Characterization Of Defects And Evaluation Of Material Quality Of Low Temperature Epitaxial Growth

Hrishikesh Das

Follow this and additional works at: https://scholarsjunction.msstate.edu/td

Recommended Citation
https://scholarsjunction.msstate.edu/td/1009

This Dissertation is brought to you for free and open access by the Theses and Dissertations at Scholars Junction. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholars Junction. For more information, please contact scholcomm@msstate.libanswers.com.
CHARACTERIZATION OF DEFECTS AND EVALUATION OF MATERIAL QUALITY OF LOW TEMPERATURE EPITAXIAL GROWTH

By

Hrishikesh Das

A Dissertation
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in Electrical Engineering
in the Department of Electrical and Computer Engineering

Mississippi State, Mississippi

May 2010
CHARACTERIZATION OF DEFECTS AND EVALUATION OF MATERIAL QUALITY OF LOW TEMPERATURE EPITAXIAL GROWTH

By

Hrishikesh Das

Approved:

Yaroslav Koshka
Associate Professor of Electrical and Computer Engineering
(Director of Dissertation)

Michael S. Mazzola
Professor of Electrical and Computer Engineering
(Committee Member)

Raymond S. Winton
Professor of Electrical and Computer Engineering
(Committee Member)

Seong-Gon Kim
Associate Professor of Physics
(Committee Member)

James E. Fowler
Professor of Electrical and Computer Engineering
(Graduate Coordinator)

Sarah A. Rajala
Dean of the Bagley College of Engineering
A novel process for low-temperature (LT) epitaxial growth of silicon carbide (SiC) by replacing the growth precursor propane with chloro-methane was recently developed at Mississippi State University. However, only limited information was available about the defects and impurity incorporation in the various types of epitaxial layers produced by this new method like blanket epitaxial layers, selectively grown epitaxial mesas, and highly doped epitaxial layers, prior to their comprehensive characterization in this work. Molten potassium hydroxide (KOH) etching, mechanical polishing and a variety of other characterizing techniques were used to delineate and identify the defects both in the epilayer and substrates.

Under optimum growth conditions, the concentration of defects in the epitaxial layers was found to be less than that in the substrate, which established the good quality of the LT growth process. Defect concentrations, on selectively grown epitaxial layers, strongly depended on the crystallographic orientation of the mesa sidewall.
The addition of HCl to the growth process, aimed at increasing the growth rate, caused a significant concentration of triangular defects (TDs) to be formed in the epitaxial layers. The TDs were traced down to the substrate by a combination of repeated polishing and molten KOH etching steps. The TDs were found not to originate from any substrate defects. Their origin was traced to polycrystalline silicon islands which form on the surface during growth and subsequently get evaporated away, which had made it impossible to detect them and suspect their influence on the TD generation prior to this work. The TDs were found to include single or multiple stacking faults bound by partial dislocations and, in some cases, inclusions of other SiC polytypes.

Gradual degradation of the epitaxial morphology was found in heavily aluminum doped p+ layers, with an increase in the level of doping, followed by much steeper degradation when approaching the solubility limit of Al in 4H-SiC. Precipitates were the dominating defect at the highest levels of doping and were observed beyond a doping of 3.5x10^{20} cm^{-3}. A dislocation generation model for heavily doped epitaxial layers was developed accounting for the stress in the lattice caused by Al doping.
DEDICATION

To my wife, Swapna
ACKNOWLEDGMENTS

I would like to first express my sincere gratitude to my major advisor, Dr. Yaroslav Koshka, without whose guidance and support this research would not have been possible. I would like to thank him for helping me and motivating me throughout the long journey of my PhD. I have learned a lot from him.

I would like to take this opportunity to thank my parents whose belief in me led to pursue this degree. Second, I would like to give special thanks to my wife Swapna who patiently supported me during my studies.

Special thanks to Dr. Michael Mazzola for introducing me to SiC and for his guidance and critical suggestions. I would also like to thank Dr. Raymond Winton and Dr. Seong-Gon Kim for serving on my dissertation committee and for their invaluable suggestions. Finally, this work would not have been successful without the teamwork and cooperation of my friends and colleagues at the Mississippi Center for Advanced Semiconductor Prototyping (MCASP) Laboratory.
TABLE OF CONTENTS

DEDICATION.................................................................................................................... ii

ACKNOWLEDGMENTS ................................................................................................. iii

LIST OF TABLES............................................................................................................. vi

LIST OF FIGURES.......................................................................................................... vii

CHAPTER

1. INTRODUCTION ...................................................................................................1

  1.1. Properties and Applications .................................................................1

  1.2. Crystal structure and polytypes..........................................................3

  1.3. Conventional Epitaxial Growth and Low Temperature Growth ............5

  1.4. Motivation and organization of this work..............................................6

2. LITERATURE REVIEW ......................................................................................10

  2.1. Conventional Epitaxial Growth .............................................................10

  2.2. Low Temperature Epitaxial Growth .....................................................11

  2.3. Selective Epitaxial growth ....................................................................13

  2.4. Defects delineation in SiC by molten Potassium Hydroxide (KOH) etching ........................................................................................................15

  2.5. Triangular defect ......................................................................................20

  2.6. Aluminum Precipitates in SiC .................................................................26

  2.7. Precipitate and Dislocation generation Models ......................................27

  2.8. Brief overview of PL characterization of the epitaxial quality of SiC ........................................................................................................31

3. EXPERIMENTAL APPROACH...........................................................................32

  3.1. Epitaxial Samples Investigated ...............................................................32

  3.2. Defect delineation in SiC by molten potassium hydroxide (KOH) etching ........................................................................................................32

  3.3. Removal of Epitaxial layers ...................................................................34
3.4. Photoluminescence ....................................................................................36
3.5. Nomarski Differential Interference Contrast (NDIC)..............................37
3.6. Raman Spectroscopy ..................................................................................39
3.7. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).........................................................41
   3.7.1. Scanning Electron Microscope ............................................................41
   3.7.2. Energy Dispersive X-ray Spectroscopy .............................................43
3.8. Focused Ion Beam (FIB) and Transmission Electron Microscope (TEM) ........................................................................................................44
   3.8.1. Transmission Electron Microscope (TEM) .........................................45

4. EXPERIMENTAL RESULTS...............................................................................47
   4.1. Characterization of defects in Low Temperature Blanket Epitaxial Growth ........................................................................................................47
      4.1.1. Comparison of blanket epitaxial growth with and without HCl.......49
      4.1.2. Defects in Optimized Low temperature blanket epitaxial growth ..........................................................50
      4.1.3. Arrays of Dislocations .....................................................................55
   4.2. Defects in Selective Epitaxial Growth.......................................................56
   4.3. Defects in heavily doped P+ epitaxial layers............................................63
      4.3.1. Defects in the P+ samples.................................................................65
      4.3.2. Photoluminescence of P+ Samples..................................................76
      4.3.3. Dislocation generation model in epitaxial layers grown at low temperature with in situ Al doping ......................................................77
   4.4. Analysis of the triangular defect generation during low-temperature epitaxial growth ..........................................................85
      4.4.1. Investigating a possible role of the substrate defects ...............86
      4.4.2. The main origin of the TDs ............................................................91
      4.4.3. The structure of the TDs .................................................................96
      4.4.4. Low-temperature Photoluminescence ........................................104

5. CONCLUSIONS AND FUTURE WORK ..........................................................107

REFERENCES ................................................................................................................110
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Properties of Common Semiconductors</td>
<td>2</td>
</tr>
<tr>
<td>4.1. Defect statistics with and without HCL</td>
<td>50</td>
</tr>
<tr>
<td>4.2. Defects in Epitaxial layer and Substrate</td>
<td>52</td>
</tr>
<tr>
<td>4.3. Epilayer to Substrate defect conversion</td>
<td>55</td>
</tr>
<tr>
<td>4.4. Defect Statistics of LTSEG Epilayer vs Substrate</td>
<td>60</td>
</tr>
<tr>
<td>4.5. Conversion statistics of LTSEG defects</td>
<td>62</td>
</tr>
<tr>
<td>4.6. Al dopant incorporation for different TMA flow rates</td>
<td>65</td>
</tr>
<tr>
<td>4.7. HAS Model parameters extracted for SiC compared to GaAs and InP from literature</td>
<td>84</td>
</tr>
<tr>
<td>4.8. Conversion statistics of epitaxial layers with large number of triangular defects</td>
<td>91</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Crystal Structure of SiC</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Polytypes in SiC</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>Good morphology of epitaxial layers grown at low temperature [21]</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>PL data comparing low temperature and regular temperature growth [23]</td>
<td>13</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic of a SEG process in Silicon</td>
<td>14</td>
</tr>
<tr>
<td>2.4</td>
<td>Optical and SEM micrographs of the various defects revealed by KOH etching.</td>
<td>17</td>
</tr>
<tr>
<td>2.5</td>
<td>Etch pits after molten KOH etch at different temperatures (Ref: [56])</td>
<td>19</td>
</tr>
<tr>
<td>2.6</td>
<td>Various reports of the Triangular defect in literature are shown in (a)[15]</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>(b)[69] (c)[63] (d)[66] (e)[72] (f)[64] (g)[65]</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>Suggested structure of the triangular defect having two BPDs at the base</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>and stacking faults between them. (Refs: a) [33] b) [70])</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>Oxidized triangular defects a) having 3C inclusions grown at 1450°C</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>and b) not having 3C inclusions grown at 1500°C (Ref: [62])</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>Raman spectra comparing the 4H and 3C peaks in different regions of a</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>triangular defect. [66]</td>
<td></td>
</tr>
<tr>
<td>2.10</td>
<td>The energy gap between the phonon replica lines in various SiC polytypes</td>
<td>25</td>
</tr>
<tr>
<td>2.11</td>
<td>PL spectra of a stacking fault at 9K (Ref: [83])</td>
<td>25</td>
</tr>
</tbody>
</table>
2.12. TEM image of aluminum precipitates in highly doped 4H-SiC (Ref: [88])..................................................................................................................27

2.13. Defects seen in epitaxial layers with doping of (a) $4 \times 10^{18}$ cm$^{-3}$ (b) $1.3 \times 10^{19}$ cm$^{-3}$........................................................................................................28

2.14. PL spectra of 4H-SiC a) IR spectra [107] b) UV Spectra [106] ......................31

3.1. Schematic of the KOH setup............................................................................33

3.2. Steps involved in characterizing defects at various levels of the epitaxial layer and the substrate: (a) investigation of defects in a blanket epitaxial layer, and (b) investigation of defects in SEG mesas........35

3.3. Schematic of the photoluminescence setup .....................................................37

3.4. Basic setup of a Nomarski Microscope ...........................................................39

3.5. Energy level diagram showing three different levels of scattering..............40

3.6. Cross section of a SEM unit.............................................................................42

3.7. Principle of EDS spectroscopy ........................................................................44

4.1. Various defect propagation scenarios from the substrate to the epitaxial layer a) micropipe - micropipe b) micropipe to several screw dislocations c) Threading – threading d) threading – carrot defect e) BPDs – ThDs f) BPDs - BPDs [104]...............................................................47

4.2. KOH etch-pits in low-temperature epilayer grown at 1300°C: (a) without HCl and (b) higher growth rate with HCl. Basal plane dislocation BPDs are encircled. Only threading dislocation (ThD) are observed in (b) indicating higher efficiency of the BPD conversion from the substrate.................................................................50

4.3. KOH etch-pits in (a) epitaxial layer and (b) in the underlying substrate. Only threading dislocation (ThD) are observed in (a). Several Basal plane dislocations BPDs observed in (b) are encircled.................................52

4.4. Defects in an epitaxial layer (a), (c) and in the underlying substrate (b). The crosses denote the vertex of the defects in the substrate. The arrows denote the direction the defects would travel after epitaxial growth. .................................................................................53

4.5. Array of dislocations seen (a) in the epilayer and (b) in the substrate beneath after polishing and molten KOH etch.................................................56
4.6. a) Defect propagation along the basal plane into an SEG mesa b) Cross-sectional SEM of an LTSEG mesa showing the defective area near the sidewalls.................................................................58

4.7. KOH etch-pits in LTSEG mesas having different sidewall orientations. Growth-induced dislocations (BPD) in mesas are observed only at sidewalls preferentially oriented upstream to the step-flow direction.........58

4.8. Defects from the substrate get replicated on the LTSEG Mesas. Arrows show the line of defects in the substrate. ...........................................59

4.9. Tracing of defects from LTSEG epilayer to substrate. The crosses denote the vertex of the defects in the substrate. The circles denote newly created ThDs during epitaxial growth............................................61

4.10. SIMS profile showing aluminum incorporation into the epilayer for different TMA flows............................................................................................64

4.11. Defect statistics of p+ doped epitaxial layers showing a) total epilayer defects and b) total epilayer defects – substrate defects in log scale...........67

4.12. Fast etching of P+ samples by KOH revealing the substrate defects underneath the epitaxial layer: (a) just after some of the epilayer has been removed by etching, (b) additional 3 minutes of etching deeper in the substrate, and (c) additional 5 min etching further deeper in the substrate. .............................................................68

4.13. Defects in the epitaxial layer and substrate of three samples grown with increasing TMA flows ..............................................................................69

4.14. Smaller etch pits appearing, growing and fading after KOH etch steps........70

4.15. SEM images of (a) ‘sharp’ and (b) ‘faded’ precipitate............................71

4.16. Optical Profilometer scans of the depth profile of faded small etch pits: (a) the topographic map of the surface with the faded etch pits circled (b) line scan of a faded etch pit overlaid over its SEM image (c)(d) line scans of other faded etch pits................................................................................72

4.17. EDS line scan showing random aluminum concentration across a threading dislocation etch pit and defect free epilayer ......................................74

4.18. EDS line scan of aluminum concentration across a small etch pit superimposed on the SEM image of the corresponding location. Higher Al concentration is seen at the core of the defect.............................75
4.19. Cross-sectional TEM images of the epitaxial layer showing a few localized small defects: (a) showing dislocations originating from the epilayer-substrate interface and defects localized at particular depths in the epitaxial layer and (b) a magnified view of a location having a few localized epitaxial defects..........................................................76

4.20. Low temperature UV-Photoluminescence of P+ samples showing progressive degradation of the crystalline quality ............................................77

4.21. Defects in the P+ samples separated into Dislocations and Precipitates........78

4.22. Calculated stress for different values of doping ........................................80

4.23. Dislocations generated over time for different values of stress.................81

4.24. Dislocations generated over time for optimized parameters of the model to fit the experimental data after 30 minutes of dislocation generation (i.e., epitaxial growth process)............................................82

4.25. Dislocation generation predicted by the HAS model versus the actual experimental data.............................................................................................83

4.26. Increase in the concentration of TDs with increase in $R_g$ .......................86

4.27. Tracing the triangular defects from the epilayer to the substrate (a) the initial step: crosses mark the location of substrate defects and (b) the final step after the epilayer has been removed: the diamonds mark the location of the triangle vertexes in the epilayer...........................................89

4.28. XRD measurements showing the presence of polycrystalline Si in the islands ..............................................................................................................94

4.29. Optical micrographs of triangular defects (TDs) in a SiC epitaxial layer grown at conditions resulting in higher $R_g$ and poly-crystalline islands formed in the upstream portion of the growth zone. Different locations on the wafer are shown: (a) upstream, (b) center, and (c) downstream. High concentration of TDs is caused by islands .........................94

4.30. Correlation of poly Si islands with triangular defect nucleation measured at various distances from the leading edge.............................................96

4.31. SEM micrographs of triangular defects after KOH of epitaxial layers formed by low-temperature epitaxial growth with HCl addition: (a) low Si/C=3.75; (b) and (c) higher Si/C=9 at two different locations on the sample. The dotted lines are used to delineate the difficult to resolve edges of the triangular defects..............................................97
4.32. Three epitaxial layers grown at different conditions with triangular defects before and after oxidation @1150°C for 6.5 hours ............................100

4.33. TDs in two different growth runs. The left column (a,a1,a2) correspond to growth at higher Rg and higher C/Si ratio than (b, b1, b2). (a),(b) as grown, (a1),(b1) after oxidation, (a2),(b2) SEM after KOH.................................................................101

4.34. Micro Raman spectra taken from a TD sample: (a) showing the points from where the spectra are obtained. (b) Showing the comparison of 4H-SiC and 3C-SiC Raman peaks inside and outside the TD.........................103

4.35. PL spectrum of a sample with very high concentration of TDs. The inset shows the disturbed surface morphology, which is caused by the longer growth time resulting in overlapping of large and smaller TDs. Sharp BE and FE PL lines can be observed in spite of the dominance of the TDs. ......................................................................................................105
Silicon carbide (SiC) is a very promising material in semiconductor technology. SiC is a wide band gap semiconductor that possesses extremely high thermal, chemical, and mechanical stability, as well as very high breakdown strength. As a consequence, SiC devices can perform under high-temperature, high-power, and high-radiation conditions in which conventional (i.e., narrow band gap) semiconductors cannot adequately perform. Its ability to function under such extreme conditions is expected to enable significant improvements to a variety of applications and systems.

