuit containing two current paths,

\[ I_v = \frac{R_p}{R_v + R_p} I_T \]

**Equation 5-4**

Where \( R_p \) is the parallel resistance and \( R_v \) the resistance of the diode membrane. Applying Equation 5-4 to the I-V trace already corrected for series resistance yields the trace shown in Figure 5-14. The effect of subtracting the series resistance is to lessen the plotted bias of each data point (i.e. the potential drop across the membrane junction is less than the measured potential drop, \( V_T \)), leading to a greater bend in the trace. The effect of accounting for the parallel resistance is to lessen the current of each data point. Thus, the parallel resistance has little effect on the current passing through the membrane at higher applied biases as is evident by the fact that the correction modifies the data.
point at the highest bias and current by ~2% (at $V_V = 1.09V$, $I_T = 682\mu A$ and $I_V = 664\mu A$). However, series resistance clearly has a more pronounced effect so that in increasing the applied bias from 1V to 1.7V, the potential drop across the diode increases by only 0.1V while the drop over the series resistance increases by 0.6V.

![I-V curve graph]

Figure 5-14. Forward bias I-V characteristics of membrane before and after correcting for the effects of series and parallel resistances.

### 5.3 Membrane temperature determination

Knowledge of any resistive heating of the membrane is essential due to the exponential thermal dependence of defect motion. Thus, the temperature of the membrane during the in-situ experiment must be known so that temperature related defect behavior can be differentiated from injection related defect behavior.

(Any temperature related defect behavior is expected to arise from the increased mobility and nucleation of dislocation kinks at higher temperatures and not from increased stress due to thermal expansion. Specifically, increased membrane temperature will not generate stress sufficient to influence defect nucleation and propagation as the already low room-temperature lattice mismatch between GaAs and AlAs of $\sim 1.5 \times 10^{-3}$
decreases further as membrane temperature increases\textsuperscript{18} (at \textasciitilde 900°\textdegree C, the lattice parameters of these two materials are equal)).

5.3.1 Theoretical membrane temperature determination

The thermal transport equation which can describe the thermal state for any point in the sample bar during the in-situ experiment is developed in Appendix-F. However, the solution of the derived second order nonlinear differential equation is not readily determined. Thus, finite elemental modeling is employed as is described below. Using this technique, the membrane thickness and overall width were varied to see the effect that membrane dimensions have on membrane temperature during in-situ electrical pumping. The findings were employed in designing an in-situ membrane geometry for which resistive heating lead to minimal temperature rise.

5.3.1.1 Finite element modeling of temperature

The membrane and sample bar volumes shown in Figure 5-15 and Figure 5-16 respectively are modeled with brick elements, each having eight nodes. Each node has temperature as its only degree of freedom. The triangular surface area elements are due to sectioning of the brick element during the meshing, or element creation, step in the model building process.

The membrane region is divided into three volumes. The center volume of the membrane (labeled H in Figure 5-15) represents the current path region and that region in which resistive heating occurs. A heat generation rate given by $I_V V_V$ per volume of the current path is applied as a body force to each node in this center volume. The outer volumes of the membrane (labeled C in Figure 5-15) represent thinned portions of the membrane through which no current passes; i.e. those areas of the membrane that contain the oxide layers. Radiation, modeled as a load on each surface node, is applied to the upper portion of the sample bar as well as to the membrane and trench surfaces. The ends and broad face of the sample bar are held at 291°K, the value given as the sample temperature by the thermocouple on the TEM holder when no heater current is applied. The applied temperature and radiation conditions act as boundary conditions for the
Numerical analysis and are necessary to achieve a converging solution. Each node is initially set to 291ºK.

Material parameters needed for a steady state analysis include the temperature dependant thermal conductivity and emissivity. The emissivity of GaAs goes from 0.08 at room temperature to 0.30 at ~600ºC and is also variable with emission wavelength. Thus an average value of 0.20 was used in the finite element analysis. The thermal conductivity of Al\textsubscript{x}Ga\textsubscript{1-x}As can be modeled by

\[
K = \frac{C}{T^{1.375}}
\]

Equation 5-5

For GaAs, \( C = 1.11 \times 10^5 \text{ Wm}^{-1}\text{K}^{0.375} \) (which is an average of seven references given by Adachi\textsuperscript{18}). For AlAs, \( C = 2.32 \times 10^5 \text{ Wm}^{-1}\text{K}^{0.375} \). However, C for a GaAs/AlAs superlattice with a period greater than 50nm (which roughly describes the VCSEL structure) has been found to be \( 0.71 \times 10^5 \text{ Wm}^{-1}\text{K}^{0.375} \), slightly lower than the value for GaAs\textsuperscript{212}. Therefore, modeling with the thermal conductivity for GaAs gives a good approximation of the temperatures attained\textsuperscript{xlviii} and is used in this work.

While the effects of radiation are fully applied in these models (per an emissivity of 0.2), it is noted that the difference in the calculated membrane temperature is only ~2K for calculations performed with an emissivity of 0.001 or 1.0 while changes in membrane geometry can lead to variations in calculated temperature on the order of \( 10^2 \text{K} \). Therefore, radiation removes only a small fraction of heat from the membrane compared to thermal conduction. (Even for 1000ºC, close to the melting temperature of these alloys, the heat flux due to thermal conduction is of order \( 10^4 \text{Wcm}^{-2} \) while that due to radiation is of order 1 \text{Wcm}^{-2}. The large thermal conduction is due to the inverse dependence of the conduction on the length of the conduction path, which for this system is ~10um).

\textsuperscript{xlviii} Modeling of the multiple layers of the VCSEL membrane is precluded due to limitations on the number of nodes available in the Ansys software. Therefore, modeling was performed for pure GaAs membranes.
Figure 5-15. Membrane geometry with loads and constraints indicated (R-radiation, H-heat generation, C-conduction, T-temperature)

Figure 5-16. Sample bar geometry.
Due to the fact that heat conduction is proportional to the cross-sectional area, it is desirable to have as great a membrane thickness as is possible while maintaining reasonable electron transparency in the TEM. Thus, the membrane thickness is fabricated as \( \sim 750\) nm. Additionally, a narrower membrane and hence, shorter heat conduction paths, will facilitate heat dissipation into the surrounding sample bar. Thus, the membrane is kept as narrow as possible while keeping the entire current path (i.e. the area between the oxide aperture) within the membrane. A short width (\(1.5\mu m\)) is thinned on each side of the current path in order to expose some of the oxide layers, which are potentially interesting areas for observation of degradation. The quantitative effect on membrane heating of varying the width and thickness of the membrane are discussed below.

The width of the current path bounded by oxide layer isolation in the VCSEL employed in this experiment was \(15\mu m\). The ideal membrane (i.e. having minimum resistive heating while maintaining electron transparency) was \(\sim 18\mu m\) wide by \(10\mu m\) deep by \(750\) nm thick. An example nodal solution for a heat generation rate of \(5mW\) applied to the membrane is shown in Figure 5-17. The highest temperature occurs in the upper middle portion of the membrane, which is farthest from the material outside the trench that acts as the heat sink.

A chart of the highest membrane temperature as a function of heat generation rate is given in Figure 5-18. Variations in highest membrane temperature with varying membrane thickness and width are depicted in Figure 5-19. As mentioned above, greater membrane thickness and smaller membrane widths give rise to lower membrane temperatures due to more efficient heat conduction paths.
Figure 5-17. Secondary electron image of finished membrane and, plot of temperature distribution in membrane for a heat generation rate of ~5mW (i.e. the product of a typical combination of membrane current, 5mA, and membrane bias, 1V).xlvi

xlvi For the sample used, the trench width away from the membrane was widened to allow for a greater range of tilt angles in the TEM. Finite elemental modeling for the same membrane dimensions and driving conditions, with and without the extra trench widening showed little difference (~1ºK) in the temperature attained. Presumably, this small difference is due to the still much greater cross-sectional area and hence, thermal conduction through the narrowed portion of the trench walls compared to the thermal conduction through the membrane.
Figure 5-18. Highest membrane temperature due to resistive heating for a membrane 750nm thick, and 20µm wide, and 10µm deep.
Thus, for typical driving conditions (<20mW), and for thick membranes (~750nm) and narrow membranes (edges less than 5µm wide), the temperature rise due to resistive heating is less than 100°C.

The thermally assisted dislocation motion in GaAs is given as \(^{213}\),

\[
\nu = \nu_o \left( \frac{\tau}{\tau_o} \right)^m e^{(-Q/k_B T)}
\]

**Equation 5-6**

For \(\alpha\) dislocations (having the highest velocity in undoped GaAs), \(\nu_o = 1.9 \times 10^3\) ms\(^{-1}\), \(\tau_o = 1\) MPa, \(m = 1.7\), and \(Q = 1.3\) eV. Thus, assuming a junction temperature of
100°C, and taking 100MPa as the upper limit of residual stress, thermally assisted dislocation motion will be of order only $10^{-10}$ m/s. Thus we can design these experiments such that thermal effects on dislocation motion can be made negligible.

### 5.4 Results and Discussion

Knowing now the diode current density, potential drop and expected temperature rise in a membrane during an in-situ experiment, it is possible to analyze observed degradation. Preliminary electrical in-situ experiments employed thinner (500nm) and wider (20um) membranes, and driving conditions (of order ~100kA/cm$^2$), such that membranes were melted due to resistive heating. Thus, thicker and wider membranes were fabricated for these experiments; the ideal geometry being 750nm thick by 18um wide by 10um deep. Typical driving conditions for these latter experiments which injected up to ~50kAcm$^2$ through the membrane (~7mA, ~1.2V after accounting for a series resistance of 531Ω) correspond to a temperature rise in the membrane of ~60°C (which is approximately twice the temperature attained in a working VCSEL). To date, using these thicker membranes, there has been no TEM-observed defects (dislocations or otherwise) that have been induced by these current densities.

However, degradation does take place as is evidenced by the gradual decrease in forward bias current over the course of an in-situ run, an example of which is shown in Figure 5-20. This gradual decrease in current (~80µA/hr) is consistent with the action of the current shunting mechanism, as discussed in Section 4.1.1, whereby passivation of dopant atoms occurs in the vicinity of the laser junction, leading to a gradual increase of the resistivity of that region.

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1 Compared to the I-V trace taken on the test pad, the I-V trace of the membrane, once it was inserted in the in-situ TEM holder, was ~300Ω less as determined by measurement of the slope of the I-V trace.
Figure 5-20. (measured Rs for this day is 531ohms. Max conditions give 8.5mW)

At the time of this writing, the data shown in Figure 5-20 represents a fraction of the 30 hours of in-situ electrical degradation with the most successful experiment to date (~40 oxide confined VCSELs have been used during these in-situ experiments, a large fraction (>50%) being destroyed prior to final completion due to such difficulties as fragile bond wires, and a large fraction of the remaining providing no interesting results due, for example, to shorting or melting). The fact that no TEM-observable degradation has occurred in this oxide-confined in-situ sample (except for melting at driving conditions above typical VCSEL operating conditions) suggests the possibility that a mechanism such as current-shunting is the operative degradation mechanism in this device. This is consistent with the fact that no preexisting defects (e.g. threading dislocations) occur in the device, which were seen in Chapter 4 to be origins of complex dislocation arrays. It further suggests that the fact that the device geometry has been greatly altered by the membrane fabrication process is not a sufficient source of damage for the nucleation of defects that lead to rapid degradation.
5.4.1 Severe membrane degradation

As mentioned previously, several preliminary samples were operated under driving conditions that resulted in local membrane melting and subsequent dislocation motion that was thus heavily dependent on thermal excitation. An example of this degradation is given in Figure 5-21. The driving conditions for this degradation were 4.6V and 47mA. Finite element modeling gave the membrane temperature at the top, center of the membrane as 3417ºK (such a value is not physically attainable but is possible in the model due to the fact that phase transformations such as melting are not accounted for). The fact that the model shows a significant portion of the membrane to be above the melting points of GaAs and AlAs (1511ºK and 2013ºK respectively) is consistent with the upper portion of the top DBR melting as shown in Figure 5-21.

