Modelling the mechanisms of nitridation of SiC based devices during anneals in NH$_3$ and NO gases

Manesh V. Mistry

A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

of

University College London.

Department of Physics and Astronomy

University College London
I, Manesh V. Mistry, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.
Abstract

The work presented in this thesis is focused on the mechanisms of processes that occur during the NO and NH$_3$ anneals of 4H-SiC/a-SiO$_2$ devices, specifically on the nitridation of performance limiting defects in a-SiO$_2$. All results are found using density functional theory (DFT) and classical molecular dynamics.

The first two results chapters of this thesis investigate the interactions of nitric oxide (NO) and ammonia (NH$_3$) with a pristine a-SiO$_2$ network. This investigation is important on two fronts, the first is that the oxide used in these devices is of high quality (CVD oxide), and the second is that these molecules have been shown to incorporate into the oxide and, in some cases, chemically interact with it. Hence one must understand the interactions of these molecules with the pristine a-SiO$_2$. My results demonstrate that neutral NO molecules only have steric repulsive interactions with the pristine network and negative NO molecule interacts with the network Si atoms electrostatically. These interactions manifest as higher NO migration barriers in the negative charge state compared to the neutral charge state. Ammonia is shown to form similar interstitials but also react with the surface silanol groups to form smaller ammonia fragments, like NH$_2$ and NH, which then lead to nitridation seen in elemental studies of such devices.

In the next chapter I examine the interaction of NO and NH$_3$ fragments with common defects in the a-SiO$_2$ network. The results in this chapter show how the charge transition levels (CTLs) of known oxide defects move deeper into the SiC/a-SiO$_2$ band gap, on nitridation, leading to the conclusion that the tunnelling probability to these defects decreases due to the large difference in energy between the SiC CBM and the nitridated defect levels. In the final chapter I present the results
Abstract

of simulations of the structure and properties of a SiC/a-SiO$_2$ interface as well as the effects of proximity of the interface for defect properties. Finally, I discuss the character of surface relaxation of the a-face of 4H-SiC.
Impact Statement

Silicon Carbide (SiC) is a wide band gap semi-conducting material which is used in high-power, high-temperature, and high-frequency applications of microelectronic devices. Its growing potential derives from many excellent properties, which include the high breakdown field, wide band gap, excellent thermal conductivity, and mechanical stability. In addition to these advantages, the native oxide of SiC is amorphous silicon dioxide (a-SiO$_2$). Since SiO$_2$ is a well-established gate oxide material, the formation of metal oxide semiconductor structures is a facile process.

Despite this promise, SiC based devices suffer from a high density of defects at the interface between SiC and SiO$_2$. These defects are known to form in a region 2 nm from the interface in both the SiC substrate and the gate oxide. The work presented here focuses on defects in the gate oxide and how their passivation with nitridating gasses, such as NO and NH$_3$, may improve the device performance. While the high temperature (1500 K) anneal in NO is the current state of the art for SiC based n-type devices, some significant reliability issues still remain. In particular, after the NO anneal there is still a significant defect concentration remaining in devices. The atomic nature of these defects is currently unknown. Identifying the nature of these defects is the focus of this thesis and will enable these defects to be eliminated from the system, hence yielding a more reliable and efficient device.
I would like to take this opportunity to thank everyone that has helped and encouraged me throughout my funding period. First and foremost, I would like to thank my supervisor, Prof. Alexander Shluger. He has made me become a better scientist through rigorous debate and has allowed my confidence to grow a thousand fold in the process. I would also like to specifically thank Dr. Jonathan Cottom and Dr. Kamal Patel who, during their respective times in the group, have made me work harder and smarter than I would ever think possible. Next, I would like to thank Dr. Gregor Pobegen and Dr. Judith Berens who have given me expertise and incite into the world of SiC and the ability to expand my knowledge beyond the modelling of materials. Thanks also go to Miss. Abbie Bray, Miss. Laura Hargreaves and Miss. Camilla DiMino who have been indomitable allies in my various plights over the last 4 years. Special thanks goes to Mr. D. Waldhöer who has helped me with coding issues and a companion on the defects in a-SiO$_2$ journey.

I would like to thank my parents, Mr. and Mrs. V. J. Mistry for all their help and support during the last 4 years. I would also like to thank Dr. H. R. Tinker, Mr. A. Mushett Cole, Mr. B. Medland, Mr. B. Kavanagh and Mr. S. Tobenhouse without whom my time in London would have been a dire affair. During the bulk of my PhD I have lived with Mr. R. Mali and Mr. S. Newcombe who have let me feel comfortable and have helped in the writing of this thesis, thank you for everything you have done and for giving me a taste of home in London. I would like to acknowledged the efforts of Dr. I. Scivetti and Dr. S. Mensa for all their help. My final thanks go to all the people at Kilburn Cosmos RFC, you have helped me through this process more than you can ever know.
List of Figures

1.1 A schematic of the work presented in this thesis and how each chapter is related to the other. ................................................................. 23

2.1 Schematic of the operation of planar (a) and trench (b) MOSFET configurations. The green section is the a-SiO$_2$ and the blue sections and the red sections are SiC the colours denote their doping (blue is n-doped and red is p-doped) and the shading is to differentiate the section of SiC in-which they reside, the areas without subscripts are areas near the electrode contact region, $n_{epi}$ is the epitaxial region of SiC and $n_{sub}$ are region deep in SiC, the white arrows in each case show where the conducting channels form. .............................. 27

2.2 A schematic of trap assisted tunnelling in SiC/a-SiO$_2$ devices. This schematic focuses on electron trapping states that are present in the oxide and whose levels sit close to the CB of SiC. ................................. 29

2.3 A 2D schematic of the structure of three common SiC polytypes and their band gaps. A,B and C are the repeating units shown both horizontally and vertically next to each polytype. The band gaps of each of the polytypes is given under each of the images. The h and k represent the two unique sites for the Si and C atoms [2]. .................. 31

2.4 A side view of the Si-face (a) and the a-face (b) along with their specific crystallographic directions (surfaces are those without H saturators). The Si-face is terminated by Si atoms and the a-face has alternating Si and C terminations and so is sometimes referred to as the stoicheometric face. .................................................... 32
2.5 Samples of $\alpha$-quartz (a) and a-SiO$_2$ (b) structures. Both structures are made of SiO$_4$ units but in the quartz sample atoms form a regular crystalline structure and in the amorphous sample they are randomly distributed. The regular distribution leads to clear channels forming in the crystalline sample, a feature which is not present in the amorphous sample. ........................................ 33

2.6 Distribution of structural properties in 20 models of 216 atom cells of a-SiO$_2$ optimised using DFT. (a) Shows a histogram of the Si-O bond lengths, (b) shows a histogram the O-Si-O bond angles, and (c) shows a histogram of the Si-O-Si bond angles [22]. .......................... 34

2.7 Schematic representation of the CTLs of all the oxide defects discussed in this section including the experimentally verified band offset of the SiC/a-SiO$_2$ device [2, 21]. ............................... 35

2.8 The atomic structure and spin density of the intrinsic electron trap in a-SiO$_2$. The SiO$_4$ tetrahedra on which the electron traps has been highlighted [40] ............................................. 39

2.9 A mechanism to form O vacancies [24]. A) the initial trapping of a second electron, B the subsequent breakage of the Si-O bond leading to the pseudo-five-coordinated Si, C the coordination and facilitation of the formation of the O$^{2-}$ interstitial and D the formation of the Si-Si interaction. ............................................. 40

2.10 An O vacancy in a-SiO$_2$. The atoms in the foreground are those that make up the O vacancy and the atoms in the background make up the rest of the a-SiO$_2$ network. The network is built-up of SiO$_4$ tetrahedra and to form the O vacancy one of these atoms has to be removed leaving two 3-coordinated Si atoms, one of O atoms for the Si on the right hand side of the image is obscured by the Si atom. Colour coding: O Red and Si yellow. ......................... 41
2.11 The H bridge defect. In this defect at H atom is placed in the gap where an oxygen atom presides. As H is only one valent, it makes a strong bond to one of the Si atoms and the other is left uncoordinated. This figure shows the H atom pointing at the three coordinated Si atom and this aids in stabilising the non-bonded electron on the Si atom. Colour coding: Si yellow, O red and H white. . . . . 45

2.12 The Hydroxyl E'-H centre defect. One of the Si-O bonds has broken (between O atom and right-hand Si atom) and the O atom is bonded to a Si atom and a H atom, the right-hand Si atom is three coordinated. The atoms in the foreground are those involved in the defect and those in the background are of the a-SiO₂. Colour coding Si yellow, O red and H white. . . . . . . . . . . . . . . . . . . . . . 46

2.13 Selected N 1s core level spectra of SiC/SiO₂ stacks after different treatments, including (a) N₂, (b) NO, (c) NH₃, and (d) NO + NH₃. Figures (a), (b) and (d) are shown at 5x magnification compared to (c) [1]. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 49

2.14 Depth profiles of SiC/SiO₂ stacks after annealing in a variety of atmospheres, including (a) N₂, (b) NO, (c) NH₃, and (d) NO + NH₃. Relative atomic% (rel. at%) for each element were determined from peak fits to the total core level areas after each sputter cycle. The coloured columns indicate which data-sets were used for detailed comparison. [1]. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 50

2.15 The two SiO₄ tetrahedron that have been used by Devynck et al. [21] to make a connection scheme for SiC/a-SiO₂ interface. A is an SiO₄ tetrahedron that has three connections to the the SiC and B is an SiO₄ tetrahedron that has two connections to the SiC [21]. . . . . 53
3.1 A schematic representation of the change in CTL position as a function of formation energy. The green line is a comparison. The blue dashed line shows what happens when the formation energy decreases (purple arrow), the CTL moves closer to the VBM (blue arrow). The red dashed line shows what happens when the formation energy increases (orange arrow), the CTL moves towards the CBM (red arrow) .......................................................... 70

4.1 A schematic representation of the sampling scheme. The green triangle represents the face of the SiO$_4$ tetrahedra being sampled, the red arrow represents the vector between the Si and the N atoms and the black arrow represents the vector between the N and the O atoms which is 1.1 Å away from the N atom. Colour coding: Si in yellow, N in blue and O in red. .......................................................... 76

4.2 The formation energy distribution of the neutral and negative interstitial, both show a range of around 3 eV. Neutral charge state in blue and negative charge state in orange. All formation energies are referenced to the valence band edge of the a-SiO$_2$ cell used in the sampling and negative formation energies are stated at this Fermi level position. .......................................................... 80

4.3 The highest (squares) and lowest (triangles) incorporation energies for interstitials that are found in the cages as determined by the Voronoi-Delaunay tessellation analysis. This energy dependence is based on the orientation of the molecule with respect to the cage. 81

4.4 Two examples of the cage structures that form the minima in the exhaustive sample and the lowest (a and c) and highest (b and d) energy NO interstitials for both cages. The asphericity delta value for each of these cages is 0.22 (a and b) and 0.01 (c and d). The difference in incorporation energy for each of the cages is 0.19 eV (a and b) and 0.06 eV (c and d). Colour coding Si yellow, N blue and O red. .......................................................... 83
4.5 The density of states (DOS) for the neutral NO molecule in a large cage. The graph is normalised so that the highest occupied state is at a Fermi level of 0 eV. All of the states shown between Fermi levels -3 eV and 6 eV are caused by the presence of NO. 84

4.6 Molecular orbital diagram of NO in the neutral (left) and negative (right) charge states. The electrons shown in green are the ones present in the neutral charge state and the electron shown in red is added on charging. 85

4.7 The majority interaction of the NO\(^-\). The N interacts with the SiO\(_4\) tetrahedron, akin to the negative NO in the literature, flattening a face of the tetrahedron. Colour coding is the same as Fig. 4.9. 86

4.8 The geometry and spin density of the interaction between NO and sites with O-Si-O bond angles of greater than 119\(^\circ\). Colour coding same as Fig. 4.9. 87

4.9 An example of the cage structures that form the minima in the exhaustively sampled a-SiO\(_2\) cell. The green line signifies two interlinking rings that make up the cage and so the NO has to move through to progress from cage to cage. Colour coding Si yellow and O red. 89

4.10 The changes in bond length between a 5 and 6 membered ring transition. The blue line in a and c illustrates the definition of ring used in this work. Colour coding same as Fig. 4.9. 90

4.11 Barrier heights of 5, 6 and 7 membered rings in a-SiO\(_2\) in the neutral (triangles) and negative (squares). The average increase in barrier height from neutral to negative is 0.2 eV. 90

5.1 The different orientations of NH\(_3\) sampled on the surface of \(\alpha\)-cristobalite. a) and b) have the principle rotation axis of NH\(_3\) perpendicular to the plane of the surface, and c) and d) have the principle rotation axis parallel to the surface. Colour coding: Si in yellow, N in blue and O in red. 96
5.2 The two different results of the orientation dependence study done on the surface of \(\alpha\)-cristobalite. a) is the H-bonded configuration and b) is the non interacting configuration. Colour coding same as Fig. 5.1.

5.3 The results of geometry optimisation calculations of \(\text{NH}_3\) on a partially hydroxylated surface. The upper image shows the formation of the \(\text{NH}_2\) fragment and the lower image shows the formation of the \(\text{NH}\) fragment. Colour coding same as Fig. 5.1.

5.4 The starting geometry for MD runs done on the surface of a-SiO\(_2\). Colour coding same as Fig. 5.1.

5.5 The nitridated geometry of the a-SiO\(_2\) surface after 1 ns of equilibration at 1500K. Colour coding same as Fig. 5.1.

5.6 The H-bonding configuration of the \(\text{NH}_3\) molecule on the surface of a-SiO\(_2\). Colour coding same as Fig. 5.1.

5.7 The incorporation energies of the singlet and triplet interstitials. On average, there is an increase of 0.5 eV in the singlet multiplicity.

5.8 Structure (a) and charge transition levels (b) of the Nitroxy Bridge. This structure forms when there is a bond length greater than 1.64 Å. Colour coding same as Fig. 5.1.

5.9 Structure (a) and charge transition levels (b) of the NH interstitial. This structure forms when there is a bond length < 1.64Å. Colour coding same as Fig. 5.1.

6.1 The 0/- CTLs and atomic structure of the Hydroxyl E’ centre. The CTLs of the Hydroxyl E’ centre were calculated over 288 O atoms in two 216-atom a-SiO\(_2\) structures. Colour coding: Si yellow, O red and H white.
6.2 A schematic representation of the 0/- CTLs of the intrinsic electron trap with and without the NO and NH\textsubscript{x} (x=1,2). The CTLs are labelled IET is the intrinsic electron trap with no N containing compounds and the CTLs labelled with NO and NH\textsubscript{x} (x=1,2) are those with their respective fragments or molecules. 114

6.3 The geometries of the intrinsic electron trap coordinated to NO and NH\textsubscript{x} (x=1,2). The Si-N bond length is 1.5 Å, with negligible variations. There is a slight contraction in the Si-O bond lengths from 1.8 Å an average of 1.78 Å with slight variations depending on the structure local to the trapping site. 114

6.4 The change in 0/-1 charge transition level before (blue) and after (Red) the addition of NO. The geometry of the O vacancy coordinated to NO is also shown. Colour coding Si-yellow, O-Red, N-blue. 116

6.5 Distribution of CTLs for each of the different geometries found for the NO coordinated to the O vacancy. a) shows a geometry where there is little change, on relaxation, from the neutral charge state, b) shows a geometry where the O atom of the NO molecule coordinates to a neighbouring, network Si atom and forms a pseudo-five-coordinated Si site and c) shows a geometry where there is an attractive interaction between one of the vacancy Si atoms. Finally, d) is the distribution for 0/- CTLs from Fig. 6.4 but split according to the different geometries. Colour coding same as Fig. 6.4. 117

6.6 Distribution of CTLs for the Hydroxyl E'-centre (blue) and its variant with NO coordinated to the dangling Si bond. The atomic configuration on the right of this figure shows the N atom of the NO molecule coordinated to the dangling network Si atom, this is the neutral charge state. The purple in the histogram denotes the overlap between the nitridated and un-nitridated variants. Colour coding same as Fig. 6.4 with H in white. 119
6.7 Gate current density as a function of the stress time for differently annealed trench MOSFET, stressed and measured at room temperature. The absolute stress bias is given in the legend and correlates with a constant \( V_{th} \) overdrive for each sample, in this case 5 MV cm\(^{-1}\) + (\( V_{th} \) of aneal under question - \( V_{th} \) of NO annealed device)/\( t_{ox} \) with the oxide thickness. The more NO was available during the anneal, the lower the leakage current is. Graph copied from [6].

7.1 The atomic structure of the Bilayer post geometry optimisation. Colour coding Si yellow, O red, H white and C in blue.

7.2 The atomic structure and projected density of stated for the interface structure. Colour coding same as Fig. 7.1.

7.3 The bond length distributions for the bulk (a) and interface (b) oxide.

7.4 The full bond angle distribution for bulk (orange bars) and interface (blue bars) systems.

7.5 The Si-Si distance as a function of the formation energy of the oxygen vacancy. This graph shows that there is still a positive correlation between Si-Si distance and the formation energy of the O vacancy.

7.6 The Si-Si relaxation distance as a function of distance to the interface. This shows that there is less relaxation of the Si-Si distance as the interface is approached.

7.7 The position of NO interstitials in the interface structures and their incorporation energies. Colour coding same as Fig. 7.1 with N in blue.

7.8 The NO interstitial in the SiC portion of the interface structures. Colour coding same as Fig. 7.1 with N in blue.

7.9 The NO interstitial in bulk 4H-SiC. Colour coding same as Fig. 7.1 with N in blue.
7.10 This is a top-down view of the a-face of SiC. It shows the surface relaxations of the a-face of 4H-SiC after geometry optimisation showing the formation of C-C clusters whose bond lengths are akin to the C-C double bond in organic chemistry. Colour coding Si-yellow and C-blue. 

A.1 The O-Si-O bond angle distribution for the 30 cells used in this thesis 147
A.2 The Si-O bond length distribution for the 30 cells used in this thesis 147
A.3 The cage volume distribution for the 30 cells used in this thesis . . . 148
A.4 The ring size distribution for the 30 cells used in this thesis . . . . 148
List of Tables

5.1 The barriers of ingress into SiO$_2$ for each of the NH$_3$ fragments. . . 98
# Contents

1 Introduction 21

2 Summary of previous work done on characterising SiC and SiO$_2$ 25
   2.1 Introduction .................................................. 25
   2.2 SiC devices used for experimental studies parallel to this work . 26
   2.3 Challenges of SiC technology ................................. 28
   2.4 Structure of SiC and SiO$_2$ .................................. 30
       2.4.1 The structure of SiC and its faces ..................... 30
       2.4.2 The structure of SiO$_2$ ................................. 32
   2.5 Defects in SiC and SiO$_2$ .................................... 35
       2.5.1 Intrinsic Defects in SiO$_2$ ............................ 37
       2.5.2 Extrinsic Defects in a-SiO$_2$ ......................... 42
       2.5.3 Defects in SiC ............................................ 46
   2.6 Post-oxidation anneals ....................................... 47
   2.7 Building the SiC/SiO$_2$ interface .......................... 52
   2.8 Concluding Remarks .......................................... 54

3 Methodology 55
   3.1 Introduction ................................................... 55
   3.2 Implementation of DFT in CP2K ............................... 57
       3.2.1 Gaussian Plane-wave method ............................ 57
       3.2.2 Pseudopotentials ....................................... 59
       3.2.3 Calculating the Energy ................................ 60
3.2.4 Exchange and correlation functionals ....................... 61
3.2.5 Self interaction error and hybrid functionals ................ 63
3.2.6 Auxiliary density matrix method .......................... 64
3.3 Auxiliary methods employed in CP2K .......................... 65
  3.3.1 Nudged Elastic Band (NEB) method ...................... 65
  3.3.2 Defect formation energy ................................ 67
3.4 Molecular Dynamics ............................................. 71
  3.4.1 Classical Potential Energy Functions ...................... 71
  3.4.2 Integration of Newton’s Law .............................. 72
  3.4.3 NVT Ensemble ........................................... 73
3.5 Concluding remarks ............................................. 73

4  Modelling the interactions and diffusion of NO in a-SiO₂ ........ 74
  4.1 Introduction ..................................................... 74
  4.2 Methodology ................................................... 75
  4.3 Results and Discussion ....................................... 79
    4.3.1 Interstitial NO configurations .......................... 79
    4.3.2 Migration of NO in a-SiO₂ ............................... 88
  4.4 Conclusion .................................................... 91

5  Modelling the interactions of NH₃ with crystalline and amorphous SiO₂ 92
  5.1 Introduction ................................................... 92
  5.2 Methods ....................................................... 94
  5.3 Results and discussion ...................................... 95
    5.3.1 Interactions of NH₃ with the surface of crystalline SiO₂ .. 95
    5.3.2 Interactions of NH₃ with the surface of a-SiO₂ ............ 99
    5.3.3 Calculations in the bulk of a-SiO₂ ........................ 101
  5.4 Conclusions ................................................... 106

6  Modelling the interactions of NO and NH₃ fragments with common oxide defects 108
  6.1 Introduction ................................................... 108
6.2 Method ................................................. 109
6.3 Results .................................................. 110
   6.3.1 The Intrinsic Electron Trap and bi-electron trap ............. 111
   6.3.2 Hydroxyl E′-centre ................................ 111
6.4 Oxide Defects coordinated to N containing compounds and fragments 113
   6.4.1 Intrinsic electron trap ................................ 113
   6.4.2 O vacancy .......................................... 115
   6.4.3 Hydroxyl E′ centre .................................. 118
6.5 Comparing theoretical results with experimental leakage current data 120
6.6 Conclusions ............................................. 124

7 Modelling the SiC/a-SiO$_2$ interface and the surface of the a-face of 4H-
SiC  ......................................................... 126
   7.1 Introduction ........................................... 126
   7.2 Method ................................................ 127
   7.3 Results and Discussion ................................ 130
      7.3.1 Structural differences between the bulk oxide and near in-
           terface oxide ........................................ 130
      7.3.2 Effects of the O vacancy and NO interstitial .............. 133
      7.3.3 Relaxations of the a-face of 4H-SiC ...................... 137
   7.4 Conclusions ........................................... 139

8 Summary and Future work ........................................... 141
   8.1 Summary ............................................... 141
   8.2 Learning outcomes ..................................... 143
   8.3 Future Work .......................................... 144

A Structural parameters of bulk a-SiO$_2$ models and raw data for NO +
Oxygen vacancy ........................................... 146
List of Publications


Chapter 1

Introduction

This thesis presents the results of a study of defects that reside at the interface between SiC and amorphous (a-) SiO$_2$. These defects are thought to be responsible for the reliability issues of SiC-based metal oxide field effect transistors (MOSFETs). This work has been done in collaboration with Dr. Gregor Pobegen and Dr. Judith Berens at Kompetenzzentrum Automobil- und Industrielektronik GmbH (KAI), which is a research subsidiary of Infineon Technologies Austria, one of the main manufacturers of SiC semiconductors. The main research question of this PhD is how one can model defects that persist at the interface between SiC and SiO$_2$ in real devices and to provide an insight into the state of these defects after an anneal with nitrogen containing molecules. The experimental characterisation of these devices by KAI and Infineon has provided vital knowledge and motivation during the course of this PhD.

The work presented here is performed theoretically, using density functional theory (DFT) and classical molecular dynamics (MD) to model the interplay between defects and passivation agents, defect levels and structural factors. Fig. 1.1 is a schematic of the content chapters of this thesis. The first two chapters of the thesis provide an overview of the relevant literature and methods used in this work, Chapter 2 provides a review of the SiC structure along with those of crystalline and amorphous SiO$_2$. Next, there is a discussion about the experimental and theoretical characterisation of defects in a-SiO$_2$ and SiC, with more emphasis put on oxide defects than SiC defects as they are the ones under study later in the thesis. Following
on from this the different post-oxidation anneals used for SiC devices is discussed with an in-depth analysis of the chemistry of the oxide and near interface regime. The final topic discussed in this chapter is the interface between SiC/a-SiO$_2$ where emphasis is placed on the electronic structure and geometry of previous models made of the interface and the techniques that are carried over to the work in an interface structure, later in this thesis. Chapter 3 summarises the main computational methods and techniques used to perform the calculations described in the thesis.

The first two results chapters show how the two main annealing agents probed in this work, NO and NH$_3$, interact with a pristine cell of SiO$_2$ in crystalline and amorphous phases. These chapters are important due to the lack of literature on this topic. We demonstrate the importance of studying the interaction of these small molecules with a pristine lattice for understanding the atomistic/network and electronic nature of these devices. Secondly, it is understood that the oxides used by Infineon are of a very high quality and during the anneal the annealing agents will have to traverse the oxide to reach the defects in the near interface region. Due to the high quality of these oxides, the majority of environments the annealing agents will see are akin to these pristine systems.