1.1. Properties and Applications

SiC belongs to a class of materials commonly referred to as wide-bandgap semiconductors. The energy gap between the valence and conduction band is much larger than in other semiconductors like silicon. This energy gap lowers the probability of thermally excited electrons being excited across the bandgap. Therefore, SiC devices can operate at temperatures exceeding 500°C.

The thermal conductivity of SiC is larger than that of other semiconductors, thus the heat generated by these devices is efficiently removed. Also, its saturated electron drift
velocity is double that of Si, resulting in much faster turn-off and higher switching speeds in devices.

SiC has many other physical properties, such as being chemically inert and radiation hardened, that make it ideal for use in many hostile environments, like nuclear reactors and outer space. Table 1.1 illustrates the differences between SiC and other semiconductor materials.

Table 1.1

Properties of Common Semiconductors

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>GaAs</th>
<th>6H-SiC</th>
<th>4H-SiC</th>
<th>3C-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap [eV]</td>
<td>1.12</td>
<td>1.43</td>
<td>3.10</td>
<td>3.26</td>
<td>2.33</td>
</tr>
<tr>
<td>Break down electric field [V/cm] @1000V</td>
<td>2.5×10^5</td>
<td>3×10^5</td>
<td>2.5×10^6</td>
<td>2.2×10^6</td>
<td>2.0×10^6</td>
</tr>
<tr>
<td>Thermal conductivity [Wcm⁻¹·K⁻¹] @ RT</td>
<td>1.5</td>
<td>0.5</td>
<td>4.9</td>
<td>4.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Electron drift velocity [cm/s]</td>
<td>1.0×10^7</td>
<td>1.0×10^7</td>
<td>2.0×10^7</td>
<td>2.0×10^7</td>
<td>2.5×10^7</td>
</tr>
</tbody>
</table>

The above properties make SiC suitable for various applications, such as electricity distribution, hybrid vehicles, more powerful solid state microwave sources for radar and communications, and other general applications of greener technologies in jet aircrafts and automobile engines. Moving from silicon to silicon carbide will radically change many power electronics applications.
1.2. Crystal structure and polytypes

Atoms in the silicon carbide unit cell are linked to each other in a tetrahedral structure. Each carbon atom is linked to four silicon atoms and vice versa. The crystals can have many different structures; the most common are cubic and hexagonal. Figure 1.1 shows how the orientations decide the final structure.

Figure 1.1 Crystal Structure of SiC

SiC exhibits a phenomenon called polytypism, which is the ability of a material to exist in more than one crystal structure. The polytypes differ just in the stacking sequence of atomic layers forming the crystal. Over 200 polytypes of SiC are known at present. Three basic orientations are possible in a hexagonal layer; these orientations are termed A, B and C. The number of layers after which the stacking repeats determines the number of the polytype. Also, the crystal structure gives the suffix alphabet, i.e., C for
cubic and H for Hexagonal. For example, the polytype with the stacking sequence ABAB is named 2H, the one with the sequence ABCABC is named 3C, the one with the sequence ABCBABC is named 4H, the sequence ABCABCABCB is named 6H, and so on. Figure 1.2 shows these examples.

![Figure 1.2. Polytypes in SiC](image)

The most commonly used polytypes are 3C, 4H and 6H. Different polytypes can be grown by Chemical Vapor Deposition by using different growth conditions. Different polytypes have a preferential tendency to grow depending on the parameters of the growth process [1] like substrate temperature, Si/C ratio, C-flux, pressure, growth rate, etc. The Si/C ratio plays a critical part in the growth. Under conditions of a high Si/C ratio or high supersaturation, the cubic 3C polytype is preferred, whereas the 4H polytype is preferred at more carbon rich conditions or low supersaturation. 6H-SiC growth occurs somewhere in the middle of the above two conditions. Also, the C-face has a stronger
relaxation than the Si-face that results in the preferential growth of 4H on the C-face under a wider range of growth conditions. Also, 3C nucleation occurs preferentially on the Si-face. Temperature also plays an important role in favoring the polytypes. At higher temperatures, there is a higher probability of growth of the hexagonal polytypes. By changing the various growth parameters, different polytypes can be grown.

1.3. Conventional Epitaxial Growth and Low Temperature Growth

Epitaxy is the process of growing a relatively thin layer on a monocrystalline substrate. Epitaxy is necessary because the SiC substrates do not have the purity required for SiC device fabrication. The active regions of the devices also need to be tailored to the specifications of the devices with appropriate doping levels.

The growth of defect free SiC epitaxial layers is critical for successful device fabrication. This growth can be accomplished by various means, including Chemical Vapor Deposition (CVD), Molecular Beam Epitaxy (MBE) or Liquid Phase Epitaxy (LPE). Generally, the same polytype needs to be grown on the substrate. This is called homoepitaxy. This can be achieved by a strict control of the growth parameters, which is not always possible. Step-controlled epitaxy [2] is a useful mechanism that ensures that homoepitaxy takes place.

Historically, all the wafers are cut perpendicular to the c-axis of the boule. If the boule orientation is tilted at an angle and then cut, this results in nano-steps on the surface of the wafer. Growth occurs along these steps, thus ensuring a replication of the stacking order.
Conventional CVD epitaxial growth processes apply silane (SiH₄) and propane (C₃H₈) as precursors. Growth temperatures in excess of 1600°C to 1700°C are used. Such high temperatures are necessary to ensure high epitaxial quality and prevent lattice defects from being created during growth. Higher temperatures also facilitate growth at higher rates. However, growth at these high temperatures has its drawbacks, including faster degradation of the reactor hardware, higher impurity release from heated parts of the reactor, and poor suitability for selective growth techniques due to mask degradation.

In previous work at Mississippi State University, epitaxial growth at much lower temperatures (down to 1300°C) has been demonstrated, providing SiC epitaxial layers with a smooth mirror-like surface [15]. This was made possible by using an unconventional chloro-carbon precursor CH₃Cl as the carbon source. The use of low temperatures, however, did not allow increasing growth rates above ~2µm/hr.

Further improvement in the growth rates, up to 5µm/hr, was achieved by the addition of HCL [21]. The low temperature epitaxial growth technique has also been successfully applied to achieve low-temperature selective epitaxial growth (LTSEG) with low temperature SiO₂ masks [24][25], which had not been possible earlier due to mask degradation at higher growth temperatures.

1.4. Motivation and organization of this work

Prior to this work, very little was known about the quality of the epitaxial layers grown at low temperature. Successful application of the low-temperature growth method requires comprehensive information about important defects that may form during the growth and their possible influences on device performance. Various applications of low
temperature growth, such as blanket epitaxial growth, selective epitaxial growth, and highly doped epitaxial layers are required for successful device fabrication. These requirements of the low temperature growth process development justified the scope of research efforts covered in this work.

In this work, a variety of characterization techniques are applied to quantitatively evaluate defects created during the low temperature blanket epitaxial growth conducted at various growth conditions. Feasibility of the low temperature growth process ensuring conversion of device killing basal plane dislocations (propagating from the substrate) into relatively harmless threading dislocations in the epilayer has been investigated. This defect conversion mechanism may be extremely useful for a variety of SiC devices.

In the low temperature growth of SiC, growth rates are limited by the silicon cluster formation in the gas phase. This problem is alleviated by the addition of HCl to the growth process that etches these clusters thus causing higher growth rates. However, epitaxial layers grown with this process suffer from the incorporation of defects that were not present at the lower growth rates. This includes the formation of triangular defects, which is the main defect seen at higher growth rates. Similar defects were extensively investigated in regular-temperature epitaxial growth; however, there is still a lack of consensus about their origin and possible ways to minimize their generation. Prior to this work, there had been no investigation of triangular defects formed in epitaxial layers grown at low temperatures. Extensive experiments have been conducted in this work to understand the origin, structure, and composition of these triangular defects.

Selective epitaxial growth in SiC has not been very successful at conventional growth temperatures for a variety of reasons including mask degradation. Growth at lower
temperatures allows us to grow epitaxial layers selectively using the conventional SiO$_2$ mask without any significant mask degradation. However, the quality of such epitaxial layers grown in mesa windows can be different from the blanket (non-selective) epitaxial growth. Several defects are seen propagating from the sidewalls of the mesas. Hence, in this work, the detailed characterization of defects in SiC grown by low-temperature selective epitaxial growth has been undertaken.

Heavily doped epitaxial layers are essential for forming good ohmic contacts in device fabrication. However, extreme doping causes epitaxial quality degradation due to the generation of dislocations and the possible formation of precipitates. This in turn causes degradation in device performance. Careful characterization is necessary for developing a low-defect-density low-temperature epitaxial growth process with a maximum possible dopant concentration. Dislocations, precipitates and other defects in highly doped layers have been quantitatively investigated to give a clear picture of the onset of crystalline quality degradation during the SiC epitaxial growth. A mathematical model for predicting defect generation as a function of doping has been developed and validated with the experimental data.

This dissertation covers the results of the experimental work summarized above and is organized as follows. Chapter 2 contains background information and a literature review of the topics relevant to this work. It provides a background on conventional and low temperature epitaxial growth of silicon carbide. It also contains an introduction to selective growth of SiC and the low temperature SEG process. A literature review of the defects in SiC characterized by their delineation using molten KOH etching is included. Various reports covering triangular defects and precipitates investigated in SiC are
summarized. A few mathematical models predicting dislocation and precipitate generation in semiconductors are discussed. A brief look at photoluminescence of a few important defects, like stacking faults, is presented.

Chapter 3 presents the experimental procedures used in this work. It contains the description of the molten KOH etching process developed and also the polishing process used to remove epitaxial layers in a controlled manner for the depth profiling of lattice defects. Other characterization techniques used in this work, including Nomarski Microscopy, Scanning Electron Microscopy, Focused Ion Beam, Transmission Electron Microscopy and Photoluminescence, are also described.

Chapter 4 contains the experimental results and discussions. The results of the characterization of both low temperature blanket epitaxial layers and low temperature selectively grown epitaxial layers are presented. Experiments to determine the structure and composition of the triangular defect are presented. A possible origin and the mechanism of the triangular defect generation in the low temperature epitaxial growth process are presented. Defects in highly aluminum doped epitaxial layers grown by the low temperature process are quantitatively investigated. A mathematical model to describe the generation of defects dependent on doping is presented. The conclusions and possible future work are presented in Chapter 5.
2.1. Conventional Epitaxial Growth

Conventional SiC epitaxial growth conducted by chemical vapor deposition (CVD) at 1500-1800°C with a SiH₄-C₃H₈-H₂ gas system relies upon the step-controlled growth mechanism [3][4][5]. The adsorbed species migrate on the surface and are incorporated into the crystal at steps where the surface potential is low. A well-known fact is that a higher growth temperature is more favorable for the step-controlled growth mechanism. In addition to growth temperature, pressure, C/Si ratio, in situ surface preparation, off-axis angle, polarity (Si-face or C-face), and a few other process parameters are critical in obtaining mirror like high quality epilayers [6][7][8].

The main reason for conducting growth at high temperatures is to obtain high quality epitaxial layers with low defect density and higher growth rates [9].

Another process to obtain thick epitaxial layers with a very high growth rate has been demonstrated using high-temperature CVD (HTCVD) [10]. Silane and hydrocarbons were used as the source precursors and the growth was carried out at 2100°C. This growth process is known as “gas fed sublimation.”

However, there are a few limitations to growing at a higher temperature, which include graphite life degradation, out diffusion of contaminants from graphite parts, and
altered C/Si ratio due to heated graphite, which would in turn affect the dopant incorporation and epilayer morphology.

The addition of HCl as a precursor gas is another attractive approach for growing high quality epilayers [11]. Growth rates of 112μm/hr have been demonstrated by Francesco et al [12]. They showed that the introduction of HCl reduces the silicon homogeneous nucleation in the gas phase, thereby enabling more silicon to be supplied to the growth surface without its depletion by the homogeneous nucleation [12].

2.2. Low Temperature Epitaxial Growth

Epitaxial growth conducted at temperatures below 1400°C was previously demonstrated on 6H-SiC substrates [13][14]. Researchers at Mississippi State University were the first to demonstrate high-quality epitaxial growth at temperatures lower than 1300°C on 4H-SiC substrates using a halo carbon growth precursor, which replaces the traditional propane [15]. The crystalline quality of epilayers grown at low temperature was reported to be as good as that in the epilayers grown at regular high temperatures [21].

The biggest advantages of conducting epitaxial growth at lower temperatures would be longer graphite life and a reduction in the process cost.

One of the main problems for conducting epitaxial growth at low temperatures is the reduced mobility of adatoms on the growing surface, which may cause 2-D nucleation [15]. This in turn can lead to the formation of a variety of defects, such as triangular defects [21], dislocations, polytype inclusions, etc. Two other major limiting factors are
the narrow process window and reduced growth rates. Further optimizing the C/Si ratio and better controlling the gas phase and surface kinetics is needed to address this issue.

The addition of HCl during low temperature growth is a promising approach in improving the surface morphology (Figure 2.1). Since the addition of HCl during epitaxial growth reduces the homogeneous nucleation in the gas phase and consequently the density of Si clusters in the gas phase, this enables a significant increase in the growth rates [21][22]. Preliminary photoluminescence data of optimized non-HCl growth suggested that the epitaxial quality is comparable to that of the regular temperature epitaxial growth (Figure 2.2) [23].

Figure 2.1. Good morphology of epitaxial layers grown at low temperature [21]
In spite of the preliminary data about the high quality of the epitaxial layers grown at low temperature described above (i.e., investigation of the surface morphology [21], and photoluminescence spectroscopy [23]), not enough is known about the generation of the main types of defects caused by low temperature growth. One of the main goals of this dissertation is to conduct a comprehensive evaluation of the overall quality and the defect contents in low temperature epitaxial layers.

2.3. Selective Epitaxial growth

Selective epitaxial growth (SEG) is a well-known process used in silicon semiconductor fabrication technologies and offers important advantages to device and IC fabrication [16]. A simple schematic of the SEG of silicon using a SiO$_2$ mask is shown in Figure 2.3. The process consists of depositing an SiO$_2$ layer on the surface of Si substrate, forming windows in the SiO$_2$ layer exposing the Si substrate, and growing Si regions.
(also called mesas) of desirable shape and dimensions selectively in the windows, without having any growth in the regions of the Si substrate protected with the SiO$_2$ mask.

However, conventional high growth temperatures (~1600°C) used in SiC epitaxial processes make it challenging to find a suitable mask for SEG of SiC.

Figure 2.3. Schematic of a SEG process in Silicon

Eshun et al demonstrated SiC SEG on SiC substrates using a graphite mask at 1500-1700°C [17] and Chen et al reported using a carbon mask at 1500°C [18]. The biggest disadvantage in using these masks during the high temperature SiC epitaxial growth is that the effective C/Si ratio above the growth surface alters locally, which may cause undesirable deposition of polycrystalline SiC on the mask.