The orientations of the planar faults shown are consistent with stacking faults on the (-1-11) and (111) planes. In addition to the stacking faults, punched-out dislocations have nucleated and grown throughout the upper DBR layers. The nucleation site in this case was a shallow and narrow trench (~50nm wide by ~500nm deep), intentionally milled into the upper DBR to help insure observable degradation within the membrane. Figure 5-22 shows several video frames of the stacking faults growing through the lower DBR layer (at a rate of ~0.12cm/s).

Figure 5-21. Degradation induced during a membrane by electrical pumping.
Figure 5-22. Time series of defect movement under electrical stress
Dislocation velocities as a function of injection current obtained for the sample above and one other where dislocation motion was observed are shown in Figure 5-23. The dislocation velocity exhibits exponential dependence on current injection. However, as was shown in Section 2.3.6.3, above ~300°C dislocation motion is primarily controlled by thermal excitation. Thus, the exponential dependence of the data in Figure 5-23 is due primarily to resistive heating of the membrane as the temperature approaches its melting point.

![Figure 5-23. Exponential dependence of dislocation velocity on membrane current.](image)

5.5 Conclusions

In order to observe material degradation in VCSEL devices in real-time, an electrical in-situ experiment has been designed whereby it is possible to pass electrical current through a TEM-transparent, sectioned VCSEL. Methods have been designed to account for current losses from parallel current paths and for potential drops across series resistances, thereby determining the precise currents and potential drops experienced by the membrane diode junction of the in-situ electrical circuit. Furthermore, finite element
modeling has been employed in order to determine the temperature rise in the membrane as a function of the driving conditions to facilitate separation of thermally assisted dislocation motion from recombination enhanced dislocation motion.

By employing excessive driving conditions, it has been possible to melt in-situ membranes and observe thermally assisted dislocation motion. The velocity of the dislocations is exponentially dependent on the level of current flowing through the membrane, although this effect is primarily due to resistive heating.

However, under more representative driving conditions (for which resistive heating is minimized), no TEM-observable degradation is detected for the VCSEL employed. However, the I-V history of the in-situ membrane does indicate that the resistance of the membrane gradually increases. This finding is consistent with a gradual degradation process, such as the current-shunting mechanism, being operative in the membrane. Furthermore, it is significant that these driving conditions (which are sufficient to cause degradation in rapidly failing samples) do not cause rapid degradation in this reliable device, even after sectioning, suggesting that these in-situ observations may be representative of the true nature of the degradation of un-sectioned device (although the high current densities and increased temperatures do likely accelerate the degradation).

Finally, the main contribution of the work described in this chapter has been the development and existence proof of an experimental procedure by which it is possible to systematically observe and characterize the degradation of laser materials in real-time on a nano-scale level in a TEM. Inherent in this experimental design is the ability to correlate the observed degradation to the precise driving conditions of the membrane junction and the resulting resistive heating.
6 Lateral Thermal oxidation kinetics of Al(Ga)As(P) and Al(In)As(P)

6.1 Motivation

Thermally grown native oxides of semiconductor materials have important functions as dielectric layers in microelectronic devices and as current blocking layers in some semiconductor laser designs. Of particular interest in the design of the AlGaAs based VCSELs discussed elsewhere in this thesis, is the amorphous oxide Al$_2$O$_3$ that is readily formed from Al$_x$Ga$_{1-x}$As (x>~90%) in a steam environment at high temperatures (>350ºC). In the III-V system, this is the most studied oxide to date. For a recent review on the mechanisms of the growth of this and other ternary III-V thermal oxides see reference$^{130}$ and the references therein.

Despite a large number of reports on the kinetics, structure and chemistry of oxides formed from ternary III-V semiconductors (e.g. (AlGa)As, (InAl)P, (InAl)As and, Al(AsSb)), there have been few known reports$^{214}$ that attempt to explain the dependencies of oxidation mechanisms on the various parameters (e.g. column V chemistry or epitaxial strain$^1$) associated with the oxidation of complex quaternary or quinternary III-V semiconductor compounds. Thus the semiconductor community lacks a comprehensive model of oxidation that would predict the oxidation behavior of any given complex III-V compound. Development of such an understanding is necessary as it is very likely that applications for a wider range of III-V oxides will arise. Furthermore, it is possible that newly understood quaternary or quinternary III-V oxides will be better suited to some current applications than currently used ternary III-V oxides. For example, the present use of the oxide formed from Al$_x$Ga$_{1-x}$As (x>0.96) in VCSELs generates a stress field$^{215,216}$ due primarily to volume changes upon oxidation, sufficient under some conditions to generate dislocations that ultimately lead to laser failure (as discussed in the preceding chapter).

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$^1$ Biaxial strain in the plane of a heterojunction is unavoidable for epitaxial growth over a wide range of III-V compounds on the three commonly used semiconductor oxides, GaAs, InP, and GaP, due to lattice mismatch.
From previous work it is known that native oxides of Al\textsubscript{x}Ga\textsubscript{1-x}As (x>0.90) occupy smaller volumes\textsuperscript{217,218,219,220} than the unoxidized crystal and that the volume ratio of oxidized to pre-oxidized material decreases with increasing Al concentration. On the contrary, native oxides of InAlP expand relative to unoxidized crystal\textsuperscript{221}. It is therefore possible that an oxide formed from intermediary compounds in the In-Al-Ga-As-P system will yield zero volume change and thus zero stress upon oxidation. Thus, investigation of the oxidation kinetics and eventually the volume changes and stresses induced by a wide range of native III-V thermal oxides will aid the design of a commercially practical (i.e. with reasonable growth behavior), minimum stress system.

Therefore, in this work we explore two quaternary oxide systems to build towards a comprehensive model to predict the oxidation behavior and properties of arbitrary III-V native thermal oxides. For this work, we have chosen to investigate the kinetics of those oxides formed from Al(Ga)As(P) and Al(In)As(P)\textsuperscript{lii}. Key parameters of the oxidation kinetics studied for these oxides are column V chemistry and epitaxial strain, where the level of strain is dependent on the column V chemistry. As previously mentioned, the current literature lacks in-depth experimental investigations of the role of either of these parameters in the III-V system.

Finally, although both vertically grown (i.e. in a direction normal to the wafer surface) and laterally grown (i.e. buried, perpendicular to the wafer normal) oxides have potential applications in device design, this work focuses on laterally grown oxides as they are most relevant to the VCSEL devices which are the focus of this thesis.

6.2 Results of oxidation experiments

6.2.1 Sample A, Al\textsubscript{x}Ga\textsubscript{1-x}As\textsubscript{y}P\textsubscript{1-y} (y 0.78) on GaAs

As determined by measurement in the FIB, oxidation lengths were on the order of 10µm (depending on oxidation time and conditions) and oxidations were clearly selective (i.e. spacers did not oxidize). The selective nature of these oxides was determined by the

\textsuperscript{lii} These two compounds encompass most III-V materials relevant to optical and electrical devices. The exceptions are materials containing Sb as a column V element, although materials with this constituent were not readily available for this work.
cycling of characteristic oxide and crystalline contrasts in the FIB as the depth increased during milling in the section of measurement (Figure 3-10).

Figure 6-1 and Figure 6-2 give the oxide length versus time for Sample A for two different temperatures\textsuperscript{iii}. The lower temperature (399°C) leads to oxidation rates that are approximately linear with time while at the higher temperature (482°C), the oxidation rate becomes parabolic with time. A change from linear to parabolic behavior is consistent with the onset of diffusion limited oxidation as the thickness of the region containing intermediate oxidation compounds at the oxide front increases at increasing temperatures\textsuperscript{135} and due to the increasing length of the diffusion path as the oxidation length increases. Thus, activation energies measured using these data from both linear and parabolic regimes are expected to be between the values of the reaction and diffusion limited activation energies. At both temperatures, the oxidation rate is slower as the phosphorus concentration, and hence tensile strain, is increased. For the lower temperature, the length of the 22% P layer does not exceed 500nm for all oxidation times measured. For the higher temperature, oxide lengths in excess of 500nm are detected although for some of the measurements, the oxide length was less than 500nm. The erratic oxide growth of the highest phosphorous content layer at higher temperatures suggests relatively greater dependence of oxidation of this layer on local fluctuations (compositional or otherwise) in the oxidizing layer.

\textsuperscript{iii} The systematic error in this data (e.g. in the relative positions of data points taken at the same time) is due to the fact that the oxidation samples were composed of five oxidizing epitaxial layers. Thus, any error that arose during the oxidation (e.g. a variation in furnace temperature) is reflected in the lengths of all five oxide layers.
Figure 6-1 Oxide lengths as a function of time at 399°C for Sample A.
Figure 6-2 Oxide lengths as a function of square root of time at 482°C for Sample A.

Arrhenius plots for each of the layers are given in Figure 6-3 through Figure 6-7. The spread in data points for a specific temperature comes from the fact that the oxidation lengths versus time for that temperature are not perfectly linear as seen in the Figure 6-1 and Figure 6-2. These deviations from perfect linearity may be due to minor fluctuations in the furnace temperature during the oxidation (e.g. while the furnace
temperature was nominally kept at a specific temperature, there were typically fluctuations of roughly ±2°C due to the temperature drop immediately following sample insertion) or long-range (tens to hundreds of microns) compositional variation within the sample. However, the computed uncertainty\textsuperscript{iv}, in activation energy from each of these Arrhenius plots incorporates the vertical scattering.

Reported linear activation energies for oxidation of AlAs reported in the literature range from $0.8\text{eV}^{222}$ to $1.6\text{eV}^{223}$, while reported parabolic activation energies range from $0.6\text{eV}^{222}$ to $0.8\text{eV}^{223}$. The range in reported values within a given mechanism may arise through several experimental factors such as differing, oxide layer thickness\textsuperscript{224}, doping levels\textsuperscript{140}, furnace configurations (e.g. water temperature\textsuperscript{154}), or proximity to other high Al content layers\textsuperscript{225}. Differences in the reported activation energies of oxidation for similar materials may also be due to different oxidation regimes (e.g. reaction limited or diffusive limited) being operative in different experiments. Specifically, if Arrhenius plot measurements are made assuming a reaction limited (i.e. linear) oxidation rate (as is done in this work, i.e. by calculating the activation energy from a plot of $\ln(\text{rate})$ vs. $t$, rather than $t^2$), the activation energy measured therefrom will be between the values of the activation energy of the diffusive (i.e. parabolic) and reaction mechanisms if for any of the oxidation lengths measured, the diffusive mechanism limits the oxidation\textsuperscript{223}. Factors known\textsuperscript{135} to favor parabolic oxidation rates are, greater oxide length (due to the greater distance over which the oxidant must transverse), increased temperature and increased Al content (apparently because of the limited rate at which intermediate products can be removed\textsuperscript{iv}).