The main results for the NO anneal show that there is a steric repulsive interaction between the network and the NO molecule leading to it relaxing into large cage-like structures in a-SiO$_2$. In each of these cages there are a range of different energies which depend on the orientation of the long axes of both the molecule and the cage in question, as the incorporation energy is lower if they are aligned. In the negative charge state, the NO molecule resides much closer to the network compared to the neutral charge state. This is a consequence of the electrostatic interaction between the N atom of the NO molecule and a network Si atom. This extra electrostatic interaction leads to an increase in migration barriers in the negative charge state by an average of 0.2 eV compared to the neutral charge state.

The static calculations of the interaction of the NH$_3$ molecule with a fully hydroxylated SiO$_2$ surface show that there is an orientational dependence upon physisorption. If the N atom of the NH$_3$ is pointed towards the surface, then the
majority interaction is a H-bonding type interaction with a surface silanol group. If the N atom is facing away from the surface, the interaction is repulsive and the NH$_3$ sits above the SiO$_2$ surface with the system energy \( \approx 0.5 \) eV higher. Upon heating to 1500 K using classical MD, corresponding to the experimental anneal temperature, the surface looses most of adsorbed water and hydrogen passivating silanol groups. The resulting interaction of NH$_3$ with the surface leads to it loosing one or two of its H atoms. Smaller NH molecules penetrate inside the a-SiO$_2$ network, as predicted by the XPS measurements [1]. In spite of the high penetration barriers into the crystalline oxide (2.39 eV), there is a migration of the NH$_3$ into the a-SiO$_2$ surface due to the presence of larger rings in the amorphous phase.

The bulk of a-SiO$_2$ was then sampled with the NH fragment. This shows that, in the singlet state, there is nitridation of the pristine network which takes the form of a defect named the nitroxy bridge. The nitroxy bridge is an important defect as it has charge transition levels (CTLs) to more positive and negative charge states near to the valence band (VB) and conduction band (CB) of SiC, respectively.

Figure 1.1: A schematic of the work presented in this thesis and how each chapter is related to the other.

In Chapter 6 I pool the knowledge gained from the first two chapters and examine the interaction of NO and NH$_x$ \((x=1-3)\) with defects in a-SiO$_2$ networks. We probe intrinsic and, H containing, extrinsic defects in bulk a-SiO$_2$. Initially, we scrutinise the defects in isolation and build distributions for their formation energies and pertinent CTLs. These defects are then coordinated with NO, NH, NH$_2$
and NH$_3$ in-order to understand the change in 0/- CTLs on nitridation. While a vast amount of work has been done on point defects in a-SiO$_2$, the specific nitridation of these defects has not been studied and the change in the distribution of CTLs on nitridation has not been discussed. When NO is coordinated to them, the 0/- CTL generally moves deeper into the band gap of a-SiO$_2$ hence moving it away from the CB of SiC and decreasing the probability of electron tunnelling to these defect states.

Finally, in Chapter 7 all the information gained from the previous three chapters is brought to a SiC/a-SiO$_2$ interface structure, to investigate how the defects behave at the SiC/a-SiO$_2$ interface. This chapter shows that the SiC increases the strain in the oxide. This is exemplified by the near-interface oxide structures having a greater number of shorter Si-O bonds, narrower bond angles and the Si-Si relaxation distance decreases as the interface is approached. Finally, this chapter presents the results of the a-face surface of 4H-SiC and shows that there is the formation of C-C bonds on the surface causing the large energy reduction between the relaxed and unrelaxed surfaces.
Chapter 2

Summary of previous work done on characterising SiC and SiO₂

2.1 Introduction

Silicon Carbide (SiC) is used as a wide band gap semiconductor which has great potential for high power and frequency applications in electrical devices which are derived from its many favourable properties like; wide band gap, high thermal conductivity, high breakdown field, high saturated drift velocity and thermal and chemical durability [2].

Despite this great potential, SiC based technologies require some development before their full potential can be realised. The devices suffer from poor channel mobilities and premature breakdown which result from the large defect density in the device [3, 4]. The defects that most greatly contribute to these detrimental processes, are those near the interface between SiC and its gate oxide amorphous Silicon Dioxide (a-SiO₂) [5]. If we compare this to Si/a-SiO₂ interface, we see that there is an order of magnitude increase in the density of near interface defects for SiC devices [2]. A greater understanding of the structure and geometry of the materials and their defects could lead to strategies to mitigate or passivate the defects.
2.2 **SiC devices used for experimental studies parallel to this work**

In SiC technologies, different device concepts have been conceived for the metal oxide semiconductor field effect transistor (MOSFET) [2]. The device concepts differ by where the conducting channel forms (i.e. which crystal plane the channel runs parallel too) [2]. The choice of crystal plane allows for control of channel mobilities and different interface properties. Commercially available SiC wafers provide the [0001] or Si face and the [000\(\overline{1}\)] or C face. The simplest device format is the planar MOSFET (Fig. 2.1a) where the conduction channel forms along the Si or C face of SiC depending on the surface onto which the gate oxide (a-SiO\(_2\)) is deposited. These devices are the most affordable as they have a simple device structure and no etching step is required, so time and energy is saved on fabrication [6].

In recent years the vertical trench MOSFET (Fig. 2.1b) has been developed which allows for the conduction channel to form over different crystal planes, namely the Si-face and the [11\(\overline{2}0\)] or a-face the latter of which offers higher channel mobilities [7]. These trench devices also have the benefit of higher channel densities per area meaning that the conducting channel can be formed far easier in these devices than their planar counter-parts hence offering superior device performance. However, the corners of trench devices suffer from gate reliability issues due to the high electric fields. This is remedied by the use of p-implantation in these regions which shields from these high electric fields.

The experimental work done in parallel to the work presented in this thesis is performed using Infineon AG trench devices. They begin as the commercially available Si-face wafers into which a trench is dug using an HF etch. Then a-SiO\(_2\) is grown in this trench via chemical vapour deposition of tetraethylorthosilicate (Si(OC\(_2\)H\(_5\))\(_4\)). After this a post oxidation annealing process in either NO, NH\(_3\), a combination of the two or N\(_2\) is performed depending on the process under examination (see chapters 4, 5 and 6 for work linked to this) these are done to reduce the near-interface defect density.
Figure 2.1: Schematic of the operation of planar (a) and trench (b) MOSFET configurations. The green section is the a-SiO$_2$ and the blue sections and the red sections are SiC the colours denote their doping (blue is n-doped and red is p-doped) and the shading is to differentiate the section of SiC in-which they reside, the areas without subscripts are areas near the electrode contact region, n$_{epi}$ is the epitaxial region of SiC and n$_{sub}$ are region deep in SiC, the white arrows in each case show where the conducting channels form.
2.3 Challenges of SiC technology

SiC is a new material in the power electronics community, relative to Si. It still suffers from a high concentration of defects [2], particularly at the interface between SiC and a-SiO$_2$ [3], making the production of reliable devices a non-trivial matter. Since the conception of SiC devices, growth defects, e.g., micropipes, vacancies, carbon impurities and stacking faults have been mitigated by advances in the growth techniques [8]. A high defect density leads SiC devices to suffer from low gate reliability (i.e., gate oxides do not function for as long as those in Si technologies), an increase in channel and gate leakage (i.e., electrons leak out of the channel either to defects or into the oxide), instabilities in the threshold gate voltage and decrease in breakdown voltage which is the minimum voltage required to make part of an insulator conducting [9].

One of the main factors exacerbating these effects is the quality of the SiC/a-SiO$_2$ interface [10]. This takes the form of decreasing interface roughness as this leads to a rough conducting channel leading to inefficient charge conduction, decreasing the concentration of trapping sites both in the SiC and a-SiO$_2$ [11]. These trapping sites will be discussed later in this section but they can take the form of acceptor states, donor states or amphoteric states, depending on the position of the level and the barrier for charge trapping [10].

The reliability concerns in SiC devices take three main forms [9]: inversion channel mobility [12], sub-threshold hysteresis [13], and bias temperature instability (BTI) [14]. Inversion channel mobility is strongly correlated to the quality of the interface [12]. Scattering processes at surface acceptor states, Coulomb scattering at fixed charges or charged interface states, interface roughness, and bulk scattering all lead to a decrease in channel mobility of these devices below the theoretical maximum of SiC [12]. Sub-threshold hysteresis manifests as a reversible increase in the threshold voltage ($V_{th}$), which is the minimum gate voltage required to form the conducting channel [13]. It has been shown to manifest in current-voltage (IV) sweep experiments as electron and hole trapping centres are charges in up and down sweeps of the band gap, respectively [15]. As the voltage (and so the Fermi level) is
2.3. Challenges of SiC technology

swept up and down the band gap of the material these IV experiments and \( V_{th} \) shift allows us to have a direct correlation between defect state concentration and defect levels [15].

Sub-threshold hysteresis shows us that charge trapping can cause shifts in the \( V_{th} \), luckily those shifts are reversible unlike those caused during BTI processes [13]. BTI is a reliability concern in power semiconductor devices which is caused due to trapped charge at the SiC/a-SiO\(_2\) interface, which then causes a permanent shift in \( V_{th} \). BTI can be observed under positive and negative gate bias, PBTI and NBTI [14], respectively, and leads to an increase in the on-resistance of the device at fixed gate biases. There is no cohesive picture of the mechanisms that cause BTI behaviour [16, 17], but it can be agreed that the process is due to the charging of defects at substrate/gate dielectric interfaces [17]. The candidates for BTI are discussed in section 2.5 and their nitridation and subsequent movement of levels are discussed in chapter 6.

![Figure 2.2: A schematic of trap assisted tunnelling in SiC/a-SiO\(_2\) devices. This schematic focuses on electron trapping states that are present in the oxide and whose levels sit close to the CB of SiC.](image)

TAT is the tunnelling of electrons or holes from one defect (or trapping centre) to another, leading to a current flowing (see Fig. 2.2) [18]. In SiC devices, this requires CTLs that are close to the band edges of SiC to reduce the barrier for electron or hole transfer from oxide defects to the SiC, the semiconducting body [18]. We require transitions to more positive charge states to occur near the VB and
transitions to more negative charge states to occur near the conduction band of SiC, for hole and electron traps, respectively [19]. As the devices we are looking at have specific problems with electron trapping, the work presented here will focus mainly on transitions to more negative charge states [18]. Fig. 2.2 shows a schematic of the the TAT mechanism. There are defects present in the SiO$_2$, on application of bias electrons can tunnel through these defects to the top electrode of the device hence decreasing the resistance of the gate oxide and diminishing its purpose. Experimental techniques, such as DLTS, show which levels are present in the band gap of SiC, before and after anneal [19]. Afanas’ev et al. [20] shown that there is a drastic decrease (99%) in the density of traps in the near interface region after an anneal in NO [20].

All of the challenges discussed in this section have the large defect concentration at the SiC/a-SiO$_2$ interface in common [20]. If there was no or a low concentration of defects, then the interface region would have the theoretical channel mobility boasted by SiC and there would be no defects to charge in the band gap of the materials, hence there would be no shifts in $V_{th}$ due to sub-threshold hysteresis or BTI. The work in this thesis looks at these defects and links them to the reliability issues mentioned and finds or explains strategies to mitigate them.

2.4 Structure of SiC and SiO$_2$

2.4.1 The structure of SiC and its faces

SiC is built up of SiC$_4$ (or C$_4$Si$_4$) tetrahedra with both Si and C being 4 coordinated. The material has mostly covalent character, with the Si and C being bonded by sp$^3$ hybridised bonds. There is a partial negative charge that sits on the C as it has a greater electronegativity and would be the anionic species if we look at the ionic picture. When SiC is built up, the tetrahedra stack in different sequences, this stacking order determines the poly-type of SiC (Fig. 2.3). Each of the different poly-types of SiC have different band gaps, which increase with increasing structure hexagonality. Devices are fabricated by forming single crystals of SiC. Then one deposits SiC’s native oxide, SiO$_2$, on top as a gate oxide [2].
2.4. Structure of SiC and SiO\textsubscript{2}

Figure 2.3: A 2D schematic of the structure of three common SiC polytypes and their band gaps. A, B, and C are the repeating units shown both horizontally and vertically next to each polytype. The band gaps of each of the polytypes is given under each of the images. The h and k represent the two unique sites for the Si and C atoms [2].

The gate oxide can be deposited or grown on the different faces of SiC (Fig. 2.4) depending on the device in question. The two main faces of interest are the Si-face and the a-face [15, 2]. These can be seen in Figs. 2.4 a and b, respectively. Both of these have different uses and channel mobilities. The Si-face is pertinent to the planar MOSFET devices and it has a channel mobility of 40 cm\textsuperscript{2}/V\textsuperscript{-2}. This is the most widely used face of SiC in devices as it is commercially available in wafer form. Trench FETs use a combination of the a-face and the Si-face. The a-face has a channel mobility of 118 cm\textsuperscript{2}/V\textsuperscript{-2} [15].

As shown in Fig. 2.4, the faces differ by the terminations of the surface. The Si-face has all Si terminations and the a-face has alternating Si and C terminations. An additional difference is in the topology of each of the surfaces. The Si face is flat while the a-face is not. This is important when building models of the interface on each of these faces. For the Si-face this has been done by Devynck \textit{et al.}[21] who has tessellated SiO\textsubscript{4} tetrahedra on the Si surface until the full coverage. Then a
2.4. Structure of SiC and SiO$_2$

Figure 2.4: A side view of the Si-face (a) and the a-face (b) along with their specific crystallographic directions (surfaces are those without H saturators). The Si-face is terminated by Si atoms and the a-face has alternating Si and C terminations and so is sometimes referred to as the stoicheometric face.

A second layer is built on top of this, forming a bi-layer. This is the method employed in this work to build the Si face interfaces in chapter 7, there is a more in-depth discussion of the methodology in chapter 7.

### 2.4.2 The structure of SiO$_2$

Like SiC, SiO$_2$ is also a covalent structure. It consists of sp$^3$ hybridised four co-ordinated Si atoms and 2 coordinated O atoms. There is a negative polarisation on the O atoms owing to their higher electronegativity. The result of this is Si being a cation-like species and the O being an anion-like, if the ionic picture is taken into account.

The Si and O atoms then come together to form corner sharing SiO$_4$ tetrahedra in the amorphous and crystalline phases. If we look at Fig. 2.5, we see that in the crystalline phase (Fig. 2.5a, $\alpha$-Quartz in this case) the tetrahedra are uniformly distributed throughout the sample. Whereas in the amorphous phase (Fig. 2.5b) the same building block is randomly distributed throughout the sample. This random
distribution of tetrahedra is characterised by a wide distribution of bond angles and bond lengths (Fig. 2.6) which give a range of different environments in the system.

**Figure 2.5:** Samples of α-quartz (a) and a-SiO$_2$ (b) structures. Both structures are made of SiO$_4$ units but in the quartz sample atoms form a regular crystalline structure and in the amorphous sample they are randomly distributed. The regular distribution leads to clear channels forming in the crystalline sample, a feature which is not present in the amorphous sample.
2.4. Structure of SiC and SiO$_2$

Figure 2.6: Distribution of structural properties in 20 models of 216 atom cells of a-SiO$_2$ optimised using DFT. (a) Shows a histogram of the Si-O bond lengths, (b) shows a histogram the O-Si-O bond angles, and (c) shows a histogram of the Si-O-Si bond angles [22].

In this thesis, a lot of emphasis will be put on the different local environments or micro-structures and the structural properties that form them in a-SiO$_2$. For example, the ring is defined as a closed micro-structure made up of different numbers of Si-O units [23]. The rings are the micro-structure that can be differentiated, not only by the number of Si-O units it contains, but also by the bond lengths and angles that make it up. These micro-structures are of vital importance to the formation of defects. The characteristic example here is the intrinsic electron trap defect. These are extra electrons trapped at structural precursor sites in a-SiO$_2$ network. These precursor sites are characterised by wide O-Si-O bond angles greater than 132$^\circ$, which are at the very tail of the angle distribution in Fig. 2.6b [22]. The intrinsic electron trap can then trap a second electron, which is an initial step in generating neutral oxygen vacancies and interstitial O ions [24]. The next section details the different oxide and carbide defects that have been shown to contribute to reliability issues in devices that use a-SiO$_2$ as the gate oxide. The structural parameters of the thirty 216-atom a-SiO$_2$ cells used in this thesis can be found in Appendix A.
2.5 Defects in SiC and SiO$_2$

This section details the defects that are thought to play a part in SiC device reliability issues (section 2.3). We mainly focus on defects in a-SiO$_2$ which can contribute to the oxide charging and leakage current through the oxide. These effects take place when electrons from the bottom of the conduction band (CBM) of SiC channel can tunnel into defects inside the SiO$_2$ film which requires the defects to have CTLs near the CBM. Further defects can be created as a consequence of charge trapping, which can lead to the oxide degradation and device failure. A schematic of the defect CTLs described in this section, relative to the experimentally verified band offset of SiC [21], is shown in Fig. 2.7. Si and C interstitials have also been shown to form in these devices but they were beyond the scope of the work presented in this thesis so are not described in this section, though the author acknowledges them.

![Schematic representation of the CTLs of all the oxide defects discussed in this section including the experimentally verified band offset of the SiC/a-SiO$_2$ device [2, 21].](image)

Electron trapping and tunnelling is a major detrimental factor in the n-channel devices, as such many of the challenges faced in developing SiC technologies (section 2.3) are thought to be because of such processes [25] (*i.e.* the $V_{th}$ shift which is a symptom of BTI is thought to be a consequence of trapped charge [26]).
2.5. Defects in SiC and SiO₂

exact atomic level nature of where these charges are trapped is unknown and so are
generally categorised as interface states (fast states) and border states (fixed oxide
charge), hence by their position within the oxide and how quickly charge can trap
and de-trap at these sites [25, 27, 28].

In Si/a-SiO₂ devices the interface, or fast, states are attributed to P₀ or P₁
defects which are three coordinated Si sites at the interface [25]. In SiC technolo-
gies these are analogous P₀ centre which are three coordinated C atoms at the
SiC/a-SiO₂ interface [29, 30, 31] which have been detected with electrically de-
tected magnetic resonance (EDMR) measurements. The impact of these defects is
thought to minimal due to their easy passivation by H atoms [32].

Border traps are of greater significance to the work presented here as they
are defects that can form the tunnelling pathways in TAT [25]. These sites are
thought to trap and de-trap electrons slower than fast interface traps [25]. One
explanation for the slower charge trap-de-trap behaviour is that electron tunnelling
probability decays exponentially with distance. Hence, these traps charge at slower
rates (compared to interface traps) simply due to an increased distance from the
channel [25]. Border traps are often associated with O vacancies (E’ centres from
optical experiment lexicon [33]) [25, 34, 35] but have also been associated with
hydrogenic centres [25, 36, 37]. These border states are thought to be the main
cause of random telegraph noise [38], which is a phenomenon in MOSFET devices
where the drain current experiences discrete fluctuations or switching events as a
function of time [39]. The main reason these border traps are more important than
interface traps to this thesis is because they are thought to cause detrimental changes
in the Vₜₘ which is a symptom of the BTI behaviours explained in section 2.3.

Based on this understanding and previous theoretical calculations [40, 22, 41,
24, 42], the defects chosen for study in this thesis are; the intrinsic electron trap,
the O vacancy and the Hydroxyl E’ centre. The H bridge defect is not included in
the study in chapter 6, as it requires H atoms to interact with O vacancies though is
included in the review for completeness. The reason for their exclusion is because,
in NO annealed devices, the concentration of H atoms is thought to be very low
2.5. Defects in SiC and SiO$_2$

(at-least below the detection limit of hard X-ray photoelectron spectroscopy [43]) and so the interaction between the two is thought to be minimal. The Hydroxyl E' centre is included because there are thought to be more long Si-O bonds present in the system than O vacancies, and if there are a small number of H atoms present in the system the probability of H interaction with a long Si-O bond is much higher than its interaction with an O vacancy (see appendix A for structural parameters of the a-SiO$_2$ cells used in this system and experimental structure distributions can be found in [44]).

2.5.1 Intrinsic Defects in SiO$_2$

For devices that use a-SiO$_2$ as a gate oxide studies about charge trapping have, in the past, been mainly linked to impurities in the network that cause these effects [45, 20, 4, 46]. There remained the question of the electron trapping ability of the pure a-SiO$_2$ network. This is particularly important to the work of this thesis for two reasons. First, apart from N-related defects detected in devices after the post oxidation anneal no other impurities have been detected because, in NO annealed devices, they are at concentrations below the detection limit, not only, of XPS and SIMS measurements[1, 47], but even if one considers hard X-ray photo-electron spectroscopy [43]. In NH$_3$ annealed devices there is a higher concentration of H, this is because the NH$_3$ molecule has three H atoms and is shown to react with the network [43, 48]. Secondly, due to the process used to grow the oxide (discussed in section 2.3), the region greater than 2 nm from the SiC/a-SiO$_2$ interface is thought to have a very low concentration of defects [49]. For these reasons the first defect discussed, the intrinsic electron trap, could be a key defect in the SiC devices discussed in section 2.2.

The work of El-Sayed et al. [22] has initially been inspired by the unexplained electron trapping level observed in device grade oxides 2.8 eV below the CB of a-SiO$_2$ (or 0.2 eV above the CB of SiC). These traps were initially seen in oxidised Si and SiC crystals by photon-simulated tunnelling experiments [20]. The low temperature capacitance [20] and Hall effect measurements [50, 51] of 4H-SiC MOS devices elucidated a density of electron trapping sites of up to $10^{14}$cm$^{-2}$eV$^{-1}$.
with a measured trap density of $10^{13}\text{cm}^{-2}$ in a 2 nm thick near interface SiO$_2$ which is around $5 \times 10^{19}\text{cm}^{-3}$ in terms of volume, which is higher than any density for any oxide defect. One of the important factors described in refs. [1, 5] to justify their assumption of electron trapping occurring in the near interface regime is the affinity for N in this region of the oxide, a further reason why the intrinsic electron trap is an important defect to the work presented here.

Molecular models, specifically a F$_3$Si-O-SiF$_3$ cluster have been used to model two SiO$_4$ tetrahedra [52] in an effort to elucidate the electron trapping ability of the a-SiO$_2$ network [52]. They added an electron to this molecular system and showed that electrons could be trapped at four coordinated Si sites which weakened Si-O bonds by localising the electron in an O p-state [52]. They then measured the O-Si-O bond angle where the electron localises showing it widened to 144°[52].

In the solid state phase, 72-atom cells of a-SiO$_2$ were used to show that electrons could be trapped in non-defective continuum random networks [53]. In this study a set of 72-atom a-SiO$_2$ cells were made using a molecular dynamics melt and quench. These structures were then optimised using a generalised gradient approximation (GGA) functional. This did not show spontaneous localisation of charge, potentially due to the self interaction error associated with GGA functionals (see chapter 3) but did show a metastable configuration with Si-O bond elongating to 1.83 Å with an expansion of the O-Si-O bond angle to 156.44°. This study also looked at the barrier to the metastable state. They found that the barrier from the delocalised state to this metastable state was 0.23 eV with the localised state being 0.17 eV higher in energy than the delocalised state.

Finally, El-Sayed et al. [40] studied the electron localisation in a pristine models of SiO$_2$ in the crystalline and amorphous phases [40]. This study shows that the intrinsic electron trap occurs when an electron is injected into the a-SiO$_2$ network and it localises at a Si which has a bond angle and a Si–O bond length at the tail of the distribution in Fig. 2.6a and 2.6b. The precursor to form such a site is a O-Si-O angle greater than 132°. Once the electron has localised, the O-Si-O bond widens to around 172° and the Si-O bonds elongate from around 1.63 Å to 1.77 Å
(Fig. 2.8).

**Figure 2.8:** The atomic structure and spin density of the intrinsic electron trap in a-SiO\(_2\). The SiO\(_4\) tetrahedra on which the electron traps has been highlighted [40]

To find the concentration of precursor sites, the structures of the three samples with 401 760, 55 296 and 8 640 atoms were analysed [22]. These samples were made via the melt-quench procedure using inter-atomic potentials, which have been used to study the structural parameters of a-SiO\(_2\) [54]. The concentration of precursor sites was found to be around 4 \(\times\) 10\(^{19}\) cm\(^{-3}\) in the larger models, agreeing well with the number of 216-atom cells that trapped electrons (4 out of 20).

The intrinsic electron trap is part of the first step in the mechanism to form oxygen vacancies in a-SiO\(_2\) proposed in ref. [24]. A diagrammatic representation of this mechanism can be found in Fig. 2.9. The mechanism starts by trapping a second electron at a wide bond angle. This increases the Si-O bond lengths to 1.81 Å and 2.26 Å, this increase can be linked to a decrease in bond order, which occurs due to filling of anti-bonding orbitals. The longer of these two bonds then cleaves to form the intermediate in Fig. 2.9c. The remaining Si-O bond breaks forming an O vacancy and interstitial O\(^{2-}\) ion.