Li et al demonstrated good surface morphology of SiC SEG on SiC substrates using a TaC mask at 1450-1550°C. They deposited Ta films on the SiC substrates and later annealed them for 30 minutes to form TaC mask subsequently used for SEG. They used
the same mask for lateral epitaxial overgrowth, since SiC does not nucleate on TaC [19]. However TaC masks are much more difficult to form than the conventional SiO$_2$ masks. Unwanted etching of the mesas was also seen under some growth conditions.

One of the challenges in device fabrication by SEG is nonuniform growth across the SEG layer, also known as local loading effect [20].

The low growth temperatures enabled by the low-temperature epitaxial growth method developed at MSU [21][22] offer an opportunity to use the low-temperature silicon dioxide and silicon nitride masking material that are successfully used in the silicon industry [15]. This growth method, subsequently called low-temperature selective epitaxial growth (LTSEG) of SiC, has been successfully demonstrated by the researchers at Mississippi State University. However, a few problems regarding the generation of some defects in the epitaxial layer remained [24][25].

Very little has been reported about defect generation in LTSEG. There is a concern that the generation of dislocations in the epitaxial SiC may be higher due to the constrained nature of the LTSEG growth. Also, orientation dependent side-wall defect generation needs to be understood.

This dissertation compares the quality of the LTSEG epitaxial layers with low temperature blanket epitaxial growth. It also examines the generation mechanisms of different defects during LTSEG, including the formation of sidewall defects.

2.4. Defects delineation in SiC by molten Potassium Hydroxide (KOH) etching

KOH etching has been used extensively in SiC bulk and epitaxial growth to delineate defects and quantify the quality of the grown material. Various imperfections in the
crystal structure may be revealed by molten KOH etching. The common defects that are seen after a KOH etch are micropipes [30], carrots [31][32], screw dislocations, threading edge dislocations, basal plane dislocations, grain boundaries, and triangular defects [31]. All these defects have a huge impact on SiC device performance [43][44]. Figure 2.4 shows various defects that can be revealed in SiC by KOH etching.

Micropipes are one of the biggest and most detrimental defects in SiC substrates and epitaxial layers. They are open core super screw dislocations with a large Burgers vector. They are known as the major device killers [26][27]. It has been shown that micropipe maps of wafers have a direct correlation to device yields [28].

Micropipes originate from the substrate and can continue into the epitaxial layer. However, sometimes they can dissociate into multiple threading dislocations. It was reported that this conversion can be promoted by using a low C/Si ratio during the epitaxial growth [29]. Micropipes show up as large hexagonal pits after etching with molten KOH (Figure 2.4 a and c).
Carrots also have a negative effect on device performance. They have been reported to cause a drop in the blocking voltage of SiC p-n diodes [33]. Carrots are believed to originate from a threading screw dislocation in the substrate [35][36]. It was also reported that the tail region of a carrot has Shockley type faults [34].

Grain boundaries are found in the substrate in which regions are surrounded by high dislocation densities [37]. These usually are packed very close to each other in straight lines and look like arrays of dislocations after a KOH etch (Figure 2.4e). Most of the time, the grain boundaries get replicated into the epilayer after epitaxial growth. However, these grain boundaries could be involved in the conversion of basal plane dislocations in the substrate to an array of threading dislocations in the epitaxial layers. The presence of these arrays is known to have a major impact on SiC devices [38].
Stacking faults (SF) are formed when there is an incorrect layer in the polytype stacking sequence. Stacking faults cause lower Schottky barrier heights and lower breakdown voltages [41]. Stacking faults can also be created by other defects under stress. It is reported that basal plane dislocations under stress cause stacking faults to appear, which increases the forward voltage drop in PiN diodes and reduces the gain of BJT devices by reducing mobility and increasing recombination [42]. SFs show up as straight lines after a KOH etch (Figure 2.4 d and f) [39][40].

The most common defects that are seen in substrates and epitaxial layers are basal plane dislocations and threading edge dislocations. Basal plane dislocations propagate through the epitaxial layer or the substrate at the off-axis cut angle. These can be identified as oval elongated etch pits after a KOH etch (Figure 2.4a) [39].

Basal plane dislocations in the epitaxial layer are known to cause a variety of problems in SiC devices [45][46][47]. They lead to the creation of stacking faults and degrade performance and cause failure. Device yield maps very closely correlate to BPD maps [46].

Various techniques have been reported to reduce BPD concentrations in the epitaxial layers. H₂ etch before the epitaxial growth reduced the BPD concentrations [48][49]. In some of the reports, performing a KOH etch of an epitaxial layer and then growing an epitaxial layer on top of the etched surface may reduce BPD concentrations [50]. More elaborate techniques involved etching the substrate, then growing a sacrificial epilayer, polishing it away, and finally growing the actual epitaxial layer [51].

BPDs in the substrate can convert to threading edge dislocations in the epitaxial layer. This is highly desirable for device applications because threading edge dislocations are
not as harmful as BPDs. It was observed that the BPDs that have a large angle to the off-cut axis have a greater probability of getting converted to threading edge dislocations [52]. The conversion percentage of BPDs to threading edge dislocations becomes an important parameter in qualifying an epitaxial growth process. Threading edge dislocations appear hexagonal in shape after a KOH etch (Figure 2.4a). However, in higher doped samples, these can look round in shape.

The etch rate of molten KOH is dependent on several factors. The etch rate of p\(^+\) samples is higher than n-type samples [53]. The etch rate on C-face SiC is higher than that on the Si-face epilayer [54]. The etch rate and the etching profiles are also highly dependent on the temperature [55][56]. Therefore, it is very important to optimize the etching process for the particular samples that are being investigated. Figure 2.5 shows the etch pits at various temperatures. The optimized etch providing the best delineation is shown in Figure 2.5d.

Figure 2.5. Etch pits after molten KOH etch at different temperatures (Ref: [56])
In this dissertation, the method of delineating defects by etching in molten KOH has been used extensively to characterize and quantify all the main defects found in epitaxial layers grown at low temperatures and under various growth conditions. Molten KOH etching also has been used to characterize the quality of LTSEG layers and to determine the structures of some defects.

2.5. Triangular defect

Triangular defects have been extensively investigated in SiC epitaxial growth. Figure 2.6 shows various observations of the triangular defect reported in literature.

![Triangular defect images](image)

Figure 2.6. Various reports of the Triangular defect in literature are shown in (a)[15] (b)[69] (c)[63] (d)[66] (e)[72] (f)[64] (g)[65]
Many factors are known to promote or suppress triangular defect formation. 3C nucleation is considered one of the reasons for defect generation in epitaxial layers. These defects can lead to the generation of triangular defects. A substrate with a lower off-cut angle (4° or lower) has larger terrace widths, promoting 2D nucleation. This increases the chances of the triangular defect formation [2]. Lower growth rates and higher off-cut substrates are supposed to reduce 3C nucleation [59][60]. Both of these factors reduce supersaturation at the terraces and thereby reduce the chances of spontaneous 2D nucleation.

Others have suggested that the origin of triangular defects is from substrate related defects [61][7]. It has also been reported that high C/Si ratios strongly increase the rate of the 3C-SiC nucleation [62]. At high C/Si ratios, the surface mobility decreases, thus causing supersaturation of adsorbed atoms and 2D nucleation. These conditions are favorable for the triangular defect formation [63][64][65][67].

Lower temperatures also promote triangular defect formation [63][65][66]. Other factors like deteriorated growth susceptors and higher temperature ramp rate also favor triangular defect formation [66]. This can be attributed to the instability at the substrate surface at the beginning of the epitaxial growth [68].

The lattice defects that define the structure of the triangular defect have been investigated by many groups. It is suggested that the triangular defect is made up of two BPDs at the base [70][33]. The two BPDs meet at the vertex of the triangular defect at the epitaxial/substrate interface, with stacking faults between them. Figure 2.7 shows this structure. Others observed screw dislocations at the vertex of the triangular defect, but they are not observed in all the triangular defects [66]. It has also been suggested that
triangular defects are formed by silicon droplets falling on the surface and forming the vertex of the triangle [71].

Figure 2.7. Suggested structure of the triangular defect having two BPDs at the base and stacking faults between them. (Refs: a) [33] b) [70])

There is conflicting evidence about the structure of the triangular defect. Many believe that it consists of 3C inclusions [72][66]. Others have shown by micro Raman analysis that the triangular defects do not contain 3C-SiC [65]. A way to detect 3C inclusions in 4H or 6H is by oxidizing the epitaxial layer and observing the color change, if any, of the defect [73][74][75]. The oxidation rates of the three polytypes are different, with the rate of 3C oxidation being more than double that of the others. Upon oxidation it was observed that some triangular defects exhibited a different color (darker) than the rest of the epitaxial layer [62]. This is indicative of 3C inclusions. However triangular defects in other samples did not exhibit this pattern. This shows that the generation of 3C inclusions in the triangular defects may or may not happen, depending on the growth conditions. Figure 2.8 shows the oxidized triangular defects.
3C-SiC inclusions in triangular defects have also been detected by Raman spectroscopy. The 4H-SiC and 3C-SiC polytypes show up as two distinct peaks in the spectra. The relative intensities of these peaks have been used as a measure to examine the composition of the defects. Figure 2.9 shows the Raman spectra taken at different locations inside a triangular defect [66]. The top part of this defect has a much higher 3C-SiC polytype peak, indicating a higher concentration there when compared to the rest of the defect. There were also reports of triangular defects that have no presence of the 3C-SiC peak when measured by Micro Raman [76], while other defects, which are triangular in nature but look different, have been found to have the presence of 3C-SiC at the top of the defect [76]. This again shows that, depending on the growth conditions and the shape and structure of the triangular defect, 3C-SiC inclusions can be present or absent.
Figure 2.9. Raman spectra comparing the 4H and 3C peaks in different regions of a triangular defect. [66]

Stacking faults have been associated with triangular defects. It is debatable whether all triangular defects have detectable stacking faults. In most cases, stacking faults are detected using photoluminescence measurements by measuring the phonon replica lines in the PL spectra. These four lines show up at the same distance from each other, regardless of the position of the zero-phonon line, and are known as the Transverse Acoustic (TA), Longitudinal Acoustic (LA), Transverse Optical (TO) and Longitudinal Optical (LO) lines, with energy differences of 46, 77, 95 and 104 meV, respectively, from the no-phonon line for 4H-SiC. The spacing between the lines depends on the bandgap of the material. Figure 2.10 shows this energy for other SiC polytypes. These lines have been used to reveal a variety of stacking faults in SiC
Figure 2.11 shows the PL spectra of an in-grown stacking fault at 9K, having peaks at 463.1nm, 468.3nm, 471.8nm and 473.1nm, representing phonon replicas with a bandgap of 2.71eV [83][84].

<table>
<thead>
<tr>
<th>Phonon branch</th>
<th>3C</th>
<th>4H</th>
<th>6H</th>
<th>21R</th>
<th>15R</th>
<th>33R</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA$_1$</td>
<td>46.3</td>
<td>46.7</td>
<td>46.3</td>
<td>46.5</td>
<td>46.3</td>
<td>46.3</td>
</tr>
<tr>
<td>TA$_2$</td>
<td>-</td>
<td>51.4</td>
<td>53.5</td>
<td>53.0</td>
<td>51.9</td>
<td>52.3</td>
</tr>
<tr>
<td>LA</td>
<td>79.5</td>
<td>76.9</td>
<td>77.0</td>
<td>77.5</td>
<td>78.2</td>
<td>77.5</td>
</tr>
<tr>
<td>TO$_1$</td>
<td>94.4</td>
<td>95.0</td>
<td>94.7</td>
<td>94.5</td>
<td>94.6</td>
<td>94.7</td>
</tr>
<tr>
<td>TO$_2$</td>
<td>-</td>
<td>-</td>
<td>95.6</td>
<td>-</td>
<td>95.7</td>
<td>95.7</td>
</tr>
<tr>
<td>LO</td>
<td>102.8</td>
<td>104.0</td>
<td>104.2</td>
<td>104</td>
<td>103.7</td>
<td>103.7</td>
</tr>
</tbody>
</table>

Figure 2.10. The energy gap between the phonon replica lines in various SiC polytypes

Figure 2.11. PL spectra of a stacking fault at 9K (Ref: [83])

In summary, there are still debates about the origin of the triangular defects and their relation to process conditions in regular epitaxial growth processes. Simultaneously, almost nothing is known about triangular defects in the low-temperature epitaxial growth process. TDs become the main type of defect at higher growth rates (growth with HCl) [21]. In this dissertation, a thorough investigation of triangular defects in epitaxial layers
grown at low temperatures has been conducted, and the structure and origin of these defects have been proposed.

2.6. Aluminum Precipitates in SiC

Highly doped epitaxial layers are required for making good ohmic contacts and for other device applications. Aluminum is the main dopant in $p^+$ SiC epitaxial layers. The problem with trying to incorporate dopants at very high concentrations is that as the number of doped atoms increase in the crystal lattice, so does the stress. It has been shown that materials with high doping form defects as a way of relieving the built-up stress. This can be observed as the formation of stacking faults in the epitaxial layers [85][86]. Beyond a certain level of doping, the solubility limit may be exceeded, and precipitates are formed. Once precipitates are formed, this severely degrades the performance and thermal stability of devices.

During precipitate formation, impurity atoms agglomerate to form clusters of a new phase. The formation of precipitates is due to favorable atomic bonding of the cluster atoms, and it is denoted as the supersaturation of the original solution. The growth rate of a precipitate may be determined by different reactions. If the growth rate of a precipitate is governed by the diffusive transport of atoms, the reaction is said to be "diffusion controlled." If the growth rate of a precipitate is determined by the rearrangement process of atoms across the interface, the reaction is said to be "interface controlled."

Precipitate formation can be classified into three major stages: nucleation, growth, and coarsening. Nucleation is considered to be a stochastic process, that is, nuclei are born as a consequence of random thermal and compositional fluctuations. The controlled
attachment of atoms to the precipitate is defined as growth. Coarsening is defined as the
dissolution of small precipitates in favor of larger ones [108].

Systematic investigation of precipitates in SiC has been relatively rare. The solubility
limit of aluminum in 6H-SiC was reported to be $7 \times 10^{20}$ cm$^{-3}$ for Si face and $9 \times 10^{20}$ cm$^{-3}$
for C face [87]. For epitaxially grown 4H-SiC, the reported solubility limit of Al is
$2 \times 10^{20}$ cm$^{-3}$ [88]. Figure 2.12 shows a TEM image of aluminum precipitates when the
total Al concentration exceeds the solubility limit. It was reported that p$^+$ doped layers do
not undergo any morphological degradation until a doping of $1 \times 10^{18}$ cm$^{-3}$ [89].

![Figure 2.12. TEM image of aluminum precipitates in highly doped 4H-SiC (Ref: [88])](image)

### 2.7. Precipitate and Dislocation generation Models

Doping causes strain in the material, which in turn causes more defects to form to
relieve this strain. The strain created in the material can be calculated by accounting for
the properties of the crystal lattice and the atomic sizes of the dopant atoms. The lattice
strain is calculated by the following formula [90]:

$$f_s = 4\pi N (r_s^3 - r_h^3) \left( \frac{3K + 4G}{27K} \right)$$
Where $f_s$ is the lattice strain, $N$ is the concentration of the dopant atoms, $r_s$ and $r_h$ are the radius of the dopant and host atoms, and $K$ and $G$ are the bulk and shear moduli calculated from the Young’s modulus.

Figure 2.13. Defects seen in epitaxial layers with doping of (a) $4 \times 10^{18} \text{ cm}^{-3}$ (b) $1.3 \times 10^{19} \text{ cm}^{-3}$
In SiC, the defects generated due to doping have not been quantitatively modeled. It has been shown qualitatively that defects increase with the increase in doping. Figure 2.13 shows the increase in defects that are caused by an increase in doping [90].