The activation energy of $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ measured here is $0.92\pm0.07\text{eV}$. The only other known reported value\textsuperscript{154} for the oxidation of $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ is $1.7\pm0.1\text{eV}^{226}$. At this time, the precise cause of this difference in measured and reported activation energies is not fully understood. However, a likely reason is the fact that the oxidation rates for the referenced activation energy were reportedly always linear, while in this work, the oxidation rates became parabolic for higher temperatures and longer oxidation lengths (so

\textsuperscript{iv} Standard Error is used as the uncertainty, which incorporates relative scatter and number of points.
\textsuperscript{iv} Briefly, a relatively dense oxide phase within the first several nanometers of the oxidation front contains $\text{As}_2\text{O}_3$, the removal of which leads to a porous oxide that is believed to facilitate rapid transport of $\text{H}_2\text{O}$. 
that the measured activation energy lies between the reaction and diffusive regimes). Though a similar temperature range (> 500°C) is used in both the referenced experiment and this work a factor which may lead to the parabolic rates observed in this work stems from geometrical considerations. Specifically, a VCSEL mesa geometry is used to measure oxidation rates for the referenced activation energy while in this work a trench geometry is used as is depicted in Figure 3-9. In the VCSEL geometry, oxidation fronts progress inward from the four edges of the VCSEL mesa leading to an increasingly smaller oxidation front circumference, while in the trench geometry, the oxidation front circumference becomes increasingly larger. Thus, while the oxide/ambient interfaces remain constant, the increasing oxidation front circumference in the case of the trench oxidation geometry means that it is possible that the trench geometry tends towards diffusion controlled rates more readily than the VCSEL geometry (i.e. in the trench geometry, the oxidant flux across the oxide/air interface must increase in order to maintain a constant oxidation rate).

The relative influences of the reaction and diffusive mechanisms in this data are considered in the later discussion. Other experimental factors (i.e. those mentioned above such as doping concentration) are internally consistent throughout the measurements taken in this work and thus are not expected to influence trends the in activation energy for oxidation.

There are no known reported values of activation energies for the lower arsenic containing compounds in Sample A. The activation energies from these plots for Sample A are given in Figure 6-8. The activation energy for oxidation increases exponentially with increasing tensile strain and phosphorus concentration.
Figure 6-3 Arrhenius plot for layer A-5. $E_A = 0.92 \pm 0.07\text{eV}$.

Figure 6-4 Arrhenius plot for A-4. $E_A = 0.96 \pm 0.10\text{eV}$. 

$1/T (1/{}^\circ\text{K})$
Figure 6-5 Arrhenius plot for A-3. $E_A = 1.04 \pm 0.15\text{eV}$.

Figure 6-6 Arrhenius plot for A-2. $E_A = 1.30 \pm 0.11\text{eV}$.
Figure 6-7 Arrhenius plot for A-1. $E_A = 1.83 \pm 0.17$ eV.

Figure 6-8. Activation energy as a function of epitaxial strain and phosphorous composition for Sample A.
6.2.2 Sample B, Al<sub>x</sub>Ga<sub>1-x</sub>As<sub>y</sub>P<sub>1-y</sub> (y < 0.2) on GaP

Measurement of oxide lengths in sample B is more challenging as the oxide lengths involved are on the order of 1μm or less. Furthermore, at higher temperatures, the oxidation of this sample is non-selective to an increasing degree (i.e. the spacers are also oxidized) so that the intended oxide layer and the oxidized spacer have similar contrast in the FIB. For this reason oxidation measurements are mostly taken in the TEM. As indicated above, TEM measurements sample only a small portion of the oxidation front (the TEM membranes are ~100nm thick) and do not allow for the determination of long-range roughness (of order >100nm) of the oxidation front. However, it is expected that any roughness, if present, will give rise to greater scatter in the Arrhenius plots of the oxidation rates, which in turn is incorporated into error calculations for activation energies.

An example of non-selective oxidation in Sample B is shown in Figure 6-9. This 004 dark field TEM image of Sample B, oxidized at 643°C for 37 minutes, indicates that the GaP spacers between the oxidizing layers have also oxidized. In contrast, Figure 6-10 is a 004 BF image showing selective oxidation of the Al<sub>x</sub>Ga<sub>1-x</sub>As<sub>y</sub>P<sub>1-y</sub> layers at 505°C for 240 minutes. The GaP spacers have not oxidized at this lower temperature.

As shown in Figure 6-10, the oxide layers have expanded horizontally with respect to their pre-oxidation state (i.e. the oxide layers extend into the trench) and have generated sufficient stress to crack the GaP spacers.

Voids present along the oxide length are likely due to TEM induced recrystallization of the oxide<sup>130</sup>. Mid-layer voids correspond to compositional fluctuations (originating from crystal growth) and have been found in a previous work<sup>130</sup> to correspond to interfaces between the chemically different oxides arising from the compositional fluctuations.

Finally, in Figure 6-10, one can detect a small region (~30nm) of different contrast at the oxidation fronts. Although it is possible that these contrast features could be caused by superposition of the front and back surfaces of the membrane under tilt, or by extreme roughness in the oxidation front, these features are visible under zone axis imaging as well as in multiple membranes, which is a strong indication that they are inherent features of the oxidation of these materials. Thus, it is believed that they are
regions of an intermediate oxidation product. Similar traits have been detected in the oxidation of $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ (with high aluminum concentrations)$^{130}$ and it is believed that these regions contain species of arsenic oxide$^{135}$, which is then removed from the oxide via reduction with free hydrogen to form the relatively volatile compound arsine ($\text{AsH}_3$), or an intermediary oxidation product$^{217}$.

Figure 6-9 (004) dark field TEM image of Sample B oxidized at 643°C for 37 minutes. 1-y indicates phosphorus concentrations. The substrate and spacer material is GaP.
Figure 6-10 (004) bright field TEM image of Sample B oxidized at 503ºC for 4 hours. Substrate and spacer material is GaP.

The oxidation of the layers in sample B at 575ºC becomes parabolic in time after an initially faster rate (for about ~2500 seconds) as is shown in Figure 6-11. This faster oxidation likely indicates that the oxidation was initially reaction controlled but that it became diffusion controlled as the oxide length increased. Compared to the higher arsenic content compounds in Sample A, oxidation rates for the high phosphorus compounds in Sample B are low. Again, as phosphorus concentration is increased (but in this case while compressive strain decreases), oxidation rates are lowered.

Figure 6-12 through Figure 6-15 give Arrhenius plots for the four oxidized layers in Sample B. The increased scatter in data is attributed to the greater error inherent in measurement of the shorter oxide lengths and due to possible roughness (with wavelength of order > 100nm) in oxidation fronts, which is not detectable using the TEM method of measuring oxide lengths due to fact that the TEM membranes employed had thicknesses of order ~100-200nm. There are no known reported values in the literature for the oxidation activation energies for these compounds.
Figure 6-11. Oxidation length versus time at 575°C for Sample B
Figure 6-12 Arrhenius plot for B-6. $E_A = 0.34 \pm 0.19$ eV.

Figure 6-13 Arrhenius plot for B-7. $E_A = 0.38 \pm 0.16$ eV.
Figure 6-14 Arrhenius plot for B-8. $E_A = 0.38 \pm 0.16 \text{eV}$.

Figure 6-15 Arrhenius plot for B-9. $E_A = 0.49 \pm 0.14 \text{eV}$. 
A plot of activation energy vs. strain is shown in Figure 6-16 for Samples A and B. Phosphorous concentrations are also indicated for reference. From this data, it is possible to determine that the column V chemistry does influence the oxidation kinetics as there is a discontinuity in activation energy for compressively strained layers (i.e. at $\varepsilon \sim 0.002$) between the samples with low P content (20% of the column V constituent) and those with high P content (78% of the column V constituent). Further conclusions concerning activation energy dependencies on strain and chemistry are deferred until after data on Samples C, D, E is presented.

![Activation energy vs. strain for Samples A and B](image)

**Figure 6-16 Activation energies as a function of strain for Samples A and B**

6.2.3 Sample C, In$_{0.5}$Al$_{0.5}$P on GaAs

The wafer containing Sample C is comprised of layers of In$_{0.5}$Al$_{0.5}$P of thicknesses, 50nm, 100nm, 150nm and 200nm, separated by GaAs spacers. Figure 6-17 shows a TEM image of Sample C at 449°C after ~4hrs. Due to the longer oxidation times used relative to Sample A, the GaAs spacers have also oxidized. Furthermore, it appears that the oxidation of In$_{0.5}$Al$_{0.5}$P has expanded into the oxidation trench.
Figure 6-17 Phase contrast image of Sample C after oxidation at 449ºC for ~4 hours.

Figure 6-18 shows a TEM image of Sample C oxidized at 505ºC after 4 hours. Again, the GaAs spacer material has oxidized. Furthermore, it appears that lateral oxidation of the In$_{0.5}$Al$_{0.5}$P has not actually occurred, but rather, most of the oxidation of In$_{0.5}$Al$_{0.5}$P has occurred vertically. This is evident due to the apparent pinch-off of the lateral oxidation within a few hundred nanometers of the oxidation trench. Furthermore, oxidation of the In$_{0.5}$Al$_{0.5}$P layers only occurs adjacent to the oxidized portions of the GaAs spacers. The bending of the lower two oxide layers is presumably due to the contraction of the GaAs volume upon oxidation. Thus, for this system, oxidation of the spacer material, GaAs, occurs more readily than the intended oxidation of In$_{0.5}$Al$_{0.5}$P, thereby limiting the usefulness of this oxide in lateral oxidation geometries.

No attempt to report oxidation kinetics data is made for this sample due to the unusual lateral oxide behavior. Furthermore, for oxides grown at lower temperatures and for shorter times for which no vertical oxidation occurs, the measured oxide lengths are of the same order as lateral oxide lengths seen in unoxidized samples (i.e. from atmospheric oxidation).
Figure 6-18 Phase contrast image of Sample C after oxidation at 505°C for 4 hours. The pinch-off of the lateral oxidation, L, by vertical oxidation, V, is indicated and represented in the inset schematic.

6.2.4 Sample D, In$_{0.47}$Al$_{0.53}$As on InP

Sample D, comprised of In$_{0.47}$Al$_{0.53}$As, generates selective and sufficiently long oxide lengths for measurement using the FIB technique. Oxide fronts were smooth except for the highest oxide temperature used (530°C) as shown in Figure 6-19. The occurrence of rougher oxidation front morphologies at higher temperatures is likely due to heterogeneous nucleation of the oxidation at the trench wall (because compositional variations would lead to rough interface morphologies at all temperatures).

Figure 6-20 gives the oxide length as a function of time at two separate temperatures for this sample. Even at longer times, the oxidation rate was linear. An Arrhenius plot for Sample D is given in Figure 6-21. Due to the linear behavior observed over the range of temperatures employed, the measured activation energy for these samples corresponds closely to the reaction mechanism. The measured activation energy
for $\text{In}_{0.47}\text{Al}_{0.53}\text{As}$ from this data of 1.36eV matches within 5% to activation energies for this material as reported in the literature$^{227}$.

Figure 6-19. Secondary electron images of the oxide fronts of Sample D for oxidation at (a) 530°C and (b) 448°C.