The oxygen vacancy (Fig. 2.10) is another very important defect for systems that use a-SiO\(_2\). The history of it can be traced back to 1956 [55] where electron paramagnetic resonance (EPR) measurements were carried out on radiation induced
2.5. Defects in SiC and SiO$_2$

Figure 2.9: A mechanism to form O vacancies [24]. A) the initial trapping of a second electron, B the subsequent breakage of the Si-O bond leading to the pseudo-five-coordinated Si, C the coordination and facilitation of the formation of the O$^{2-}$ interstitial and D the formation of the Si-Si interaction.

Defects in crystalline and amorphous SiO$_2$, showing distinct resonances in these samples [55, 33]. Later in 1960, these EPR studies were correlated to optical spectra labelling the defects E$_n^\prime$, where the n is the signal label and the prime and double prime et cetera, being used to indicate the number of electrons involved [56, 57]. From the two studies it was suggested that the main defect responsible for these signals was the O vacancy [56, 57].

In 1961 [58], a further detailed analysis of the E$^\prime$ EPR signal found that it originated at an unpaired Si electron (i.e. a Si dangling bond) hence concluding that the signal came from an O vacancy [58], though noting that the signal could not be from a "normal" O vacancy as the 2 unpaired electrons on the three coordinated Si atoms neighbouring the O vacancy would pair up [58]. Hence the defect would become diamagnetic and be invisible to EPR, though the work offers no alternative defect [58, 33]. A 1974 study [59] proposed an asymmetric relaxation of the two Si atoms of the O vacancy, with one of them keeping a pyramidal geometry and the other relaxing through the plane of its three O atoms and coordinating to a nearby network O atom, which was unrelated to the O vacancy at this point [59]. This was supported by small cluster cluster calculations of SiO$_2$ [59, 33]. Much later in 1987 [60], semi-emperical calculations of large SiO$_2$ clusters proposed that in the neutral charge state the Si atoms of the O vacancy would relax (or "rebound") [60] to form a Si-Si dimer and in the positive charge state there would be the asymmetric relaxation mentioned above.
2.5. Defects in SiC and SiO$_2$

**Figure 2.10:** An O vacancy in a-SiO$_2$. The atoms in the foreground are those that make up the O vacancy and the atoms in the background make up the rest of the a-SiO$_2$ network. The network is built-up of SiO$_4$ tetrahedra and to form the O vacancy one of these atoms has to be removed leaving two 3-coordinated Si atoms, one of O atoms for the Si on the right hand side of the image is obscured by the Si atom. Colour coding: O Red and Si yellow.

In the late 1980s it was possible to identify two distinct centres, namely the E$'_{\gamma}$ and the E$'_{\delta}$ [61], the former being the E$'_{1}$ defect from ref. [55] formed by asymmetric relaxation of the dangling Si atom and the latter being 2 neighbouring O vacancies hence 4 dangling Si bonds around a centre [62, 63]. The matter of E$'_{\gamma}$ versus E$'_{\delta}$ was seemingly de-convoluted by first principle density functional calculations in 1990 [64] and 1997 [65] with the signal for the E$'_{\gamma}$ being attributed to O vacancies in the crystalline phase and signals for the E$'_{\delta}$ being attributed to the amorphous phase [33]. These calculations also further conclude that the O vacancy preferentially formed the Si-Si dimer configuration in the neutral charge state and the asymmetrically relaxed geometry in the positive charge state [64, 65]. In 2002, further calculation of the E$'$ centre was done to probe the topological dependence of the geometry of the O vacancy. It found a geometry similar to the asymmetrically relaxed O vacancy though the Si atom that strongly relaxes forms an interaction with
2.5. Defects in SiC and SiO$_2$

a network Si atom and a network O atom and becomes 5 coordinated, as opposed to the earlier strongly relaxed Si atom which forms an interaction with a network Si atom [66]. Finally in 2007 the CTLs of the different O vacancies configurations were calculated finding that the dimer formed very shallow levels due to the delocalised nature of the wave-function and the $E'_g$ centre forms very deep levels as the wave-function is very localised [67].

All of this work then feeds into a study from 2009 [68] in which the geometry, electronic structure and spectroscopic properties were predicted for the O vacancy in charge states ranging from +2 to -2, using embedded cluster calculations [68]. This study shows that the O vacancy can be responsible for electron and hole trapping within the band gap of a-SiO$_2$ hence showing that the CTLs given in Fig. 6.6. Earlier in this section, one of the assumptions made about the SiC devices in this thesis is that there is not a high concentration of O vacancies in regions of the oxide greater than 2 nm from the SiC/a-SiO$_2$ interface. However, in the near interface regime, due to the high levels of stress put on the oxide by the SiC, it is thought that O vacancies do manifest as the system tries to decrease this stress [69].

2.5.2 Extrinsic Defects in a-SiO$_2$

The intrinsic electron trap and the O vacancy are two important intrinsic oxide defects, but we must also consider extrinsic defects, which are defects formed by species other than Si or O. A pragmatic approach to understand the defects present in the device is to consider the steps involved in device fabrication. After the SiC is grown, the oxide is deposited or grown on different faces of the SiC crystal (Si-face for planar MOSFETs and a-face and Si-face for trench MOSFETs). In the work presented here, it is assumed that the oxide is deposited by CVD as described in section 2.2. CVD oxides have been shown to form the highest quality oxide films. After CVD the system is heated to 1200°C in the presence of a nitridating atmosphere, in the annealing step [2]. The annealing processes discussed in section 2.6 are done in the presence of ambient gases meaning that moisture and other atmospheric gases are present in the chamber. Water has been shown to break up the network causing H related defects [70]. The main H related defects present in a-SiO$_2$ are the
2.5. Defects in SiC and SiO\(_2\)

Hydroxyl E'-centre and the H-bridge (H\(_B\)).

These hydrogenic centres are thought to be key defects in BTI processes (see section 2.3) as they have CTLs near the band edges of SiC (Fig. 2.7) and so are thought to trap both holes and electrons hence being involved in NBTI and PBTI depending on the device doping. The category of hydrogenic defect that is pertinent to this thesis is those which can be described as border traps, hence can be seen as fixed trap centres. Due to their electron trapping levels residing close to the CBM of SiC (Fig. 2.7) they can also be seen as part of TAT pathways and so they will be discussed in both contexts in chapter 6, with slightly more emphasis being placed on their effect on TAT, as this is the experimental work we have to compare too.

There are a multitude of species present in the atmosphere that are also present in the anneal chamber. The most important species here are water (H\(_2\)O) and H\(_2\) which create the hydrogen related defects mentioned previously [42, 70]. Bakos et al. [70] have investigated the interactions of H\(_2\)O in a-SiO\(_2\). In this system, if an H\(_2\)O molecule is reacted with a ring of less than six Si-O members then it forms two silanol groups with a barrier of 1.5 eV depending on the local environment of the ring [70]. Wimmer et al. [42] investigated the appearance and disappearance of defect related signals, in so-called volatile behaviour, and show that H atoms can disassociate from hydrogenic centres, particularly the Hydroxyl E'-centre [42]. This means that, if H atoms or H related defects are present in the a-SiO\(_2\) network, then they are mobile and may cause further network damage resulting in further defect levels [42].

Forming gas, a mixture of H\(_2\) and N\(_2\), has been used as an annealing agent in Si/SiO\(_2\) as it passivates under coordinated Si atoms by bonding them with H, and removes these levels from the band gap [71]. However, if too a high concentration of H\(_2\) is used it can induce H defects in a-SiO\(_2\) in a similar manner to hydrolytic weakening in quartz [72]. Hydrolytic weakening can be induced by thermally treating a-SiO\(_2\) with H\(_2\). There is a dramatic increase in the EPR signal associated with these H centres and so an increase in defect densities, which have been shown to be predominantly under-coordinated Si atoms in the bulk of a-SiO\(_2\) [71] or at the inter-
2.5. Defects in SiC and SiO\textsubscript{2}

face between it and the semiconductor body. H atoms that come in close proximity to one another recombine to form H\textsubscript{2} molecules as the system gains 4.7 eV from this recombination. All of this means that H alone would not be an efficient annealing agent.

A defect that is a direct result of the forming gas anneal is the H\textsubscript{B} (Fig. 2.11). This defect occurs when a H atom interacts with an O vacancy. On relaxation the H moves towards one of the Si atoms and caps its dangling bond. The shorter Si-H distance averages at 1.47 Å with a range of between 1.44-1.57 Å. The longer Si-H distance averages at 2.21 Å and has a range of 1.74-3.13 Å. The H\textsubscript{B} shows the negative-U behaviour in its CTLs. This is where the charged state of the defect is more thermodynamically stable across some range of Fermi levels than the neutral charge state. In the work done by El-Sayed et al. [41] they show that, out of the 10 H\textsubscript{B} defects computed, 2 of them show this behaviour, with the remaining 8 having their neutral charge state being the most stable across the band gap. This defect has a 0/- CTL 6 eV above the a-SiO\textsubscript{2} valence band (0.2 eV below the SiC conduction band) and a +/0 CTL 3.2 eV above the above the a-SiO\textsubscript{2} valence band (0.5 eV above the VB of SiC).

This work also shows that the binding energy of the H\textsubscript{B} defects is on average of 2.76 eV, but has a range of 4 eV. This broad range is attributed to the reformation of the Si-Si interaction. The binding energy tells us that the H is strongly bound onto the Si atom and so, even under high anneal temperatures, it is unlikely to disassociate [41]. The large range further proves that all processes in a-SiO\textsubscript{2} have a component that is linked to the steric environment that a particular defect is placed in. As there is a positive correlation between the Si-Si distance, post relaxation, and the formation energy of the O vacancy, one can infer that some steric component has caused this large range in disassociation energies [73]. As mentioned earlier, the H anneal can also form new defects, and a defect that is thought to be formed is the Hydroxyl E' centre.
2.5. Defects in SiC and SiO$_2$

Figure 2.11: The H bridge defect. In this defect at H atom is placed in the gap where an oxygen atom presides. As H is only one valent, it makes a strong bond to one of the Si atoms and the other is left uncoordinated. This figure shows the H atom pointing at the three coordinated Si atom and this aids in stabilising the non-bonded electron on the Si atom. Colour coding: Si yellow, O red and H white.

The E$'$-H (Fig. 2.12) is the result of a reaction between a H atom and an lengthened Si-O bond, the reaction barrier being around 0.8 eV in a-SiO$_2$. On relaxation there is a slight interaction between the partially negative O and partially positive Si. The E$'$-H has a 0/- CTL 6 eV and a +/-0 CTL 4.5 eV above the a-SiO$_2$ valence band, placing them isoelectronic to the SiC conduction band and 1.5 eV above the SiC valence band, respectively [41, 42]. The samples taken by El-Sayed et al. [41] show that the E$'$-H defects does not have negative-U behaviour, like the H$_B$. It is shown to be thermodynamically stable in the neutral charge state.

In this section, four defects in a-SiO$_2$ have been discussed; the intrinsic electron trap, the O vacancy, H bridge and the E$'$-H. The structural properties and the appropriate CTLs of each are have been outlined and throughout quoting the values referenced to the a-SiO$_2$ valence band and an appropriate band edge in SiC (Fig. 2.7) These CTLs allow us to link the theoretical calculations to the operation of the device. As described earlier, an important property of a gate oxide is that it is insulating. To test this, time dependant dielectric breakdown (TDDB) experiments are done to find the current density in the oxide, giving an idea of the degree to which current can flow through the oxide.
2.5. Defects in SiC and SiO₂

Figure 2.12: The Hydroxyl E’-H centre defect. One of the Si-O bonds has broken (between O atom and right-hand Si atom) and the O atom is bonded to a Si atom and a H atom, the right-hand Si atom is three coordinated. The atoms in the foreground are those involved in the defect and those in the background are of the a-SiO₂. Colour coding Si yellow, O red and H white.

2.5.3 Defects in SiC

Macroscopic defects include; voids [74], polytypic inclusions[75], low-angle boundaries, graphitisation and Si droplets, micropipes and stacking faults [76]. As mentioned earlier in this chapter the structure of SiC dictates its electronic structure and so its purpose [2]. However, these defects have been kept at a low concentration and have a limited effect on the performance of the device as their concentrations have been kept low by advances in the growth process. This however, has increased the complexity of the process and so the cost of the of the synthetic process has been increased.

Microscopic defects are categorised into vacancies (missing atoms), antisites (atoms in the wrong positions) and interstials (extra atomic species) [8]. Each of these can involve both Si and C atoms in the lattice of SiC. The main defects that are detrimental to channel mobility are the C and Si vacancies and divacancies, Si antisites, C antisites and carbon clusters [2].

As with the defects in a-SiO₂, SiC defects have also been studied experimen-
2.6 Post-oxidation anneals

In this section the main annealing processes for n-type SiC MOSFETs are outlined. This process occurs after SiC growth and deposition of a-SiO$_2$ and involves heating the device in a chamber filled with either NO, N$_2$, NH$_3$ or a combination of NO and NH$_3$. In each case, the gas concentration is dominated by N$_2$ as it functions as the carrier gas [5, 80, 81]. N$_2$ has been used as it does not create a nitrogen signal to the XPS and SIMS data [47, 1]. The temperature of the chamber is increased to 1200° C (1500 K) and the annealing agents are thought to diffuse into the near interface and part way into the SiC [47, 1]. An important concept or term that needs to be discussed is that of nitridation. Nitridation derives from the term oxidation and in this thesis it is meant as direct bonding or coordination of N or N containing molecules or fragments to the a-SiO$_2$ network or SiC lattice.

Si device technologies are more mature than SiC and so can be seen as precursor devices to SiC and many of the post-oxidation anneals have also been performed on Si devices and on a-SiO$_2$ films [82, 48, 83]. The NH$_3$ anneal was performed earlier than the the NO anneal, because the NH$_3$ molecule is much more readily available than the NO [84]. These early studies with NH$_3$ started the assertion that high temperature treatments of a-SiO$_2$ increase the concentration of N in the oxide [84] hence showing that NH$_3$ readily reacts with the films [83] which is a concept...
that is directly applicable for SiC devices annealed in NH$_3$, as they also suffer from nitridation of the gate oxide [1]. The NO anneal has been used in non-SiC devices to form a Si-O-N film to inhibit atomic transport [85]. Though it has come into the fore as the state of the art post-oxidation annealing technique for SiC materials [86].

Experimental work on SiC/a-SiO$_2$ devices has shown that this anneal procedure reduces the near interface defect density ($D_{it}$) by 99% [3]. The work of Rozen et al. [5] demonstrates that the NO enters and diffuses to the near interface and that there is no nitridation in regions of the interface greater than 2 nm from the interface [49]. This work also identifies the optimal annealing time to be 30 minutes [80]. If the device is left to anneal for less than 30 minutes, then some defects in the near interface region persist. Beyond 30 minutes there are marginal gains in the channel mobility of the device [5, 49, 80, 81], though there is not comment in this study about the dielectric strength of the oxide [5, 49, 80, 81].

Gruber et al. [86] did secondary ion mass spectrometry (SIMS), which shows that the nitridation starts 2 nm above the SiC/a-SiO$_2$, in the oxide and persists, to around 2 nm into the SiC, meaning that there is a degree of penetration into the semiconducting body [86]. This was later confirmed by Regoutz et al. [1] who performed high resolution X-ray photo-electron spectroscopy (XPS) on 4H-SiC/a-SiO$_2$ devices [1]. This work also confirms that there is no appreciable nitridation of the bulk oxide during the NO anneal [1]. This latter study was performed on wafers that were made using an established industrial process (discussed in section 2.2), which were then treated with NO, NH$_3$ or both. In the NO annealed devices a nitrogen peak is only seen at the interface (Fig. 2.13) [1].
2.6. Post-oxidation anneals

Figure 2.13: Selected N 1s core level spectra of SiC/SiO₂ stacks after different treatments, including (a) N₂, (b) NO, (c) NH₃, and (d) NO + NH₃. Figures (a), (b) and (d) are shown at 5x magnification compared to (c) [1].

Another annealing technique used to passivate defects in SiC/SiO₂ devices is a similar procedure but using NH₃, it was conceived due to NO being a caustic and dangerous gas [87]. Another reason that the NH₃ was thought to give an improved device performance was because the NO anneal was deemed inefficient due to side reactions forming N₂ and O₂ [87, 88]. This, however, is incorrect as the probability for NO to split into N₂ and O₂ is very low, without the presence of a catalyst, exemplified by the use of catalytic converters in motor vehicles.

A further reason the NH₃ is a factor here is that H₂ has long been used as a passivisation agent for devices that use a-SiO₂ as their gate oxide by way of the forming gas anneal [71]. The logic follows that, if nitridation during the NO anneal reduces the density of defects by 99%, then adding H might remove the remaining 1%. There is also the argument that H reduces the effect of the P₀₃ centre on channel
mobilities and so an anneal in NH$_3$ can be used to nitridate near interface (border) oxide defects and interface defects in one procedure [29]. This, however, is not the case. NH$_3$ annealed devices have been shown to have great initial mobilities and cycling hysteresis’ but then they suffer from accelerated gate leakage with respect to their NO counter parts [87, 88], which is a consequence of dielectric weakening [87, 88]. The work of Regoutz et al. [1] shows that the ammonia annealed devices have nitridation throughout the oxide, not only at the interface between a-SiO$_2$ as with the NO annealed devices. The nitridation is predominant at the surface of a-SiO$_2$ and then decays towards the SiC/a-SiO$_2$ interface (Fig. 2.14). This nitridation is posited to be the cause of the dielectric weakening [87].

![Figure 2.14: Depth profiles of SiC/SiO$_2$ stacks after annealing in a variety of atmospheres, including (a) N$_2$, (b) NO, (c) NH$_3$, and (d) NO + NH$_3$. Relative atomic% (rel. at%) for each element were determined from peak fits to the total core level areas after each sputter cycle. The coloured columns indicate which data-sets were used for detailed comparison. [1].](image-url)
An additional important feature of the XPS spectra is the intensity of the N peak at the interface. It is five times higher for NH$_3$ annealed devices compared to NO annealed devices [1], which leads to the authors positing that there is an increased concentration of N at the interface post an anneal in NH$_3$ [1, 87]. As with NO annealed devices, this increase in concentration of N is thought to be a consequence of the defect density at the interface between SiC and a-SiO$_2$ (Fig. 2.13).

To gain a better understanding of the nature of this nitridation one can look at anneals done with isotopically labelled NH$_3$ as done by Baumvol et al.[48, 83, 84]. In this work NH$_3$ that was labelled as $^{15}$NH$_3$ was used to treat thin films of a-SiO$_2$ [84]. Through the course of this work it was shown that both N$^{14}$ and N$^{15}$ was incorporated into the a-SiO$_2$ layer. The works also suggests a set of reaction pathways that could be responsible for the nitridation [48].

The work in this thesis emphasises the lack of atomistic understanding behind the experimental results. The XPS and SIMS data shows that for the NO annealed devices there is little (if present lower than the detection limit) nitridation of the bulk oxide. However, for the NH$_3$ annealed devices there is a large amount of nitridation of the bulk oxide. From electronic experiments there is a sizeable difference between the two anneals too, showing that the NH$_3$ annealed devices have an enhanced gate leakage current compared to their NO annealed counter parts [87]. Both electrical and elemental analysis are linked but this link is missing. The work presented in chapters 4, 5 and 6 looks to explain this using DFT and classical MD calculations. The first two chapters looks at the interactions of NO and NH$_3$ with pristine a-SiO$_2$ cells and chapter 6 looks at their interactions with a defective a-SiO$_2$ network.

In this section we have detailed the different annealing techniques that have been used to improve the reliability, performance and longevity of SiC/a-SiO$_2$ devices. To summarise, the NO anneal removes around 99% of defect states at the SiC/a-SiO$_2$ interface without causing dielectric weakening to the silica layer. The NH$_3$ anneal initially makes devices that perform better than the NO annealed de-
vice but then they suffer from accelerated gate leakage compared to their NO annealed counter parts. One explanation for this is that the NH$_3$ anneal causes dielectric weakening in the gate oxide. The nature of this dielectric weakening is thought to be a consequence of the nitridation of the oxide shown via isotopic labelled anneals with NH$_3$ and XPS studies.

2.7 Building the SiC/SiO$_2$ interface

In the previous sections we have discussed a host of defects and annealing agents that passivate defects in an oxide region 2 nm from the SiC/a-SiO$_2$ interface. All of this raises important questions: what effect does the interface have on the oxide structure and could the interface between SiC and a-SiO$_2$ explain why it is plagued with such a magnitude of defects?

The first factor to consider in order to answer this question is the density of a-SiO$_2$ and SiC, which is 2.2 g cm$^{-3}$ and 3.2 g cm$^{-3}$, respectively. This is an increase of over 45% going from a-SiO$_2$ to SiC meaning that there cannot be a smooth transition between the oxide and the semiconducting channel [21]. Devices using Si as the channel and a-SiO$_2$ as the oxide contain a region of higher than average oxide density (2.4 g cm$^{-3}$) at less than 2 nm from the interface, which is shown in x-ray reflectometry data [21]. The density mismatch between these two materials (density of Si is 2.6 g cm$^{-3}$) is not as significant as the density difference between SiC and a-SiO$_2$. However, there is still a 10% increase in oxide density which means there could be an even more dense oxide in the near interface regime in SiC devices [89].

The near interface oxide density is used by Devynck et al. [90] as part of the justification of their 4H-SiC/a-SiO$_2$ interface built on the Si-face of 4H-SiC. The author regards this interface models as the most effective model because it replicates the band offset experimentally found in real devices and is the only method that gives an in-depth methodology about how one creates the structure. The other interface models found by the author (Akiyama et al. [91] and Deak et al. [79]) have excellent electronic structures but are missing explicit instructions on the steps
2.7. Building the SiC/SiO$_2$ interface

Figure 2.15: The two SiO$_4$ tetrahedron that have been used by Devynck et al. [21] to make a connection scheme for SiC/a-SiO$_2$ interface. A is an SiO$_4$ tetrahedron that has three connections to the the SiC and B is an SiO$_4$ tetrahedron that has two connections to the SiC [21].

to reliably create the interface structure. The band offset of this model is shown in Fig. 2.7, where the SiC VB sits 3 eV above the VB of a-SiO$_2$.

An important consideration is how one connects the two materials together. The most rigorous method to make an interface uses a connection scheme [21]. In this method, two basic shapes were used to connect the two materials together; the first is where three of the oxygen atoms of a SiO$_4$ tetrahedron are connected to the SiC (Fig. 2.15A) and the second where only two of the oxygen atoms are connected (Fig. 2.15B) [21]. These constructions are then interspersed on top of the Si-face of 4H-SiC to form a single layer of SiO$_2$ above which one adds enough oxide layers that it becomes bulk like (i.e. where there is little molecular movement on ion relaxation)[21].

This model was created on the Si (or [0001]) face of 4H-SiC. SiC has two other faces where the oxide can be grown/deposited these are the C-face and the a-face. There is no theoretical work done on the a-face of SiC. The c-face has also been investigated as it has been used to grow single graphene sheets in 6H-SiC, however, this has no clues on how one can build an interface, it is only a surface science study [2]. The work of Akiyama et al. [91] looks at the different wet oxidation rates using a fairly simple interface model for both the Si and C faces of SiC, again giving no clues on the electronic properties of the interface [91].
2.8 Concluding Remarks

In this chapter, the structure and electronic properties of a-SiO$_2$ and SiC which form the gate oxide and the semiconducting channel, respectively, in SiC/a-SiO$_2$ devices as been reviewed. This is followed by a brief review of the defects that have been shown to form in devices using a-SiO$_2$ as the gate oxide. Finally, a short review of how an interface structure can be made and some examples on different faces of SiC have been shown.

The work in this thesis is focused on the interactions of the annealing agents with pristine and defective SiO$_2$ structures in the amorphous and crystalline phases. The first two results chapters show the interactions of the annealing agents NO and NH$_3$ with the pristine structures. As shown by the literature review this is not considered in the literature but forms an important part of the understanding the chemical make up of the differently annealed devices. Then the next chapter focuses on the interaction of these annealing agents with common defects in a-SiO$_2$, putting an emphasis on how the CTLs change when annealing agents are coordinated to them and how this relates to the tunnelling characteristics of these differently annealed devices. The last results chapter looks at all of these factors at the interface between SiC and a-SiO$_2$.

In the following chapter I give an introduction to the methods employed in this thesis, namely DFT and classical MD. This is then followed by four chapters that include the results that have been attained over the funding period. Fig. 1.1 shows the outline of the content chapters and how they feed into one another.
Chapter 3

Methodology

3.1 Introduction

The work presented in this thesis has been performed using a combined approach based on classical molecular dynamics (MD) and density functional theory (DFT). Classical MD is used to build models of a-SiO$_2$ and to explore the interactions of NH$_3$ with the SiO$_2$ surface at elevated temperatures. Below I provide a brief summary of the computational procedure and then discuss each of the methods in more detail in the following sections.