Dislocation generation models dependent on strain have been developed for semiconductors [91][92][93]. Of these, the Haasen Sumino (HAS) model has been applied to semiconductors like Si, Ge, GaAs, and InP to determine the dislocation generation in those materials due to stresses during growth [95][96][97][98]. The Hassen Sumino model is a phenomenological model that predicts the generation and multiplications of dislocations in a material due to stress. Phenomenological models describe empirical observations of phenomena that are consistent with fundamental theory. However the model itself is not derived directly from theory. The Hassen Sumino model was originally based on mechanical testing data collected on float zone silicon growth. The HAS model describes the plastic deformation of the crystals under stress and the generation of dislocations and their multiplication which result from it.

The equation used to model the dislocations created is a differential equation which is described as follows:

\[
\frac{dN}{dt} = K k_0 N e^{\frac{-Q}{k T}} (\sqrt{J - D\sqrt{N - \tau_d}})^p (\sqrt{J - D\sqrt{N}})^{\lambda}
\]

Where \( N \) is the density of dislocations (cm\(^{-2}\)); \( J \) is the material stress; \( Q \) is Peierls potential (eV); \( k \) is Boltzmann’s constant 8.617x10\(^{-5}\) (eV/K); \( T \) is the absolute temperature (K); \( K \) is a material constant (cm/dyn); \( D \) is the strain hardening factor (dyn/cm); \( k_0 \) is a material constant (cm\(^{2p+1}\)/dyn\(^p\) S); \( \tau_d \) is the drag-stress (dyn/cm\(^2\)); and \( p \) and \( \lambda \) are dimensionless material constants [99][100][101][102]. This equation can be
numerically solved to give the number of dislocations formed for the particular value of stress. Given experimental data, this model can be used to derive material parameters like the strain hardening factor, the multiplication factor, and the material constants to give qualitative agreement between the experiment and the theory [103].

Precipitate models quantitatively describing defect formation have not been reported for SiC. Precipitate formation of oxygen in silicon has been studied in detail [109], offering various models for precipitate formation. The basic models involve simulating homogenous nucleation without taking strain into consideration. The Nucleation rate \( J_0 \) in this case is given by:

\[
J_0 = 4\pi c \frac{D}{d} Zn(r_c)
\]

\[
r_c = \frac{2\gamma \nu_p}{k_B T \ln(C_{ox}/C_{ox}^*)}
\]

Where \( r_c \) is the critical radius beyond which the precipitates are stable, \( c \) is the number of nucleation sites per unit volume, \( D \) is the diffusion coefficient, \( d \) is the atomic jump distance, \( Z \) is the Zeldovich factor, \( \gamma \) is the interface energy per unit area, \( \nu_p \) is the particle volume per precipitate atom, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( C_{ox} \) is the concentration of oxygen in the lattice, and \( C_{ox}^* \) is the solubility limit of oxygen [109].

However, more complex models require the incorporation of the strain factor into the equations as the volume occupied by the precipitate species becomes appreciable. Also, the nucleation of precipitates can occur at defect centers or intrinsic defects. These factors require heterogeneous nucleation models [109].

In this work, a quantitative evaluation of dislocation and precipitate formation during low-temperature epitaxial growth across a varied doping range has been undertaken, with
an emphasis on determining the onset of precipitation and epitaxial quality degradation. A mathematical model based on the Haasen Sumino model has been adapted to SiC to describe dislocation generation data.

2.8. Brief overview of PL characterization of the epitaxial quality of SiC

Photoluminescence can be a powerful method to determine the defect levels in a material. Different PL lines can give information about various levels in the bandgap. Ultraviolet (UV) PL reveals shallow levels, while Visible-Infrared (IR) PL shows deep levels. Some defect levels reflect the quality of epitaxial layers. Figure 2.14a shows IR spectra of some deep defects in 4H-SiC, including Vanadium levels and the UD-1/UD-3 levels [107]. Figure 2.14b shows UV spectra of shallow peaks of the lattice damage related $D_I$ defect that is used to judge the epitaxial layer quality [106]. In this work, PL has been used as a method of confirming the absence of the common radiative intrinsic defect levels in a variety of epitaxial samples grown at low temperature.

Figure 2.14. PL spectra of 4H-SiC a) IR spectra [107] b) UV Spectra [106]
CHAPTER 3
EXPERIMENTAL APPROACH

3.1. Epitaxial Samples Investigated

Many types of low-temperature epitaxial samples were investigated in this work. They fall broadly into three categories: (1) blanket epitaxial layers, (2) SEG epitaxial layers and (3) heavily doped epitaxial layers. Blanket epilayer samples include those samples grown with and without HCl and at different growth conditions. Low temperature SEG samples include epitaxial samples grown using an optimized growth process that minimized formation of visible defects on the mesas. Samples with varying types of triangular defects with different concentrations were investigated. Epitaxial layers grown at low temperature doped with varying amounts of aluminum acceptors ranging from $2.4 \times 10^{19} \text{ cm}^{-3}$ to $4.3 \times 10^{20} \text{ cm}^{-3}$ were also investigated.

3.2. Defect delineation in SiC by molten potassium hydroxide (KOH) etching

Etching by molten KOH is used to delineate defects in a material. This is because of the difference between etching rates of defects and the SiC epitaxial layer or substrate. This is very useful in evaluating the quality of epitaxial layers quantitatively.

A molten KOH etching system was designed and built consisting of a MTI Corp. CF-1200X crucible furnace. Solid KOH pellets from Cole Palmer were used as a source for
KOH, which was contained in an MTIAlbany nickel crucible. A ceramic base was used as a buffer between the base of the crucible furnace and the crucible. A sample carrier, designed from a solid nickel mesh, was used to dip samples into the molten KOH solution. The temperature of the melt was monitored by the internal crucible furnace sensor. Figure 3.1 shows the schematic of the KOH etching setup.

Figure 3.1. Schematic of the KOH setup

The furnace was covered with a lid to maintain a stable temperature during the etch process. Temperature control is critical for KOH etching as variation in temperature leads to variable etch rates and different etch pit profiles. Before any etching the system is heated up to the target temperature and allowed to stabilize for a period of two hours.

The KOH etching processes had to be customized for a variety of samples such as low doped epitaxial layers, high doped epitaxial layers, substrates etc. This is because a difference in crystalline quality and doping causes a difference in the etch rates, and thus requires tailored processes for different kinds of samples. The temperature and the etch time were varied to get desirable size of the defect pits. The overall blanket etch rate, i.e.
the removal of non-defective epitaxial material, was also monitored using the changes in the epitaxial layer thickness measured by Fourier Transform Infrared Spectroscopy (FTIR) to ensure that no over-etching takes place.

3.3. Removal of Epitaxial layers

To study the defects in SiC at various depths in the material and to correlate them to defects in the substrate, there is a need to remove the epitaxial layer in a controlled manner homogenously. After a KOH etch, the epitaxial layer surface is full of etch pits. To delineate defects deeper in the epitaxial layers, the surface must be ‘reset’ or smoothened, so that fresh defects can appear in the underlying layers without the interference from previously etched defects in the removed upper portion of the epitaxial layer.

To achieve these objectives a mechanical polishing process was developed. A Buehler Polimet I Mechanical polisher having variable RPM control was used. Polishing of SiC requires a diamond based slurry/abrasive because of the hardness of SiC. Buehler Metadi supreme polycrystalline diamond suspensions were used on Buehler Texmet 1500 8” polishing cloth. The diamond slurry used was of 0.1µm, 0.25µm, and 1µm grit size depending on the process. A special sample holder was designed and fabricated to ensure the best polishing homogeneity. The optimum weight and the RPM were chosen as a tradeoff between polishing rate and surface morphology and homogeneity. Material removal rate was closely monitored using reflective FTIR measurements of the remaining epitaxial layer thicknesses.
It was found that the mechanical polishing leaves a thin layer of mechanical damage on the surface of the samples. This damaged layer was not immediately visible upon inspection, but was revealed upon further etching by KOH. To minimize this, a final polish with 0.1µm grit size was employed to remove this layer. Though this helped a little, some surface damage still remained. An Inductively Coupled Plasma (ICP) etch was also performed on the samples, which was very effective in completely removing the damaged layer. This process was successfully employed for investigating defects in SEG samples, enabling damage/scratch free inspection of underlying depths after polishing. Figure 3.2 shows the steps involved in the removal of the epitaxial layers and revealing defects at different depths of the epitaxial layer and the substrate.

Figure 3.2. Steps involved in characterizing defects at various levels of the epitaxial layer and the substrate: (a) investigation of defects in a blanket epitaxial layer, and (b) investigation of defects in SEG mesas.

In order to take advantage of the higher KOH etch rates of some of the higher doped epitaxial layers, another process was developed to examine the defects in the underlying substrate. It was established KOH applied to heavily doped epitaxial layers can be used
for complete removal of the epitaxial layer by etching, in order to reveal the substrate underneath. The etch pits related to the epitaxial layer defects fade away as the substrate is reached, and only the substrate defects are delineated sharply. This provided an excellent opportunity to study both the epitaxial layer defects and substrate defects at the same time, due to the fact that the epitaxial layer defects appear faded and the substrate defects appear sharp.

Prolonged etching for a sufficient time completely removes the epitaxial layer and leaves only substrate defects to be observed under the microscope. This method can be used as a replacement for mechanical polishing and ICP etching for investigating a few types of suitable samples.

3.4. Photoluminescence

Photoluminescence (PL) measurements are applied to detect various energy levels in the bandgap of SiC. PL spectra enable a qualitative comparison of epitaxial layer quality and can be used to monitor the formation of defect levels.

PL spectra were analyzed using a SPEX 500M grating spectrometer coupled with a liquid nitrogen cooled Edinburg Instruments E1-L Ge detector for the infrared (IR) part of the spectra. To measure IR photoluminescence, the excitation beam is modulated with a mechanical chopper, and the PL response is converted by a germanium detector to a signal monitored with a Stanford Research Systems SR830DSP lock-in amplifier. A Hamamatsu R928 multi-alkali photo-multiplier tube (PMT) was used for the visible and the ultraviolet (UV) photoluminescence. Visible and UV photoluminescence are detected using photon counting. A Horiba Jobin Yvon Symphony 2048×512 CCD detector is also
used to detect UV and Visible spectra. This setup allows for much faster acquisitions and better resolution. Low temperature PL spectra are measured by mounting the samples on the cold finger of a variable temperature liquid He closed cycle cryostat operating in a temperature range between 6.5 and 300 K. Figure 3.3 shows the schematic of the photoluminescence setup.

![Figure 3.3. Schematic of the photoluminescence setup](image)

3.5. Nomarski Differential Interference Contrast (NDIC)

Nomarski Differential Interference Contrast also known as Nomarski Microscopy relies on the interference contrast illumination technique. The technique involves differential splitting of plane polarized light that produces adjacent beams that are separated by few microns [110][111]. The separation depends upon the resolving power of the microscope. Differential beam splitting is achieved via a Nomarski prism. The incident light is polarized, and upon hitting the Nomarski prism, which is perpendicular to its surface, the beam splits into two plane polarized waves that are 90° to each other.
and 45° to the incident wave. The wave travels at different speeds within the prism because the refractive index of the crystal determines the propagation velocity of the wave. Upon exiting the prism, the two polarized waves hit the sample after being focused by the condenser. The emergent beams travel in parallel paths and are slightly offset with respect to each other. The two polarized waves are then recombined together into a single beam using a second Nomarski prism. Upon exiting the second prism, the beam passes through the analyzer that is perpendicular to the polarizer. At this point, an intermediate image is produced that can be viewed through the eye piece. An interference contrast appears in the adjacent beams caused by the different paths taken by the beams due to the minor variations in the refractive index or thickness of the sample. The background color is characteristic of the equipment, and it can be changed by variable positions of the prisms. The destructive and constructive interference of white light allows appropriate phase adjustment by effectively eliminating certain wavelengths that results in optimum contrast [112]. Figure 3.4 shows the basic setup of a Nomarski microscope. In this dissertation, these types of microscopic images have been used to identify defects in the as-grown epitaxial layer and also defects delineated after molten KOH etching.
3.6. Raman Spectroscopy

Raman Spectroscopy is based on the Raman Effect, which is a light scattering spectroscopic technique. It is due to inelastic scattering of monochromatic light, usually a laser beam in the near infrared (NIR), visible (Vis), or ultraviolet (UV) range. It was first discovered in 1928 by an Indian physicist, C.V. Raman. Upon interaction with the sample the frequency of photons in the laser source changes, i.e. the incident photon excites the molecule into a virtual state. The frequency of photons that are absorbed and reemitted by the sample is shifted up or down with respect to the original monochromatic light source frequency [113][114]. This shift gives information about various transitions in molecules.
(like rotational, vibrational, and other low frequency transitions), which makes it a powerful tool to study solid, liquid, and gaseous samples.

Typically a basic Raman system consists of four major components, monochromatic laser light source, light collection optics, wavelength sensor, and detector. The laser light source excites molecules and transforms them into dipoles. These oscillating dipoles emit light of mainly three different frequencies: Rayleigh scattering, Stokes scattering, and Anti-Stokes scattering, as shown in Figure 3.5. Spontaneous Raman scattering is weak, therefore special measures are needed in separating the weak inelastic Raman scattered light from the predominant elastic Rayleigh scattered light. Stray light from the Rayleigh scattering may cause interference and mask the useful Raman signal. This could be resolved by using holographic gratings and multiple dispersion stages that eliminate interference near the spectral range close to the laser line where the stray light has the
maximum effect. Raman spectroscopy has proven to be a useful tool for studying the crystal orientation. The polarization of laser light with respect to the crystal and the polarization of Raman scattered light can be used to determine the crystal orientation [115].

In this work, Raman spectroscopy is used to detect the presence of 3C-SiC inclusions in 4H-SiC epitaxial layers. A Micro Raman spectrometer was used to locally probe different triangular defects to determine their composition. A Horiba LabRam HR with a laser excitation wavelength of 633 nm and a spot size of 2 µm was used to obtain the Raman spectra.

3.7. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

3.7.1. Scanning Electron Microscope

Scanning Electron Microscope (SEM) is a powerful tool that creates magnified images by using electrons in a raster scan pattern instead of the light waves in a conventional optical microscope. The popularity of SEM is due to its capability of providing very detailed images of a wide range of materials at much higher magnifications and depth of focus. Since the SEM uses electromagnets rather than lenses, it gives more control on the degree of magnification, in addition to large depth of field. All these features coupled together make SEM one of the most useful instruments in research [116].
Figure 3.6. Cross section of a SEM unit

Figure 3.6 shows a typical cross-section of a SEM unit. The SEM uses an electron gun that produces a stream of monochromatic electrons. The electron beam follows a vertical path and travels through condenser lenses, an electromagnetic field, and scanning coils. The set of coils scan the beam in a grid or raster fashion. The final objective lens focuses the beam down towards the sample. When the primary electron beam interacts with the sample for a few microseconds, various interactions such as elastic scattering, inelastic scattering, and electromagnetic radiation occur that are detected by different specialized detectors. Once the beam hits the sample, the types of signals that are produced would be electrons (secondary electrons, back scattered electrons, transmitted
electrons), and X-rays. Depending on the application, the type of detector is selected. For example, the secondary electron (SE) detector will be useful for making morphological observations on the sample surface (high resolution surface information, high edge contrast and so on.) The backscattered electron (BSE) detector will be useful in conducting observations with edge contrast suppressed and observing specimen composition information [117].

3.7.2. Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS) is an analytical technique that helps in identifying the elemental composition of the sample [118]. EDS detects x-rays that are emitted from the sample when the primary beam interacts with the atoms in the sample causing shell transitions. The energy of the emitted x-ray is characteristic of the parent element. Figure 3.7 shows this process and the lines that are emitted from the orbital transitions. The efficiency with which characteristic x-rays are excited from the sample and the spatial resolution of the x-ray signal depend on the accelerating voltage used in the electron column. Higher voltages causes more efficient excitation (due to higher energy electrons), but result in lower resolution. The EDS x-ray detector counts the number of emitted x-ray photons for an energy range. Percentage elemental composition of the sample can be determined from this data. The energy spectrum versus the relative counts provides both qualitative and quantitative elemental analysis. However, creation of spectrum (energy level associated with any detected x-ray photon) has two types of errors associated with it, random and systematic error. Therefore, careful statistical analysis is required in obtaining good elemental analyses.
Figure 3.7. Principle of EDS spectroscopy

In this work, a JEOL Field Emission SEM with accelerating voltage up to 30 kV and magnification of 500,000X was used to analyze the defects revealed by molten KOH etching. The concentration of aluminum in defect etch pits was estimated with the EDS Kα spectra.