Figure 6-20 Oxidation length versus time for Sample D
Figure 6-21 Arrhenius plot for Sample D. \( E_A = 1.36 \pm 0.18 \text{ eV} \).

6.2.5 Sample E, \( \text{Al}_x\text{Ga}_{1-x}\text{P} \) on GaP

Sample E is comprised of \( \text{Al}_x\text{Ga}_{1-x}\text{P} / \text{GaP} \) with three layers of \( x = 0.80, 0.90, \) and \( 0.97 \). The three layers are unintentionally grown to different thicknesses of 81nm, 75nm and 54nm, respectively. Although for \( \text{Al}_{0.98}\text{Ga}_{0.02}\text{As}^{154} \) and \( \text{AlAs}_{0.56}\text{Sb}_{0.44}^{228,229} \), lateral oxidation rates are thickness independent above 50nm, such data is not available for the \( \text{Al}_x\text{Ga}_{1-x}\text{P} \) system.

All layers of Sample E exhibited short oxide lengths on the order of 100nm and are thus, measured by TEM. Oxide length as a function of time for the \( \text{Al}_{0.80}\text{Ga}_{0.20}\text{P} \) layer (E-3) is given in Figure 6-23 for 575°C. The \( \text{Al}_{0.90}\text{Ga}_{0.10}\text{P} \) layer exhibited oxide lengths of the same order as unoxidized samples. The \( \text{Al}_{0.97}\text{Ga}_{0.03}\text{P} \) layer exhibited oxide lengths an order of magnitude greater than those seen in unoxidized samples. However, the oxidization of this layer was erratic, compromising the usefulness determining an activation energy via an Arrhenius plot. The \( \text{Al}_{0.80}\text{Ga}_{0.20}\text{P} \) layer was not susceptible to...
atmospheric oxidation and the oxidation front was relatively uniform. Thus, the Arrhenius plot for the Al$_{80}$Ga$_{20}$P layer in this sample is given in Figure 6-24.

Figure 6-22  004 bright field TEM image of Sample E.
Figure 6-23 Oxidation length vs. time for sample E-3 at 575°C.

Figure 6-24. Arrhenius plot for E-3. $E_A = 0.79 \pm 0.08$ eV.
6.3 Discussion

A mechanistic discussion of the results of the oxidation experiments is now given. The activation energies for all of the compounds discussed above are plotted in Figure 6-25 as a function of the controlled experimental parameter, biaxial strain\textsuperscript{1ivi}. Also given in the graph is the P fraction of the column V constituent for each compound.

As discussed in Section 6.2.2, from Figure 6-16 a strong effect of column V chemistry on the activation energy was observed. However, the dependence of the activation energy on column V chemistry for the samples under compressive strain (e.g. $y < 0.21$) has a trend which is opposite of the trend for the samples under tensile strain, indicating that no single parameter is likely to explain all of the data. Thus, a discussion of additional parameters, such as oxide compression, which were not experimentally controlled parameters but which likely affected the oxidation process is included below.

The relative significance of the reaction and diffusion mechanisms is also discussed. For reference, the activation energy of the diffusive mechanism is lower than the activation energy of the reaction mechanism for the wet oxidation of Si (e.g. 0.71eV compared to 1.26eV)\textsuperscript{132} and AlAs (e.g. 0.8eV compared to 1.6eV)\textsuperscript{223}, which is consistent with the dominance of the diffusive mechanism at high oxidation temperatures.

\textsuperscript{1ivi} Though we show here that multiple factors affect the activation energy of oxidation, in practice, plotting the activation energy data as a function of biaxial strain does show some clear trends.
Figure 6-25. Activation energy (closed circles) of oxidation as a function of biaxial strain and of the P content (open circles) of the compounds.

It was suggested in Section 2.4.1.5 that the stored strain energy (due to lattice mismatch) in the oxidation layers might be the mechanism by which epitaxial strain influences activation energies. Specifically, it was suggested that the released strain energy would provide some of the energy necessary to initiate the oxidation process thereby lowering the measured activation energy. However, the trend seen (i.e. increase in activation energy for increased tensile and compressive strains) is opposite to that expected from this proposed mechanism (i.e. decreasing activation energy for greater strains) suggesting the dominance of other parameters. Furthermore, it is calculated below that the value of strain energies involved are small in comparison to the variation in activation energy seen. Specifically, the strain energy per volume is given as

\[
E_e = \frac{1}{2} \sigma e = \frac{Y}{2(1-\nu)} e^2
\]

Equation 6-1
where $Y$ is the elastic modulus (or Young’s modulus) and $\nu$ is Poisson’s ratio for the material. Applying unit analysis, and multiplying by the inverse molecular density gives the elastic modulus for AlP for example, in relevant units of eV/molecule:

$$Y = 0.9 \times 10^{12} \frac{dyne \cdot cm}{cm^3} \times \frac{6.25 \times 10^{11} eV}{dyne \cdot cm} \times \frac{(0.5467 \times 10^{-7} \ cm)^3}{4 \text{molecules}} = 92 \frac{eV}{\text{molecule}}$$

**Equation 6-2**

For the epitaxial layer used in this work with the highest strain (Al$_{0.97}$Ga$_{0.03}$P, Sample B-6) the biaxial strain is $\varepsilon = 9.7 \times 10^{-3}$ and Poisson’s ratio is 0.32 so that (using the elastic moduli of AlP),

$$E_{\varepsilon} = \frac{1}{2(1-0.32)} \times 92 \frac{eV}{\text{molecule}} \times (9.7 \times 10^{-3})^2 = 6.4 \frac{meV}{\text{molecule}}$$

**Equation 6-3**

Thus, this level of stored strain energy is between two and three orders of magnitude lower than the variation in measured activation energies between the layers with the lowest and highest levels of strain.

There is a small body of literature\(^{230,231,232}\) on the effect of pressure for the oxidation of silicon, though no similar reports were found for the oxidation of III-V compounds. Such pressure is due to the volume constraint of the normally expanding oxide by the surrounding crystal. The effect of pressure on the diffusion of the oxidant through the oxide is such that the diffusivity of the oxidant is modified as,

$$D_{ox} \sim D \exp\left(-\frac{PV_d}{kT}\right)$$

**Equation 6-4**

where $P$ is the hydrostatic pressure experienced by the oxide layer, $D$ is the pressure-free diffusivity and $V_d$ is the activation volume of diffusivity. Thus, the term
PV_d will be a component of the measured activation energy. The activation volume term is representative of the volume change due to the creation or passage of a defect through a unit cell\textsuperscript{lvii} and so the term PV_d is effectively the work done against the pressure in the displacement of neighboring atoms during the passage of an oxidant molecule\textsuperscript{lviii}.

The pressure is given by

$$P = -\frac{B\Delta V}{V}$$

Equation 6-5

where B is the bulk modulus of the material and \(\Delta V\) is the volume change.

The activation volume of water through amorphous Al\textsubscript{2}O\textsubscript{3} (the main constituent in these oxides) was not found in the literature. However, the value of activation volume for water through the extensively studied oxide, SiO\textsubscript{2} is given as 0.075nm\textsuperscript{3} (from experimental measurements)\textsuperscript{230}. A value of 100GPa has been reported for the bulk modulus of amorphous Al\textsubscript{2}O\textsubscript{3}\textsuperscript{233}. However, the pressures induced in the oxides cannot be calculated due to the difficulty in quantifying the extent to which the oxide is constrained (i.e. there is some expansion into the surrounding trench). For a rough estimate however, we consider the surface grown oxide of In\textsubscript{0.5}Al\textsubscript{0.5}P which was studied in a previous work\textsuperscript{130} and for which volume expansions of 30% were measured. The increased volume for In\textsubscript{0.5}Al\textsubscript{0.5}P is likely due to the retention of P-oxide as discussed in Section 2.4.1.3. This is assumed to contribute to volume expansion seen in the other samples in this work as well. Thus, assuming that the lateral oxide of In\textsubscript{0.5}Al\textsubscript{0.5}P (Sample C) is fully constrained (and using in this approximation the bulk modulus for amorphous Al\textsubscript{2}O\textsubscript{3}),

\textsuperscript{lvii} Though the term “unit cell” does not correspond directly to an amorphous oxide, the same principle applies.

\textsuperscript{lviii} There can also be a term to account for the work done by the change in volume during the conversion of one III-V molecule into a III-oxide and V-oxide molecule. For the oxidation of Si, the corresponding increase in activation energy is of the same magnitude as the term modifying the diffusivity.
Activation energies of the magnitude determined in Equation 6-6 are not physically reasonable and were not measured in this work, but this is likely due in part to pressure relaxation from growth into the trench (i.e. newly forming oxide pushing existing oxide into the trench) or flow of the oxide into the trench (i.e. forcing of the oxide to expand horizontally due to the vertical constraint from the spacer layers). The use of the empirically determined activation volume for SiO$_2$ may also give a higher than actual energy term (it is not known to what extent the volume of a unit cell of III-V-oxide is increased if a water molecule is introduced into it).

In light of the relative effects of the various oxidation parameters discussed above, the increasing activation energy with increasing tensile strain (e.g. Sample A) is then likely partially explained by the increase in pressure as the P-content is increased. However, it was found for Sample A that the oxidation exhibited parabolic behavior for higher temperatures indicating that the activation energies (measured assuming linear oxidation rates) would be between the respective activation energies of the reaction and diffusion mechanisms. Furthermore, the diffusive mechanism is known to become increasingly dominant in the oxidation of Al$_x$Ga$_{1-x}$As as the oxidation rate increases (due primarily to the limited rate at which intermediate oxidation products can be removed)\textsuperscript{135}. Thus, the observed decrease in activation energy for decreasing P content in Sample A is also consistent with a trend towards a lower activation energy diffusive limited regime as the respective oxidation rates increase.

The compounds with the highest P content however (e.g. Sample B) have the lowest activation energies. Thus, the pressure term does not seem to dominate in the oxidation of these materials (Sample B) or else the activation energies would be comparable or greater than those measured in Sample A for which the P content and thus induced pressure is expected to be lower. However, a significant factor which likely favors a diffusive mechanism, despite the relative short oxide lengths involved, is the...
more significant level of P retention (discussed in Section 2.4.1.3) compared to the As release from the oxidation of AlAs. Thus, whereas the release of As leads to a porous oxide that enhances diffusion and therefore increases the probability that the oxidation is reaction limited, the lower porosity of the high P containing oxides makes it more likely that the processes is diffusion limited, thus having a lower activation energy.

The measured activation energy of $\text{Al}_{0.80}\text{Ga}_{0.20}\text{P}$ is also consistent with this explanation. Typically, the activation energy for oxidation of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ increases exponentially with increasing Ga content$^{154}$. Accordingly, the activation energy of $\text{Al}_{0.80}\text{Ga}_{0.20}\text{P}$ (Sample E-3) is higher than the activation energy of $\text{Al}_{0.97}\text{Ga}_{0.03}\text{P}$ (Sample B-6) which has the same column V chemistry. However, the activation energy of Sample E-3 ($\text{Al}_{0.80}\text{Ga}_{0.20}\text{P}$) is lower than the activation energy of $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ (Sample A-1) despite the higher Ga content. Thus, as was discussed in the previous paragraph, an additional factor, likely the lower porosity of the high P containing oxide, leads to a diffusion limited regime corresponding to a lower activation energy.