Amorphous materials present a formidable modelling challenge, they require large cells and extensive statistics to allow structures within the materials to be sampled. The first step is to make models of the amorphous material that match the physical experimental properties (e.g. density, bond length and angle distribution) of the system at hand. The method used to make all the a-SiO$_2$ models here is similar to refs. [92, 40, 93], in which a classical molecular dynamics melt-quench is used. The melt-quench method is used for glass structures as it mimicks their fabrication and has been used in a myriad of studies to make similar models in similar defect and structural studies (see Refs. [92, 40, 93, 94]). The method involves heating the material to a high temperature, equilibrating at this high temperature then quickly quenching the system, as one would during the fabrication of glass. In the work presented in this thesis the models start of as a 216-atom cubic cell of $\beta$-cristobalite, they are then melted and quenched a reactive forcefield (ReaxFF)
in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) using periodic boundary conditions.[95, 96, 97] This is the first part of constructing the continuum random network model.

When the melt-quench procedure is completed, the resulting structures are further optimised using DFT and the electronic structure is calculated. The calculations in this work are done with periodic boundary conditions so each of 216-atom cells is amorphous but the calculation as a whole is periodic. The a-SiO2 cells used in this work have an extra processing step, in that they go through a DFT cell optimisation using the hybrid functional PBE0 TR LRC. This provides the full relaxation of internal stresses and the mean density of the a-SiO2 cells to be closer to the experimental density of 2.2 g cm\(^{-3}\). A full overview of this procedure is given in ref. [94].

After all of these processing steps, defects and interstitials are added to the system. Subtle changes in the structure of amorphous materials can cause the facile formation of defects. An example of this is the intrinsic electron trap discussed above, which traps electrons in a seemingly non-defective sample and facilitates the formation of O vacancies [40, 24]. Another example of this is the interaction of H atoms with Si-O bonds greater than 1.64 Å which make the Hydroxyl E’-centre. To this end we have made and optimised 30 structures and for all defect calculations in this work a minimum of two cells is fully sampled with hybrid DFT, this means that interstitials (NO and NH) were placed on the faces of all SiO\(_4\) tetrahedra and each of the 144 O sites in the 216 atoms cells were individually made defective. This yields \(\approx 190\) interstitial positions and 144 defect sites in 2 cells. For interstitials, we employ an exhaustive sampling procedure in which the interstitial is placed in different positions in a structure that is at the experimental density of SiO\(_2\), 2.2 g cm\(^{-3}\), a full explanation of this procedure can be found in chapter 4.

DFT is used to investigate defect levels and the interactions of molecules with a SiO\(_2\) surface and bulk. The results of these calculations are used to explain the nitrogen passivation of real devices, requiring models which accurately replicate the band gap of a-SiO\(_2\). Standard DFT has the issue of underestimating the band
gaps of materials and the method used to correct this is hybrid functionals. Hybrid functionals mix exchange from standard DFT and Hartree-Fock (HF) to attain the correct band gaps for materials. Hybrid functionals are very computationally intense hence require strategies to mitigate computational cost, this is done using the auxiliary density matrix method (ADMM). An additional cost saving feature is the use of a range truncating functional, in this case PBE0_TR_LRC which truncates the HF exchange to a certain radius from each of the atoms. The DFT calculations are done in the CP2K code, it is primarily a $\Gamma$-point code which allows for the cheap calculation of larger volumes of configurational space as one extends the system in real space as opposed to the $k$-space. CP2K also uses the Gaussian plane wave (GPW) method, this takes all the positive elements of local basis set and plane-wave basis sets to create an efficient and accurate procedure to model the atoms in the system.

The rest of this chapter will provide more detail of the methods used in calculations. First, we detail DFT specifically looking at the implementation in CP2K. For a complete derivation of DFT the reader is directed to [98]. I then describe the molecular dynamics and the final section is on the method used to calculate migration and reaction barriers and charge transition levels.

3.2 Implementation of DFT in CP2K

This section details the DFT implementation in CP2K. CP2K is primarily a $\Gamma$-point code which means that the system is expanded in real space as opposed to in reciprocal space, which is not the case in codes such as VASP and CASTEP [99, 100, 101]. The $\Gamma$-point approach allows for facile and accurate calculation of amorphous systems which, by definition, have no long range order.

3.2.1 Gaussian Plane-wave method

DFT calculations use local basis sets, such as Gaussian basis sets, or non-local basis sets, such as plane wave basis sets, to model valence electrons. Each of the methods have their own advantages and disadvantages [102, 103]. Gaussian functions have been used ubiquitously in DFT codes due to their efficient implementation; this
is because the product of two Gaussians is a Gaussian, which is important when calculating integrals. One of the issue with Gaussians is that they do not properly describe orbitals near atomic nuclei.

Plane wave basis sets have also been widely used in DFT codes; they derive from Bloch waves and allow for the wave-function of a system to be represented by a set of plane waves. Plane waves are thought to be more complete basis sets compared to local basis sets, which are often incomplete. The major benefit of plane wave basis sets is the ability to efficiently perform fast Fourier transforms on them allowing for efficient calculation of the Hartree energy. The drawback is the indifference of plane-waves to free space and so regions with atoms and regions of vacuum equally have the same number of plane-waves projected onto them. Further to this, the electron density derived from a plane-wave wave-function requires many more basis functions than that of localised basis sets [98]. There is an argument that plane-wave basis sets are more complete than local basis sets, but the counter argument is that local basis sets are less computationally demanding and give similar results.

The GPW method, implemented in CP2K uses both Gaussians and plane waves as basis sets which allows for a faster calculation whilst also retaining accuracy [104, 105]. Gaussian basis sets are used to find the potential and kinetic energies, analytically. The density from the Gaussian basis set is then mapped onto the plane wave basis set, allowing for the utilisation of fast Fourier transform for the calculation of the Hartree energy. All of this means that the combined GPW method is much more efficient and as accurate as using local and plane-wave basis sets in isolation. The density represented using Gaussian basis sets is given by [105];

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$  \hspace{1cm} (3.1)

where $\rho(r)$ the density, $N$ is the number of electrons and $\psi_i(r)$ is the $i$’th molecular orbital. Molecular spin orbitals can then be expressed as a linear combination of atomic orbitals [98]:

$$\psi_i = \sum_{\mu=1}^{K} c_{i\mu} \phi_{\mu}$$  \hspace{1cm} (3.2)
where $c_{i\mu}$ is the mixing coefficient and $\phi_\mu$ is one of $K$ atomic orbitals. Each atomic orbital is in turn a contracted sum of Gaussians [98]:

$$\phi_\mu = \sum_{k=1}^{L} d_{\mu k} \phi_k(\alpha_{\mu k})$$  \hspace{1cm} (3.3)

where $d_{\mu k}$ is the coefficient of the primitive Gaussian function $\phi_k$ which has the exponent $\alpha_{\mu k}$, and $L$ is the number of functions in the expansion. During the calculation, the coefficients for the atomic orbitals $d_{\mu k}$ are generally kept constant, and the coefficients for the molecular orbitals $c_{i\mu}$ are varied to obtain the ground state density. The density obtained using the Gaussian basis sets is then mapped onto the plane wave basis, described as:

$$\tilde{\rho}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\Gamma} \tilde{\rho}(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}},$$  \hspace{1cm} (3.4)

where $\tilde{\rho}(\mathbf{r})$ is the density, $\Omega$ is the volume of the cell, $\tilde{\rho}(\mathbf{G})$ are the expansion coefficients and $\mathbf{G}$ are the reciprocal lattice vectors. This then allows the Hartree energy to be calculated using the plane wave basis set, via fast Fourier transforms.

This section looks at how valence electrons are treated in CP2K’s implementation of DFT. However, the question of how core electrons are treated still has not been addressed. The next section details pseudopotentials used to describe core electrons [106].

### 3.2.2 Pseudopotentials

The potentials of both core and valence electrons are represented by the pseudopotential. Core electrons are assumed to be minimally perturbed during chemical interactions with other atoms. As such, fewer Gaussians are required to represent the cusp behaviour at the nucleus. This, smooth varying nature of pseudopotentials allows fewer plane waves to be used in calculations hence leaving the valence electrons to be solved completely during calculation. In this thesis the Goedecker-Teter-Hutter (GTH) pseudopotentials have been used, which are fitted to provide optimal accuracy and efficiency when using a plane waves basis set [106]. The GTH pseudopotentials have been used extensively by CP2K users [107, 108, 40, 109], with versions that work for a number of exchange correlation functionals [110]. A detailed description of the GTH pseudopotentials can be found in [106, 111].
3.2. Implementation of DFT in CP2K

So far we have shown how valence and core electrons are mathematically represented by the GPW method and pseudopotentials, respectively. The next section will briefly look at how the energy is calculated in DFT calculations, by introducing the Kohn-Sham formulations, then we will focus on strategies to attain accurate material properties in the DFT framework, primarily focusing on the use of hybrid functionals.

3.2.3 Calculating the Energy

The development of efficient density functionals started in 1964 with Hohenberg and Kohn [112]. They have shown that for a given electron system there is a one-to-one mapping between the external potentials and the electronic density [112]. In addition to this they show that one can variationally minimise the energy of a system to gain the ground state electron density. Hence in theory, one could obtain the ground state energy of a system by finding its ground state electron density [112].

However, the Hohenberg and Kohn theorems do not show us the functional form of the dependence of the energy and density, it just tells us that it exists. To this end, in 1965, Kohn and Sham [113] derived a set of one electron equations from which the electron density could be derived. They demonstrate that the exact ground state electronic energy $E$ of an $n$ electron system can be formalised as [113],

$$ E[\rho] = -\frac{\hbar}{2m_e} \sum_{i=1}^{n} \psi_i^*(\mathbf{r}_1) \nabla_1^2 (r_1) d\mathbf{r}_1 - \frac{e^2}{4\pi\varepsilon_0} \sum_{I=1}^{N} \frac{Z_I}{r_{I1}} \rho(\mathbf{r}_1) d\mathbf{r}_1 + \frac{e^2}{8\pi\varepsilon_0} \int \rho(\mathbf{r}_1)(\mathbf{r}_2) (r_{12}) + E_{XC}[\rho], $$

where the one-electron spatial orbitals $\psi_i (i=1,2,...,n)$ are the Kohn-Sham orbitals [114]. The exact ground state electron density is given by,

$$ \rho(\mathbf{r}) = \sum_{i=1}^{n} |\psi_i(\mathbf{r})|^2. $$

In equation 3.5 the first term is the kinetic energy, the second term is the electron-
3.2. Implementation of DFT in CP2K

nucleus attraction where the sum is over all \( N \) nuclei with index \( I \) and atomic number \( Z_I \), the third term is the Coulomb interaction between total electron distribution (summed over all Kohn-Sham orbitals) at \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) and the last term is the exchange-correlation (XC) energy of the system which is also a functional of the total electron density \([113, 114]\). Kohn-Sham orbitals can then be obtained using the Kohn-Sham equations, which can be derived by applying the variational principle on the electronic energy \( E[\rho] \) with the electron density given in equation 3.6 \([113, 114]\). The Kohn-Sham equations for the one-electron orbitals, \( \psi_i(\mathbf{r}_i) \), has the form,

\[
\left( -\frac{\hbar^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0} \sum_{i=1}^{N} \frac{Z_I}{r_{1i}} + j_0 \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) \right) \psi_i(\mathbf{r}_1) = \varepsilon_i \psi_i(\mathbf{r}_i), \tag{3.7}
\]

where \( \varepsilon_i \) are the Kohn-Sham orbital energies and \( V_{XC} \) is the XC potential which is the functional derivative of exchange correlation energy,

\[
V_{XC}[\rho] = \frac{\delta E_{XC}[\rho]}{\delta \rho} \tag{3.8}
\]

The non-interacting set of electrons are then projected on to the interaction electrons and the interaction potential is put into the XC potential \( (V_{XC} \text{ in equations 3.8 and 3.7}) \), which is unknown \([114]\). The next section details the approximations used for the XC term, starting off with a short discussion about the local density approximation (LDA) and the generalised gradient approximation (GGA) then looking at the hybrid functionals used in the work presented in this thesis.

### 3.2.4 Exchange and correlation functionals

The two most widely used approximations for the XC functional are LDA and GGA. LDA determines the XC energy by considering the electron density at each point in space of a system to be the same. It assumes that each point in an inhomogeneous electron distribution will have the same XC energy as a point in a homogeneous electron gas (HEG) with the same electron density \([115]\) in a system with no external potential. In this approach, the XC energy is typically approximated using the homogeneous electron gas model, where positive charges (nuclei) are distributed equally in a volume such that the electron density is also a uniform quantity in
space. The number of nuclei and electrons (N) as well as the volume (V) are then taken to infinity such that the density \( \rho = N/V \) is finite and constant. The exchange energy \( E_{\text{LDA}}^{\text{LDA}} \) of a HEG can then be solved analytically \[116\]:

\[
E_{\text{LDA}}^{\text{LDA}}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho(r)^{4/3} \, dr
\] (3.9)

and the correlation energy can be calculated using quantum Monte Carlo simulations or many-body perturbation theory. In practice, the exchange and correlation energies are calculated for a small volume around each spacial point in the system and integrated over the whole electron density:

\[
E_{\text{LDA}}^{\text{XC}} = \int \rho(r) \varepsilon_{\text{XC}}(\rho(r)) \, dr.
\] (3.10)

LDA has been shown to perform well in systems where the electron density does not vary a great deal across the system (e.g. metals), but poorly for systems that do have large variations in electron density, such as covalent or ionic systems, hence the advent of GGA functionals \[117\]. GGA functionals include the gradient of the electron density at each point hence being more applicable to ionic and covalent systems \[118\]:

\[
E_{\text{GGA}}^{\text{GGA}} = E_{\text{XC}}^{\text{GGA}}[\rho(r), \nabla \rho(r)].
\] (3.11)

There is a wide variety of functionals that utilise GGA, for example PBE, BLYP and PW91. \[119, 120, 121\] Each of these give vastly improved structural representations and energies for a plethora of systems with ionic or covalent character. However, despite the good representations of the energy and structure of many materials, the band gaps of insulating systems remain under-estimated by LDA and GGA functionals. This is because of the self-interaction error (SIE) in the Hartree energy term of the Kohn-Sham equations. The next section details the nature of the SIE and the use of hybrid functionals. Hybrids mix a small proportion of Hartree-Fock (or exact) exchange with GGA exchange and are used to mitigate the effect of the SIE on calculations, hence leading to experimentally verified band gaps.
3.2.5 Self interaction error and hybrid functionals

The SIE manifests in the Hartree energy term, defined as [122, 123, 124]:

\[ E_H[\rho(r)] = \frac{1}{2} \iiint \rho(r_1) \rho(r_2) \frac{d|r_1 - r_2|}{d(r_1 dr_2)}. \]  (3.12)

If one uses the above formulation, then each electron in the system will feel a repulsive force from all the other electrons in the system, including itself. This extra repulsion leads to the electron density being more delocalised resulting in both LDA and GGA functionals underestimating the band gap and limiting their ability to model localised states. To reduce the SIE, hybrid functionals can be used. In which a fraction, \( \alpha \), of Hartree-Fock exchange is added to LDA and GGA functionals. In Hartree-Fock theory, the self-interaction does not occur as the self interacting terms reduce to zero upon expansion of the Slater determinant. The exchange correlation energy when using hybrid functionals \( E_{XC}^{Hyb} \) can be calculated as,

\[ E_{XC}^{Hyb} = \alpha_{Hyb} E_{HF} + (1 - \alpha) E_{DFT}^{HF} + E_{DFT}^{XC}. \]  (3.13)

The work presented in this work uses the PBE0_TC_LRC functional which uses the PBE0 functional as a base functional [125, 126]. The PBE0_TC_LRC functional is formalised as [126],

\[ E_{xc}^{PBE0-TC-LRC} = \alpha E_{HF,TC}^{x} + \alpha E_{HF,LRC}^{x} + (1 - \alpha) E_{PBE}^{x} + E_{PBE}^{c}, \]  (3.14)

where \( \alpha \) is a parameter that controls how much Hartree-Fock exchange is used in the system. It is generally defined as 0.2 in the literature but this work uses a value of 0.25 [127]. TC is a truncation operator which is used to limit the calculation of Hartree-Fock integrals within a certain range of atomic centres, which in all calculations done with this functional is 2 Å. The justification for using this functional is that it has been widely used to calculate similar systems as those presented in this thesis. These works can be seen in refs. [40, 22, 41, 108, 109, 128] to name a few. To decrease the cost of these calculations the auxiliary density matrix method (ADMM) is used and so is detailed in the next section.
3.2.6 Auxiliary density matrix method

ADMM is used in CP2K to reduce the computational intensity of calculating the HF exchange [129]. The ADMM method constructs a coarse density matrix which uses less basis functions than the original Gaussian basis set. The Hartree-Fock exchange is calculated on the reduced density matrix hence requiring far fewer calculations as a result and so significantly reduces the computational time. The auxiliary basis set is given as [129]:

\[ \psi_i' = \sum_{\mu} C_{\mu i} \psi_i'(r) \] (3.15)

where \( \psi' \) is the wave function in the smaller auxiliary basis set, \( C_{\mu i} \) is the orbital coefficient and \( \psi_i'(r) \) is the orbital. The density matrix can then be constructed from the orbital coefficients as [129]:

\[ P_{\mu \nu} = \sum_i C_{\mu i} C_{\nu i}. \] (3.16)

The orbital coefficients for the auxiliary basis set and auxiliary density matrix can be obtained by minimising the square difference between the wave functions in the original basis set and the auxiliary basis set. The Hartree-Fock exchange energy can then be calculated as [130]:

\[ E_{x}^{\text{HF}}[\rho] = E_{x}^{\text{HF}}[\rho'] + (E_{x}^{\text{HF}}[\rho] - E_{x}^{\text{HF}}[\rho']), \] (3.17)

\[ E_{x}^{\text{HF}}[\rho] \approx E_{x}^{\text{HF}}[\rho'] + (E_{x}^{\text{DFT}}[\rho] - E_{x}^{\text{DFT}}[\rho']), \] (3.18)

where \( E_{x}^{\text{HF}}[\rho'] \) is the Hartree-Fock exchange energy and \( E_{x}^{\text{DFT}}[\rho] \) is the exchange energy calculated using the GGA functional. If the difference in the exchange energy calculated on the auxiliary density matrix and the original density matrix is zero then the calculation proceeds, if not the auxiliary matrix is reconfigured and the calculation is repeated until the difference is zero. Using the auxiliary density matrix can greatly reduce the cost of a DFT calculation when using a hybrid functional.

This chapter has shown how CP2K implements DFT calculations. In the next section I describe the specific methods used to calculate defect levels and barriers.
for migration and reactions. First I describe the nudged elastic band (NEB) method, which is used to calculate the barriers for migration and reaction using DFT. Next we look at the how defect formation energy is used to calculate charge transition levels (CTLs), which allows comparison between DFT calculations and experiments by showing the probability for charge trapping at specified Fermi level positions; there will also be a short description about the corrections used when calculating CTLs for charged defects.

3.3 Auxiliary methods employed in CP2K

DFT gives the total energy and geometry of a given system in a given charge state. Below I describe how the adiabatic barriers for defect migration and charge transition levels of defects are calculated using this information.

3.3.1 Nudged Elastic Band (NEB) method

A reaction can be defined as a change from one stable configuration to another, over some transition state. The minimum energy path (MEP) and can be used to calculate the kinetics and thermodynamics of a reaction, by finding the saddle point of the reaction which happens at the transition state [131]. To this end, the nudged elastic band (NEB) method can be used to calculate saddle points and minimum energy paths along a reaction [132, 133]. The method uses linear interpolation to create a series of intermediate images (bands) along the reaction path between the initial and final configurations of the reaction. These images are then optimised such that each image finds the minimum energy possible whilst maintaining equal spacing to neighbouring images. The overall system is constrained by adding spring forces between the images, which project out the component of the force due to the potential perpendicular to the band. The NEB method originates from the plain elastic band (PEB) method where the force $F$ acting on an image $i$ is given by [134]:

$$F_i = -\nabla V(r_i) + F^\text{spring}_i.$$  (3.19)
3.3. Auxiliary methods employed in CP2K

Here $V(r_i)$ is the total potential energy of the image $i$ and $F_{i}^{\text{spring}}$ is the force on image $i$ due to the springs attached which are formalised as,

$$F_{i}^{\text{spring}} = k_{i+1}(r_{i+1} - r_i) - k_i(r_i - r_{i-1}),$$  \hspace{1cm} (3.20)

where $k_i$ is the spring constant. The PEB method is an example of a chain of state method, where several images (or ‘states’) of a system are connected together to trace out a path. The object function is defined as [133],

$$S^{\text{PEB}}(r_1, \ldots, r_{P-1}) = \sum_{i=0}^{P} V(r_i) + \sum_{i=1}^{P} \frac{P_i}{2}(r_i - r_{i-1})^2,$$  \hspace{1cm} (3.21)

where the first term sums the potential energies of each of the images and the second term sums the potential energies arising due to the springs connecting the images.

To find the MEP in PEB method, the object function is minimised with respect to the intermediate images while keeping the start and end point images $r_0$ and $r_P$ fixed.

However, the PEB does not provide the MEP in most situations. When the spring constant is high, the elastic band becomes too stiff such that the path cuts corners in the energy landscape, this can lead to the saddle point being ill-defined. This is a consequence of the component of the spring force which is perpendicular to the path which tends to pull images away from the MEP. When a smaller spring constant is used, the elastic band becomes closer to the saddle point but the images slide down avoiding the barrier region hence reducing the resolution of the band in the transition state region. This is due to the component of the true force $\vec{\nabla}V(r_i)$ in the direction of the path. The distance between images becomes uneven such that the net spring force balances out the parallel component of the true potential force.

In the NEB method, the elastic band is minimised such that the perpendicular component of the spring force and the parallel component of the true force are projected out. The force on image $i$ becomes,

$$F^0_i = -\vec{\nabla}V(r_i)\big|_{\perp} + F_{i}^{\text{spring}} \cdot \hat{\tau}_{\parallel} \|\hat{\tau}_{\parallel},$$  \hspace{1cm} (3.22)

where $\hat{\tau}_{\parallel}$ is the unit tangent to the path. The perpendicular component of the true force $-\vec{\nabla}V(r_i)$ is given by,

$$-\vec{\nabla}V(r_i)\big|_{\perp} = \vec{\nabla}V(r_i) - \vec{\nabla}V(r_i) \cdot \hat{\tau}_{\parallel} \|\hat{\tau}_{\parallel},$$  \hspace{1cm} (3.23)
This method of force projection separated the dynamics of a path from the images distributed along it. Now the spring force does not interfere with the relaxation of the images perpendicular to the path. As a result, the relaxed configuration of the images satisfies $-\vec{\nabla}V(r_i)\mid_\perp = 0$ such that the images lie on the MEP. Because the spring force only affects the distribution of the images within the path, the choice of the spring constant becomes less restrained. This separation of the relaxation of the path and the discrete representation of the path is essential to ensure convergence to the MEP. A further improvement is the climbing image nudged elastic band (CI-NEB) [132]. In this case the springs connected to the highest energy image are allowed to relax giving a better approximation of the saddle point.

In the work presented in this thesis the CI-NEB method is used to calculate the migration barriers of small molecules and reaction barriers on the surface and in the bulk of SiO$_2$. Despite all the schemes employed by CP2K to reduce the computational intensity of calculations, the NEB method remains quite an expensive method. For a 216-atom cell of a-SiO$_2$ with 5 bands, it requires a minimum of 96 cores per band and 24 hours of wall time. To mitigate the need to do many of these calculations, the micro-structures in a-SiO$_2$ are analysed to give statically significant results without doing hundreds of these expensive calculations.

### 3.3.2 Defect formation energy

DFT can be used to find the thermodynamic, electronic and optical parameters of defect systems. The work presented in this thesis looks at how changes to these systems affect their properties. This is done using the defect formation energy calculations. This is an important parameter, defined as the energy difference between an investigated system and the components of the system in their reference states. In this project, the formalism of Northrup and Zhang is employed [135],

$$E_{form} = E_{Defect} - E_{Bulk} - \sum_i \mu_i n_i + q (\mu_e + E_{Band}) + E_{corr}, \quad (3.24)$$

where $E_{form}$ is the defect formation energy, $E_{Defect}$ is the energy of the system with the defect, $E_{Bulk}$ is the energy of the defect free system, $\mu_i$ is the chemical potential of the defect species $i$, $n_i$ is the number species of type $i$ added ($n_i > 0$) or removed
(\(n_i < 0\)) from the system, q is the charge of the system, \(\mu_e\) is a free parameter representing the electron chemical potential, \(E_{\text{Band}}\) is the energy eigenvalue of the band edge taken from calculation of the bulk pristine cell, and \(E_{\text{corr}}\) is the charge correction and is only applied if there is charge present in the system.