3.8. Focused Ion Beam (FIB) and Transmission Electron Microscope (TEM) 
Focused Ion beam

Focused Ion Beam (FIB) is a technique that uses a finely focused beam of gallium (Ga⁺) ions to raster scan the surface of a sample. It is very similar to scanning electron microscope that uses focused beam of electrons. The generated secondary ions are collected to form an image of the surface of the sample. The FIB systems use a focused ion beam that can be operated at low beam currents for imaging or high beam currents for removing material from localized sites, thus enabling cross-sectional images of the structure. At low beam currents, an image resolution of 5 nm can be achieved since only
very little material is sputtered. However, at high beam currents more material is sputtered from the surface, thus allowing precise milling down to the sub micron level. FIB is an ideal tool in semiconductor industry for examining sub surface particles, defect analysis, circuit modifications, and difficult to access features. FIB is commonly used to prepare ultra thin samples that are a few nanometers in thickness for transmission electron microscopy [119][120].

3.8.1. Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) is a technique that uses an electron beam instead of light to be transmitted through a sample to create an image. TEM uses an electromagnetic lens that can focus the electrons fired from the electron gun into a very thin electron beam of desired wavelength or size. When the electron beam travels through the sample, three different interactions can be observed, unscattered electrons (transmitted electrons), elastically scattered electrons, and inelastically scattered electrons. The transmitted electrons are converted to light and a magnified image is formed. The resultant image is brighter if more electrons pass through (less dense) the sample, and vice versa a darker image is formed if fewer electrons pass through the sample.

Through the use of different types of electrons and apertures, different images can be obtained, bright field image versus a dark field image. The compositional and crystallographic information of the sample down to its atomic level can be obtained using TEM. The extremely high resolution of TEM down to near atomic levels of approximately 0.2 nm makes it a valuable tool in semiconductor materials research.
However, TEM is an expensive technique, and it is difficult to achieve extremely thin samples during sample preparation. Also, utmost expertise is needed to interpret the results accurately from a well calibrated tool [121].

In this work Cross-sectional TEM samples were prepared using a FEI Quanta 3D Dual Beam Focused Ion Beam (FIB). These samples were characterized with a FEI Tecnai F-20 200KV TEM.
CHAPTER 4

EXPERIMENTAL RESULTS

4.1. Characterization of defects in Low Temperature Blanket Epitaxial Growth

As was described above, previously available information about the quality of the epitaxial layers formed by the low-temperature epitaxial growth process was limited to Nomarski micrographs and scarce photoluminescence data. Nothing was known about the lattice defects and the defect concentrations in the epitaxial layers. For successful utilization of the low-temperature growth technique in commercial power-electronic devices, it is critical to investigate and unearth any device killing or device performance reducing defects that are created, incorporated, or propagated during the growth process.

Figure 4.1. Various defect propagation scenarios from the substrate to the epitaxial layer a) micropipe - micropipe b) micropipe to several screw dislocations c) Threading – threading d) threading – carrot defect e) BPDs – ThDs f) BPDs - BPDs [104]

47
Various samples with epitaxial layers grown using different growth conditions were treated using the KOH technique to delineate the lattice defects. Statistics of the defects revealed were then collected and analyzed. The following issues were investigated.

First, defect propagation from substrate to epitaxial layers can occur following a variety of scenarios as shown in Figure 4.1 [104]. In general, a defect can propagate through while maintaining its type, or it can get converted to another type of defect. It is desirable in the epitaxial growth of SiC to have device killing defects like micropipes and basal plane dislocations (BPDs) converted to threading dislocations (ThDs). We will look at these processes as they occur in low temperature growth.

The second point of emphasis of the KOH study was generation of new defects during the low-temperature epitaxial growth, especially when attempts were made to increase the growth rate of the low-temperature technique. As was described in the introduction, homogeneous nucleation of silicon gas-phase clusters is particularly pronounced at low growth temperatures [21][22]. This mechanism severely depletes the silicon growth species and serves as a bottleneck for epitaxial growth rate. To alleviate this problem, addition of HCl was used in the previous work [21][22]. HCl caused etching of the gas-phase clusters, improvement of the surface morphology, and most importantly almost doubling of the growth rate. However, this also gave rise to new problems like the generation of triangular defects, so it was very important to compare differences in the epitaxial quality with and without HCl and investigate the mechanisms of the new defect generation.
4.1.1. Comparison of blanket epitaxial growth with and without HCl

First, two samples with epitaxial layers grown with and without HCl were analyzed. In the sample with HCl, higher growth rate was achieved (~5 µm/hr with HCl vs ~2 µm/hr without HCl).

High concentration (~1x10^5 cm^2) of threading dislocations (ThD) was revealed by KOH in the sample grown without HCl (Figure 4.2a). While Figure 4.2a shows a location on the wafer having a high concentration of the basal plane dislocations (BPD), the average BPD concentration of 3x10^4 cm^2 was almost an order of magnitude lower than that of ThDs.

Growth at higher growth rate with HCl addition (at higher growth rate of ~5 µm/hr compared to no-HCl growth) caused an additional order of magnitude reduction of the BPD concentration (4.4x10^3 cm^2) (Figure 4.2b), thus indicating that higher growth rate, as well as a possible change in the effective Si/C ratio due to HCl-induced dissociation of the Si gas-phase clusters, caused enhancement of BPD conversion during the growth. Table 4.1 summarizes the statistics of growth with and without HCl, counted from 30 sites in both the samples.
Figure 4.2. KOH etch-pits in low-temperature epilayer grown at 1300°C: (a) without 
HCl and (b) higher growth rate with HCl. Basal plane dislocation BPDs are 
encircled. Only threading dislocation (ThD) are observed in (b) indicating 
higher efficiency of the BPD conversion from the substrate.

Table 4.1
Defect statistics with and without HCL

<table>
<thead>
<tr>
<th>Growth Condition</th>
<th>ThDs (Avg/cm²)</th>
<th>BPDs (Avg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without HCL</td>
<td>1.389 x10⁵</td>
<td>3.570 x10⁴</td>
</tr>
<tr>
<td>With HCL</td>
<td>1.391 x10⁵</td>
<td>4.424 x10³</td>
</tr>
</tbody>
</table>

4.1.2. Defects in Optimized Low temperature blanket epitaxial growth

Next, the relative amount of defects in the substrate and the epitaxial layers were 
analyzed. This is important because it can tell us whether we create new defects during 
the epitaxial growth or decrease the defect concentration by suppressing defect 
propagation from the substrate into the epitaxial layer. This can be used to give a good 
measure of the epitaxial quality because the total concentration of epitaxial defects minus 
the total concentration of substrate defects can be used as a reliable and convenient 
measure of epitaxial layer quality.
To evaluate defects in our low-temperature epitaxial process, an epitaxial layer of good quality grown at optimized growth conditions was chosen. The sample had an epitaxial layer thickness of 0.8µm.

Figure 4.3a shows defects revealed after the KOH etch. It shows mostly ThDs in the epitaxial layer. The sample was then mechanically polished to remove the epitaxial layer and reveal the substrate underneath. The sample was then treated by KOH again to delineate the defects in the substrate.

The substrate shows a much larger concentration of BPDs (marked by the circles in Figure 4.3b). Figure 4.3b also includes the scratches caused by the mechanical polishing, which should be ignored.

Table 4.2 presents the statistics of defects in the epitaxial layer and the substrate. It shows that the total number of defects is approximately the same. This implies that at our optimized growth conditions, we do not create extra defects in the epitaxial layer. This is very important to know that at optimized conditions there is no difference in the defects in the substrate and the epitaxial layer, and that any increase in this difference is the result of non-optimal growth conditions resulting in degradation of epitaxial quality.

The statistics also show an order of magnitude reduction of BPDs in the epitaxial layer, which possibly happens due to BPD conversion to ThD. This mechanism is confirmed below.
Figure 4.3. KOH etch-pits in (a) epitaxial layer and (b) in the underlying substrate. Only threading dislocation (ThD) are observed in (a). Several Basal plane dislocations BPDs observed in (b) are encircled.

Table 4.2

<table>
<thead>
<tr>
<th></th>
<th>ThDs (Avg/cm²)</th>
<th>BPDs (Avg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epilayer</td>
<td>7.011 x10⁴</td>
<td>9.677 x10²</td>
</tr>
<tr>
<td>Substrate</td>
<td>7.072 x10⁴</td>
<td>7.072 x10³</td>
</tr>
</tbody>
</table>

Next, we tried to trace the same defects from the substrate to the epitaxial layer, to see how they change after the epitaxial growth. To achieve this, a few easily identifiable locations on the epitaxial layer were chosen. These locations had deep markings on the sample surface that would be identifiable even after the mechanical polishing that removes the epitaxial layer and reveals the substrate. Several locations with micropipes were chosen. Figure 4.4a shows such a location on the epitaxial layer after a KOH etch. It shows a micropipe surrounded by a large number of ThDs.
Figure 4.4. Defects in an epitaxial layer (a), (c) and in the underlying substrate (b). The crosses denote the vertex of the defects in the substrate. The arrows denote the direction the defects would travel after epitaxial growth.
The sample was then mechanically polished to remove the epitaxial layer and reveal the substrate. After the KOH etch to reveal the defects in the substrate, the same location was examined (Figure 4.4b). The vertexes of all the defects are marked by crosses, while arrows denote the direction in which the dislocations subsequently propagated during the epitaxial growth. This set of crosses and vertexes are then superimposed on the epilayer image (Figure 4.4a), which results in Figure 4.4c.

It can be seen from Figure 4.4c that each of the defects in the substrate (BPD or ThD) corresponds to a ThD in the epitaxial layer. The position of the defects in the epitaxial layer is also correctly predicted by the arrows. This shift is determined by the angle of the corresponding dislocation propagation with respect to the crystal lattice. A 1:1 correspondence of epilayer to substrate defects is seen. This further supports the statistics that no defects are created or destroyed but only converted to a different type during epitaxial growth at these growth conditions.

Table 4.3 shows the conversion statistics from a few such sites where the defects were traced from the epitaxial layer to the substrate. This shows that the overwhelming process is the conversion of BPDs in the substrate into ThDs in the epitaxial layer. The other processes of defect creation and defect annihilation are negligible. This supports the conclusion that the number of defects in the epilayer and substrate are approximately equal.
Table 4.3
Epilayer to Substrate defect conversion

<table>
<thead>
<tr>
<th>Site</th>
<th>BPD_{sub} \rightarrow \text{ThD}_{epi}</th>
<th>BPD_{sub} \rightarrow \text{No Defect in Epilayer}</th>
<th>No Defect in Sub \rightarrow \text{ThD}_{epi}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>31</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>26</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Avg/cm^2</td>
<td>4.30 \times 10^5</td>
<td>4.30 \times 10^3</td>
<td>8.60 \times 10^3</td>
</tr>
</tbody>
</table>

4.1.3. Arrays of Dislocations

In some of the blanket epitaxial layers, a type of defect resembling an array of defects is seen after molten KOH etching. These arrays are very densely packed and are very bad for any device. It is very important to determine whether these arrays originate due to the epitaxial growth or are caused by substrate defects.

After close examination and further KOH etching, it is seen that all the individual dislocations in these arrays on the epitaxial layer are threading dislocations. After polishing away the epilayer and applying molten KOH etching to the substrate, it is seen that the entire array is present in the substrate. A closer examination also reveals that all these defects in the substrate are BPDs. Figure 4.5 shows an array of defects both in the epitaxial layer and at the same location in the underlying substrate after polishing.
In summary, a quantitative investigation of dislocations in blanket epitaxial layers grown by the low-temperature epitaxial growth technique was conducted for the first time. We have established that under optimal conditions the blanket epitaxial growth at lower temperatures does not suffer from creation of new defects in the epitaxial layer. All dislocations observed in the epilayers are caused by dislocation propagation from the substrate.

In addition, we have seen an efficient conversion of BPDs to ThDs, which is highly desirable in an epitaxial growth process of SiC. Addition of HCl to the growth process enhances this conversion efficiency, though introducing a few problems of its own that will be investigated in Section 4.4.

4.2. Defects in Selective Epitaxial Growth

KOH etching was applied to samples having an epitaxial pattern produced by Low Temperature Selective Epitaxial Growth (LTSEG).
The average concentration of dislocations in LTSEG epitaxial layers away from the mesa edges was a little higher but comparable to the blanket growth (Figure 4.7). The ThD arrays in Figure 4.7 are substrate-related and are not reflective of the epitaxial process.

High concentrations of BPDs were found at some mesa edges. It was established that BPDs predominantly generate at the edges oriented roughly perpendicular to the off-axis cut ([11-20] direction) and located at the “upstream” side of the mesa with respect to the step-flow direction. Little or no edge BPDs appear at the mesa edges oriented downstream, along, or at a small angle to the step-flow direction.

Upon examining a higher growth rate SEG sample before KOH that had much more pronounced visible defects at the edges, these defects were found to be due to a high concentration of the triangular defects (similar to the triangular defects described in Section 4.4). These triangular defects originate at the epilayer-substrate interface at or close to the sidewalls of the SiO$_2$ mask and grow in the basal plane in the off-cut direction as result of interrupted step flow growth.

For lower growth rate conditions as in the sample being examined, the conditions are less favorable for triangular defect formation. In this case, the defects propagate only when the step flow direction is perpendicular and away from the mesa growth edge, where they are originally created (Figure 4.6a).

Obtaining cross-sectional SEM images of these samples enabled us to confirm that the defects originated from the sidewall at the epilayer-substrate interface and propagated along the direction of the basal plane of the SiC lattice towards the surface.
[25]. Figure 4.6b shows the cross-sectional SEM of an LTSEG mesa showing the defect propagation from the SiO₂ sidewalls into the epitaxial layer causing the defective area.

![Cross-sectional SEM of an LTSEG mesa showing the defective area](image)

**Figure 4.6.** a) Defect propagation along the basal plane into an SEG mesa b) Cross-sectional SEM of an LTSEG mesa showing the defective area near the sidewalls

![KOH etch-pits in LTSEG mesas having different sidewall orientations](image)

**Figure 4.7.** KOH etch-pits in LTSEG mesas having different sidewall orientations. Growth-induced dislocations (BPD) in mesas are observed only at sidewalls preferentially oriented upstream to the step-flow direction.
Tracing the defects in the LTSEG epitaxial layer is significantly simplified by the presence of the mesa pattern. Dense arrays of dislocations observed in Figure 4.7 were clearly traced back to the corresponding dislocation arrays in the substrate as also seen in Figure 4.8. High concentrations of BPDs were found at some mesa edges as explained earlier.

Statistics of all the other defects in the epilayer were taken. The SEG sample was then mechanically polished just enough to remove the KOH etch pits. It was then etched by inductively coupled plasma down to the substrate. After the epitaxial layer was entirely removed in the mesa regions, with the mesa-patterned structure still preserved, it was further etched by KOH to reveal the substrate defects.

Table 4.4 summarizes the defect statistics of the SEG mesas versus the underlying substrate. The number of epilayer ThD defects is considerably higher than the substrate defects. This implies that new ThDs are created during LTSEG growth. The
concentration of BPDs is an order of magnitude lower than that in the substrate, implying good conversion efficiency.