The greater activation energy of $\text{In}_{0.47}\text{Al}_{0.53}\text{As}$ (Sample D) relative to that of $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ (Sample A-1) is consistent with the reduced amount of Al in Sample D. Specifically, it has been observed that replacing Al in these compounds with either Ga$^{154}$ or In$^{227}$ increases the activation energy for oxidation (due in part presumably to the much greater oxidation potential of Al, as given in Table 2-1).

Finally, although structural characterization of the oxides was not performed in this work, these materials may yield different oxide phases for different oxidation temperatures. If multiple phases have been grown in this work for the range of temperatures employed, it likely that the measured activation energies will reflect some complex average of the activation energies associated with the growth of both phases. Structural characterization conducted prior to the work presented in this thesis$^{130}$ of the oxides of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and InAlP (grown under conditions similar to those employed in this work) indicated that the dominant oxide phase was amorphous $\text{Al}_2\text{O}_3$.

6.4 Conclusions

The conclusions to be drawn from these experiments are as follows. Lateral oxidation of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ ($y \ 0.78$, Sample A) is selective with respect to the GaAs
spacers for the full range of column V ratios and temperatures tested. For the oxidation length versus time experiments, the oxidation rate was approximately linear for all compositions (except the highest phosphorous content layer) at the lower temperature of 399°C while for the higher temperature of 482°C the oxidation became parabolic. This switch to parabolic behavior for the oxidation of AlAs has been reported in the literature and attributed to the greater buildup of As$_2$O$_3$ at the oxidation front at higher temperatures. For both temperatures tested, increased phosphorous composition led to slower oxidation rates. For the highest phosphorous containing layers and low temperatures, the oxidation is asymptotic with time, never extending above 1um length in total. At higher temperatures, the oxidation is erratic, presumably due to heterogeneous nucleation of the oxide. Activation energies range from 0.92eV for the lowest phosphorous containing layer to 1.83eV for the highest phosphorous containing layer.

Lateral oxidation of Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ (y = 0.20, Sample B) with GaP spacers has a relatively low oxidation rate (0.1µm/hr at 575°C). Similarly to Sample A (y = 0.78), the oxidation rate decreases for increasing phosphorous concentration. Oxidation of these materials is non-selective with respect to the GaP spacers at high temperatures (643°C). At the lower temperatures investigated (575°C), where oxidation is selective, the oxidation is parabolic with time, although there may be an initial transient for which the oxidation rate is more rapid (similar to the transient seen for the oxidation of Si$^{132}$). Furthermore, the oxide undergoes volume expansion causing the oxide to extend into the oxidation trench and demonstrating that the oxide is in a state of compression. Activation energies for oxidation range from 0.49eV for the lowest phosphorous containing compound to 0.34eV for the highest phosphorous containing compound.

Rate data for the lateral oxidation of In$_{0.5}$Al$_{0.5}$P (Sample C) with GaAs spacers was unattainable due to non-selective oxidation behavior. Lower temperatures that did not cause oxidation of the GaAs spacers yielded no oxidation of the In$_{0.5}$Al$_{0.5}$P while higher temperatures showed similar oxidation rates of the In$_{0.5}$Al$_{0.5}$P and GaAs or no lateral oxidation of the In$_{0.5}$Al$_{0.5}$P whatsoever. When oxidation of the In$_{0.5}$Al$_{0.5}$P did occur (albeit concomitant with GaAs oxidation) the oxide grew into the trench which is consistent with previous studies$^{130}$ that found that surface oxidation of In$_{0.5}$Al$_{0.5}$P
underwent a ~30% volume increase. No measurement of activation energy for this material was possible under the experimental conditions employed here.

Lateral oxidation of In$_{0.47}$Al$_{0.53}$As (Sample D) was selective with respect to the InP for the temperatures used. At the highest temperature used (530°C) the oxidation fronts were uneven presumably due to heterogeneous initiation of the oxidation along the trench wall. The oxidation rate was linear for the temperatures for which the length versus time was checked (530°C and 448°C). The activation energy for oxidation was measured to be 1.36eV, similar to that reported in the literature$^{227}$. The rate of lateral oxidation of Al$_x$Ga$_{1-x}$P (Sample E) was relatively low (<0.4µm/hr). For the highest Al containing layer, oxidation rates were too uneven to measure an activation energy. For the slightly lower Al content, the oxidation rate was more consistent but the oxide lengths observed were similar to those seen in samples that were not thermally oxidized (but which presumably underwent atmospheric oxidation). The lowest Al containing layer was not susceptible to atmospheric oxidation and the activation energy determined for this material was 0.79eV.

In general, the pressure induced by the volume constraint of the oxides (which would normally expand) corresponds to an extra work component of the activation energy, which is likely significant compared to the measured activation energies, whereas the biaxial strain is believed to have an insignificant effect. For compounds using As as the main constituent of the column V chemistry, the diffusive mechanism increasingly becomes the rate limiting mechanism for the compounds having the greatest oxidation rates leading to lower measured activation energies. It also appears that using P as the main constituent in the column V chemistry, which likely leads to lower porosity of the oxide, supports the dominance of a diffusive mechanism having lower activation energy.

In sum, it has been possible to assess the effects that chemistry, strain and pressure have for a wide range of III-V compounds. Of engineering relevance is the fact that despite lower activation energies, compounds with high phosphorous concentrations have very low oxidation rates. Of the materials studied, only Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ ($y \approx 0.78$) produces selective lateral oxides of considerable length (>1µm) in short times (~minutes). The possibility that a composition could be found which would yield zero expansion upon oxidation is well supported by the proceeding data. Specifically, it appears that the
quaternary Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ may provide a suitable compound as it was found here that increasing the P content leads to expansion upon oxidation and it is known from the literature that Al$_x$Ga$_{1-x}$As contracts upon oxidation.
7 Summary and future work

Several new and important results have been discussed in this thesis. For the first time a technique has been developed whereby it is possible to view the entire active region of a solid state laser in a TEM and thereby conclusively identify the degradation mechanisms that lead to laser failure. These technique has been systematically applied to the characterization of a single, rapidly failing VCSEL device structure thus showing the evolution of material failure in the device and ultimately linking the material failure to the output characteristics of the device. Additional examples of degraded VCSELs, drawn from a wider set of failure conditions, were examined to give breadth to our understanding of VCSEL failure mechanisms. In sum, the results of these ex-situ degradation studies are of immediate interest to the VCSEL industry for the development of long-lifetime devices and more generally, they are of importance in the advancement of our understanding of material degradation mechanisms in III-V semiconductor materials.

In order to observe material degradation in VCSEL devices in real-time, an electrical in-situ experiment has been designed whereby it is possible to pass electrical current through a TEM-transparent, sectioned VCSEL. Methods have been designed to account for current losses from parallel current paths and for potential drops across series resistances, thereby determining the precise currents and potential drops experienced by the membrane diode junction of the in-situ electrical circuit. Furthermore, finite element modeling has been employed in order to determine the temperature rise in the membrane as a function of the driving conditions to facilitate separation of thermally assisted dislocation motion from recombination enhanced dislocation motion. The main contribution of the electrical in-situ work has been the development and existence proof of an experimental procedure by which it is possible to systematically observe and characterize the degradation of laser materials in real-time on a nano-scale level in a TEM knowing the precise driving conditions of the membrane junction and the resulting resistive heating.
Finally, it has been possible to assess the effects that chemistry, strain and pressure have for a wide range of III-V compounds. Of engineering relevance is the fact that despite lower activation energies, compounds with high phosphorous concentrations have very low oxidation rates. Of the materials studied, only Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ ($y \approx 0.78$) produces selective lateral oxides of considerable length (>1µm) in short times (~minutes). The initial goal that a composition could be found which would yield zero expansion upon oxidation is well supported by the proceeding data. Specifically, it appears that the quaternary Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ may provide a suitable compound as it was found here that Al$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ ($y \approx 0.2$) expands upon oxidation and it is known from the literature that Al$_x$Ga$_{1-x}$As contracts upon oxidation.

7.1 Future work

Several avenues of future work can be proposed based on the results of this work. The observation of complex dislocation patterns in the ex-situ degraded VCSEL samples suggests that it would be telling if computer code could be developed that would model the patterns that dislocations would create based on controlling parameters such as residual stress fields, non-radiative recombination, and which would take into account the possible effects of the Mullen-Sekerka instability (as discussed in D).

In order to compliment the in-situ TEM experiment exploring the effects of current injection on III-V semiconductor degradation behavior, experiments exploring in real-time and on a nanoscale level, the degradation behavior of III-V materials under high optical injection and under the influence of electric fields should be developed. Thus, details of a partially developed optical in-situ experiment are discussed in Appendix G.

While the focus of the in-situ studies described in this work has been on sectioned VCSEL samples, the residual stress state in a VCSEL is complex and cannot be easily determined. Thus, by employing simpler structures in which the stress state can be engineered (i.e. from lattice mismatch), a correlation between the degradation behavior and the stress state can be made.
It is known from the oxide studies described in this thesis that the compositions in the range of $\text{Al}_{x}\text{Ga}_{1-x}\text{As}_{y}\text{P}_{1-y}$ ($y > 0.80$) undergo rapid thermal oxidation in which a volume expansion occurs (presumably due to the retention of P oxides). Thus additional characterization of these oxides, particularly using a surface oxide geometry, needs to be performed in order to determine that composition for which volume change upon oxidation is minimized. Presumably, a lateral oxide of the composition thus determined can be used as an oxide-confinement layer in a VCSEL to minimize the degree of stress induced.

Furthermore, as was shown in Equation 2-10, the oxidation of semiconductor materials can be modeled as the summation of the reaction limited (linear) growth and diffusion limited (parabolic) growth contributions to the overall oxide length. It is thus possible to explicitly determine the activation energies of the diffusion and reaction limited processes by first fitting the functional form given in Equation 2-10 to a plot of oxide length versus time for a specific oxidation temperature to extract the parameters $k_l$ and $k_p$ (from Equation 2-10). The coefficients thus obtained, which contain the activation energy terms, can be plotted using the Arrhenius method for which the measured slopes are equal to the activation energies. This method is demonstrated for the oxidation of Si in reference 132 and for the oxidation of AlAs in reference 223. Thus, additional characterization of the oxide lengths with time and temperature, especially for the commercially interesting oxide of $\text{Al}_{x}\text{Ga}_{1-x}\text{As}_{y}\text{P}_{1-y}$ ($y < 0.78$) will provide such information.

Finally, further insight into the relative effects of the reactive and diffusive mechanisms on the oxidation of III-V materials may be gained by characterizing chemical profiles in the vicinity of the oxide front. Presumably, for conditions of strong diffusive dependence (i.e. the time required to complete the reaction at the oxidation front is small compared to the time required for the oxidant to reach the front), there will be high chemical gradients across the oxidation front.
A Oxidation furnace configuration

Following is a brief description of the oxidation furnace designed for these experiments. The entire system is shown in Figure A-1. The end cap on the right (Figure A-2) has an outlet for exhaust gas, an outlet for the sample paddle, and a free outlet. The free outlet was connected to the pressure gauge when the system pressure was checked. The stainless steel fitting on the sample paddle outlet can be loosened to allow for positioning of the sample under the tip of the thermocouple measuring the furnace temperature. The entire end cap must be removed (paddle attached) in order to place a sample on the end of the paddle. The gas mixing system is shown on the left (Figure A-3 and Figure A-4). N₂ gas is bubbled through a frit into at least 1 liter of distilled water. The N₂ flow is set to 2.92 splm. A drip vessel is used to replace water lost to the furnace. The temperature of the water is kept at 90ºC (measured by a second thermocouple). All tubing past the water heater is heated to above 100ºC with heating tape to prevent condensation.