The chemical potential of a species is defined as the energy that is absorbed or released due to a change in the particle number of that species [127]. The most important part of choosing the chemical potential is to use one that corresponds to the process we are trying to model. In the case of the work presented here, we look at interstitials and defects in the bulk. For all instances in this work we take the energy of defect atoms in the gas phase. These are calculated as,

\[
\mu_{\text{mol}} = \frac{1}{n} E_{\text{mol DFT}}. \tag{3.25}
\]

Here \(\mu_{\text{mol}}\) is the chemical potential of a molecule or atom removed or added to a bulk system, \(E_{\text{mol DFT}}\) is the DFT energy of the molecule in the gas phase calculated with the same parameters as the bulk and bulk defect calculation, and the \(\frac{1}{n}\) factor is changed depending on the chemical potential used. This is exemplified by a defect calculation of an O vacancy in a-SiO\(_2\). We remove one O atom from the network so we need to add the energy of this back in the third term of equation 3.24; so we calculate the DFT energy of an O\(_2\) molecule in the gas phase and divide it by two (as we only remove one O atom from the a-SiO\(_2\) network, so \(\frac{1}{n}\) in equation 3.25 becomes \(\frac{1}{2}\)) and is used as the chemical potential in equation 3.24 to calculate the formation energy of the defect.

As stated earlier in the chapter, I am interested in electron trapping by defects in a-SiO\(_2\). When extra charge is added to a system in DFT, a neutralising background charge is applied in periodic boundary conditions so that the energies can be calculated. This can shift CTLs and place them at incorrect positions. To correct this, a charge correction term is added to equation 3.24. In the work presented in this thesis the Lany-Zunger charge correction is used [136], which has a form:

\[
E_{\text{LZ}} = \left[1 - c_{\text{sh}} \left(1 - \frac{1}{\varepsilon}\right)\right] \frac{q^2 \alpha}{2\varepsilon L}, \tag{3.26}
\]
where $E_{LZ}$ is the Lany-Zunger correction energy, $c_{sh}$ is the shape factor, $\varepsilon$ is the dielectric constant (the calculations which have charge present in them use a value of 3.7 [137]), $q$ is the charge state, $\alpha$ is the Madelung constant and $L$ is the separation between defects [138, 139]. The total correction applied to the charged calculations was 0.375 eV. Another important consideration is the interaction of defect centres in neighbouring periodic images. This can be particularly problematic in charged defect centres which have long range interactions. While removing this error is out of the realms of current DFT cell sizes its effects can be partially mitigated by having sufficiently separated defects in cells that are large enough to have non-interacting defects. One way of reducing this error is to converge the formation energy and CTL of a defect with the size of the cell.

Equation 3.24 is then plotted across the band gap of the material. The fourth term in equation 3.24 gives the variance in formation energy across the band gap for the charged defects. Fig. 3.1 shows a schematic of a charge transition level diagram, the neutral charge state is the horizontal line and does not vary across the band gap of the material as the fourth term in equation 3.24 becomes zero as $q = 0$. The three diagonal lines represent the negative charge states whose energies do vary across the band gap due to $q \neq 0$. The gradient of these lines is dictated by the charge of the defect (i.e. if the charge state is positive then the line will have a positive gradient, if the charge state is negative the line will have a negative gradient and the line will be steeper if we are in higher charge states) [127].

The formation energy of the charged defect can also shift (purple and orange arrows in Fig. 3.1) due to stabilisation or steric effects. The points where the neutral and negative lines cross are the CTLs which tell us the Fermi level position where the defect is going to trap a charge at 0 K. These crossing points can also change if there is stabilisation or steric effects (blue and red arrows in Fig. 3.1). As stated previously, amorphous materials require large statistics to find the full distribution of their behaviours so it would be impractical to plot this diagram for every defect found. Later, chapters will show distributions of CTLs and they are found by simultaneously solving the $y=mx+c$ lines formed by this analysis. This analysis allows
3.3. Auxiliary methods employed in CP2K

Figure 3.1: A schematic representation of the change in CTL position as a function of formation energy. The green line is a comparison. The blue dashed line shows what happens when the formation energy decreases (purple arrow), the CTL moves closer to the VBM (blue arrow). The red dashed line shows what happens when the formation energy increases (orange arrow), the CTL moves towards the CBM (red arrow)
3.4 Molecular Dynamics

for direct comparison between DFT calculations and experimental techniques, such as DLTS and TDDB [127].

This section has detailed the methods used in tandem with DFT to gain parameters that can be compared with experimental data. We first discussed the NEB method which uses linear interpolation to find the MEP and hence the barriers for migration and reaction. Then the defect formation energy was discussed, which allows the calculation of CTLs required for comparison between theory and experiment. The next section looks at molecular dynamics. The work in this thesis only uses classical molecular dynamics, which is implemented in the Lammmps code.

3.4 Molecular Dynamics

Molecular dynamics (MD) computes the dynamics of a system of interacting particles by integrating Newton’s laws of motion [140], resulting in a trajectory showing how the positions and velocities of the particles in the system evolve with time. Classical MD methods use interatomic potentials (IP) to model the interactions between particles and so the potential energy landscape. Hence the accuracy of the calculation depends on the IP and how well it represents the system. In theory, a well selected IP will give equally accurate predictions of particle dynamics as \textit{ab initio} methods at a fraction of the computation cost. This is particularly useful when considering large systems to be studied here, where \textit{ab initio} MD simulations are computationally prohibiting.

3.4.1 Classical Potential Energy Functions

A large number of IPs have been developed to give simplified descriptions of the potential energy surface [141]. The form of these functions, or potentials, can range in levels of complexity and vary with the type of bonding. An intuitive method to describe the potential energy surface is to expand it in terms of single-body, two-body and higher order terms,

\[
V_{pot}(\mathbf{r}_1 \ldots \mathbf{r}_n) = \sum_i v_1 (\mathbf{r}_i) + \sum_i \sum_{j>i} v_2 (\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3 (\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \ldots,
\]

(3.27)
where \( v_1 \) represents the effect of an externally applied field and the remaining terms represent inter-atomic interactions. \( v_1 \) is usually set to zero in periodic calculations and the potential is evaluated starting from the two-body term. In general, evaluating the two-body term alone can give a good representation of the PES, especially for describing systems with ionic or van der Waals bonding. The most commonly used two-body potential is the Lennard-Jones potential \([142]\), which can be fitted to experimental or theoretical data for a given system:

\[
v_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],
\]

(3.28)

where \( \varepsilon \) is the potential well depth, \( \sigma \) is the finite distance at which the inter-particle potential is zero and \( r \) is the distance between the particles. If electrostatic charges are present, the Coulomb potentials are added,

\[
v_{\text{Coulomb}}(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r},
\]

(3.29)

where \( Q_1 \) and \( Q_2 \) are the charges of each particle and \( \varepsilon_0 \) is the permittivity of free space.

### 3.4.2 Integration of Newton’s Law

Once a potential energy surface has been defined, one must still integrate Newton’s equation of motion. The Verlet algorithm, is commonly used and can be derived by making the Taylor expansion of the position coordinate both forward and backward in time \([143]\),

\[
r(t + \Delta t) = r(t) + v(t) \Delta t + \frac{1}{2} a(t) \Delta t^2 + \ldots,
\]

(3.30)

\[
r(t - \Delta t) = r(t) - v(t) \Delta t + \frac{1}{2} a(t) \Delta t^2 + \ldots
\]

(3.31)

These two equations can be added together to create the Verlet algorithm, which is a symmetric function in which time is conserved in both directions,

\[
r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t) \Delta t^2 + O(\Delta t^4).
\]

(3.32)

The algorithm is properly centered such that \( r(t + \Delta t) \) and \( r(t - \Delta t) \) play symmetrical roles, making it time-reversible and it shows excellent energy-conserving properties over long times. It is assumed that the forces only depend on the position
coordinates. The velocities do not enter explicitly in the algorithm but they are needed for estimating the kinetic energy and hence the temperature. They can be obtained by subtracting Eq. 3.30 with Eq. 3.32.

\[
v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t} + O(\Delta t^2).
\] (3.33)

### 3.4.3 NVT Ensemble

Molecular dynamics simulations rely on thermodynamic ensembles, which are used to allow the properties of real thermodynamic systems to be extracted from the calculations [144]. One example of this is the canonical ensemble (NVT) [145], which is used for all molecular dynamics simulations carried out in this thesis. In the NVT ensemble, the number of atoms (N), volume (V) and temperature (T) are conserved quantities. Subsequently, the energy of the endothermic and exothermic processes in the simulation are exchanged with a thermostat. In this way, control of the thermostat provides a way to add and remove energy from the boundaries of the system in a realistic way, approximating the canonical ensemble. An in depth discussion of the practical applications of the NVT ensemble in molecular dynamics simulations can be found in the literature [145].

### 3.5 Concluding remarks

In this section the formulation of DFT that is used in CP2K has been discussed. Then the implications of different functionals was explained with a short explanation of the SIE and how it can be mitigated using hybrid functionals. Next methods that are used in tandem with DFT and CP2K are discussed, the first of these is the NEB method which allows for the calculation of barriers of migration and reaction by finding the minimum energy path and relaxing images along it hence finding saddle points in the potential energy landscape. the second is the defect formation energy which allows for the calculation of defect levels showing the probability of charge trapping at different Fermi level positions. The following chapters present the results of simulations of incorporation of NO and NH$_3$ molecules in the pristine a-SiO$_2$ network and then move onto defective networks and finally discussing an interface structure.
Chapter 4

Modelling the interactions and diffusion of NO in a-SiO$_2$


4.1 Introduction

The work in this chapter discusses the interactions of the NO interstital (NO$_i$) with a pristine a-SiO$_2$ network. As mentioned earlier, the anneal in NO represents the current state of the art for SiC/a-SiO$_2$ devices as it removes 99% of defects in these devices [20]. An important aspect to introduce this work pertains to the chemistry and electronic behaviour of NO annealed devices. An in-depth discussion of both of these aspects can be found in chapter 2 and in refs. [1, 80, 86]. However, the important factors for the assumptions used in this chapter will be that the NO molecule has little or no interaction with regions of the oxide greater than 2 nm from the interface between a-SiO$_2$ and SiC and the nitridation is concentrated in a region less than 2 nm from the interface. This leads us to the assumption that the NO molecule is neutral when it enters the oxide and only becomes charged in this region 2 nm from the interface, which is consistent with the Mott-Cabrera mechanism used to describe the oxidation of Si to form a-SiO$_2$ [146]. This assumption allows us to split our calculations up into the neutral charge state, representing NO in the far from interface regime, and the negative charge state, representing NO in the near
4.2. Methodology

An ensemble of thirty a-SiO$_2$ structures was produced by performing classical molecular dynamics (MD) melt-quench simulations on 216-atom periodic cells of bulk, crystalline SiO$_2$ (β-cristobalite) using the method outlined by Patel et al. [147]. In this method a classical molecular dynamics melt-quench was performed with the ReaxFF force field implemented in the LAMMPS code, [95, 96] using an NPT ensemble and a cooling rate of 6 Kps$^{-1}$. The ion positions and lattice vectors of the MD structures were then relaxed using Density Functional Theory (DFT) as implemented in CP2K using the PBE0_TCLRC functional with a 2 Å truncation radius and 25% Hartree-Fock exchange [130, 148, 149, 150]. The DZVP-MOLOPT basis set and a converged plane wave cut-off of 550 Ry and relative cut off of 50 Ry were used. The efficient calculation of exchange integrals was facilitated by application of the ADMM approximation [151]. The models generated by this procedure have densities ranging between 2.100 g cm$^{-3}$ and 2.286 g cm$^{-3}$.

A single 216-atom periodic cell with a density approximately equal to the mean density of the parent population (2.2 g cm$^{-3}$ [2]) was selected for further studies. All sites present in this structure were then sampled using the scheme shown in Fig. 4.1. A sampling grid of initial positions of NO was created by taking the centre point between three out of the four O atoms hence sampling all seventy-two SiO$_4$ tetrahedra present in the 216-atom cell. The NO molecule is then placed along the vector between the mid-point of the face and the Si-atom at the distance equal to or greater than 1.5 Å away from the network atoms. This 1.5Å distance is measured from the network Si atom to the N atom of the NO molecule and other distances are measured between the N and O atoms of NO molecule and nearby

interface regime. Fig. 1.1 is a schematic representation of the results chapters in this thesis. This chapter is about NO in a pristine network of a-SiO$_2$. It represents the first step in understanding the mechanisms that take place during the NO anneal. This chapter will only look at a pristine network and so no defects, apart from the interstitial NO, are discussed.
4.2. Methodology

Figure 4.1: A schematic representation of the sampling scheme. The green triangle represents the face of the SiO$_4$ tetrahedra being sampled, the red arrow represents the vector between the Si and the N atoms and the black arrow represents the vector between the N and the O atoms which is 1.1 Å away from the N atom. Colour coding: Si in yellow, N in blue and O in red.

Network atoms (see red arrow in Fig. 4.1). Placing the molecule with N or O towards the Si atom does not change the results. Placing the molecule at distances < 1.5 Å leads to nonphysical network relaxation and, if the NO is placed further away, the adjacent grid points become too close to one another, hence reducing sampling.

Before the sampling commenced two tests were performed to validate the use of the method and code. The first was a neutral geometry optimisation in the VASP code. VASP is a code that uses plane-wave basis sets instead of the gaussian-plane wave basis sets implemented in CP2K. The calculations were run with the same PBE0 functional as in CP2K. The VASP calculation took around 50% longer than
4.2. Methodology

the calculation in CP2K with no appreciable change in incorporation energy or end geometry. The second test was to look at the affect of having Van der Waals dispersion corrections in the calculation. To test this 10 geometries of the sampling grid were geometry optimised with and without dispersion corrections and the incorporation energies were calculated. In each case the energy and end geometry were almost identical with the calculations with dispersion corrections taking 25% longer than without.

This procedure results in 187 initial configurations. The atomic positions of these structures are relaxed in the neutral and negative charge states using the DFT setup described above. The calculations of \( \text{NO}^{-1} \) were carried out in the triplet state, this is shown to be the ground state and is in agreement with the previous work [70, 152]. The incorporation energies of the NO\(_t\) in the amorphous network are then calculated using the standard formalism by Northrup and Zhang [153],

\[
E_f = E_{ds} - E_{bulk} - \sum_s n_s \mu_s + q(E_v + \mu_e),
\]

where \( E_{ds} \) is the energy of the system with incorporated NO, \( E_{bulk} \) is the energy of the a-SiO\(_2\) network without NO, \( \mu_s \) is the chemical potential of NO, \( E_v \) is the energy of the valence band maximum, \( \mu_e \) is the Fermi level position and \( q \) is the defect’s charge. We apply the Lany-Zunger charge correction to the calculations done in the negative charge state [154]. As the chemical potential we use the total DFT energy of the NO molecule in the gas phase at 0 K, calculated using the same parameters as the production calculations. This method of calculating the chemical potential is used because it accurately describes the process during the anneal in which the NO molecule starts off in the gas phase and then moves into the network.

The relaxed configurations of the NO\(_t\) then give initial and final states for diffusion trajectories calculated using a climbing image nudged elastic band (CI-NEB) method implemented in the CP2K code [155]. These trajectories were then classified by analysing the steric crowding at the transition state usually situated at the centre of a ring. The usual definition of a ring in a-SiO\(_2\) network as a closed structure with some number of Si-O units [23]. These ring sizes show the steric
effect on the molecule (i.e. smaller rings have a greater steric effect and vice versa).

As we show below, the stable configurations of the NO\textsubscript{i} in a-SiO\textsubscript{2} are located inside cages, such as the one shown in Fig. 4.9. These cages are made up of rings and so to move between them the molecule has to traverse these rings. The 6-membered ring is the most prevalent [156], so four trajectories were selected representing the range of possible 6-membered ring geometries, then two of both 5- and 7-membered rings were probed using the same logic but in this case bracketing the most and least strained variants (see Appendix A for distributions of ring sizes). By choosing a relaxed structure at either side of a ring, the minima are then connected in the NEB calculations and the barrier calculated using the CI-NEB method. It should be noted that this limited sampling is aimed to probe the structural motifs the NO molecule might encounter on its journey to the interface without probing every ring using the very computationally expensive NEB method.

In order to identify the aforementioned cages, we have used a methodology based on the Voronoi S-network, which is a generalisation of the Voronoi-Delaunay tessellation for multi-component systems [157, 158, 159, 160]. This approach has been used in the past to identify regions of empty space in semiconducting alloys [161], to study density fluctuations in super-cooled liquids [162, 163, 164] and even to investigate proton diffusion in water [165]. The relevant methodological details can be found in Refs. [157, 162]; for the purposes of this discussion it is important to note that the size distribution of the cages - and indeed, broadly speaking, the identification of empty space within disordered systems, such as amorphous solids - is not unique. The methodology we have used relies chiefly on two parameters, \( R_P \) and \( R_B \) (see ref.[162]), which determine the minimum size of the cage and the minimum contact area between two cages to be considered as one, respectively. Thus, we have verified that different choices in terms of either \( R_P \) or \( R_B \) do not impact any the qualitative trends reported in the results and discussion section. Importantly, our methodology provides direct access to the volume of the cages and it allows to unequivocally assign a given cage to an interstitial NO molecule. The distribution of cage volumes can be found in appendix A.
4.3 Results and Discussion

In this section the results of sampling the pristine a-SiO$_2$ network are discussed. In the first section we will look at the energies and geometries of the neutral and negatively charged NO interstitial molecules, then we will go on to discuss the barriers for migration through cages for the NO in the neutral and negative charge states. As mentioned previously, in this chapter we use the neutral and negative charge states as facsimiles for the near and far from interface regime, respectively, as we assume that the NO can pick up an electron from the valence band of SiC by way of tunnelling.

4.3.1 Interstitial NO configurations

When NO is placed into an a-SiO$_2$ network and the ion positions are relaxed in the neutral charge state, the NO molecule has a repulsive interaction with the network. This gives a range of different interstitial configurations and incorporation energies, depending on the size and shape of the cage.

Fig. 4.2 shows the distribution of incorporation energies of NO interstitial molecules in the a-SiO$_2$ network with the blue bars showing the neutral state energies. As the system is amorphous, there is a large range of incorporation energies despite there being a singular repulsive steric interaction between the network and molecule. This extensively sampled silica periodic cell gave a range of incorporation energies from -0.05-3.1 eV (see Fig. 4.2). The negative incorporation energy comes from a small attractive dipole interaction between the partial negative charge of N in NO with the partially positive network Si atoms.

Previous literature calculations performed in the crystalline $\alpha$-quartz show that there is an energetic cost of around 3.5 eV for the incorporation of O$_2$ [70]. Despite the small differences in electron distribution between NO and O$_2$, the two molecules are quite similar. As the main interaction in the neutral charge state is a steric repulsion, the mass of the two molecules is the most important feature. They only differ by 1 mass unit so can be directly compared in the neutral charge state to make a comparison based on their stericics. Other than the mass, both molecules are diatomic with a rod like C shape.
Figure 4.2: The formation energy distribution of the neutral and negative interstitial, both show a range of around 3 eV. Neutral charge state in blue and negative charge state in orange. All formation energies are referenced to the valence band edge of the a-SiO$_2$ cell used in the sampling and negative formation energies are stated at this Fermi level position.

As the steric repulsion is the major interaction in the neutral charge state, the free space in the network must be characterised. ref. [166] shows that the crystalline $\alpha$-cristobalite has very uniform, small cage volumes of 33 Å$^3$, which give an incorporation energy of O$_2$ of around 3.5 eV. Whereas in the amorphous phase of SiO$_2$ cage volumes range from 25 Å$^3$ to 250 Å$^3$, with an average of around 65 Å$^3$ [166, 167]. If one considers the densities and structure of the two phases then the reason for these differences becomes clear. Both phases are made up of corner sharing tetrahedra, but in the amorphous phase the tetrahedra are randomly distributed in space while there is a regular distribution of tetrahedra in the crystalline phase. The crystalline phase has a mass density of 2.6 g cm$^{-3}$ and the amorphous phase has a density of 2.2 g cm$^{-3}$. As the crystalline phase has a higher density than that
of the amorphous phase, it can be inferred that its lattice has less free space, hence explaining the existence of the larger voids in the amorphous phase and the higher average void volume than is found in the crystalline phase. The random distribution of tetrahedra in the amorphous phase leads to the range of cage volumes that is found.

Figure 4.3: The highest (squares) and lowest (triangles) incorporation energies for interstitials that are found in the cages as determined by the Voronoi-Delaunay tessellation analysis. This energy dependence is based on the orientation of the molecule with respect to the cage.

The extensively sampled a-SiO\textsubscript{2} cell used to gather results in this chapter has a range of cage volumes between 20 Å\textsuperscript{3} and 60 Å\textsuperscript{3} (Fig. 4.3). As expected, there is an inverse correlation between the cage volume and the incorporation energy within each one of them. This is due to the smaller cages having a higher degree of steric crowding compared to the larger ones, resulting in higher incorporation energies. This can be explained by thinking about the relaxations the molecule must go through in order to get to each minima. In smaller cages, the NO will interact with a larger number of atoms compared to the larger cages, meaning that more atoms must displace to accommodate it, giving rise to a higher energy.

Fig. 4.3 also elucidates that there is a distribution not only in a range in
4.3. Results and Discussion

the full sample but also in each of the cages. In the studies like the one of ref. [166] where Voronoi analysis is used, the free space is assumed to be spherical. If this assumption was correct for a-SiO\textsubscript{2} then one would not observe any range within a cage, as all minima that were slight rotations of the molecule in a cage specific global minima would have the same energy, as the network atoms would be regularly distributed about molecule. This is clearly not the case and the reason is because the cages found in a-SiO\textsubscript{2} are not fully spherical. The primary rotational axis of the NO molecule goes through the N and O parallel to the N-O bond and can be referred to as the long axis of the molecule. The orientation of this axis with respect to the cage axis is an important factor for considering the the interaction of the NO with the a-SiO\textsubscript{2} network.

In Fig. 4.4, two cages found in the Voronoi-Delaunay analysis are shown. Those in Fig. 4.4 a and b are much less spherical than those in Fig. 4.4 c and d. This point is clear by visual inspection but this difference can be quantified using the asphericity delta. This value is a measure of how aspherical the cages are and so a larger number shows a more ”rod-like” cage. The difference in energy between the minima in Fig. 4.4 a and b is much higher than that for Fig. 4.4 c and d. In both cases the difference can be attributed to the long axis of the molecule being mis-aligned with the long axis of the cage, but this makes much more difference when the cage is more rod-like. The atoms around more spherical cages are more homogeneously distributed and so the orientation of the molecule with respect to them has less of an energetic penalty compared to the rod-like cages.

An important concept to consider is the Fermi level of the device as a whole. The SiC devices under investigation are n-doped which means that electron rich species are added to the channel raising the Fermi level of the device from the VB of SiC to a widely accepted value of 4.5 eV above the a-SiO\textsubscript{2} VB, this being the centre of the SiC band gap when the band offset of the device is considered [2, 47]. The modal peak of the 0/-1 CTL for the NO\textsuperscript{i} sits 4.35 eV above the a-SiO\textsubscript{2} VB. This means that there is a high probability of NO to pick up an electron from the system. Fig. 4.5 shows the density of states of an NO molecule in a large cage.
Figure 4.4: Two examples of the cage structures that form the minima in the exhaustive sample and the lowest (a and c) and highest (b and d) energy NO interstitials for both cages. The asphericity delta value for each of these cages is 0.22 (a and b) and 0.01 (c and d). The difference in incorporation energy for each of the cages is 0.19 eV (a and b) and 0.06 eV (c and d). Colour coding Si yellow, N blue and O red.

These are states at Fermi level positions of 0 eV, 3 eV and 5 eV which are formed due to the NO being present in the cage (these have a variance of 1 eV with fig. 4.5 representing the mode) hence are below the Fermi level of the N-type device. This means that there is a high probability that the NO will become charged when it is in the near interface region.

While all of this shows that negative NO is feasible, the ability of electrons to tunnel is highly dependant on the distance between donor and acceptor states. Mott and Cabrerra proposed a model for electron tunnelling for the oxidation of Si to form MOS structures. Their findings show that an electron will tunnel from
4.3. Results and Discussion

Figure 4.5: The density of states (DOS) for the neutral NO molecule in a large cage. The graph is normalised so that the highest occupied state is at a Fermi level of 0 eV. All of the states shown between Fermi levels -3 eV and 6 eV are caused by the presence of NO.

The VB of Si to the O$_2$ molecule when the molecule is within 2 nm of the Si thus directing the diffusion of the O$_2$ molecule making oxidation facile [146]. SIMS measurements of NO annealed SiC/a-SiO$_2$ devices show that there is nitridation of the near interface region (a region $\leq$ 2 nm from the SiC/a-SiO$_2$ interface) of a-SiO$_2$ [86]. This result is also verified by XPS measurements [1]. This means that at least some of the NO molecules can become negatively charged when they reach this near interface oxide region.

The negatively charged NO molecule is iso-electronic to the O$_2$ molecule and one can expect that its ground state will be a triplet. Fig. 4.6 shows the electron arrangement for neutral and negative NO. In the neutral charge state there is an empty molecular orbital and a half filled orbital. In this case Hund’s rule states that the next electron should be placed in the empty orbital as spin pairing two electrons costs extra energy. This means that theoretically the negative NO molecule will be in the triplet spin state not in the singlet multiplicity. When calculations are performed in the singlet and triplet multiplicity, the latter is lower in energy and
Figure 4.6: Molecular orbital diagram of NO in the neutral (left) and negative (right) charge states. The electrons shown in green are the ones present in the neutral charge state and the electron shown in red is added on charging.

hence is the ground state.