Table 4.4
Defect Statistics of LTSEG Epilayer vs Substrate

<table>
<thead>
<tr>
<th></th>
<th>ThDs (Avg/cm²)</th>
<th>BPDs (Avg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epilayer</td>
<td>2.02 x10⁵</td>
<td>3.17 x10⁴</td>
</tr>
<tr>
<td>Substrate</td>
<td>7.392 x10⁴</td>
<td>1.585 x10⁴</td>
</tr>
</tbody>
</table>

Tracing the SEG defects to the substrate was done on multiple sites. The procedure was similar to what was done in blanket epitaxial growth tracing. Figure 4.9a shows the patterned epilayer after a KOH etch. Figure 4.9b shows the same region after a polish followed by an ICP etch and again followed by a KOH etch. The crosses denote the vertexes of the substrate defects. Figure 4.9c shows the crosses superimposed on the epilayer etch pits. The newly created defects are encircled. Again we see that all the substrate defects have a corresponding converted epilayer defect.
Figure 4.9. Tracing of defects from LTSEG epilayer to substrate. The crosses denote the vertex of the defects in the substrate. The circles denote newly created ThDs during epitaxial growth.

Conversion statistics are collected from all the sites where defects are traced from the epitaxial layer to the substrate. Table 4.5 summarizes the major conversion processes.
from the substrate to the epitaxial layer. It shows that the BPDs in the substrate do get converted efficiently to ThDs in the epitaxial layer. The major difference in this case from low temperature blanket epitaxial growth is that new ThDs introduced by the epitaxial growth process unrelated to substrate defects are an appreciable fraction of the total defects in the epilayer. This confirms our previous observation that there is an appreciable increase of the ThDs in the epitaxial layer compared to the substrate.

Table 4.5
Conversion statistics of LTSEG defects

<table>
<thead>
<tr>
<th>Site #</th>
<th>BPD_{sub} → ThD_{epi}</th>
<th>ThD_{epi} Created</th>
</tr>
</thead>
<tbody>
<tr>
<td>R25R</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>R25R</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>R26R</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>R26R</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>R59R</td>
<td>14</td>
<td>3</td>
</tr>
<tr>
<td>R55R</td>
<td>43</td>
<td>12</td>
</tr>
<tr>
<td>R12R</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Avg(/cm²)</td>
<td>5.53 x10⁴</td>
<td>1.61 x10⁴</td>
</tr>
</tbody>
</table>

To make sure that the substrate did not contain defects that were not readily seen or etched, a much more extensive molten KOH etch was done on the substrate for a prolonged amount of time. Only the defects that were seen earlier grew larger in size, and no additional defects were revealed.

In summary, defects in LTSEG layers have been investigated for the first time. Defects originating from the sidewall of the mesas have been identified, and a possible mechanism for their formation was suggested. It was observed that in the epitaxial layers
away from the sidewalls, not many extra ThDs were created during SEG growth. This is in slight contrast to low temperature blanket epitaxial growth where no new defects were created. However, it was established that BPDs are mostly absent in the LTSEG mesas (except for those at the mesa sidewalls), which owes to a very efficient conversion of BPDs from the substrate to ThDs in the epitaxial layer.

### 4.3. Defects in heavily doped P⁺ epitaxial layers

Epitaxial layers heavily doped with aluminum are very useful for device applications. For example, very low resistive contacts can be fabricated with high P⁺ doping of the epitaxial layers. This is accomplished by increasing the TMA (trimethylaluminum) flow during the growth.

However, it is critical to monitor the epitaxial layer quality as the amount of aluminum content is increased. This is because once the solubility limit is reached, the chance of forming precipitates increases rapidly. Also, extremely high doping can cause dislocations in the epitaxial layers due to stress and other side effects like change in the lattice constant. Therefore, it is essential to know the onset of epitaxial degradation and precipitate formation. While this information is available for the epitaxial growth conducted at regular high temperature, there is no knowledge about the precipitate formation during low-temperature epitaxial growth. In this section, the results of defect analysis of various P⁺ samples are presented.

Eight samples with varying TMA flows were chosen for this analysis. While the doping efficiency or the amount of shallow acceptor formation is beyond the scope of this work, SIMS and CV data were instrumental in monitoring the amount of Al incorporation
during the epitaxial growth. An epilayer was grown on a control sample during all the runs involving aluminum. SIMS measurements on this sample provided the information about the aluminum incorporation into the epitaxial layers for all the TMA flow rates used.

Figure 4.10 shows the amount of aluminum that was incorporated into the epitaxial layers for various TMA flow rates. Table 4.6 lists all the samples analyzed with the SIMS doping measured versus TMA flow rates. A wide and high range of Al doping incorporation up to \(4.3 \times 10^{20} \text{ cm}^{-3}\) is obtained.

![SIMS profile of Aluminum concentration as a function of TMA flow](image)

Figure 4.10. SIMS profile showing aluminum incorporation into the epilayer for different TMA flows
Table 4.6

Al dopant incorporation for different TMA flow rates

<table>
<thead>
<tr>
<th>TMA Flow (sccm)</th>
<th>Al SIMS (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.034</td>
<td>2.4726 x 10¹⁹</td>
</tr>
<tr>
<td>0.07</td>
<td>4.5919 x 10¹⁹</td>
</tr>
<tr>
<td>0.14</td>
<td>9.891 x 10¹⁹</td>
</tr>
<tr>
<td>0.2</td>
<td>1.5672 x 10²⁰</td>
</tr>
<tr>
<td>0.29</td>
<td>2.6486 x 10²⁰</td>
</tr>
<tr>
<td>0.35</td>
<td>3.5125 x 10²⁰</td>
</tr>
<tr>
<td>0.37</td>
<td>3.8258 x 10²⁰</td>
</tr>
<tr>
<td>0.4</td>
<td>4.3197 x 10²⁰</td>
</tr>
</tbody>
</table>

4.3.1. Defects in the P⁺ samples

All the samples were treated by molten KOH. The resulting etch pits from various defects in epitaxial layers were counted from 30 sites over the whole sample. Figure 4.11a shows the total number of epitaxial defects plotted against Al concentration determined by SIMS. It is seen that the number of defects increase as the doping concentration increases, though some samples appear to deviate from this trend.

In interpreting the results of Figure 4.11a, one needs to make sure that only new dislocations generated during the epitaxial growth (and not those propagating from the
substrate) are considered. In order to separate the newly-generated defects, the epitaxial layer needs to be removed to reveal the substrate underneath. In our prior experiments described in Section 4.1, this was accomplished with the mechanical polishing of the samples. But as discussed above, this leaves scratches on the surface, often masking the defect etch pits.

A different approach could be used with P\textsuperscript{+} samples. It was observed that the heavily doped epilayers get etched very fast during the KOH process itself, which is an advantage not available when dealing with lower-doped epitaxial layers. So, molten KOH etching can be used both for defect delineation and for removing the epitaxial layer and exposing the substrate.

A process was developed to remove the epitaxial layer by etching in the KOH melt and reveal the substrate defects underneath. After the epitaxial layer was removed by molten KOH etching, the etch pits of the dislocations generated by the epitaxial growth (i.e., not having their origin in the substrate) became larger and shallower and eventually faded away, thereby not interfering with the substrate defects which get prominently revealed (Figure 4.12). With this new process, all the P\textsuperscript{+} samples were etched until the substrate defects were revealed and counted.
Figure 4.11. Defect statistics of p⁺ doped epitaxial layers showing a) total epilayer defects and b) total epilayer defects – substrate defects in log scale
Figure 4.12. Fast etching of P⁺ samples by KOH revealing the substrate defects underneath the epitaxial layer: (a) just after some of the epilayer has been removed by etching, (b) additional 3 minutes of etching deeper in the substrate, and (c) additional 5 min etching further deeper in the substrate.

Analysis of the etch pits counted using this procedure (Figure 4.11b) provided the information about the concentration of defects generated during the epitaxial growth. Comparing to Figure 4.11a, a more monotonous trend without any anomalies was obtained.

The analysis of the trend in Figure 4.11b showed that increasingly more defects are generated during the epitaxial growth as the TMA flow (i.e., Al incorporation) is increased. This trend will be discussed later.

Figure 4.13 illustrates the degradation of the epitaxial layers in three different samples as the TMA flows increase. All the faded etch pits are due to dislocations formed during the epitaxial growth. Defects in the substrate pictures are also shown after the epitaxial layer was etched away (Figure 4.13 d, e, f). The concentration of the defects
generated during the epitaxial growth increase exponentially with increase in the TMA flow.

![Figure 4.13. Defects in the epitaxial layer and substrate of three samples grown with increasing TMA flows](image)

Another interesting observation in these samples is the formation of smaller etch pits after KOH etching that behave differently from the regular dislocation etch pits. The onset of appearance of those very small etch pits is seen in the higher doped samples with TMA flows of $\geq 0.35$ sccm. These small etch pits increase exponentially in number as the TMA flows are increased. At the highest TMA flows, the number of small pits dominate over the regular larger etch pits. We speculated that these small etch pits could be due to precipitates caused by excessive TMA flows, which is supported by the following observations.
While the defects responsible for the regular etch pits appear to propagate through the entire epilayer thickness (i.e., generate at epilayer/substrate interface and propagate along with epitaxial growth), the small etch pits behave as defects that are localized at certain (and apparently different) depths in the epitaxial layer.

The regular big sized etch pits persist all the way through the KOH treatment until the epilayer is entirely removed and the substrate is exposed. The smaller pits show three basic stages of behavior vs KOH etching time: (1) they appear only after a certain portion of the epilayer has been removed, (2) they grow bigger; (3) they fade away, while new ones appear at a different depth. When the pit appears and grows bigger with KOH etching, it means that sufficient epilayer thickness has already been removed to expose the precipitate. When the pit starts fading away, it means that the precipitate has been etched away completely, and the epitaxial layer in that region remains free from the defect. When an etch pit appears, it means that the precipitate was not present near the original epilayer surface before etching, but is present in the currently exposed deeper locations inside the epilayer. This behavior was observed with all the smaller etch pits. Figure 4.14 shows all the behaviors exhibited by the smaller etch pits occurring at a particular region of the sample.

Scanning Electron Microscope (SEM) high magnification images were taken of all the etch pits. Figure 4.15 shows a sharp etch pit of a precipitate (a) and faded etch pits of the precipitates after they had already been removed by etching (b). The defects still remaining in the epitaxial layer are sharp whereas the pits with no defect remaining on the other hand are featureless, as expected.
Figure 4.14. Smaller etch pits appearing, growing and fading after KOH etch steps

Figure 4.15. SEM images of (a) ‘sharp’ and (b) ‘faded’ precipitate
Figure 4.16. Optical Profilometer scans of the depth profile of faded small etch pits: (a) the topographic map of the surface with the faded etch pits circled (b) line scan of a faded etch pit overlaid over its SEM image (c)(d) line scans of other faded etch pits.
To confirm that the faded etch pits do not propagate to the interface between the substrate and the epitaxial layer, an optical profilometer was used to measure the depth of these faded pits. This was important in order to determine whether the defect has terminated within the epitaxial layer (i.e., that those defects are not dislocations propagating from the epilayer-substrate interface).

Figure 4.16 shows the results of the profilometer scans. Figure 4.16a shows the topographic view of an etched site. The two faded pits identified in this site are encircled. The epitaxial layer thickness of this sample is 1.1µm as measured by FTIR. The line scan from one of the faded etch pits is shown in Figure 4.16b. It is superimposed on the SEM image of that same defect. It can be seen that the pit is very shallow, extending less than 0.16µm from the surface. Figure 4.16c and Figure 4.16d show line scans from other faded etch pits. All of them show that the faded pits have a depth of 0.15 - 0.2µms. The profile data shows that the faded pits of the small defects (and consequently the defects themselves) are indeed localized in the epitaxial layer. This behavior is indicative of precipitate related defects.

Energy Dispersion Spectroscopy (EDS) is a convenient technique to measure the elemental presence of aluminum at relatively small locations of the defect etch pits formed after KOH. EDS scans were performed at the locations of the etch pits corresponding to threading edge dislocations, as well as at the locations of the smaller etch pits. Each scan also covered an area surrounding the selected etch pit.

The line scans around the threading dislocations showed no variation in the Al concentration between the epitaxial layer and inside the etch pit (Figure 4.17). In contrast, the EDS line scans across the smaller etch pits had a characteristic spike of the aluminum
concentration right at the core of the etch pit as compared to the much lower Al concentration in the epilayer surrounding the small etch pits (Figure 4.18). This indicated that aluminum accumulation exists in the small area of the core of these small etch pits (i.e., aluminum precipitation apparently takes place at the corresponding defect).

Figure 4.17. EDS line scan showing random aluminum concentration across a threading dislocation etch pit and defect free epilayer
Figure 4.18  EDS line scan of aluminum concentration across a small etch pit superimposed on the SEM image of the corresponding location. Higher Al concentration is seen at the core of the defect.

A cross-section of one of the higher doped samples (a sample with Al concentration of about 4.3×10^{20} cm^{-3}) was prepared by a Focused Ion Beam. It was then investigated by TEM. Figure 4.19 shows the TEM images from this sample. As can be seen, localized defects are present in the epitaxial region of the images. The size of these defects range from 20 nm to 100 nm, and their concentration is similar to the small etch pits uncovered by molten KOH etching. This observation confirms that the smaller etch pits observed at higher values of Al doping are indeed due to defects localized at a certain depths inside the epilayer (i.e., are likely to be Al precipitates) rather than due to dislocations.
Small defects

Figure 4.19. Cross-sectional TEM images of the epitaxial layer showing a few localized small defects: (a) showing dislocations originating from the epilayer-substrate interface and defects localized at particular depths in the epitaxial layer and (b) a magnified view of a location having a few localized epitaxial defects.

In summary, nothing had been known about dislocation generation at high doping conditions during the low-temperature growth. Clear evidence of increasing dislocation generation with increasing TMA flows was obtained. Onset of precipitation was established. It was shown that the precipitate concentration dominates over dislocations at very high doping levels. A new convenient method for precipitate investigation in thin layers was developed. Two uniquely identifiable etch pits of defects were found and were classified as threading dislocations and precipitate related defects.

4.3.2. Photoluminescence of P⁺ Samples

Photoluminescence spectra of several P⁺ samples in situ doped with Al with increasing Al concentrations were measured. Figure 4.20 shows three such spectra plotted, which are indicative of the trend that is seen. As the Al doping increases, the Al
and N₂ bound exitonic peaks become smaller in intensity. This signifies a decline in the crystal quality. This is also accompanied by a rise in the aluminum donor acceptor pair related PL peaks showing higher incorporation of the dopant.

![PL spectra of Al doped P⁺ samples](image)

Figure 4.20. Low temperature UV-Photoluminescence of P⁺ samples showing progressive degradation of the crystalline quality

4.3.3. Dislocation generation model in epitaxial layers grown at low temperature with in situ Al doping

As described in earlier sections, the defects in the P⁺ samples were distinctly classified into dislocations and precipitate related defects. Figure 4.21 shows change in concentrations of both defects with increasing the Al doping after they are both separated. As follows from Figure 4.21, the threading dislocations dominate at lower Al doping. At
higher doping, the precipitate defects rapidly increase in concentration dominating the total defect count.

![Defects in the P⁺ samples separated into Dislocations and Precipitates](image)

Figure 4.21. Defects in the P⁺ samples separated into Dislocations and Precipitates

We took the experimentally determined dislocation concentration and model this generation of dislocations as a function of strain in the lattice caused by doping. For this purpose, we adapted the Hassen-Sumino (HAS) model for dislocation generation. The HAS model is defined by the following differential equation.

$$
\frac{dN}{dt} = Kk_0Ne^{Q/kT} \left( \sqrt{J - D\sqrt{N} - \tau_d} \right)^p \left( \sqrt{J - D\sqrt{N}} \right)^q
$$

Where $N$ is the density of dislocations (cm⁻²); $J$ is the Material Stress; $Q$ is Peierls potential (eV); $k$ is Boltzmann’s constant $8.617 \times 10^{-5}$ (eV/K); $T$ is the absolute temperature (K); $K$ is a material constant (cm/dyn); $D$ is the strain hardening factor (dyn/cm); $k_0$ is a material constant (cm²⁺¹/dyn¹ S); $\tau_d$ is the drag-stress (dyn/cm²); and $p$
and $\lambda$ are dimensionless material constants. In this model the $(\sqrt{J - D\sqrt{N} - \tau_d})^p$ term is related to the generation of the dislocations. The $(\sqrt{J - D\sqrt{N}})^\lambda$ term is related to the multiplication of the dislocations.