Figure A-1. Oxidation furnace
Figure A-2. Gas exhaust and sample insertion system

Figure A-3. H$_2$O-N$_2$ mixing system
Figure A-4. H$_2$O-N$_2$ mixing system
B Determination of strain relief in oxide samples

Strain relief was measured via misfit dislocation counting in the TEM. Ideally, dislocation counting is performed over as large and area as possible for the most accurate measurement of strain relief. However, due to the fact that in this work, multiple sample layers were grown on single wafers, large area TEM transparent regions of single interfaces were not readily made (i.e. by chemical or wide-area ion milling). Thus, the FIB was employed to fabricate a ~10x10µm TEM membrane for each layer.

The axis having the highest density of dislocations was chosen to represent the strain relief value giving the maximum strain relief present. Furthermore, if no dislocations were observed, the lower limit of dislocation spacing was taken as 10µm, the membrane dimension. The average dislocation spacing, \( \rho \), was calculated as the number of dislocations per membrane dimension. The strain relief, \( \Delta \varepsilon \), was calculated as

\[
\Delta \varepsilon = \frac{b \cos \phi}{\rho}
\]

Equation B-1

Where \( b \) is the magnitude of the burgers vector and \( \phi \) is the angle between the burgers vector and the normal to the dislocation line in the plane of the interface (i.e. typically 60° for a misfit dislocation on a 001 interface in III-V materials). The strain relief thus determined is given in Table B-1.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal strain ($10^{-3}$)</th>
<th>Membrane dimension (µm)</th>
<th>Number of dislocations visible</th>
<th>Average dislocation spacing (µm)</th>
<th>Strain relief ($10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>-5.7</td>
<td>6.5</td>
<td>10</td>
<td>0.64</td>
<td>0.34</td>
</tr>
<tr>
<td>A-2</td>
<td>-4.7</td>
<td>9.7</td>
<td>13</td>
<td>0.75</td>
<td>0.27</td>
</tr>
<tr>
<td>A-3</td>
<td>-2.3</td>
<td>9.4</td>
<td>9</td>
<td>1.04</td>
<td>0.19</td>
</tr>
<tr>
<td>A-4</td>
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<td>9.8</td>
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<td>0.22</td>
</tr>
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<td>A-5</td>
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<td>3</td>
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</tr>
<tr>
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<td>4.62</td>
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</tr>
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<td>3</td>
<td>3.00</td>
<td>-0.06</td>
</tr>
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<td>2</td>
<td>4.50</td>
<td>-0.04</td>
</tr>
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<td>8.9</td>
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<td>8.9</td>
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</tr>
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<td>8.4</td>
<td>7</td>
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Table B-1. Strain relief determination
C  Growth and processing data for VCSEL V1

The table below gives the composition, thickness, doping characteristics and growth temperatures for the layers of VCSEL V1. Growth, by MOCVD, starts at the bottom of the table. The column “loops” gives the number of times a set of layers was repeated (i.e. the layer order between a “Start # and Stop #” is repeated # times). The interfaces are graded as indicated by the “Al/In start” and “Al/In end” (i.e. the ratio of Al or In to Ga). The p-type dopant is carbon and the n-type is silicon.

A contact structure of 200 Å Ti / 200 Å Pt / 2000 Å Au is deposited and is annealed during the oxidation step at 440ºC for 15 minutes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Al/In start</th>
<th>Al/In end</th>
<th>Layer thickness (Å)</th>
<th>Dopant type (n,p, or uid)</th>
<th>Dopant concentration c.c.</th>
<th>Growth Temp ºC</th>
<th>Loops</th>
</tr>
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<td>GaAs</td>
<td></td>
<td></td>
<td>134.9</td>
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<td>352.7</td>
<td>p</td>
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<td>p</td>
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<td>640</td>
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<tr>
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<td></td>
<td>417.6</td>
<td>p</td>
<td>4.0E+18</td>
<td>750</td>
<td>Stop 15</td>
</tr>
<tr>
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<td>0.16</td>
<td>298.1</td>
<td>p</td>
<td>4.0E+18</td>
<td>750</td>
<td>15</td>
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<td>p</td>
<td>4.0E+18</td>
<td>750</td>
<td>15</td>
</tr>
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<td>Stop 15</td>
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<td>156.1</td>
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Table C-1. Growth table for VCSEL V1.
**D Complex patterned growth**

There is a large, and long standing\textsuperscript{234} body of literature on the nature of complex growth in natural systems. For example, the literature contains an extensive treatment of dendritic (and similar) growth patterns as they pertain to phase transformations, chemical reactions, etc. (for a recent review of this branch of science refer to the text by Feder\textsuperscript{235}, or Langer\textsuperscript{236}). An understanding of the dynamics of complex pattern growth is expected to be applicable to a wide range of situations in the natural sciences\textsuperscript{237}.

**D.1 Extended growth patterns in other branches of science.**

A brief synopsis of the salient features of complex patterned growth, also known as extended growth, is given to help in understanding the complex dislocation patterns shown in this thesis. Extended growth patterns occur in many physical systems, such as during the electrolytic growth of metals, or during the growth of dust particles. These patterns fall into several categories that can be classified by shape, and which vary according to driving and environmental conditions. Examples of relevant driving condition parameters include supercooling in the case of solidification, and applied voltage in the case of electrolytic growth. Examples of important environmental parameters that determine the nature of the pattern include the surface tension between the growing substance and the host material, the availability of solute material, and the degree of anisotropy of the host material. Many of the possible shapes are shown in Figure D-1. Two examples of the shape dependence of extended patterns on growth conditions are given in Figure D-2 and Figure D-3. Brief details of the conditions leading to these growth shapes are given below.
Figure D-1. Various extended pattern growth shapes. (DLA-diffusion limited aggregation. DBM-dense branching morphology)

Figure D-2. Dependence of pattern type on growth conditions (solute concentration, C, and driving voltage, V)\textsuperscript{242}. The example given is for electrolytic growth of Zn from a concentration, C(M), of ZnSO\textsubscript{4}. 
D.1.1 Dendritic patterns

Dendritic patterns, with branches that follow specific crystallographic directions, arise under a range of driving forces (e.g. supercooling or applied voltage) and when the host material exhibits some degree of anisotropy. In the extreme case, for high anisotropy, high driving force, and high particle concentration, a needle like, or stringy pattern is produced with minimal side branching$^{242,238}$. There is increased side branching as the driving force is lowered$^{242}$.

D.1.2 Dense branching morphology (DBM)

DBMs are radial in nature and have no fractal nature (i.e. are not produced by self-similar structures of increasing size)$^{248}$. These patterns arise in systems with little or no anisotropy, little or no surface tension of the growing phase, a range of driving forces, and medium concentration gradients$^{242}$.

D.1.3 Diffusion-limited aggregation

DLA patterns are formed under low driving forces, with low particle concentration gradients, and when the host material has little or no anisotropy$^{238}$. In contrast to dendritic growth, they exhibit no preferred growth directions$^{242}$. They are formed by irreversible aggregation (i.e. a particle, once affixed to the pattern, remains
stationary) similar to the following manner\textsuperscript{239,240}. An initial seed particle sits in the center of a large container. A second particle is introduced on a random site a large distance from the origin (say on the perimeter of the container). The particle randomly diffuses unless it touches the seed particle at which point it becomes stationary. The process of introducing a particle is repeated some number of times. The effect produces a random branching pattern in which the outer site of the branches grow and split more rapidly than the inner sites which are shadowed by the outer sites (i.e. the particles are more likely to be captured by the outer sites). As the name implies, the rate-limiting step in the growth of these patterns is the rate of diffusion of particles to the aggregate.

**D.2 Nature of dislocation patterns seen in degraded VCSELs**

The complex nature of some of the dislocation patterns shown in Section 4.1.2 warrants some consideration of the mechanisms responsible for such pattern growth. Although previous investigations into the dislocations structures present in degraded edge emitting lasers has revealed branching dislocation patterns, there has been little known published consideration into the fundamental mechanisms responsible for the complex branching patterns. What has been published are a few models for the dislocation history that might give rise to the observed patterns (e.g. Matsui’s multiple cross slip model\textsuperscript{58}). What’s not explicitly discussed in detail is why the dislocation has such motion.

Of the possible complex patterns discussed above, we focus the following discussion primarily on dendritic growth and diffusion limited aggregation (DLA) as they contain characteristics most relevant to the dislocation patterns observed. Extensive literature searching found no published treatment of dendritic dislocation patterns apart from an article by A.A. Pisarev et al\textsuperscript{241} who have shown similar dislocation patterns (albeit, on the order of only 100nm in diameter) in steel after helium ion bombardment.

There are three general mechanisms that control complex growth patterns. One of these is the magnitude of the force driving the growth\textsuperscript{242,243}. In the case of solidification, this includes, for example, the degree of undercooling. A second mechanism is the degree of instability of the growth interface\textsuperscript{237,244,245}. An interface is said to be stable if infinitesimal perturbations do not grow, thereby leaving a smooth interface at the molecular level. The degree of stability depends on the competition between driving and
opposing forces\textsuperscript{237,246}. For example, thermal gradients destabilize a planar interface (i.e. heat dissipation is more efficient over a larger surface area) while surface tension acts to stabilize it\textsuperscript{236}. The last mechanism is the degree of anisotropy of the involved materials which will dictate the overall shape of the pattern\textsuperscript{237}. Again, for the case of solidification, this may be manifested as a preferred growth orientation.

Aspects of diffusion-limited aggregation are also relevant to the dislocation patterns seen in Section 4.1.2. As discussed above, a complex pattern with many outward reaching branches is formed if diffusing species are blocked from entering the center of the pattern due to the trapping nature of the branches. Furthermore, it has been found that DLA patterns are favored over dendritic patterns for cases where there is no anisotropy affecting the surface tension of the growing phase\textsuperscript{247,248}.

In light of the above brief review of complex patterns in nature, we can draw several parallels to the complex patterned dislocation networks in VCSELS (especially, V2, V3 and V4). For dipole formation, there will be a combination of driving forces due to stress fields (mechanical) and point defect gradients (chemical) while dislocation line tension acts to minimize the dislocation line length\textsuperscript{83}. Thus, noting the conditions that lead to uniformly branching patterns (described above), the dislocation patterns observed in V2 and V3 are likely formed under conditions of relatively lower anisotropy and relatively lower driving force, compared to the linear dislocation arrays found to be associated with DLDs in edge emitting lasers. The lower anisotropy is possibly manifested as a biaxial stress field at the active region of the VCSEL as opposed to an axial stress field (the favoring of one direction of dislocation array growth due to an anisotropy in residual stress was briefly discussed in Sections 2.3.3.3 and 2.3.3.5).