Fig. 4.2 (orange bars) shows that the formation energy of negative NO molecules, when the Fermi level of the system is the VB of a-SiO$_2$ is distributed from 2.05 eV to 5.75 eV. The general increase in formation energy is because the VB of a-SiO$_2$ is not the Fermi level position at which the negative charge state of NO is most favourable but showing these values allows us to easily show that there is a distribution of energies even in the negative charge state and that the distribution is different to the neutral charge state. This is explained by the extra electrostatic interactions of NO$^-_i$ compared to NO$_i$.

In the majority of cases, the nitrogen of the NO$^-_i$ is located around 2 Å from a network silicon (Fig. 4.7). This is similar to the Si-N distance found in the literature [152]. The electrostatic interaction is accommodated by the flattening of the face of an SiO$_4$ tetrahedra (Fig. 4.7). This occurs by the oxygen atoms moving into the plane of the Si. The NO$^-_i$ in these minima have a closer Si-N distance than in the neutral charge state, due to the extra electrostatic interaction with the network.

Another configuration is formed when NO$^-_i$ comes across a wide O-Si-O
Figure 4.7: The majority interaction of the NO\(^-\). The N interacts with the SiO\(_4\) tetrahedron, akin to the negative NO in the literature, flattening a face of the tetrahedron. Colour coding is the same as Fig. 4.9.

bond angle site (see Fig. 4.8). It has been shown in ref. [40] that sites with an O-Si-O bond angle greater than 132° can trap electrons in strongly localised states located deep in the band gap. The fully optimised a-SiO\(_2\) structures considered here are denser and have a more narrow O-Si-O angle distribution than those studied in ref. [40] (distribution of O-Si-O bond angles can be found in Appendix A). The spontaneous electron trapping in these structures takes place at precursor sites with O-Si-O angles exceeding 119°. Such sites represent the tail of the bond angle distribution for a-SiO\(_2\). NO\(_I^-\) ions strongly interact with the Si of the wide bond angle site, with a Si-N distance of 1.5 Å. Fig. 4.8 shows that the spin density in this configuration is mostly localised on the NO\(_I^-\), with a small amount on the network atoms.

In this section the differences between neutral and negative NO interstitials have been discussed. It has been shown that NO\(_I^-\) has a repulsive steric interac-
4.3. Results and Discussion

Figure 4.8: The geometry and spin density of the interaction between NO and sites with O-Si-O bond angles of greater than 119°. Colour coding same as Fig. 4.9.

tion with the a-SiO$_2$ network and there are some attractive interactions that lead to negative incorporation energies due to interactions between the partial negative and positive charges on the N and Si atoms, respectively. It is also shown that there is an energetic dependence on the orientation of the long axis of the molecule with respect to the long axis of the cage in which it resides. If these axes are aligned then the molecule will have a lower incorporation energy than if they are misaligned. This orientational dependence is connected to the shapes of the cages forming the minima in the neutral charge state. The difference in incorporation energy is more drastic when the cage is more rod like than spherical. This is because the steric space around the NO molecule is more homogeneous for spherical cages compared to the rod like cages.

In the negative charge state, the NO molecule resides much closer to the a-SiO$_2$ network than in the neutral charge state. This is due to the electrostatic interaction between the NO and the a-SiO$_2$ network, specifically the negatively charged
4.3. Results and Discussion

NO and the partially positive network Si atom. There is also an interaction that spontaneously forms between the NO$_{i}^-$ and O-Si-O bond angles greater than 119°, where NO$_{i}^-$ blocks the electron trapping sites, which can reduce the rate of degradation of a-SiO$_2$ due to the electron trapping from SiC.

4.3.2 Migration of NO in a-SiO$_2$

In this chapter so far we have discussed the static interactions of the NO interstitial in a-SiO$_2$. In the neutral charge state the NO wants to be as far from the network as feasibly possible, whereas in the negative charge state one may have to overcome some kind of electrostatic interaction to migrate or diffuse.

Before going through the results it is important to have a short discussion about the structure of a-SiO$_2$ and how one can use this to understand the microstructures that NO will encounter on its journey to the interface. Fig. 4.9 shows an isolated cage that makes up the minima found in the previous section. The cage structure can be viewed as made up of Si-O units forming some irregular polyhedral shape. The faces of the polyhedra are the rings (highlighted in green in Fig. 4.9) the NO molecule must traverse in order to make progress towards the interface.

The barrier height for migration depends on the size of the ring. The energetic barrier for migration through a ring increases with decreasing ring size, as shown in Fig. 4.11, but there are large variations between barriers through rings of the same size which are caused by differences in the steric environment of each ring. If the ring under investigation is in a dense region, then the breathing distortions in Fig. 4.10 are constrained hence increasing barrier for migration. If the ring migrated through is in a less dense region of the oxide, then breathing distortions are easily facilitated hence yielding a lower barrier.

We observe large variations in the migration barriers between different ring sizes. There is less space for migration through 5 when compared to 6 member rings and a large energetic difference between migration mechanisms through these rings. Figs. 4.10a and b show the geometries of the initial and transition states for migration through the 6 member ring. The ring distortion in the transition state can be characterised by a breathing motion, where the largest change in Si-O bond
Figure 4.9: An example of the cage structures that form the minima in the exhaustively sampled a-SiO$_2$ cell. The green line signifies two interlinking rings that make up the cage and so the NO has to move through to progress from cage to cage. Colour coding Si yellow and O red.

length is from 1.62 Å to 1.64 Å. For the transfer through the 5 member ring (Figs. 4.10c and 4.10d) there is still a breathing distortion but the distortion is even more drastic, with the largest change in bond length being from 1.64 Å to 1.71 Å. This is caused by the further decreased free space and reduced diameter of the ring and results in the increased barrier for migration [90]. For NO$_2^-$, there is a greater increase in the barrier height through the 5 and 6 membered rings (Fig. 4.11). Again, one can link this to the distance between the NO$_2^-$ and the network atoms. There is a decrease in the distance between the NO$_2^-$ molecule and the network and so the interaction is stronger causing an increase in the barrier for migration with respect to the NO$_i$.

Migrations through 7 member rings have the lowest barriers and show little variation between charge states as there is the largest amount of free space along the migration path. In the neutral charge state this means that the NO has a smaller number of network atoms to repel. The barriers for migration in the negative charge state are, on average 0.2 eV higher than the neutral charge state. This is attributed to
4.3. Results and Discussion

**Figure 4.10:** The changes in bond length between a 5 and 6 membered ring transition. The blue line in a and c illustrates the definition of ring used in this work. Colour coding same as Fig. 4.9.

**Figure 4.11:** Barrier heights of 5, 6 and 7 membered rings in a-SiO$_2$ in the neutral (triangles) and negative (squares). The average increase in barrier height from neutral to negative is 0.2 eV.

the electrostatic interactions that are shown for the negative NO$_i^-$. This electrostatic interaction attaches an energetic penalty for the NO$_i^-$ to move from one cage to another.
4.4 Conclusion

In this chapter the interactions of NO in a pristine a-SiO$_2$ have been discussed. The Mott-Cabrerra model has been used to justify considering NO being neutral far from the interface and negatively charged close to the interface where electron tunnelling from SiC is possible.

For static calculations in the neutral charge state we show that there is overwhelmingly a steric repulsive interaction between the NO molecule and the a-SiO$_2$ network, with some attractive interactions between the partially negative N atom of the NO molecule and a partially positive network Si atom. In the negative charge state there are two interactions between the negatively charged NO$^-$ and the a-SiO$_2$ network. The majority interaction is where the NO$^-$ interacts with an SiO$_4$ tetrahedra, sitting 2 Å from the central Si atom and flattening the face of the tetrahedra. The minority interaction is the interaction between NO and a O-Si-O bond angle greater than 119°.

In the barrier calculations, an inverse correlation between the size of the ring and the migration barrier through it was found. This was attributed to the decrease in free space going from larger rings to smaller ones holding true for the negative charge state too. However, here there is an increase in the average migration barrier by 0.2 eV attributed to the extra electrostatic interaction, as seen in the static calculations.

The next chapter deals with the interactions of another annealing agent, ammonia (NH$_3$), with pristine SiO$_2$ in both the crystalline and amorphous phases.
Chapter 5

Modelling the interactions of NH$_3$ with crystalline and amorphous SiO$_2$

5.1 Introduction

This chapter describes the results of calculations of the interaction of NH$_3$ with pristine SiO$_2$ in both the crystalline and amorphous phases. Fig. 1.1 shows its relation to other chapters in this thesis. It builds on the knowledge gleaned from chapter 4 to look at the interactions of NH$_3$ with pristine SiO$_2$. It sets about tackling the dissociation, migration, and incorporation of NH$_3$ from an atomistic perspective, to provide insights into the NH$_3$ anneal and the different modes of interaction and incorporation. From this, an understanding of the energetic landscape can be built-up, giving important insights into whether passivation approaches utilising NH$_3$ can ever be tuned to improve upon the NO anneal, or if the N-incorporation in the bulk oxide and the surface of a-SiO$_2$ cannot be avoided and hence, NH$_3$ annealed devices will always be susceptible to the accelerated gate leakage compared to the NO annealed systems.

While NO represents the current state of the art for annealing agents in SiC/a-SiO$_2$ technologies, there have been some issues identified with the annealing procedure. It has been posited in the literature that this process is inefficient as 2 molecules of NO can thermally disassociate into N$_2$ and O$_2$, so the passivation of defects in the device is in competition with the thermal cleavage of NO [168, 87, 88].
Though this is unlikely as it generally requires the use of precious metal catalysts like in catalytic converters. Another justification for different anneals is that NO is a very harmful gas. NO\textsubscript{x} gasses which form from incomplete combustion of vehicular fuel are actively removed from car exhaust gasses, using catalytic converters. So, in an effort to preserve the safety of the engineers who fabricate these devices another annealing agent was sought. NH\textsubscript{3} was thought to be a good alternative as, while it is toxic in large quantities, it is much less caustic than NO.

During these anneal procedures the passivisation agent incorporates into the oxide and is envisaged to interact with the interface defects removing them. Afanas’ev \textit{et al.} [169] have shown that after the anneal with NO, SiC devices exhibit a drastic decrease in the density of interface defect states. However, regardless of how the procedure is tuned, around 1\% of the defect states persist [169]. These can be attributed to unpassivated defects that are in someway sterically inaccessible to the passivant. Alternatively, as will be explained later in this thesis, it is also possible that the defect states observed post passivisation are in fact N-related states introduced as a result of passivisation.

Previous studies have indicated that anneals in NH\textsubscript{3} can target defects that are impervious to the NO anneal. This has been attributed to NH\textsubscript{3} introducing both N and H, targeting distinct defects in a-SiO\textsubscript{2} and at the interface. This was born from the use of the forming gas, a mixture of N\textsubscript{2} and H\textsubscript{2}, anneal being used to passivate defects in Si/a-SiO\textsubscript{2} devices so NH\textsubscript{3} was thought to be a ”perfect storm” annealing agent for SiC/a-SiO\textsubscript{2} devices [170, 171, 85]. However, anneals in NH\textsubscript{3} have been shown to result in an enhanced leakage current [87, 88, 6]. This has been explained to result from the nitrogen incorporation in both the bulk oxide and interface region of the device, although the nature of ‘incorporation’ is unclear. Though elemental analysis, such as XPS, show nitrogen signals in the bulk oxide of NH\textsubscript{3} annealed devices, which would only be present if the N is bonded to the network [1, 47].

There has been a concerted attempt in the literature to untangle the atomistic effects of the NH\textsubscript{3} anneal and shed light on the mode of N-incorporation. Pitthan \textit{et al.} [87, 88] performed the NH\textsubscript{3} annealing procedure on 4H-SiC devices using
5.2 Methods

The work in this section details the interactions of NH₃ and its fragments (NH and NH₂) with the hydroxylated surfaces of SiO₂ in both amorphous and crystalline phases. Then we look at the interactions of the NH fragment with the bulk of a-SiO₂. The NH fragment was chosen because its incorporation energy in SiO₂ is shown to be vastly lower than those for NH₂ and NH₃, being 1.6 eV and 2 eV lower, respectively.

Classical MD and DFT calculations were performed to elucidate the interactions of NH₃ with fully and partially hydroxylated surfaces of SiO₂. a-SiO₂ surfaces have a hydroxylation level of ≈ 8 nm⁻² and the crystalline surface have a hydroxylation level of ≈ 5 nm⁻². The crystalline phase of SiO₂ that is used here is α-cristobalite.

On both surfaces, we first performed classical MD simulations. We place NH₃ on the surface and heat the sample up to 1500 K; these structures are then kept at 1500 K for 1 ns and this procedure is repeated 100 times. A cell without NH₃ present is also treated with the same classical MD method, as a control. These classical MD simulations used the Reaxx force field within the Lammps code [95, 96].

The next set of calculations treat the interactions of the NH fragment with the bulk of a-SiO₂. The bulk of a-SiO₂ is sampled using the same method as in

5.2 Methods

isotopically labelled $^{15}$NH₃. The XPS results show that there is a large concentration of Si-N bonds in the bulk oxide [87, 88]. This is complemented by the results of Regoutz et al. [1] who performed depth profiling XPS measurements on devices annealed in N₂, NO, NH₃ and NH₃ + NO [1]. This study was an etch step XPS experiment where a layer of the oxide was removed after it had been probed with X-rays. It detected a large nitrogen signal at the surface of a-SiO₂ and that there was a decaying signal towards the SiC/a-SiO₂ interface. This work also measured an ≈ 5 fold larger N signal at the interface of NH₃ annealed devices compared to NO annealed devices at comparable conditions.
chapter 4. All of the DFT calculations were done in CP2K using the PBE0-TC-LRC functional (exchange truncation radius of 2 Å and 25% exact exchange) with the DZVP-MOLOPT basis set and a converged plane wave cut-off of 550 Ry [130, 148, 149, 150]. The efficient calculations of exchange integrals were facilitated by application of the ADMM approximation using the pFIT3 basis set [129].

5.3 Results and discussion

5.3.1 Interactions of NH\textsubscript{3} with the surface of crystalline SiO\textsubscript{2}

This section looks at the interactions of NH\textsubscript{3} with the SiO\textsubscript{2} surfaces. First, we examine the orientation dependence of the NH\textsubscript{3} molecule with respect to the surface. The principle rotational axis of the NH\textsubscript{3} molecule is the C\textsubscript{3} axis that goes through the N and perpendicular to the plane of the three H atoms. These calculations were done using the hybrid DFT parameters mentioned in section 5.2 using geometry optimisations. Four orientations of this molecule were examined, two with the principle axis perpendicular (Fig. 5.1a and 5.1b) to the plane of the surface and two with this axis parallel to the plane of the surface (Fig. 5.1c and 5.1d). For each of the orientations a 5 by 5 grid was used to sample the surface, giving a total of 100 structures.

The 100 calculations on the surface of α-cristobalite yield 2 different relaxed geometries (Fig. 5.2). Fig. 5.2a shows the H bonded interaction and 5.2b shows the non interacting configuration. The difference in energy between these two configurations is 0.5 eV, with the H-bonded configuration being more stable than the other.

The number of each configuration occurring strongly depends on the starting geometry. If the N atom is pointing towards the surface (Fig. 5.1b), the H-bonded configuration occurs most often (in 15 out of 25 samples) whereas if the N molecule is pointing away from the surface (Fig. 5.1a), it occurs less often (2 out of 25 samples). This is most likely to be a consequence of the distance between the partially negative N and the partially positive H atoms on the surface silanol groups.

These calculations show the different configurations that can be formed on the
Figure 5.1: The different orientations of NH$_3$ sampled on the surface of $\alpha$-cristobalite. a) and b) have the principle rotation axis of NH$_3$ perpendicular to the plane of the surface, and c) and d) have the principle rotation axis parallel to the surface. Colour coding: Si in yellow, N in blue and O in red.

surface of a fully hydroxylated and idealised SiO$_2$ surface. They also demonstrate the factors that would affect physisorption. During the anneal, some NH$_3$ molecules have to penetrate from the gas phase of the chamber into the bulk of a-SiO$_2$. Intuitively, one would assume that the intervening step would be some physisorption on the surface of a-SiO$_2$. Our calculations show that, when the NH$_3$ molecule approaches the surface of a-SiO$_2$ with its N facing the surface, it is more likely to physisorb compared to when it approaches the surface with its N facing away from the surface. This may have two consequences, the first is that these physisorbed molecules will be more likely to react on the surface, and the second being that there might be a lower barrier for ingress into the oxide. Each of these consequences result from the molecule having less degrees of freedom when physisorbed than when they are in the gas phase.

These calculations look at the interactions of NH$_3$ with a fully hydroxylated surface of $\alpha$-cristobalite, with a hydroxylation level of 5 nm$^{-2}$ which is near that of a-SiO$_2$ at 300 K [172]. However, during the anneal the temperature is much higher
5.3. Results and discussion

Figure 5.2: The two different results of the orientation dependence study done on the surface of $\alpha$-cristobalite. a) is the H-bonded configuration and b) is the non-interacting configuration. Colour coding same as Fig. 5.1.

and the hydroxylation level is reduced due to desorption of hydrogen [172]. Hence one must look at the interactions of NH$_3$ with an under-passivated surface.

In this part of the study we removed one and then the second H from the surface and performed geometry optimisation calculation with the NH$_3$ next to these under-coordinated bonds using DFT. The results show that the H atoms would switch from the ammonia molecule to the under-coordinated O atoms. When NEB calculations are performed, the reaction is shown to be barrier-less. This can be explained by the respective bond enthalpies of N-H and O-H bonds. The former has a bond enthalpy of 391 kJ mol$^{-1}$ and the latter 467 kJ mol$^{-1}$. This means that the system as a whole is 76 kJ mol$^{-1}$ more stable, per O-H bond formed, on hydroxylation of the surface compared to having dangling bonds (Fig. 5.3).

Now we must detail the barriers for migration into SiO$_2$. This was done on the $\alpha$-cristobalite surface using NEB calculations. Table 5.1 shows these barriers for each of the fragments. The difference in these barriers increases with the increasing size of the fragment, meaning that the migration into the $\alpha$-cristobalite is wholly
5.3. Results and discussion

Figure 5.3: The results of geometry optimisation calculations of NH$_3$ on a partially hydroxylated surface. The upper image shows the formation of the NH$_2$ fragment and the lower image shows the formation of the NH fragment. Colour coding same as Fig. 5.1.

Table 5.1: The barriers of ingress into SiO$_2$ for each of the NH$_3$ fragments.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>NH</th>
<th>NH$_2$</th>
<th>NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrier [eV]</td>
<td>0.2</td>
<td>1.61</td>
<td>2.39</td>
</tr>
</tbody>
</table>

In this section we have looked at the interactions of NH$_3$ with a crystalline surface of SiO$_2$. This study allows us to understand the major interactions that can occur when NH$_3$ interacts with the surface of SiO$_2$ during the anneal. It has been demonstrated that the orientation of the C$_3$ axis of the NH$_3$ is important to the H-bonding interactions that can occur on a fully hydroxylated surface. Then we show that, when NH$_3$ interacts with a partially hydroxylated surface, the H atoms can be abstracted to form NH$_2$ and NH. The migration barriers of these fragments are such that the smallest fragment, NH, is the most likely to penetrate into the crystalline surface as it has the lowest barrier for ingress. In the next section MD simulations of NH$_3$ on an amorphous surface are described.
5.3. Results and discussion

5.3.2 Interactions of NH$_3$ with the surface of a-SiO$_2$

This section details the results of classical MD simulations of NH$_3$ on the surface a-SiO$_2$. The starting geometry of these simulations is shown in Fig. 5.4. During the ramp stage of the MD run the silanol groups on the surface of a-SiO$_2$ start to rotate, as would be expected at elevated temperatures. Then during the equilibration stage water is liberated from the surface. This leads to the formation of strained siloxane rings, the reaction proceeds in a manner similar to that described by Commas-Vives et al. [172]. Strained rings have long been seen as reactive centres in chemistry e.g. the epoxide group is a 3 membered ring consisting of two C atoms and an O atom, which are the centres for addition reactions in organic chemistry [173]. The main stated reason for the epoxide group being reactive is the strain of the C-C-O bond angles. The C atom is sp$^3$ hybridised and so would prefer to be in a tetrahedral geometry with bond angles of 109.5$^\circ$ and bond lengths of 1.43 Å. However, the epoxide group is approximated as an equilateral triangle and so the C-C-O bond angles are contracted to 60$^\circ$ [174]. A similar case can be made for the smaller siloxane rings. Si is also sp$^3$ and so would prefer to have bond angles of 109.5$^\circ$ which is similar to the internal angles of a six membered ring. The smaller rings, such as 4 and 5 membered rings, which are the result of the water formation, have angles closer to 90$^\circ$ and so are more reactive compared to the larger rings and can be seen as active sites for the reaction of NH$_3$ with the surface of SiO$_2$.

The reaction of NH$_3$ with the surface of SiO$_2$ proceeds with the interaction of the NH$_3$ with a surface Si atom. The vibration of the Si-O bond leads to interactions between the partially positive Si and the partially negative N atom. There is then coordination of the Si and N and also the O and H, which then leads to the formation of a Si-N bond and a O-H bond, forming the water molecule.

The above reaction happens in about 50% of MD runs. In most other cases the NH$_3$ remains unreacted and generally migrates from one silanol group to another in H bonding configurations (Fig. 5.6). This migration process is a consequence of the weak inter-molecular interactions, compared to the covalent bonding in the rest of the system. This is exemplified by the gas phase NH$_3$ molecule in section 5.3.1.
5.3. Results and discussion

Figure 5.4: The starting geometry for MD runs done on the surface of a-SiO$_2$. Colour coding same as Fig. 5.1.

being 0.5 eV less favourable than the H-bonded NH$_3$ meaning that 0.5 eV is gained on H-bonding compared to the 4.5 eV gained from forming a Si-O bond.

Another important point to note is the ingress of the molecule into the network. In the previous section it was shown that only the smaller fragments have the ability to move into SiO$_2$. However, if the NH$_3$ stays unreacted, it can gain access to the system. The difference here is that there are larger rings on the surface that have the required space to allow the NH$_3$ molecule to move into the oxide. After the molecule moves into the network, it sits in one of the cage structures described in chapter 4. After the NH$_3$ molecule moves into this cage, it stays there until finally it leaves back through the ring it moved through. This suggests that the NH$_3$ molecule is too big to get too far into the oxide, at least without significant distortion of the a-SiO$_2$ network.
5.3. Results and discussion

5.3.3 Calculations in the bulk of a-SiO$_2$

The results in the previous section show that the ammonia molecule can break up into smaller fragments at the surface. These results agree with some of the experimental observations in refs. [48, 83, 175], which indicate that NH$_2$ and NH are more mobile inside the SiO$_2$ network. The previous section showed that the abstraction of two H atoms on a partially hydroxylated surface is a facile process, in that it happens on geometry optimisation. This partially hydroxylated surface is justified by the works of Commas-Vives et al. [172] which shows that there is an inverse correlation between the distance between Si-OH groups on the surface and the barrier to form water and to lose the amount of H that is required some H must be lost from long range Si-OH groups hence essentially leading to long Si-O bonds and so near under coordinated Si atoms. This section details the interactions of the NH fragment with the a-SiO$_2$ network.

In the first part of this work we looked at neutral NH in the triplet state thus extending the work done by Bakos et al. [70] and Orelana et al. [152] They have shown that the triplet state of NH is 2 eV lower in energy than the singlet state in the gas phase [70, 152]. The 216 atom cell of a-SiO$_2$ was exhaustively sampled by placing NH in 187 different positions and then relaxing the ion positions in the triplet and singlet states. The energy distributions can be seen in Fig. 5.7. They are similar to that of the NO molecule in SiO$_2$ in ref. [176] and chapter 4 leading to a
similar conclusion that was drawn there, the incorporation energy of the interstitial is largely determined by steric environment it is in. Each of the relaxed structures are formed an interstitial configuration, as shown in 5.9. This is at odds with the experimental work by Pittan et al. [87] and Regoutz et al. [1] who see nitridation of the bulk oxide [1, 87]. Our assumptions state that the bulk oxide of these devices has a very low concentration of defects and hence the N signals observed in these experiments are unlikely to result from reactions of NH$_3$ with defects.

The results of Orelana et al. [152] show that, in the gas phase, the NH fragment has a spin triplet (S=1) ground state as the spin singlet configuration is 2.06 eV higher in energy [152]. However within our computational setup the NH fragment in the gas phase is isoenergetic in both the triplet and singlet states. Hence we then re-sampled the a-SiO$_2$ in the singlet multiplicity. In the a-SiO$_2$ network, when the triplet NH is an interstitial it is an average of 0.5 eV lower in energy than the singlet interstitial.