The equation needs to be numerically solved to obtain a solution of the dislocations generated with respect to time. At a given stress in the material, the generation of new dislocations stops after a sufficiently long period of time, and their concentration saturates to a certain level. Given that the stress in the material changes with doping, we get different saturation limits of dislocations for different doping levels. However, our typical epitaxial growth experiments lasted for 30 minutes, which is not necessarily a sufficiently long time to achieve saturation of dislocation content. Therefore, we modeled the dislocation generation for that specific growth duration. We applied a few simplifications and assumptions to this model. We assume the stress in the crystal lattice is isotropic and that the generation and multiplication are both affected by the dopant-dislocation interaction. The value of the multiplication exponent ‘$\lambda$’ depends on the model that is used [122]. In the case of the HAS model it has been experimentally determined to be 1. In other models like the Johnston-Gillman model it is set to ‘0’ [94]. Applying these simplifications, the exponent part of the equation reduces to $(Stress_{\text{effective}})^{p+1}$.

In this model the important parameters that we expected to extract from fitting the experimental data with the model are $K$, $D$, and $p$. $K$ is also called the multiplication factor. It determines how fast the dislocations multiply and their concentration increases towards the saturation limit. $D$ is the strain hardening factor and in conjunction with the
actual stress in the crystal, determines the saturation limit of the dislocation generation. ‘p’ is the material constant exponent which gives an indication of how rapidly the dislocations grow with increase in stress.

The stress in the lattice due to doping is calculated from the strain, which is given by the following:

\[ f_s = 4\pi N (r_s^3 - r_h^3) \left( \frac{3K + 4G}{27K} \right) \]

Where \( f_s \) is the lattice strain; \( N \) is the concentration of the dopant atoms; \( r_s \) and \( r_h \) are the radius of the dopant and host atoms; and \( K \) and \( G \) are the bulk and shear moduli calculated from the Young’s modulus.

The calculated stress values for our range of doping are shown in Figure 4.22. These values are used in the model to calculate the number of dislocations generated after the selected growth time.

![Stress vs Doping](image)

Figure 4.22. Calculated stress for different values of doping
The solution of differential equation of the HAS model provided the amount of dislocations generated over time for different levels of stress (Figure 4.23). In this figure, the saturation value of the dislocations depends on the value of stress which is generated by the doping. The rate at which the dislocations saturate to this value (the transient) is dependent on the other parameters of the model.

![Figure 4.23. Dislocations generated over time for different values of stress.](image)

In our calculations, the parameters were adjusted to give the best fit for the experimental data at the growth time of 1800 seconds (30mins). Figure 4.24 shows the set of dislocation generation curves at different values of stress (i.e., doping). The simulated number of generated dislocations after 1800 seconds is plotted along with the experimental data in Figure 4.25. As can be seen, a reasonable agreement is obtained between the simulation and the experiment. Some deviation from the model is observed.
at low Al concentration. This is because though the calculated strain due to doping reduces, there are other sources of strain in the lattice, which contribute to a higher real strain in the lattice. This causes a higher generation of dislocations in the lattice when compared to the theoretical modeled value.

Figure 4.24. Dislocations generated over time for optimized parameters of the model to fit the experimental data after 30 minutes of dislocation generation (i.e., epitaxial growth process)
Figure 4.25. Dislocation generation predicted by the HAS model versus the actual experimental data

The parameters extracted from this model for our low temperature 4H-SiC growth of P⁺ layers are compared to those for other semiconductors obtained from literature in Table 4.7.
Table 4.7
HAS Model parameters extracted for SiC compared to GaAs and InP from literature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>4H-SiC</th>
<th>GaAs</th>
<th>InP</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (m/dyn)</td>
<td>$5.98 \times 10^{-9}$</td>
<td>$7 \times 10^{-8}$</td>
<td>$1.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>D (dyn/m)</td>
<td>$2.45 \times 10^4$</td>
<td>$3.1 \times 10^5$</td>
<td>$3 \times 10^5$</td>
</tr>
<tr>
<td>p</td>
<td>1.33</td>
<td>1.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The extracted parameters are in line with expectations and give insight about the generation of dislocations in 4H-SiC. With the multiplication factor K being lower in 4H-SiC than GaAs and InP, the generation of the dislocations takes longer in our growth conditions. The strain hardening factor being lower is expected in SiC, as it depends on the shear modulus of the material. This results in more dislocations being created in SiC than the other semiconductors for the same amount of stress. The value of the extracted material constant exponent ‘p’ results in a slightly slower rate of saturation.

In summary, the HAS model was for the first time applied to our low temperature 4H-SiC growth of Al doped epitaxial layers. There was a very good agreement between the modeled and the experimental data. The parameters extracted from the model give some insight about material properties relevant to dislocation generation during low temperature SiC growth.
4.4. Analysis of the triangular defect generation during low-temperature epitaxial growth

Low-temperature epitaxial growth was conducted using standard SiH$_4$ and CH$_3$Cl precursors typically at flow rates of 30 sccm and 4 sccm respectively [15]. The precursor flows have been varied in a wide range and no triangular defects (TDs) were observed. As was reported earlier, in order to achieve higher growth rate ($R_g$), the SiH$_4$ and CH$_3$Cl flow rates were increased while keeping the effective (input) C/Si ratio constant, which resulted in morphology degradation [15]. When $R_g$ was further increased, surface roughening was observed at the downstream of the growth zone and was gradually progressing towards the upstream. This degradation of the surface morphology can be explained by homogeneous nucleation and formation of Si gas-phase clusters depleting supply of Si to the growth surface, which means that there is an unintentional increase in the real C/Si ratio in the growth zone even though the input C/Si was kept unchanged. However, even for the wide process window, the Si gas-phase condensation was not causing formation of Si droplets at the growth surface. Additionally, absence of TDs also confirms that there are no step-flow growth obstructions caused by Si droplets at the growth surface. Typically, the droplets serve as nucleation centers for TDs.

The low-temperature epitaxial growth with addition of HCl resulted in an increase in $R_g$, which was attributed to the significant reduction of the Si precursor depletion by the gas-phase homogeneous nucleation [123]. However, this increase in $R_g$ was accompanied by a significant increase in the generation of TDs. Qualitatively similar behavior was seen when higher $R_g$ was achieved by replacing the SiH$_4$ precursor with a SiCl$_4$ precursor [124].
Even though the concentration of the TDs in the epitaxial layers was not exactly reproducible run to run, it was noted that the average TD concentration increased as the R_g was increased from 1.5 to 6 μm/hr by increasing the precursor flow rates. Figure 4.26 shows this trend of increase in the concentration of TDs vs R_g. It can be seen that the trend can be fitted reasonably well with an exponential dependence. A similar trend of TDs was observed when the SiH_4 was replaced with SiCl_4.

![Graph showing increase in TDs vs R_g](image)

Figure 4.26. Increase in the concentration of TDs with increase in R_g

### 4.4.1. Investigating a possible role of the substrate defects

As follows from our experiments, the concentration of the TDs increases with an increase in R_g (depending on Si and C precursor flow rates). This indicates that the growth conditions play an important role in TD generation. However, the possibility that the TD nucleation takes place at certain defects in the substrate should also be
considered. If this is the case, then the problem of TDs generation in the low-temperature epitaxial growth could be resolved by merely improving the crystalline quality of the substrates (i.e., eliminating the particular defects serving as the nucleation centers).

The experimentally observed TD concentration from run to run had an appreciable statistical deviation; hence, reliable comparison of TD generation in low-temperature epitaxial layers grown on different substrates from different vendors was difficult. However, there was no clear trend observed in TD generation when moving from one wafer/vendor type to another (or between different wafers and different vendors). This could imply three different scenarios: (1) the TD nucleation centers are not related to any defects in the substrate; (2) the particular unknown substrate defects responsible for TD generation have similar concentrations in different commercially available wafers; and (3) the TDs are not substrate related and are caused instead by the epitaxial growth itself. One way to reliably answer this question is to see if individual TDs have corresponding defects in the substrate that serve as nucleation centers (i.e., a substrate dislocation at the vertex of the triangle).

When thick epitaxial layers were analyzed, an approach based on tracing TDs back to substrate defects by removing epilayers through polishing was previously found very challenging. This is due to the fact that removal of a few microns of material might result in a significant shift of the dislocation etch pits from their position at the epilayer surface, especially if a particular dislocation propagated at a significant angle to the surface. As a result of such significant shift, keeping track of a particular defect may become complicated.
In this work, TDs in thin epitaxial layers of thickness ranging from 1 to 3 µm grown with an \( R_g \) from ~2 to 6µm/hr were investigated. KOH etching was conducted on each sample to reveal and account for all detectable dislocations and possibly relate them to the generation of the TDs (Figure 4.27a). However, it should be noted that the observed dislocations could be generated during the epitaxial growth or could propagate from the substrate. Using a Nomarski optical microscope, a number of different locations (more than 6 sites) were carefully investigated across the entire sample area, as well as in different samples grown under different growth conditions and \( R_g \). Utmost care was taken to keep track of the exact position on the sample when analyzing these defects. This was achieved by forming a periodical pattern of deep numbered marks down to the depth significantly exceeding the epilayer thickness by ICP etching.

The entire epitaxial layer was removed in incremental steps by mechanical polishing, while the remaining thickness after each step was measured using the reflective FTIR technique. The complete removal of the epitaxial layer was confirmed by Hg CV doping measurements (typically the substrate doping was in \( 10^{18} - 10^{19} \) range). After some of the intermediate polishing steps, KOH etching was done and Nomarski optical micrographs were re-acquired in order to keep track of each of the TDs and dislocation etch pits.
Figure 4.27. Tracing the triangular defects from the epilayer to the substrate (a) the initial step: crosses mark the location of substrate defects and (b) the final step after the epilayer has been removed: the diamonds mark the location of the triangle vertexes in the epilayer.
Figure 4.27b shows KOH etch pits of the substrate, where the epilayer is completely removed by polishing, at exactly the same location as that of Figure 4.27a. In Figure 4.27b the initial vertex position of each of the TDs present in the epitaxial layer are represented by diamonds. Comparing Figure 4.27a and Figure 4.27b, it can seen that not a single TD had a corresponding substrate dislocation (i.e., a dislocation etch pit) anywhere close to the location of the vertex of the triangle. It was observed that there was no correlation between the TDs in the epitaxial layers and the etch pits of the substrate dislocations at any of the investigated locations.

Basal plane dislocations (BPDs) revealed in the substrate can be distinguished as the characteristic oval KOH etch pits and are encircled (Figure 4.27b). The corresponding locations of these BPDs are shown as crosses in Figure 4.27a. The arrows indicate the direction of the BPD propagating through the epitaxial layer during the epilayer growth. The tail of the arrow corresponds to the dislocation position that is deeper inside the substrate below the epitaxial layer, as taken from Figure 4.27b. The head of the arrow, therefore, points at the final position of the dislocation at the surface of the epilayer. It can be seen that most of the substrate BPDs, shown as crosses in Figure 4.27a, end up as dislocation etch pits in the epitaxial layer (small pits in Figure 4.27a). Additionally, higher resolution analysis revealed that most of the dislocations in the epitaxial layer propagating from the substrate are converted from BPDs to primarily threading edge dislocations.
Table 4.8

Conversion statistics of epitaxial layers with large number of triangular defects

<table>
<thead>
<tr>
<th>Site #</th>
<th>Triangles Formed #</th>
<th>BPD_{sub} → ThD_{epi}</th>
<th>BPD_{sub} Destroyed</th>
<th>ThD_{epi} Created</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55</td>
<td>10</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>54</td>
<td>10</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>51</td>
<td>12</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>76</td>
<td>7</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>64</td>
<td>7</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>73</td>
<td>10</td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Avg /cm²</td>
<td>1.385 x10^5</td>
<td>2.080 x10^4</td>
<td>1.114 x10^3</td>
</tr>
</tbody>
</table>

We analyzed the conversion statistics of the various defects in the sample from all the six sites (Table 4.8). Again, we see that all BPDs in the substrate are converted to ThDs in the epitaxial layer. The important statistic here is that the number of new ThDs created in the epitaxial layer is appreciable. This again points to the non-optimal growth conditions due to which triangular defects and more ThDs are created.

The main conclusion that can be made is that while substrate BPDs could be observed at all locations of the investigated samples, none of these substrate dislocations caused the generation of the TDs.

4.4.2. The main origin of the TDs

As described in the previous section, it has been established that substrate defects do not serve as the nucleation center for TDs. Therefore, it had to be concluded that the nucleation centers must be introduced by the epitaxial process itself. It was established that the sizes of many, though not all, of the TDs is consistent to their generation at the
very epilayer/substrate interface, assuming that the triangle of a TD is always positioned in the basal plane of the off-axis grown epitaxial layer [33][70]. However, an attempt to reduce the TD concentration by adjusting the initial process conditions, such as much lower growth rate and different C/Si ratio did not cause any improvement. Therefore, a two stage growth process was attempted; initially very low $R_g$ that was previously shown not to generate any TDs, followed by a higher $R_g$ that caused TD generation. The size of the TDs indicated that many of them start generating exactly when the epitaxial growth conditions switch to the higher value of $R_g$, while few other TDs generate later during the growth. This however indicated that the TD generation is not limited to the initial startup stage of the epitaxial growth process conditions.

It has been shown that the Si droplets can cause obstructions in the step-flow growth, thus generating TDs during the growth process [71]. However, in our experiments the Si droplet formation at the surface was not observed. Moreover, TDs were not observed in the standard experiments when SiH$_4$ and CH$_3$Cl precursors were used without HCl addition, even though severe Si vapor condensation was clearly observed inside the susceptor due to dense vapor cloud and gas-phase cluster formation, confirmed by the growth trends reported in Ref [15].

It was reported earlier that the additional supply of chlorine is beneficial for the suppression of the homogeneous nucleation of Si during the low-temperature epitaxial growth [123][124]. However, the suppressed formation of the gas-phase clusters or premature dissociation may lead to formation of polycrystalline Si islands at the colder upstream portion of the hot zone, due to the increased supply of Si growth species [123]. The concentration of polycrystalline islands reduced and was not observed on the
epitaxial layer inside the growth zone, especially when approaching the higher-
temperature growth zone. However, it was also demonstrated that the polycrystalline
deposits may extend well inside the growth zone and spoil the epilayer surface at some
growth conditions, particularly at the upstream portion, for instance at higher H\textsubscript{2} carrier
gas flow velocity in both SiCl\textsubscript{4} and HCl experiments [123][124].

If the polycrystalline Si islands are suggested to act as possible nucleation center for
the TDs, then it should be explained why those islands are not observed in most of the
samples with high concentrations of TDs. To address this issue, an epitaxial growth
experiment with SiCl\textsubscript{4} and CH\textsubscript{3}Cl precursor gases flown at 24 and 4 sccm respectively,
and inhomogeneous R\textsubscript{g} from 4 to 2.5 μm/hr from upstream to downstream was designed
to achieve relatively small sizes and concentration of the polycrystalline islands at the
upstream portion of the growth zone.

After the epitaxial growth, it was noted that the polycrystalline islands from \(~5\ \mu\text{m}\) to
\(~20\ \mu\text{m}\) wide appeared at the upstream portion of the substrate (Figure 4.29a). X-ray
Powder Diffraction (XRD) measurements were performed for phase identification of the
crystalline material. It was confirmed that the islands had polycrystalline Si as seen in
Figure 4.28 [123].
Figure 4.28. XRD measurements showing the presence of polycrystalline Si in the islands

![XRD spectrum](image)

Figure 4.29. Optical micrographs of triangular defects (TDs) in a SiC epitaxial layer grown at conditions resulting in higher Rg and poly-crystalline islands formed in the upstream portion of the growth zone. Different locations on the wafer are shown: (a) upstream, (b) center, and (c) downstream. High concentration of TDs is caused by islands.