The branching of the dipoles (seen for the VCSELS and in edge emitting lasers) is likely due to an instability between the force driving the growth and the dislocation line tension. This instability is likely related to the radiation enhanced defect motion (REDM) mechanism. Specifically, as mentioned in Section 2.3.2, phonon energy due to multiple non-radiative recombination events is absorbed by the lattice giving rise to kinks or jogs in the dislocation\textsuperscript{48-51}. However, there is no strong driving force due to residual stress which, if present would manifest itself as a clear preferred orientation for dislocation growth. The driving force for the dislocation motion for this configuration then is
possibly a chemical gradient of point defects leading to an osmotic force for climb. Such a force is explained by Hirth and Lothe\textsuperscript{249} as follows. There is an equilibrium concentration of point defects in the vicinity of a dislocation (which contains an edge component) that is dependent on the dislocation-free equilibrium point defect concentration of the material, and the stress experienced by the dislocation. However, if a concentration gradient of the point defects exists between the location of the dislocation and a location far from it, there will be diffusive flow of point defects according to the sign of the gradient. Therefore, the dislocation will emit or absorb point defects to maintain the equilibrium concentration of point defects near it and in doing so, will undergo climb motion. Thus, applying instability theory, as a jog is formed (by a REDM event) which extends into the gradient, the gradient field is increased in the region of the extension (as depicted in Figure D-4), leading to an increased driving force for further extension\textsuperscript{236}. This instability (i.e. as opposed to a stable competition between the increased line length and the line tension opposing growth) and the source of energy via REDM (which in turn increases as the dislocation motion increases) may thus lead to the rapid extension of narrow arms of the dislocation dipole.

![Figure D-4.](image)

Finally, we note that the dislocation arrays, specifically in VCSELs V2 and V3 are similar to patterns attributed to the diffusion limited aggregation (DLA). Specifically, the dislocation patterns exhibit semi-radial patterns of long and narrow dislocation extensions similar to the extension seen for DLA in Figure D-1. This would suggest that
the point defects necessary for pattern growth are limited from reaching the center of the pattern due to the end of the dislocation arms acting as point defect sinks. This further suggests that point defects do not vertically migrate to the dislocation array from within the DBR layers but instead migrate horizontally from within the layers of the active region (point defect migration towards the dislocation array from the vertical direction would presumably favor widening existing dipoles rather than extending them). This is again consistent with point defect assisted migration due to the REDM mechanism allowed by the carrier recombination within the active region of the device. Possible sources for these defects are the interfaces within the active region or the structures used for current confinement (e.g. the oxide layers).

In sum, the shape of the complex pattered dislocation arrays are shown to resemble complex patterns from other branches of science. The theoretical mechanisms leading to complex patterned growth have been applied to the growth of the complex pattered dislocation arrays. In contrast to the conditions leading to the formation of DLDs, the formation of radial dislocation patterns is likely due to a relatively lower amount of residual stress that is also relatively isotropic. The branching nature of the dislocation dipoles may be due to an instability in the pattern growth caused in part by the REDM effect. The occurrence of long thin dislocation arms may be in part due to the diffusion limited aggregation mechanism.

E Data acquisition for electrical in-situ work (Chapter 6)

E.1 Electric circuitry

An electrical breadboard was used to make the necessary connections between the power source, sample holder and monitoring equipment as shown in Figure E-1. A computer equipped with a NI-DAQ data acquisition board (model AT-MIO-16E-10) was used to gather real-time data during the experiment. The software package LabView (v. 4.1) was used to create an interface to control the data acquisition as discussed later. A VCR acquiring electron diffraction image footage of the degradation

lix National Instruments Corporation; 6504 Point Parkway Austin, TX 78730-5039.
was synced to the data collection interface for easy comparison of degradation conditions (e.g. drive potential, specimen current) to degradation behavior after the experiment. The power was either provided by the Ni-DAQ board (-10V $V_D$ 10V) or by an external power supply ($|V_D|<10V$) when higher driving potentials were desired.

![Figure E-1. Schematic of setup for in-situ electrical degradation experiment](image)

The electric circuit used to drive the experiment and to acquire experimental parameters and measurements is shown in Figure E-2. A manual switch was used to change the power supply driving the circuit.
Figure E-2. Wiring diagram for in situ electrical circuit. Pa represents the external power supply and Pc represents the NiDAQ power supply.

The circuit consisted of two parallel branches. The upper branch, a voltage divider, acted as a voltmeter for the lower branch, which contained the membrane. The voltage divider was used due to the fact that the maximum input on the NiDAQ board was ±11V. Thus, $R_2$ was chosen as 10% of $R_1$ so that driving potentials greater than 11V could be measured. Furthermore, the total of $R_1$ and $R_2$ was chosen as $1.1 \times 10^6 \Omega$ (a value at least an order of magnitude greater than the resistance of a membrane under low bias) so that the voltmeter did not draw off a significant portion of the total circuit current. The measured drive potential was calculated as,

$$V_D = V_A \frac{R_1 + R_2}{R_2}$$

Equation E-1

In the lower branch of the circuit a reference resistance, $R_r$, needed to determine current flow through the membrane, was chosen so that ideally it was a relatively small fraction of the total circuit resistance and hence dropped a small fraction of the total drive
potential. However, the minimum useful (i.e. significant compared to noise) measurable potential was 24.41µV. Therefore, the reference resistance had to be high enough to drop a portion of the total applied potential that allowed for reasonably fine voltage (and hence current) measurements for the desired range of measurement. For this work, a reference resistor of 100Ω was typically used, as it was found to be a reasonable compromise between providing for measurement sensitivity and being relatively small (compared to the membrane resistance) over a range of smaller applied biases (e.g. less than a few volts).

At high voltages (e.g. approaching 10V) the resistance of the diode decreased rapidly\(^{13}\) causing the reference resistor to drop a more significant portion of the total potential. Thus, whereas the NiDAQ board may have supplied the maximum of ±10V, the potential drop across the membrane was much less than ±10V.

The current through the sample was calculated as,

\[
I_r = \frac{V_r}{R_r}
\]

**Equation E-2**

where \(V_r\) was the measured potential drop across the reference resistor, \(R_r\). The approximate potential drop (e.g. ignoring the potential drop across wires and contacts which are accounted for in Section 5.2) across the sample was then calculated by,

\[
V_T = V_D - V_r
\]

**Equation E-3**

---

\(^{13}\) Briefly, as the applied forward bias is increased, the barrier for electron transport through the junction is lowered leading to greater current flow per applied bias, and hence lower resistance.
Finally, the resistance for the diode membrane at any current was calculated by,

\[ R_T = \frac{dV_T}{dI_T} \approx \frac{V_T}{I_T} \]

Equation E-4

E.2 Data acquisition module used in electrical in-situ studies

A screen capture of the LabView user interface developed by this author for data acquisition in this experiment is shown in Figure E-3. All measurements and calculated values were stored to a buffer after every iteration and could be saved as described below. In step one, the reference resistance being employed was entered (typically 100 Ω as mentioned above). During data acquisition, the membrane resistance and portion of potential drop across the in-situ circuit were shown on this line and were also recorded to the buffer. In step 2, the grab rate was chosen. This value was also recorded to a buffer and could be changed during a data acquisition run. For this particular data acquisition interface, it was found that the maximum grab rate was \( \sim 25 \text{sec}^{-1} \) (as determined by the looping speed of the software).

In step three, a VCR frame number was entered in HH:MM:SS format that corresponded to the VCR frame number at which the acquisition was begun, thereby accomplishing a manual sync of the data acquisition to the VCR-recorded TEM images. This line also read out the updated VCR frame in decimal time (the value which is recorded) as well in the HH:MM:SS.S format. The total time of the current data acquisition run as well as the number of data lines stored to the buffer was also given on this line. In step 4, if the NiDAQ board was used as the power source, the circuit voltage was controlled by the slider bar or by keypad input. At the end of the data acquisition period, if saving the data was desired, the button in step 5 was pushed.

Three real-time updating charts were also included in the user interface as shown in Figure E-3 (i.e. the three large black blocks). The charts labeled “I&V traces” showed the circuit current, \( I_T \), and applied potential, \( V_A \), as a function of time. A real time trace of \( I_T \) versus \( V_T \), was also shown for quick determination of ohmic and rectifying behavior.
For the $I_T$ versus $V_T$ real-time chart a second buffer could be set which determined the number of data points given in the chart and thereby, the rate at which the chart was refreshed. In the lower right, the voltmeter sensitivity was chosen by setting the maximum and lower allowed voltages. For lower voltage ranges, the sensitivity was increased with the trade-off that voltages outside the range were not detected. A table at the right gave the allowable configurations. A thermometer-like graphic gave an indication of how close the voltage was to approaching the selected upper voltage limit.
Figure E-3. User interface of LabView data acquisition program.

LabView uses an icon driven program language to create tools such as the data acquisition module used in this work. Figure E-4 gives a screen capture of the program that controlled the data acquisition module used in this work. Most labels correspond to the labels seen in the front panel, although other comments are included. The individual
familiar with LabView programming (and possessing a magnifying glass) should be able to duplicate the data acquisition interface used in this work based on Figure E-4.

Figure E-4. Icon driven programming of LabView data acquisition program.
Table E-1 shows an example of the data file generated if the data from the buffer was saved to disk in step 5. The categories: VCR time, circuit voltage, membrane current prefactor, voltage for current high and voltage for current low (the sensitivities set by the user), and grabs per sec were entered by the user or directly measured from the NiDAQ board. The value, membrane current prefactor, corresponds to the factor used to convert the initial calculation of current in amps to the final displayed and recorded value in micro-amps, and was included in the data acquisition to avoid confusion in data analysis after the experiment. Membrane current was calculated based on a measurement of potential drop across the reference resistor. Membrane resistance, and sample voltage were calculated as discussed above.

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<th>VCR time (sec)</th>
<th>circuit voltage (volts)</th>
<th>membrane current (µA)</th>
<th>membrane resistance (ohm)</th>
<th>membrane current prefactor</th>
<th>voltage for current high</th>
<th>voltage for current low</th>
<th>grabs per sec</th>
<th>reference voltage</th>
<th>sample voltage</th>
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</table>
The thermal transport equation, including effects of conduction, radiation, and resistive heating, is a second order nonlinear differential equation with no analytical solution. Thus, a finite element model has been developed in order to determine the relation between the temperature distribution in our in-situ TEM membrane and driving conditions. The thermal transport equations used by the finite element software are developed below. Time dependence is included in the derivation although steady state analysis is carried out in the finite elemental analysis. Much of the development of these thermal equations follows the treatment of heat conduction in solids by Carslaw and Jaeger.

Consider current flowing through a parallelepiped in the z direction. In three dimensions, it can be shown that the heat flux by conduction at any point is given by,

\[ \mathbf{f} = -K \nabla T \]

**Equation F-1**

where K is the thermal conductivity. It can then be shown that the rate of heat gain in a volume element is given by,

\[ -8 \rho \varepsilon \nabla \cdot (\nabla \cdot \mathbf{f}) \]

**Equation F-2**

and by,

\[ 8 \rho \varepsilon \frac{dT}{dt} dx dy dz \]

**Equation F-3**

\(^{15}A simple method using only magnitudes of heat quantities and ignoring spatial dependencies of heat flow has been attempted. However, the temperature equation based on these simplifications yields temperatures greater than the melting point of Al\(_{x}\)Ga\(_{1-x}\)As for drive currents commonly used in the experiment and so the more precise solution is sought.
where \( \rho \) and \( c \) are the material density and specific heat respectively. Thus, equating Equation F-2 and Equation F-3,

\[
\rho c \frac{\partial T}{\partial t} - (\frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z}) = 0
\]

**Equation F-4**

However, the terms for thermal conductivity and specific heat are temperature dependent,\(^{\text{lxii}}\) thus Equation F-4 becomes (after substituting Equation F-1 in Equation F-4),

\[
\rho(T)c(T) \frac{\partial T}{\partial t} - K(T)\nabla^2 T - \frac{\partial K(T)}{\partial T}\left((\frac{\partial T}{\partial x})^2 + (\frac{\partial T}{\partial y})^2 + (\frac{\partial T}{\partial z})^2\right) = 0
\]

**Equation F-5**

\( K(T) \) for the \( \text{Al}_x\text{Ga}_{1-x}\text{As} \) system (and many other III-V binaries) varies as,

\[
K(T) = \frac{K_0}{T^n}
\]

**Equation F-6**

where \( n \) for \( \text{Al}_x\text{Ga}_{1-x}\text{As} \) is \(~1.375\) (reference 18).