In the singlet multiplicity, 17.6% of the structures form a nitroxy bridge defect
5.3. Results and discussion

Figure 5.7: The incorporation energies of the singlet and triplet interstitials. On average, there is an increase of 0.5 eV in the singlet multiplicity.

(Fig. 5.8) on ion relaxation. This defect has a formation energy 1 eV lower than the NH interstitial in the singlet state and 0.2 eV lower energy than the NH interstitial in the triplet state. This energy gain is attributed to two effects. The first one is the relaxation of strained environments in the oxide on NH insertion as this always occurs at bond lengths greater than 1.64 Å. The second can be demonstrated using
the bond enthalpy of the Si-O, Si-N and O-N bonds. The Si-O bond (bond enthalpy of 4.68 eV) is broken and Si-N and O-N bonds (enthalpies of 3.68 eV and 2.08 eV, respectively) are formed, giving a total energy gain of 1.08 eV. Despite this gain, the nitroxy bridge forms the minority of our sample. We attribute this to the requirement of a structural precursor. The nitroxy bridge structure forms at sites having a Si-O bond that is longer than those of the modal bond length (1.63 Å). The NH molecule, on geometry optimisation, inserts itself into a Si–O bond which is greater than 1.64 Å. This forms a structure with a similar stoichiometry as those found in the oxide of NH\textsubscript{3} annealed devices, as shown by XPS measurements [1].

![Image of nitroxy bridge structure and graph](image)

**Figure 5.8:** Structure (a) and charge transition levels (b) of the Nitroxy Bridge. This structure forms when there is a bond length greater than 1.64 Å. Colour coding same as Fig. 5.1.

The forward barrier to form the nitroxy bridge is 0.8 eV and the reverse barrier
to reform the interstitial geometry is 1.2 eV. These results show that in the singlet multiplicity there is an easily accessible barrier for the reaction of NH with the network. The reverse barrier which, while accessible at anneal temperatures, would require the system moving to a geometry with higher energy.

![Figure 5.9](image)

**Figure 5.9:** Structure (a) and charge transition levels (b) of the NH interstitial. This structure forms when there is a bond length $< 1.64 \text{Å}$. Colour coding same as Fig. 5.1.

The NH interstitial and the nitroxy bridge have 2 different electronic behaviours. The interstitial configuration only has a 0/- charge transition level at a
5.4. Conclusions

Fermi level of 2 eV within the band gap of SiO$_2$. If the Fermi level of the SiC/a-SiO$_2$ device lies at 4.5 eV in Fig. 5.9 then the NH interstitial would become negative when there is an available electron, chapter 6 looks at the interactions of the NH fragment with the intrinsic electron trap. This can occur when it is less than 2 nm from the SiC/a-SiO$_2$ interface where an electron can tunnel from the SiC valence band to the NH molecule. This is similar behaviour to the NO interstitial (seen in chapter 4).

The nitroxy bridge has both 0/+1 and -1/0 levels at 2 eV and 6.5 eV above the a-SiO$_2$ valence band, respectively. The nitroxy bridge adds more transition levels into the band gap of a-SiO$_2$ which could point towards charging of the oxide on device operation. Devices annealed in NH$_3$ have excellent mobility on initial operation but that they then fail faster than their NO alternatives [87]. The initial mobility can be attributed to the NH$_3$ anneal bringing $\approx$ 5 times more nitrogen to the interface than the NO anneal.

5.4 Conclusions

This chapter has summarised the interactions that NH$_3$ and its fragments have with the surface of a-SiO$_2$. On a fully hydroxylated surface, there is a dependence on the orientation of the molecule on the type of interactions that form on the surface. If the N atom of the NH$_3$ is pointing at the surface then it is much more likely to form H-bonding type interactions with the surface of a-SiO$_2$ which decreases the molecules degrees of freedom leading to it being easier for the molecule to react with the surface or gain entry into it.

We observe the formation of the nitroxy bridge defect in the bulk of a-SiO$_2$, which is the NH fragment inserted in a Si-O bond. The barrier to form this from an interstitial NH is 0.8 eV and the reverse barrier is 1.2 eV. This reaction happens only when NH molecule in the singlet state interacts with elongated Si–O bonds greater than 1.64 Å. When the CTLs of the nitroxy bridge and the NH interstitial are calculated, the former is seen to trap holes and electrons in the band gap of a-SiO$_2$ and the latter is seen to just trap electrons. The electron and hole trapping
5.4. Conclusions

CTLs of the nitroxy bridge defect are near the CBM and VBM of SiC, respectively, when the band offset of the device is taken into account. Hence, there is a high probability for electron tunnelling from the conduction band of SiC and holes being trapped in the a-SiO₂, which could lead to recombination centres. All of this means that the nitroxy bridge should be included in the list of potential defects that cause gate leakage current and TAT tunnelling pathways, specifically in NH₃ annealed devices. In the triplet multiplicity the NH fragment only forms the interstitial.

The data in this chapter shows that, during the NH₃ anneal nitridation is a facile process at any point in the oxide. The precursor required to form the nitroxy bridge (bonds 1.64 Å or greater) and analysis of the structure shows that these bonds are in high density high strain regions of the oxide. The density of the oxide in Si/SiO₂ has been shown to increase by around 10% in the near interface meaning that the concentration of these high strain environments in the near interface region increases. This combined with the high defect density at the interface may explain why one finds more N in the near interface region during the NH₃ anneal compared to the NO anneal.

The previous two chapters considered the interaction of NO and NH₃ with the pristine networks and lattices of SiO₂ at different distances from the SiC/SiO₂ interface giving an idea of what the mobile species are in the anneals. The next chapter considers the interactions of these molecules and fragments with defects in a-SiO₂.
Chapter 6

Modelling the interactions of NO and NH$_3$ fragments with common oxide defects

6.1 Introduction

This chapter presents the results of modelling the nitridation of common oxide defects in a-SiO$_2$. An in-depth discussion of the challenges associated with SiC/a-SiO$_2$ devices and the annealing techniques used is presented in chapter 2. Briefly, SiC/a-SiO$_2$ devices suffer from a high density of near interface defects which cause effects, such as TAT, sub-threshold hysteresis, bias temperature instability, and inversion channel mobility. The latter of these occurs due to defects in the channel \((i.e.\) in the SiC not the a-SiO$_2$) and the nitridation of them has been discussed in ref. [177]. The remaining three occur due to defects in the gate oxide. A post-oxidation anneal procedure has been used to mitigate these effects, with the anneal in an NO atmosphere being the current state of the art.

In this chapter we present three oxide defects that are believed to be linked to the reliability issues mentioned above. These are the intrinsic electron trap, the O vacancy and the Hydroxyl $E'$ centre. First, the defects themselves are discussed if their computation here differs from the literature. Then the defects are coordinated to the NO molecule with the intrinsic electron trap also being coordinated to
the NH$_2$ and NH fragments. The change of the 0/- CTL on coordination of these N containing molecules and fragments is discussed, in each case there is a discussion about the tunnelling characteristics of the defect pre- and post- coordination, with reference to the TDDB measurements done parallel to the theoretical study performed here. The next section details the methodology used during this investigation.

6.2 Method

The investigation carried out in this chapter uses the same a-SiO$_2$ structures as in chapters 4 and 5 as well as the same DFT parameters. These are: 550 Ry cut-off and 50 Ry relative cut-off, using the PBE0_TCL functional with 25% exact exchange, and the DZVP-GTH-MOLOPT basis sets with ADMM basis sets used to facilitate the calculation of the computationally demanding exact exchange integrals, all within the CP2K code. A full discussion of the DFT methodology can be found in chapter 3 and the procedure to make the a-SiO$_2$ structures is discussed briefly in chapter 4 with a more in-depth discussion found in ref. [108]. The rest of this section details the method unique to this chapter, with reference to work in previous chapters where appropriate.

From the library of thirty structures, two structures were fully sampled. They have densities of 2.2 g cm$^{-3}$ and 2.286 g cm$^{-3}$. The latter of these has the highest density of the thirty structures and was chosen to try and emulate a higher density oxide as would be found in the near interface regime. However, on comparison of CTLs and formation energies, no difference was found. In the two structures, each of the 144 oxygen sites is sampled with the Hydroxyl E$'$ centre and the O vacancy. After the samples have relaxed in the neutral and negative charge states (adding the positive charge state for the Hydroxyl E$'$ centre), we collect the CTLs and produce the formation energy diagrams. Next, we consider the interaction of the N containing fragments and molecules with these defects.

In the thirty structures, we find that five structures spontaneously form the intrinsic electron trap so we also take these defects and add the nitrogen compounds
to all of them and collect the 0/- CTLs. For each of the defects (both nitridated and not), we first relax the ion positions in the neutral and then in the negative charge states. All defects and N containing counterparts are made and checked by manual inspection. The justification for the defects presented can be sought in chapter 2.

Another consideration that must be made is the method of defect formation energy calculation. The usual procedure for the calculation of defect formation energies is outlined in chapter 3 and is used to calculate the formation energies and CTLs of the defects without the N compounds. However, as stated in chapter 3, one must calculate these parameters in a way that mimics the process used to form them. In the case of passivation of defects with N containing molecules, the agent is added to an already defective network so the standard formulation should be changed to:

\[
E_f = E_{N(ds)} - E_{ds} - \sum_s n_s \mu_s + q(E_v + \mu_e),
\]  

(6.1)

where \( E_{N(ds)} \) is the total energy of the nitridated defect and \( E_{ds} \) is the energy of the original defected cell. Each of the defects coordinated to the N containing compounds is referenced back to the original defect. This allows us to calculate a formation energy using the initial conditions that accurately relate to the device during anneal (i.e. that the defects are present in the oxide and the N containing compounds interact with them during the anneal). The chemical potential for each N contain compound is its DFT energy in the gas phase, again as this is how they start off during the anneal procedure. Finally, we apply the Lany-Zunger charge correction to the calculations done in charged states [154].

6.3 Results

This section details the CTLs of defects, both in the presence of nitridating gas molecules and without. The first section looks at just the oxide defects and the second examines these defects in the presence of NO, NH and NH\(_2\). The oxide defects are well studied in the literature (see section 2.5) and so the results in the first section will focus on the differences between the defects that are calculated in the library of structures made with the above method. We start by looking at the
intrinsic electron trap and move to a short discussion on Hydroxyl E' centre.

6.3.1 The Intrinsic Electron Trap and bi-electron trap

The intrinsic electron trap has been shown, theoretically, to form when extra electrons are injected into a pristine a-SiO$_2$ network from an electrode. The electrons have been shown to spontaneously localise at O-Si-O bond angles wider than 132°. [40] The structures used in this study have very few angles greater than 132° but spontaneous electron trapping is still a feature of them. The electrons trap at O-Si-O bond angles greater than 122° and a Si-O bond length greater than 1.64 Å present both of these structural parameters are still at the very tail of the distribution (appendix A) meaning that electron trapping still occurs at rare structural features. In the thirty structures, spontaneous electron trapping occurs in five structures.

The 0/-1 CTL for this defect is reported to be 6 eV above the VB of a-SiO$_2$ which puts it iso-enegetic with the conduction band of SiC, when the band offset of the device is considered. The intrinsic electron trap can trap a second electron and this has been shown to be the first step in a mechanism to form O vacancies [24]. This mechanism relies on there being large repulsive interactions causing bond breaking. When a second electron traps at the wide bond angle site there is a large increase in the Si-O atomic distances, the longer of the two increasing from 1.75 Å to 2.42 Å. These bond lengths are not explicitly stated in ref. [24] so are stated here for completeness.

6.3.2 Hydroxyl E'-centre

As mentioned previously, the Hydroxyl E'-centre has to be considered because H or H containing molecules (H$_2$, H$_2$O etc.) are ubiquitous to all systems and have been shown to create defects when present in certain concentrations. It is also suggested that, when anneals in NH$_3$ are performed, there is an increased gate leakage current with respect to the NO annealed device. As shown in Fig. 6.6, the Hydroxyl E'-centre has 0/- CTLs close to the band edges of both SiC and a-SiO$_2$ meaning it is a prime candidate for TAT in these devices. When the Hydroxyl E'-centre is charged, the charge localises on the Si dangling bond of the defect. In the neutral charge
6.3. Results

Figure 6.1: The 0/- CTLs and atomic structure of the Hydroxyl E' centre. The CTLs of the Hydroxyl E' centre were calculated over 288 O atoms in two 216-atom a-SiO\textsubscript{2} structures. Colour coding: Si yellow, O red and H white.

state, there is an unpaired electron on the Si and the electron is paired and removed in the negative and positive charge states, respectively.

An important characteristic that is viewed differently between the defects calculated here and those calculated in the literature is the formation of negative-U centres. A negative-U centre is where the defects most stable in the charged states compared to the neutral state, in some range. El-Sayed et al. [41] have shown that, when the Si/a-SiO\textsubscript{2} band offset is considered, within the Si band gap range, there is no negative-U behaviour. However, 4H-SiC has a wider band gap of 3.2 eV and so within this range there are around twenty Hydroxyl E'-centres that show negative-U behaviour [41]. This could mean that for SiC/a-SiO\textsubscript{2} devices the Hydroxyl E'-centre is of bigger concern due to potential charge trapping on fabrication of the device.
6.4 Oxide Defects coordinated to N containing compounds and fragments

Above we have discussed the differences between the results found in this study and the results of the literature. This section will discuss how the CTLs and geometry of the intrinsic electron trap, O vacancy and the Hydroxyl E′ centre change on nitridation.

6.4.1 Intrinsic electron trap

In chapter 4 the NO$^-i$ was shown to spontaneously interact with O-Si-O bond angles of greater than 120°, with a Si-N distance of 1.5 Å (Fig. 4.8). Due to this, the only geometry that is tested is the N atom of the the NO molecule facing the Si of the intrinsic electron trap. In chapter 4 it was posited that the NO can block potential precursor sites and hence reduce the concentration of these electron trapping sites. For the NH$^x$ fragments, the orientation by the H end towards the Si ion with extra electron was thought to be the lowest energy configuration, due to the H atom having a partially positive charge. However, this did not show any appreciable change in the CTL as the H atom in these fragments generally interacted with the O atoms and not the trapped electron on the Si atom, so no appreciable stabilisation occurred.

For all of the nitrogen containing compounds and fragments, the 0/- CTL moves down towards the VB of a-SiO$_2$ sitting ≈ 2.5 eV above the a-SiO$_2$ VB, and 0.4 eV below the VB of SiC (Fig. 6.2). This means that the level is moved far away from the CB of both a-SiO$_2$ and SiC hence the probability of electrons tunnelling to these centres is drastically reduced and so removes them from BTI and TAT processes.

The geometry of the intrinsic electron trap coordinated to NO and NH$^x$ (x=1,2) is shown in Fig. 6.3. The Si-N distance in each case is ≈ 1.5 Å , again with some variation due to the structure local to the defect. In each case there is a contraction of the Si-O bonds from ≈ 1.8 Å to an average of 1.78 Å. This is caused by the partial transfer of the electron from the network Si atom to the NO and NH$^x$, for the NO molecule this is shown in Fig. 4.8.
6.4. Oxide Defects coordinated to N containing compounds and fragments

**Figure 6.2:** A schematic representation of the 0/- CTLs of the intrinsic electron trap with and without the NO and NH$_x$ (x=1,2). The CTLs are labelled IET is the intrinsic electron trap with no N containing compounds and the CTLs labelled with NO and NH$_x$ (x=1,2) are those with their respective fragments or molecules.

**Figure 6.3:** The geometries of the intrinsic electron trap coordinated to NO and NH$_x$ (x=1,2). The Si-N bond length is 1.5 Å, with negligible variations. There is a slight contraction in the Si-O bond lengths from 1.8 Å an average of 1.78 Å with slight variations depending on the structure local to the trapping site.

The intrinsic electron trap can trap a second electron and this has been shown to be the first step in a mechanism to form O vacancies (Fig. 2.9). As discussed above, when the second electron traps at the wide O-Si-O bond angle site, there is a large increase in the Si-O bond lengths. When the bi-electron trap is coordinated to
6.4. Oxide Defects coordinated to N containing compounds and fragments

the to NO and NH\(_x\) (x=1,2), the longer bond length decreases from and average of 2.42 Å to 1.88 Å. Long bonds are seen as precursors to bond breaking and a shorter bond points to the network being stronger at these bi-electron trap sites meaning there should be an increase in the barrier for the process in Fig. 2.9.

These results show that the anneal in NO and NH\(_3\) leads to a gate oxide that is less susceptible to electron trapping due to the 0/- CTL of the intrinsic electron trap moving below the VB of SiC on coordination with NO and NH\(_x\). These annealing procedures also make the gate oxide less susceptible to the formation of O vacancies during operation, as the Si-O bonds around the bi-electron trap are contracted on coordination with NO and NH\(_x\), meaning that the device, post anneal, can be more reliable.

6.4.2 O vacancy

In this section we discuss the change in geometry and CTLs of O vacancy in a-SiO\(_2\) on coordination with NO. This work has been started by Dr. A.-M. El-Sayed and some of his preliminary unpublished results are shown as a part of this thesis. These preliminary calculations were done in a-SiO\(_2\) periodic cells that were not cell optimised. I have repeated these calculations to check if there was any difference and these are the results that are presented in this section.

The NO molecule can incorporate into the O vacancy either by its O or N atom. My calculations demonstrate that N atom coordinating with the dangling Si atoms of the O vacancy is the lowest energy configuration by an average 0.5 eV. This is a result of the slight positive polarisation on the N atom of the NO molecule interacting with the O vacancy.

When the NO molecule is added to the vacancy, the modal peak of the 0/- level moves from 6.75 eV to 4.5 eV (ranging from 3 eV to 6 eV) above the a-SiO\(_2\) valence band, which is much deeper in the band gap of the device (Fig. 6.4).
6.4. Oxide Defects coordinated to N containing compounds and fragments

Figure 6.4: The change in 0/-1 charge transition level before (blue) and after (Red) the addition of NO. The geometry of the O vacancy coordinated to NO is also shown. Colour coding Si-yellow, O-Red, N-blue.

In the negative charge state, the NO coordinated O vacancy has a different geometry depending on the local environment of the defect. Fig. 6.5 shows the three different geometries and their respective 0/-1 CTLs. Fig. 6.5a is a negative state geometry where there is little change from the neutral geometry shown in Fig. 6.4. It generally manifests where the NO molecule is facing a large cage and so there are not any Si atoms in close proximity. Generally, the closest network Si atom to the O atom of the NO molecule is at a distance of around 3 Å before the relaxation. Fig. 6.5b shows a system where the O atom of the NO molecule is coordinated to a next nearest neighbour Si atom forming a pseudo-five-coordinated Si site (The Si atom is psudo five coordinated due to the lack of bonding orbitals). This geometry is similar to the one found in the work by Gao et al. [109] One of the steps in forming the Frankel pair defects is coordination of an under coordinated O atom to a network Si atom [109]. In the geometry presented in Fig. 6.5b, the O-Si-O bond angle of the pseudo-five coordinated Si atom goes from 120° to 140°. Finally, Fig. 6.5c shows an NO molecule where there is some interactions between the O atom and the Si atom of the O vacancy. This again is not a bonding type interaction, as the difference in formation energy at the VB is an average 0.5 eV between the geometry in Fig. 6.5a and Fig. 6.5c. This is similar to the energy difference between H-bonded and gas phase interactions from chapter 5.
6.4. Oxide Defects coordinated to N containing compounds and fragments

**Figure 6.5:** Distribution of CTLs for each of the different geometries found for the NO coordinated to the O vacancy. a) shows a geometry where there is little change, on relaxation, from the neutral charge state, b) shows a geometry where the O atom of the NO molecule coordinates to a neighbouring, network Si atom and forms a pseudo-five-coordinated Si site and c) shows a geometry where there is an attractive interaction between one of the vacancy Si atoms. Finally, d) is the distribution for 0/- CTLs from Fig. 6.4 but split according to the different geometries. Colour coding same as Fig. 6.4.
Fig. 6.5d shows the 0/- CTLs for each of the of the different geometries. The CTLs for the geometry in Fig. 6.5a are the closest to the CB of SiC and then the model peaks of the geometries in Figs. 6.5b and 6.5c are the next closest. This is due to the extra stabilisation of charge for the geometries in Figs. 6.5b and 6.5c. Fig. 3.1 is what happens to the CTLs when the formation energy of the charged defect changes. If the formation energy decreases, then the CTL moves closed to the VB and vice versa. The stabilisation of the O atom seems to reduce the formation energy of the NO coordinated to the O vacancy across the band gap hence leading to levels shifting deeper in the gap.

Another factor that must be discussed is the ability of nitridated O vacancy to accept electrons and be involved in BTI and TAT processes. In Fig. 6.4 there are very few 0/- CTLs that resonate with the CB of SiC and so there is a low probability for electrons to tunnel to these defects as the system would have to expend energy to charge them.

6.4.3 Hydroxyl E’ centre

This section details the interactions of the NO molecule and the Hydroxyl E’ centre. As mentioned in chapter 2, this defect is thought to be a major contributor to BTI effects for devices that use a-SiO$_2$ as the gate dielectric as it can trap holes and electrons at levels near the VB and CB, respectively, of SiC and Si. This section will focus on its electron trapping ability as this is the most important factor for the devices under examination.

The molecular orbital diagram for the NO molecule (Fig. 4.6) shows that it has an unpaired, on-bonding electron in the neutral charge state and two unpaired electrons in the negative charge state (ground state multiplicity is triplet). As O is generally two coordinated and N three coordinated, one can make the assumption that the unpaired electron resides on the N atom. This means that the N atom of the NO molecule should coordinate with the defect. Coordination of the O atom was tried but, over twenty defect configurations, it was an average 0.6 eV higher in energy and the Si-O distance was an average 0.5 Å longer than the equivalent Si-N interaction.
6.4. Oxide Defects coordinated to N containing compounds and fragments

**Figure 6.6:** Distribution of CTLs for the Hydroxyl E′-centre (blue) and its variant with NO coordinated to the dangling Si bond. The atomic configuration on the right of this figure shows the N atom of the NO molecule coordinated to the dangling network Si atom, this is the neutral charge state. The purple in the histogram denotes the overlap between the nitridated and un-nitridated variants. Colour coding same as Fig. 6.4 with H in white.

The 0/- CTLs of the Hydroxyl E′ centre shifts deeper into the band gap of the device, on coordination of the NO molecule. However, the shift is not as drastic as the one for the O vacancy, with the modal peak moving from around 6 eV to 5 eV above the VB of a-SiO$_2$, or isoelectronic with the CB of SiC to 1 eV below it. There is also a significant overlap of the two distributions (purple section of Fig. 6.6) with some of the NO coordinated levels located above the CB of SiC. When the difference between the interaction of the NO molecule with the O vacancy is compared to the Hydroxyl E′ centre, it shows that the latter only makes one bond with the NO molecule and so the interaction is weaker hence leading to the energy of the NO coordinated variant of the Hydroxyl E′ centres to be higher across the band gap of the device, hence shifting its CTL towards the CB.

On examination of negative charge state geometries for the nitridated Hydroxyl E′ centre, a distinction between local geometries around the defect cannot be made as the NO molecule that is coordinated to the Hydroxyl E′ centre does not change geometries. Hence the wider structure of the system was examined as the variance in the CTLs seems to come solely from the steric environment of the defect. A
similar conclusion being drawn for the NO$_i$ from chapter 4. If the NO feels less steric crowding, then the neutral formation energy of the defect is going to be lower and, leading to a shift in the $0/-$ CTL closer to the VB vice versa. In chapter 4 the incorporation energy of the NO molecule was attributed to the local steric environment, with a higher incorporation energy coming from smaller volume cages. These smaller cages are made up of smaller rings the migration barrier through which was also larger. All of this means in the real device the Hydroxyl E$'$ centre that are present in the larger cages are better passivated than those in smaller strained environments.

Another important factor to consider is the probability of electron tunnelling to the NO coordinated Hydroxyl E$'$ centre compared to the defect centre without NO. Generally if electron trapping levels resonate with the conduction band then there will be facile electron tunnelling to them. In the case of the nitridated Hydroxyl E$'$ centre there are still many sites (Fig. 2.12) that are close to the SiC CB and so tunnelling to these states requires less energy evolution than for the states that have moved deeper in the conduction band. Hence, compared to the nitridated O vacancy the nitridated Hydroxyl E$'$ centre more readily accepts electrons and so is still plays a part in TAT and potentially in BTI processes.

6.5 Comparing theoretical results with experimental leakage current data

In this chapter the results of coordinating NO to the O vacancy, Hydroxyl E$'$ centre and intrinsic electron trap have been discussed. It has been shown that, on coordination, the $0/-$ CTLs of all of these defects move deeper into the band gap. With the O vacancy and the intrinsic electron trap CTLs moving the deepest into the gap. This section brings together these results and the results of chapter 5 with the results of leakage current and TDDB experiments of these differently annealed devices to explain what happens to the device post anneal. Gate current density as a function of the stress time for differently annealed trench MOSFET, stressed and measured at room temperature are shown in Fig. 6.7 and have been previously published in
6.5. Comparing theoretical results with experimental leakage current data

Figure 6.7: Gate current density as a function of the stress time for differently annealed trench MOSFET, stressed and measured at room temperature. The absolute stress bias is given in the legend and correlates with a constant $V_{th}$ overdrive for each sample, in this case $5 \text{ MV cm}^{-1} + (V_{th} \text{ of aneal under question} - V_{th} \text{ of NO annealed device})/t_{ox}$ with the oxide thickness. The more NO was available during the anneal, the lower the leakage current is. Graph copied from [6].

ref. [6].