Multiple overlapping TDs were formed aligned along the step-flow direction of the epitaxial growth at the downstream side of each island (Figure 4.29a), and the vertexes of the triangles were located inside the corresponding island. However, bigger islands
caused more TDs, and different parts of the islands were serving as a nucleation centers for different TDs.

At the location close to the center of the sample, the polycrystalline Si islands were absent (Figure 4.29b). However, there are clear traces of smaller islands that were present at the surface at early stages during the epitaxial growth and evaporated later. Those traces can be observed as disturbed roughly circular regions on the epitaxial layer surface (Figure 4.29b). It is evident that the evaporated islands apparently served as nucleation centers for at least one or couple of TDs originated in these locations of the epitaxial layer. However, with the evaporated islands being smaller, each of them did not serve as a nucleation center for multiple TDs, as compared to the bigger islands seen in Figure 4.29a.

Close to the optimized growth conditions but at high growth rates in our HCl-assisted growth experiments or experiments with SiCl₄ replacing SiH₄, much lower concentration of TDs were observed in the downstream portion of the growth (similar to Figure 4.29c). The TDs formed at those conditions did not have any islands at the vertex of the triangle (which is typical for most of our TDs). By observing the trend in Figure 4.29a and Figure 4.29b, it can be concluded that at the downstream location of the sample a smaller number of smaller-size polycrystalline Si islands were formed as shown in Figure 4.29c. Due to the much smaller size of these islands, they evaporate easily from the epilayer surface after staying there for a short time. However, this time is sufficient to cause a disturbance in the step flow growth, which would result in the TD generation. The number of poly Si islands and the number of nucleated triangular defects that are not obviously associated with the islands (i.e. those which nucleate outside the visible
islands) are counted as a function of distance from the leading edge of a sample. Both of these statistics are highly correlated as seen in Figure 4.30. This confirms that the poly Si islands play the major role in the triangular defect nucleation.

![Figure 4.30. Correlation of the concentration of poly Si islands with the concentration of the triangular defects nucleated at various distances from the leading edge](image)

**4.4.3. The structure of the TDs.**

KOH defect delineation technique was applied to investigate the crystallographic structure of the TDs. TDs formed in different epitaxial layers grown at different process conditions are shown in Figure 4.31. A common feature that was observed in the vicinity of the vertex of the triangle was at least one or often multiple threading dislocations present. It is clearly evident from the previous section that a brief presence of Si polycrystalline islands (that are different from a Si droplet), which is small enough to
evaporate after causing a disturbance, could result in the generation of the dislocations at the vertexes of the TDs and TDs themselves.

Figure 4.31. SEM micrographs of triangular defects after KOH of epitaxial layers formed by low-temperature epitaxial growth with HCl addition: (a) low Si/C=3.75; (b) and (c) higher Si/C=9 at two different locations on the sample. The dotted lines are used to delineate the difficult to resolve edges of the triangular defects.
It was also observed that some of the TDs did not seem to have threading dislocations at their vertexes (e.g., one of the TDs in Figure 4.31a), which is a clear indication that the presence of these dislocations is just an accompanying feature of the TD generation rather than their origin. It was observed that all of the TDs are bound by at least one partial dislocation (PD) on each side, showing up between the side and the base of the triangle as a very elongated etch pit (at the corner of the triangle). In most of the cases, at least one more dislocation was seen propagating in the basal plane along the median of the triangle (e.g., Figure 4.31a). However, in some of the TDs, one of the two bounding PDs was absent, which means that only half of the triangle was present. As shown earlier, in the TDs formed during the conventional high temperature epitaxial growth [70], the area of the TDs in between the PDs is represented by a stacking fault (SF).

The more pronounced and well-defined TDs (as seen before KOH etching), after KOH etching, revealed multiple PD etch pits lined-up along the sides of the triangle (Figure 4.31a). The multiple PDs formed in some of the TDs normally propagate at the same angle (i.e., along the same well defined side of the triangle). However, in some cases, more disordered arrays of PDs are formed that propagate not only along the sides and the median of the triangle but also at different angles with respect to the triangle median (Figure 4.31c).

In line with previous observations [125][126], the angle between the PDs on both sides of the triangle, in other words the width of the TD, depends on the process growth conditions. The main factor determining the shape of the TD is established to be the Si/C ratio. Lower Si/C ratio resulted in wider TDs (Figure 4.31a), as compared to higher Si/C ratio (Figure 4.31b and Figure 4.31c). It was verified the effect is indeed due to Si/C
ratio, due to changes in doping caused by changes in Si/C ratio following the site-competition mechanism, or changes in $R_g$. No clear correlation of the TD shape with $R_g$ or doping could be established. The intentional doping with N$_2$ and Al did not seem to have any effect on the shape of the TDs, which further confirmed that the propagation of PDs defining the sides of the TDs is indeed influenced directly by the Si/C ratio.

The next important question that needed to be addressed was the possibility of formation of 3C-SiC polytype inclusions in the areas of the TDs, which was frequently observed in the previous reports [65][66][72]. In this work, one of the simplest (if not entirely unambiguous) approaches to detecting the polytype transformation based on thermal oxidation was used [73]. Oxidation rates ($R_{ox}$) are different for the 4H and 3C polytypes, with the rate of oxidation being higher for the 3C polytype (more than two times higher than 4H). Three sets of low-temperature SiC epitaxial samples grown with HCl addition, which had TDs, were subjected to steam oxidation at 1150°C for 6.5 hours. The three sets of samples had quite distinctively different looking triangular defects. Figure 4.32 shows the triangular defects in the three samples before and after oxidation.

It can be seen from Figure 4.32 that the sample 114 had a distinctive color change indicating different SiO$_2$ thickness, which serves as evidence of a different SiC polytype inside the triangular defects. The sample 51 did not show any color change. To determine the cause of this difference a closer look at the structure of the triangular defects was taken.
Nomarski optical micrographs of two different samples, at similar locations on the wafer before and after oxidation, are compared to SEM images obtained after KOH defect delineation (Figure 4.33).

In some of the investigated samples, no change in the oxidation rate was observed, which implies that there is no polytype transformation in the TD areas (e.g., Figure 4.33a and Figure 4.33a1). In few other samples, formation of 3C-SiC polytype was clearly observed, evidenced by darker color of the triangles owing to much higher oxidation rate (Figure 4.33b and Figure 4.33b1). Even for certain growth conditions that lead to 3C polytype formation, it was observed that sometimes only half of the triangle would reveal the presence of 3C polytype, and not all triangles experience the polytype transformation (Figure 4.33b1).
Figure 4.33. TDs in two different growth runs. The left column (a,a1,a2) correspond to growth at higher Rg and higher C/Si ratio than (b, b1, b2). (a),(b) as grown, (a1),(b1) after oxidation, (a2),(b2) SEM after KOH.

KOH defect delineation revealed a higher density of the partial dislocations at the triangle periphery accompanying the polytype transformation inside the TDs (Figure 4.33b2 compared to Figure 4.33a2). It was often seen that half of the triangle that did not have a polytype inclusion had just a few or one PD along the given side of the triangle, while the other half of the triangle showing a polytype inclusion had a dense array of PD etch pits (Figure 4.33b2).

Multiple stacking faults, which are located in the basal plane and are relatively close to each other, lead to formation of multiple partial dislocations. Additionally, observation of very dense arrays of PDs is also an indication that individual stacking faults when
clubbed together form a region of different polytype (and most likely the 3C polytype which has higher oxidation rates).

The two samples shown in Figure 4.33 had different growth conditions; the sample without the polytype inclusions in the TDs was grown at higher $R_g$, and at a higher value of C/Si ratio.

In addition to oxidation, a micro-Raman analysis was also used as an independent way to establish the presence of 3C-SiC inclusions in some of the triangular defects. Raman spectra were obtained at selected points inside the triangular defects and outside them in the blanket epitaxial layer. Figure 4.34a shows the locations from which the Raman spectra were measured. Figure 4.34b shows the Raman spectra inside and outside the triangular defect. The 4H-SiC and 3C-SiC TO phonon peaks are seen. The 4H-SiC peaks are of much higher intensity. However, a clear difference is seen in the 3C-SiC peaks. The intensity of the 3C peak inside the TD was more than double than that observed outside in the defect-free epitaxial layer. This sample had showed a color change in the TDs upon oxidation, which confirmed the Raman data indicating the presence of 3C-SiC inclusions. The Raman spectra taken from the samples that did not show the color change after oxidation had a weak 3C-SiC peak similar in intensity to the surrounding defect-free epitaxial layer.
Figure 4.34. Micro Raman spectra taken from a TD sample: (a) showing the points from where the spectra are obtained. (b) Showing the comparison of 4H-SiC and 3C-SiC Raman peaks inside and outside the TD
4.4.4. Low-temperature Photoluminescence.

A significant progress has recently been achieved in applying Low-Temperature Photoluminescence (LTPL) spectroscopy in investigating the optical properties of different kinds of stacking faults (SF) [79][127][128]. A large difference was observed in the excitonic bandgap determining the energy of the zero phonon line, for a variety of SF types. The standard PL lines of SF-related bound excitons, such as TA, LA, TO and LO phonon lines, always correspond to the well known phonons replicas in SiC, which simplifies their identification [82].

In epitaxial layers grown at conventional high temperatures, SF PL was detected in the vicinity of TDs [81]. A similar trend was expected from TDs formed during the low-temperature epitaxial growth.

However, no evidence of SF LTPL lines were observed in the epitaxial layers, even in those having relatively dense TDs. Standard photoluminescence spectra dominated by nitrogen bound excitons were measured at approximately 15 K. It was speculated that TDs take insufficient fraction of the area probed by PL.

Due to the unavailability of microscopic PL for this project, another approach was applied in an attempt to maximize contribution of the TDs to the LTPL emission. A thicker sample (>15 µm-thick) with very high TDs concentration was grown at a much longer time to produce merging and overlapping TDs. Nomarski optical micrograph of this epitaxial layer was obtained as shown in Figure 4.35. This sample had much rougher surface than normal, which is merely due to overlapping TDs, and also smaller TDs were generated inside the area of the bigger TDs at the later stages of growth. It was observed
that the sample had dense network of intersecting SF, which should have made it easier to obtain SF contribution to the PL emission.

Figure 4.35. PL spectrum of a sample with very high concentration of TDs. The inset shows the disturbed surface morphology, which is caused by the longer growth time resulting in overlapping of large and smaller TDs. Sharp BE and FE PL lines can be observed in spite of the dominance of the TDs.

Surprisingly, absolutely no SF luminescence could be observed even in this sample (Figure 4.35). An attempt to identify the presence of the 3C-related PL emission was also unsuccessful. While the spectrum of this n-type sample is dominated by nitrogen bound excitons (notice that the $Q_0$ nitrogen BE line is scaled down an order of magnitude), the spectrum also has clear free exciton lines. The observation of strong and sharp free and bound excitons lines is evidence of a decent crystallographic quality. A distinguishing feature of the LTPL in this sample was a rather strong intrinsic defect-related $D_1$ lines (the $M_1$ and $L_1$ components dominating at this particular measurement temperature). Also, the new features that were absent in the samples with smaller concentration and not
overlapping TDs are two PL lines at approximately 4151 and 4159 Å lines. At this stage the origin of the new two lines remains unclear.

It remains to be explained why SFs, which are apparently an inherent part of the TDs formed by the low-temperature halo-carbon epitaxial growth technique, did not show up as the characteristic emission lines in the investigated LTPL spectra. One possibility is that in the relatively small triangular defects investigated in this work, with a large number of basal plane dislocations, a non-radiative recombination would be more favorable for the carriers trapped in the potential well of the stacking fault. Alternatively, a larger number of closely spaced SFs, which are characteristic for the TDs formed during the low-temperature epitaxial growth, may exhibit different optical emission properties, possibly including more favorable non-radiative recombination.
CHAPTER 5
CONCLUSIONS AND FUTURE WORK

A comprehensive characterization of a variety of defects in low temperature epitaxial layers was undertaken in this work. Blanket epitaxial layers, layers grown by selective epitaxial growth, and heavily Al doped P⁺ layers were analyzed. A molten KOH etching process along with a polishing process was developed to characterize defects in any type of SiC material at any depth.

Under optimized growth conditions, the number of dislocations in the blanket epitaxial layer was found to be less than or equal to the defects in the substrate. This means that the low temperature epitaxial growth process does not contribute to any new lattice defects. Low-temperature growth with HCl addition showed a much higher conversion efficiency of the harmful basal plane dislocations (BPDs) into much less harmful threading dislocations (ThDs) than the low temperature growth without HCl. However, epitaxial layers grown with a higher growth rate in the presence of HCl show a generation of new ThDs and triangular defects in the epitaxial layer.

LTSEG also shows an increased creation of ThDs compared to the blanket epitaxial growth. Basal plane dislocation formation is also extensive along mesa edges oriented roughly perpendicular to the off-axis cut ([11-20] direction) and located at the “upstream” side of the mesa with respect to the step-flow growth direction.
Crystalline quality of P+ epitaxial layers grown by the low-temperature halo-carbon epitaxial growth technique with in situ Al doping was investigated. Degradation in epilayer quality (i.e., lattice defect generation) took place when the aluminum doping approached the previously reported solubility limit. After the substrate defects were excluded from the consideration, a monotonic trend of enhanced defect generation versus aluminum doping was established. Two types of defects were identified. Threading dislocations were present in all the samples, and their concentration increased with Al doping. The other type of defect was found only in the higher doped epitaxial samples (with Al doping concentration above 3.5x10^{20} cm^{-3}). It was established that these defects are localized at certain (and different) depths inside the epitaxial layers by both profilometer measurements and TEM measurements. Energy dispersive spectroscopy data also confirmed the presence of aluminum inside the defect core. This allowed us to suggest that these defects are precipitates or precipitate related defects.

A dislocation generation model based on the Haasen Sumino model was developed for the low temperature epitaxial growth of Al doped 4H-SiC P+ epitaxial layers. A good agreement between the model and the experimental data was achieved. The extracted parameters give us insight about the factors influencing the dislocation generation process in 4H-SiC low temperature growth.

The triangular defects that form during the low-temperature halo-carbon growth and act as the main problem in the way of increasing the growth rate were investigated. While different origins were previously identified for similar TDs in more conventional higher-temperature epitaxial growth techniques, the nucleation centers for the TDs in the low-temperature growth were unambiguously identified as typically very small
polycrystalline Si islands (but not droplets) that tend to evaporate after briefly causing disruption of the step-flow growth. No substrate defects were found involved in the TD formation, which eliminated a possibility to eventually improve the quality and the growth rate of the low-temperature epitaxy by reducing the dislocation content in the substrates.

The structure of the triangular defects was studied by SEM and molten KOH etching. Some of the triangular defects were found to have a small spherical polycrystalline deposit at the vertex. These triangular defects were bound by sparse partial dislocations originating from the stacking fault at the base. Other triangular defects were found to be densely bounded by partial dislocations. The densely bound triangular defects (multiple partial dislocations at the edges of the triangular defect) exhibit presence of polytype inclusions (3C-SiC) within its boundary as revealed by oxidation and Raman spectroscopy. Generation of multiple stacking faults is suggested as the origin of this polytype violation.

Several avenues of future work are suggested for continuation of the various topics pursued in this dissertation. Characterization of defects in different precursor systems like SiCl₄ is an interesting possibility. Quantifying the number of triangular defects formed in the presence of HCl with respect to growth rate could offer important insight into the defect formation process. Additional possibilities for reducing nucleation of the polycrystalline islands at the growth surface need to be investigated. The growth parameters during selective epitaxial growth can be studied to reduce and eliminate the generation of new threading dislocations during growth. The precipitate related defect in the P⁺ epitaxial layers can be investigated further to better understand their structure.
REFERENCES