\(^{\text{lxii}}\) The thermal expansion coefficient is of order \( 10^6/K \) which corresponds to a \(~2\%\) change in density at a temperature rise of 1000\(^\circ\)K. In contrast, the heat capacity varies by \(~10\%\) and the thermal conductivity by \(~30\%\) at a temperature rise of only 100\(^\circ\)K above room temperature\(^{18}\).
If heat is supplied by current, the heat generation rate in a volume element is:

\[ \rho c(T) \frac{\partial T}{\partial t} = \frac{I^2}{\sigma A_i^2} = \frac{IV}{V_i} \]

\textit{Equation F-7}

where \( A_i \) is the area of the current flow region, \( \sigma \) is the conductivity of the membrane, \( I \) and \( V \) are the membrane current and bias respectively, and \( V_i \) is the membrane volume. Though the \( I^2 \) term is commonly used in thermal calculations for metals, in the VCSEL system the conductivity, \( \sigma \), depends on the sophisticated doping profiles used, and is thus difficult to employ in modeling. However, both \( V \) (for the membrane) and \( I \) are directly measured during the experiment, and thus this formulation for power generation is used in these calculations.

If radiation from the surfaces of the membrane is considered, the Stephan-Boltzmann law gives the rate of heat loss per volume as,

\[ \rho c(T) \frac{\partial T}{\partial t} = 2e\sigma_{SB}(T^4 - T_o^4) \frac{D}{D} \]

\textit{Equation F-8}

The factor of 2 takes into account radiation from both sides of the membrane, \( e \) and \( \sigma_{SB} \) are the emissivity of the membrane and the Stephan-Boltzmann constant respectively, and \( D \) is the thickness of the membrane. The \( T_o \) term accounts for radiation into the membrane from the ambient atmosphere. Convection can also be accounted for in this term with the appropriate constants. However, as the experiments take place in the TEM vacuum, convection is ignored.
Incorporating Equation F-7 and Equation F-8 into Equation F-5 gives

\[ \rho c(T) \frac{\partial T}{\partial t} = K(T) V^2 T + \frac{\partial K(T)}{\partial T} \left( \left( \frac{\partial T}{\partial x} \right)^2 + \left( \frac{\partial T}{\partial y} \right)^2 + \left( \frac{\partial T}{\partial z} \right)^2 \right) + \frac{IV}{V_i} - \frac{2e\sigma_{SB}(T^4 - T_0^4)}{D} \]

Equation F-9

For steady state analysis, the left hand side of the above equation is set to zero. As mentioned previously, no analytical solution to this equation is readily derived. Thus a numerical solution is obtained in the finite element software Ansys (v5.7).

G Optical In-situ degradation

An additional in-situ TEM method has been partially developed to explore the degradation caused by the high optical fluxes typically present in operating VCSELs. Briefly, in this experiment, optical field densities up to 5 kW/cm² provided by an Ar⁺ ion laser are directed onto a plan-view-sectioned VCSEL sample and the resulting material behavior is monitored by TEM. A brief description of the experimental design and technique as well as some preliminary results are given below.

For comparison of the optical density provided by the in-situ setup and the output density present in an operating VCSEL, several examples of typical VCSEL output power densities reported in the literature are given in Table G-1. The optical power density at the active region within the VCSEL is typically an order of magnitude greater than the value cited in the table due to the high reflectivity of the DBR stacks employed as the cavity mirrors (i.e. the majority of photons are reflected back into the optical cavity by the mirror). For reference, VCSEL V1 which was used for a majority of the ex-situ degradation experiments described in Chapter 4, emitted a maximum power output of ~0.4 kW/cm² before degradation ensued.
### Table G-1. Examples of optical output intensities for various VCSEL designs

<table>
<thead>
<tr>
<th>Maximum output power kW/cm²</th>
<th>VCSEL design</th>
<th>Emission Wavelength (nm)</th>
<th>Reference number</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>3.5x3.5µm², oxide confined</td>
<td>850</td>
<td>251</td>
</tr>
<tr>
<td>12.5</td>
<td>4x3µm², oxide confined</td>
<td>~950</td>
<td>252</td>
</tr>
<tr>
<td>4.2</td>
<td>4.5x8µm², oxide confined</td>
<td>986</td>
<td>253</td>
</tr>
<tr>
<td>1.5</td>
<td>14.4x18 µm², oxide confined</td>
<td>969</td>
<td>253</td>
</tr>
<tr>
<td>0.4</td>
<td>6x6µm², oxide confined</td>
<td>~1100</td>
<td>254</td>
</tr>
<tr>
<td>0.06</td>
<td>10µm diameter, ion implant confined</td>
<td>670</td>
<td>255</td>
</tr>
</tbody>
</table>

**G.1 Optical in-situ experimental design**

A 300mW Ar ion laser\(^{lxiii}\) emitting three component wavelengths simultaneously (458 nm, 488 nm, 514.5 nm) is used as the light source for this experiment. The energy of this light is above the bandgap of all III-V materials generally used in VCSEL designs and so the photon energy will be absorbed in all parts of the VCSEL sample. This situation differs from an operating VCSEL where, the emission wavelength is such that the energy of the output light is below the bandgap of the mirror layers. The room temperature absorption coefficient, \(\alpha\)^{lxiv}, for 488 nm photons in GaAs is \(1.1\times10^5\) cm\(^{-1}\) corresponding to a penetration depth of \(~90\) nm\(^{18}\).

A 50µm diameter multimode\(^{lxv}\) fiber\(^{lxvi}\) is used to couple the Ar\(^+\) ion laser to the TEM sample via an optical in-situ TEM holder\(^{lxvii}\) shown in Figure G-1.

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\(^{lxiii}\) Spectra Physics model 177 argon ion laser with maximum output power of 300mW.

\(^{lxiv}\) The optical flux density will decrease by a factor of \(e^1\) after propagating a distance (termed the penetration depth) of \(1/\alpha\).

\(^{lxv}\) The term “multimode” refers to the fact that this fiber is composed of a bundle of smaller diameter fibers. It is generally easier to couple laser light into a multimode fiber.

\(^{lxvi}\) Fiber has 50mm core, 125mm cladding and 250mm outer diameters. Part number is CS-94-0509, available from Thorlabs, Newton NJ.

\(^{lxvii}\) Made by Gatan Inc.
G.1.1 Fiber insertion

The fibers used in this experiment, especially when stripped of their cladding, had a tendency to break due to the stresses generated in the bends of the sample holder fiber tube. Thus, the following method has been developed to position the fiber end at the sample area without breaking it:

1. Apply a very minute amount of vacuum grease to the end of the fiber.
2. Thread the fiber through the fiber feed-through tube from the exposed end of the holder (i.e. the end that does not go into the TEM) and pull through several feet of fiber. During the threading process, the fiber will typically stop at constrictions or bends in the feed-through tube. However, repeatedly pushing and pulling the fiber, (holding onto the fiber as near to the exposed end as possible so that the force being applied does not cause bending of the exposed portion of the fiber) will eventually result in the fiber moving past the obstacles.
3. Strip the cladding from about 5 cm of the end of the fiber in a vial of Dichloromethane. To do so, dip the end of the fiber in the vial for approximately 1-2 minutes. Remove the fiber and lightly hold the soaked end of the fiber in the crease of a folder piece of filter paper and pull.
4. Cleave the end of the fiber so that only ~1mm remains stripped. To produce the cleanest cleave, tape the fiber to a table so that the exposed fiber
overhangs the edge of the table. Then, very lightly score (i.e. just barely touch) the exposed fiber with a diamond scribe ~1mm past the end of the jacket. Put one drop of water on the scribe mark ($\text{H}_2\text{O}$ facilities bond breaking in Si based fibers). Apply pressure with a finger to the taped portion of the fiber and gently pull the exposed portion of the fiber. The fiber will cleave at the scribe mark.

5. To position the fiber end at the sample location, use a pair of soft tweezers (e.g. made of Teflon) to hold the fiber back towards the rear end of the holder as is shown in Figure G-2 (essentially, you close off most of the sample area with the tweezers leaving just about a fiber’s width of area for the fiber to move through). This gives the correct angle, whereas not holding the fiber in this position results in a frictional force between the fiber and the feed-through tube that is sufficient to break the fiber when the fiber is moved. Pull from exposed end of the holder until the fiber is at the desired location (e.g. until it just falls past tip of tweezers).

6. Clean any excess grease from the sample area with a sharp toothpick or cotton swab that has been dipped in a mild solvent.

![Figure G-2. Schematic of how to hold the fiber when pulling it back through the feed-through tube.](image)

Measurement of the fiber power output is more accurate if taken after the fiber is installed in the TEM holder as the bending of the fiber in the holder, or cracks developed
during the fiber insertion may induce some optical losses. Thus, the power delivered to the sample is determined as shown in Figure G-3. After inserting the fiber into the holder but prior to inserting the sample (so that the light exits the holder as is shown in the upper half of Figure G-3), the range of power delivered by the laser through the fiber is measured with a thermopile detector. Due to the fact that the optical fiber is positioned so that it is nearly touching the sample (e.g. so that there is minimal beam spreading), the optical density incident on the sample is then approximately the known power per fiber area.

![Figure G-3. Technique for determining optical density impinging on sample](image)

G.1.2 Sample heating

As was the case in the electrical in-situ experiment, determination of sample temperature is essential to separating temperature related effects from radiation-induced effects.

As mentioned above, the extent of the energy absorbed by the sample from the laser beam is characterized by the sample’s absorption coefficient. For GaAs, the absorption coefficient can be calculated using the absorption coefficient of GaAs.

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lxviii Briefly, the thermopile detector measures optical power using the electrical signal generated from a series of thermocouples, which have been heated due to the absorbed incident light. The detector used has uniform absorption characteristics over a wide range of wavelengths (250nm - 1100nm) and is capable of detecting a range of power, 5mW to 20W.
absorption coefficient close to the melting temperature (1513K) for the photon energies employed here decreases to $\approx 5 \times 10^4 \text{cm}^{-1}$.[256-260] It remains to develop a finite element model so that membrane temperatures can be estimated based on the optical power delivered.

G.1.3 Preliminary results

Several defect free plan-view oxide-confined VCSEL samples have been tested using the method described above. However, it was observed that no degradation occurred until a threshold optical density of $\approx 3 \text{kWcm}^{-2}$ was incident on the sample, at which point the sample rapidly melted. Thus, additional experimental development is needed to attain a sample geometry for which sample heating is minimized.

In sum, it is believed that the in-situ experimental method described above, with additional development, will make it possible to observe in real-time and on a nano-scale level, the behavior of semiconductor materials under optical injection.
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