The defects discussed above have been chosen because they have 0/- CTLs near the CB edge of SiC, when the band offset of the device is taken into account, and so are prime candidates in oxide tunnelling mechanisms and BTI processes. There are two important mechanisms for tunnelling in these devices. The first one is the Fowler-Nordheim (FN) tunnelling where electrons tunnel into the states in the conduction band of a-SiO$_2$, and the second one is TAT where electrons tunnel between defects in the oxide. Each of these is affected by oxide defects, the former is inhibited by electrons trapped at defects close to the conduction band and the latter is enhanced by defects as, the greater their concentration, the closer they are to
one another and the higher the probability for electrons to tunnel between them. In this section we will compare the tunnelling current attained in differently annealed devices (Fig. 6.7) and link them to the CTLs presented in this chapter.

In the TDDB study, charge is pumped between the source and gate electrodes and the charge density is measured, hence giving an idea of the amount of leakage current in the oxide for each of the differently annealed oxides (Fig. 6.7). During the N$_2$ anneal, a multitude of experimental results show that there is little or no nitridation of the oxide [1]. As the oxide is a high quality CVD oxide the bulk oxide is likely to be free from defects that break the network, but may be susceptible to intrinsic electron traps. The 0/- CTL of the intrinsic electron trap is 6 eV above the a-SiO$_2$ VBM and isoelectronic to the CB of SiC (Fig. 6.3), meaning that electrons can easily tunnel to this defect. If the electron is trapped at this defect, then it is sat close to the conduction band of a-SiO$_2$. Fig. 6.7 shows that at low voltages (35 V) the gate current density of N$_2$ annealed devices starts off at a value of around $10^{-9}$ A/cm$^2$ then decreases to $10^{-10}$ A/cm$^2$ at the end of the run. We posit that the primary tunnelling mechanism in these devices is FN tunnelling and so as the stress time increases electrons fall into intrinsic electron trap precursor sites and get trapped leading to a decrease in current density due to the build up of electrons near the band edge of a-SiO$_2$. However, the current still remains high as the near interface defects have not been passivated. These N$_2$ annealed devices will be used as a baseline for the NH$_3$ and NO annealed devices.

Experiments performed on a-SiO$_2$ devices annealed in NO show that there is a relatively small nitridation in regions greater than 2 nm from the SiC/a-SiO$_2$ interface.[5, 80, 1]. As the bulk oxide is not fully nitridated, one can assume that the intrinsic electron traps still persists. The previous section shows that, when NO is coordinated to O vacancies, the 0/- level moves from 6 eV above the a-SiO$_2$ VB to 4.5 eV above the a-SiO$_2$ VB (Fig. 6.4). The 0/- level of the intrinsic electron trap also moves toward the a-SiO$_2$ VBM on NO coordination. This has two consequences on the current density through the oxide. Firstly, both the intrinsic electron trap and O vacancies that are in the near interface region are passivated
6.5. **Comparing theoretical results with experimental leakage current data**

as their levels have moved drastically away from the CB of both SiC and a-SiO$_2$ meaning that the initial current density within the device will be lower than for the N$_2$ annealed devices (Fig. 6.7). Secondly, electrons moving through the CB of a-SiO$_2$ can still be trapped at intrinsic electron trap precursor sites in the bulk oxide as they have not been nitridated. In Fig. 6.7 the NO annealed devices have an initial oxide charge density of $10^{-10}$ A/cm$^2$ which is lower than the initial charge density of the N$_2$ annealed devices confirming that there are less defects near the interface for the electrons to tunnel to. This current density then drops to a value of $10^{-12}$ A/cm$^2$ when electrons from the CB of a-SiO$_2$ become trapped at the bulk intrinsic electron trap precursor sites. The layer of nitridation creates a blockade for electrons giving a total decrease in current density compared to the N$_2$ annealed devices.

Elemental analysis of devices annealed in NH$_3$ show that there is nitridation of all areas of the oxide, with maxima at the surface of a-SiO$_2$ and at the interface between a-SiO$_2$ and SiC [1]. Calculations presented in chapter 5 present ideas for the bonding of N into the surface and bulk of SiO$_2$. The nitroxy bridge defect has electron and hole trapping levels near the CB and VB of SiC, hence could be the defect that enhances the TAT pathways [48, 83].

Fig. 6.7 demonstrates the NH$_3$ annealed devices have an oxide current density greater than $10^{-6}$ A/cm$^2$, much higher than the NO and N$_2$ annealed oxides. This current density is relatively constant all the way through the experiment with a negligibly small drop at $10^4$ seconds. This suggests that the main tunnelling mechanism in these devices is TAT, with some minor FN tunnelling that seems to be ubiquitous regardless of annealing agent. The results of all experimental work show that there is a significant chemical change of the oxide which has been theorised to be substitution of the network O with N. This bonding of N into the a-SiO$_2$ network leads to levels in the band gap of a-SiO$_2$ which contribute to TAT pathways.
6.6 Conclusions

This chapter has detailed the geometry and 0/- CTLs of common oxide defects and how they change on coordination of NO and NH$_3$ fragments. We initially looked at the defects without nitridating molecules and shown the differences between the literature and the calculations performed during the course of this study. For the intrinsic electron trap we find that the precursor angle for electron trapping moves from 132° to 120°, this is thought to be a consequence of the different procedures used to make the a-SiO$_2$ models, the previous study relied on a geometry optimisation, post melt-quench, which allowed for these wider bond angles to be included in the structure, mostly due to a larger density variation between structures compared to those used in this study which have been cell optimised before production calculations.

The next section details the extrinsic Hydroxyl E' centre defect which has some interesting variations between the literature and the results in this study. We find that, when a significant number of defects are sampled (288 samples over 2 a-SiO$_2$ cells), there is a subset that shows negative U behaviour. This means that the Hydroxyl E' centre would be charged when the device is not under stress meaning that there is facile trapping of electrons and holes depending on the Fermi level of the device.

Next we looked at the geometry and CTLs of each of these defects when coordinated with the NO molecule and NH$_3$ fragments. The results for all of these defects shows that, on coordination, the modal peak for the 0/- CTL shifts deeper into the a-SiO$_2$ band gap, thus shifting it away from the band edges of both a-SiO$_2$ and SiC when the band offset model is considered. However, for the Hydroxyl E' centre, there is still a proportion of defect levels that sit within 1 eV of the SiC CB, hence are still active in tunnelling processes. This means that for the O vacancy and intrinsic electron trap there is a lower probability of electrons tunnelling to these defects, hence decreasing the number of TAT pathways and decreasing the probability electrons trap at these defect sites. This is experimentally proven in the TDDB measurements that show NO annealed devices lead to the lowest gate leakage for
all the anneals tested in Fig. 6.7.

The next chapter looks at the structure and defects at the interface between SiC/a-SiO$_2$. We first discuss model building and how the SiC and a-SiO$_2$ were connected to make the interface structure. Then we characterise the structure of the interface oxide, comparing it to the bulk structures used throughout this work. Finally, the O vacancy in a-SiO$_2$ and the NO interstitial are studied in the near interface comparing the results to the bulk calculations and work previously done in the literature.
Chapter 7

Modelling the SiC/a-SiO$_2$ interface
and the surface of the a-face of
4H-SiC

7.1 Introduction

This section details the results of my work on modelling the interface between SiC and a-SiO$_2$. A brief discussion on the methods used for constructing the interface structures is given in section 2.7. Of particular importance for the work in this section is the method by Devynck et al. [21] which utilises a connection scheme.

Fig. 1.1 shows a schematic representation of the chapters in this thesis. This chapter takes some of the results discussed so far to the interface between SiC and a-SiO$_2$. Initially, we will look at the method used to make the interface structure focusing on forming the connection scheme between the Si-face of 4H-SiC and a-SiO$_2$. The bond length and angle distributions of the near interface oxide are then compared to these values for the bulk oxide. Finally, we look at the formation of the O vacancy and a NO interstitial at the interface and compare their geometries to those in the bulk a-SiO$_2$ structures (full structural parameteres can be found in appendix A). We also look at the interactions of the NO interstitial in the bulk of SiC to compare it to the the geometry in the interface structures. Finally, some initial work on the structure relaxation that occurs on the a-face of 4H-SiC is discussed.
7.2 Method

The calculations presented in the previous chapters used the PBE0_TR_LRC hybrid functional. The systems used in all of these chapters included either a 216-atom cell of a-SiO$_2$ or a 450-atom cell of crystalline α-cristobalite. The systems studied in this section are generally greater than 1000 atoms, with the exception of a model of the a-face surface, which is around 500 atoms. Despite all the techniques CP2K uses to decrease the computational cost of calculations (see chapter 3), performing hybrid DFT calculations for systems of this size is computationally unfeasible. Hence, all the calculations in this chapter are carried out using the standard GGA PBE functional with a 550 Ry cut off and 50 Ry relative cut off. Another change made here is the use of the TZVP basis set as previous calculations of SiC show that the band gap is better represented with TZVP compared to DZVP and, as we are using a standard GGA functional, the best electronic structure available is required [177].

The interface structure is made in a similar manner to that in ref. [21]. SiO$_4$ tetrahedra are tessellated across the Si-face surface generally making two and three connections with the surface of SiC. Once all the Si atoms on the surface of SiC were saturated, a second layer of oxide was added, making a bi-layer of oxide. This bi-layer was then capped with H atoms and a geometry optimisation was performed in DFT (Fig. 7.1).

After the geometry optimisation, the H atoms used to cap the structure were removed along with the SiC. Then a bespoke a-SiO$_2$ network is melted and quenched on top of this structure using the van Beest–Kramer–van Santen (BKS) force field [178]. Other interface structures, which include a-SiO$_2$ use the Reaxx force field [179] but during this study it was found that the BKS force field gave defect-free structures more reliably than the Reaxx force field (with an average of one defect per 2000 atoms compared to one defect every 600 atoms, for a testing sample of
As the BKS force field was tabulated for another study, it was also found to be around twelve times faster than Reaxx. Bulk a-SiO$_2$ structures made with Reaxx and BKS have been compared in ref. [22]. The classical MD calculations were done 3D periodically with the bi-layer (shown in Fig. 7.1) that was attached to the SiC being static throughout the calculation, hence eliminating the oxidation effects that occurred when the SiC was present. The calculation involved a temperature ramp to 3000 K lasting 0.1 ns, then an equilibration at 3000 K lasting 1 ns and finally a quench to 0 K lasting 5 ns.

After the classical MD melt-quench step, the SiC is added back to the structure and the top and bottom of the structure is capped with H atoms to fully saturate bonds. The H capping leads to a clean band gap similar to those found in the literature when standard GGA functionals are used (Fig. 7.2) [21, 90]. Another processing step that was added was the search for under-coordinated or defect states, which were generally passivated with H atoms for the same electronic reasons as they are used on the surface. Fig. 7.2 shows the interface structure and the projected density of states for the structure. The band offset is characterised by C and O character for SiC and a-SiO$_2$, respectively. This is done because the C is unique to

**Figure 7.1:** The atomic structure of the Bilayer post geometry optimisation. Colour coding Si yellow, O red, H white and C in blue.
the SiC and the O is unique to the a-SiO$_2$.

The structural parameters for the bulk oxide structures were found using the R.I.N.G.S code [23] but it does not allow us to analyse slab and multi-component (i.e. ternary systems and interface systems), hence an analysis software in the atomic simulation environment (ASE), implemented in python 3, was used. The code is new and requires some development, and so currently cannot differentiate between O-Si-O and Si-O-Si bond angles, so the total combined bond angle distribution was computed for the near interface and bulk oxide structures.

Each of the near interface oxide structures is between 12 and 15 Å thick and contains between 900 and 1000 atoms. As ASE is an object based coding system, the computational intensity of computation relies on the size of the object and the complexity of the operation being performed. The calculations of bond lengths is a facile process and is done by taking the modular distance between two atoms, so for the interface systems requires the calculation of around a million distances to which some cut-off criteria are added to make sure the atoms are adjacent, generally taking a range of between 1.4 and 1.8 Å. This range was chosen due to the analysis if bond lengths in bulk a-SiO$_2$. The minimum Si-O distance is generally no less than 1.5 Å, and the minimum distance for atoms to be deemed "non-bonded" is 1.8 Å.
The calculation of angles is done by taking the cross product between three atoms which are within the above mentioned distance cut-off range, this requires the calculation of around 8 billion matrix elements and so is very computationally intense, particularly with the lack of multi-processor support. To limit the computational cost, around half of the atoms in the interface system are used to calculate the bond lengths and angles, being careful to choose those closest to the SiC/a-SiO$_2$ interface.

7.3 Results and Discussion

This section discusses the results gained using the interface structures. First, the differences between the structure of the interface oxide and the bulk oxide are discussed, then we look at the geometries and energies of O vacancies and NO interstitials in the interface structures.

7.3.1 Structural differences between the bulk oxide and near interface oxide

In this section we discuss the differences between the bulk and near interface structures of a-SiO$_2$. As mentioned in section 2.7, the density of the near interface oxide is thought to be around 2.4 g cm$^{-3}$, meaning the change in structural features is very important.

Fig. 7.3a shows the Si-O bond length distribution for the interface structure and Fig. 7.3b shows this distribution for the 30 bulk structures used throughout the thesis. There are two striking features, the first is that the distribution of bond lengths is much tighter for the bulk structures than for the interface structures, and the second is that the distribution of bond lengths for the interface structures has been shifted to lower values with the modal peak moving from $\approx 1.62$ Å in the bulk structures to $\approx 1.60$ Å.

The shorter modal bond length in the interface oxide means that the oxide is literally being squeezed so that the SiC and a-SiO$_2$ can be bonded to one another. This leads to the wider distribution in bond lengths as there has to be a place where the system can release strain. The wider distribution has the consequence that there
Figure 7.3: The bond length distributions for the bulk (a) and interface (b) oxide.

is a greater variety of environments in the interface oxide compared to the bulk oxide as the distribution of bond lengths appears to have much greater extrema in the interface structures compared to the bulk structures ($\text{Min}_{\text{int}} = 1.5 \, \text{Å}, \text{Min}_{\text{bulk}} = 1.55 \, \text{Å}, \text{Max}_{\text{int}} = 1.8 \, \text{Å} \text{ and } \text{Max}_{\text{bulk}} = 1.68$). This means that, when SiC is introduced, the strain is being balanced by bond extensions further from the interface.

Elongated bonds have long been linked to the facile formation of defects (e.g. in [40]) meaning that this strain and subsequent release of strain is the reason why there is a larger density of defects at the SiC/a-SiO$_2$ interface compared to Si/a-SiO$_2$ devices. This can be linked directly to the density mismatch by the fact that there is a decrease in overall bond lengths as the a-SiO$_2$ must be squeezed into a smaller space in-order to fully bond with the SiC.
7.3. **Results and Discussion**

**Figure 7.4:** The full bond angle distribution for bulk (orange bars) and interface (blue bars) systems.

Fig. 7.4 shows the distributions of all bond angle in both the bulk and interface structures. The distribution shows very well defined modal bond length for bulk structures at around $110^\circ$ and a tail from around 110 to $160^\circ$. The interface systems have a more varied structure with a similar, if broadened, modal peak around $110^\circ$. There is also a peak around $130^\circ$ which does not appear in the bulk distribution.

The varied environments in the interface structures is attributed to the extra strain due to the interface and to the increase in density that is present in these structures. The narrower bonds present at the interface due to full connection between SiC and a-SiO$_2$ and, as with the short bonds, the bonds being squeezed into a space vastly smaller that in the bulk. These extremely strained environments are then balanced out by wider bonds further from the interface, hence the wide distribution of bond angles.

Strained environments lead to the formation of defects and so this section has shown that the near interface oxide structure is much more strained than the bulk structure. This gives an idea of why the defect density at the SiC/a-SiO$_2$ interface is so much higher than at the Si/a-SiO$_2$ interface. As this region of the oxide is the
most under strain, it will have the shortest bond lengths and narrowest bond angles, at least in a situation where there is near perfect connection between the SiC and a-SiO$_2$. That means that these bonds will be easily broken, while this would have an energy penalty associated with it, the system as a whole would become more stable by minimising the strain in the near interface region.

This section has looked at the bond length and band angle distributions for the interface structures and compared these with the same distributions in the bulk structures. The section demonstrated that the large strain put on the oxide leads to large variations in the structure between the bulk and interfaces oxides. These large variations are a consequence of balancing the large strain at the interface causing shorter and narrower bond lengths and angles nearer the interface and longer and wider bond lengths and angles in areas further from the interface. This inherent strain does not exist in the bulk structures but it too has areas of high and low strain, as discussed in chapter 4. However, the variations in the bulk structures are not as drastic as those in the interface structures. The next section looks at the O vacancy and NO interstitial in the interface structures and includes a comparison of their interactions in the bulk and interface oxides.

7.3.2 Effects of the O vacancy and NO interstitial

First, we consider the O vacancy in the interface structures, then we will move on to look at the NO interstitial at different points in the oxide and SiC. The calculations of the NO interstitial will be compared to the results in chapter 4.

As the oxygen vacancy is one of the most widely studied defects in the bulk of a-SiO$_2$, it allows for a convenient comparison for the interface oxide structures. Kimmel et al. [68] found that there was a strong positive correlation between the formation energy of the O vacancy and the Si-Si distance post geometry optimisation [68].

Fig. 7.5 correlates the O vacancy formation energy in the interface structures with the Si-Si distance post geometry optimisation. It shows that about 75% of the points show a strong, positive correlation. The remaining 25% are the O vacancies that were formed in the connection region. They are unable to fully relax due to
Figure 7.5: The Si-Si distance as a function of the formation energy of the oxygen vacancy. This graph shows that there is still a positive correlation between Si-Si distance and the formation energy of the O vacancy.

Figure 7.6: The Si-Si relaxation distance as a function of distance to the interface. This shows that there is less relaxation of the Si-Si distance as the interface is approached.
	heir proximity to the SiC. This behaviour can be explained using the structural parameters outlined in the previous section. As shown, there are generally shorter bonds and narrower bond angles in the near interface region and so there is less room for relaxation. This is attributed to the increased density of the near interface oxide structures. This is pictorially represented by Fig. 7.6. It shows the Si-Si distance relaxes on geometry optimisation in regions less than 8 Å from the interface. There is little change in the relaxation distance until a point 4 Å from the interface at which point there is a linear decrease at distances less than 4 Å.

Chapter 4 presents the results of my study of the NO interstitial in an a-SiO₂
network. The reader is directed to this chapter or ref. [176] for a more in-depth discussion. However, as a brief summary the chapter discusses the dependence of local steric structure on the incorporation energy. It presents the idea that there is an increase in the incorporation energy when there is more steric crowding.

Figure 7.7: The position of NO interstitials in the interface structures and their incorporation energies. Colour coding same as Fig. 7.1 with N in blue.

If we take this knowledge to the interface, then we have a substantial amount of analysis for comparison. The first thing would be to analyse the average distances from the network to the centre of the molecule as a similar Voronoi-Delaunay analysis for large structures is currently impossible. In Fig. 7.8 there are two NO interstitials that are very close in the network but have drastically different incorporation energies (0.7 and 2.55 eV). If the average distance to the network for each one is taken, then the one with the lower incorporation energy has an average distance to the network of 3.3 Å and the higher incorporation has an average distance of 2.4 Å, meaning that the system that has lower incorporation energy is, on average, further
from the network.

Figure 7.8: The NO interstitial in the SiC portion of the interface structures. Colour coding same as Fig. 7.1 with N in blue.

In chapter 4 we showed that the NO molecule sits much closer to the a-SiO$_2$ network compared to the neutral molecule. While the NO molecule does sit closer to the network in the interface structures, there is no flattening of SiO$_4$ tetrahedra or widening of O-Si-O bond angles that was characteristic of the negative NO interstitial, hence one must conclude there is not charging of the NO in these structures. The examination of the local density of states, Mulliken and Hirshfeld charge analysis confirm this.

As SIMS and XPS measurements of NO annealed devices exhibit a N signal inside the SiC portion of the interface system. Therefore the NO molecule was also placed in the SiC portion of the interface systems. These calculations indicate that there is cleavage of the NO molecule and incorporation of the N and O atoms into the SiC lattice, with the NO bond length increasing from 1.1 Å to 2.3 Å. Initially, this was thought to be a consequence of the free surface at the bottom of the interface allowing the SiC lattice to flex in a non-physical manner and the elongation of bonds leading to the nitridation due to this proximity. To test whether this is an artefact, the NO interstitial was placed into a 96-atom bulk cell of 4H-SiC. These calculations showed a similar behaviour to the interface structures (Fig. 7.9), with the NO bond length increasing from 1.1 Å to 2.42 Å suggesting that the cleavage is physical. This effect is barrier less in the bulk 4H-SiC structures. However, barriers have not
7.3 Results and Discussion

Figure 7.9: The NO interstitial in bulk 4H-SiC. Colour coding same as Fig. 7.1 with N in blue.

been tested in the interface structures as performing a NEB calculation using them is computationally unfeasible.

7.3.3 Relaxations of the a-face of 4H-SiC

In this chapter the structure of the near interface has been discussed and used to explain the interactions, geometry and energy of the O vacancy and the NO interstitials. The results in the interface structures have been compared back to calculations in the bulk both from earlier chapters in this work and also in the literature where appropriate.

All of this work has been done on an interface structure that is made on the Si-face of 4H-SiC. The devices that were tested via TDDB in chapter 6.6 and the devices used in the work of Regoutz et al. [1] are all trench MOSFETs which make use of both the Si- and a- faces as the interface between the device and the gate oxide (see section 2.2)[1]. While the characterisation of defects and structures in an a-face interface is beyond the scope of this work, the structure of the surface has
been examined. The fabrication procedure for these devices has been discussed at length in chapter 2. However, it is important to re-iterate that there is some time gap between the growth of the single crystal 4H-SiC and the deposition of the oxide. These calculations examine the relaxations at the a-face surface itself as it tries to minimise its energy and so look at the interface directly after crystal growth. It is the first step in understanding the structure of the SiC pre-oxidation.

**Figure 7.10:** This is a top-down view of the a-face of SiC. It shows the surface relaxations of the a-face of 4H-SiC after geometry optimisation showing the formation of C-C clusters whose bond lengths are akin to the C-C double bond in organic chemistry. Colour coding Si-yellow and C-blue.

When geometry optimisation calculations are performed on the a-face surface, the two coordinated C atoms on the surface pair up with their distances decreasing from 2.4 Å to 1.4 Å, which is the C-C double bond length [173]. Fig. 7.10 shows a birds eye view of the the a-face before and after the relaxation. The upper image is the relaxation without moving any atoms and the lower image is where, pre-relaxation, the C atoms are moved 0.1 Å closer to one another to make the formation
of the regular bond structure more likely. The relaxation energy of the latter surface shows that 3.5 eV are gained per C-C bond formed on the surface.

This has two potential outcomes, first that the C atoms are now saturated and so do not require further bonding, hence are not involved in any bonds to the a-SiO$_2$. This potentially means that there are local areas of lower density at the a-face of 4H-SiC which could offset the vastly increased density of the near interface oxide meaning that less defects are likely to spontaneously form. Secondly, these C-C double bonds on the surface could be the precursors to C-cluster defects that have long been theorised in the literature [10]. Devices with a CVD oxides have lower C-cluster concentrations than sputter deposited oxides or oxides made through wet oxidation of SiC [2]. This is because the surface of SiC is minimally disrupted by ALD, while the others do significantly disrupt the oxide.

7.4 Conclusions

This chapter has detailed the results in a Si-face SiC/a-SiO$_2$ interface and the a-face surface of 4H-SiC. Initially, the differences between the structure of the near interface oxide and the bulk oxide were discussed. It was concluded that the near interface has a greater variety of environments compared to the bulk structures due to its wider distributions of bond lengths and angles. This wider distribution is thought to be a consequence of greater mass density of the near interface a-SiO$_2$, with angles and bonds near the interface being shorter and narrower, respectively, than those further from the interface.

These structural results were then used to explain the behaviour of the NO interstitial and the O vacancy in these interface structures, comparing their geometries and energy distributions to calculations in chapter 4 and in the literature, respectively. For the O vacancy in the interface oxide structure the direct correlation between the Si-Si distance, post oxidation, and the formation energy of the defect is retained, accept in cases where the O vacancy is formed in the connection scheme. The relaxation of these Si-Si distances was then shown to decrease as the interface is approached. The NO interstitial was not shown to spontaneously charge neg-
atively in these structures, despite being closer to the a-SiO$_2$ network than in the bulk. Instead this was seen to be a consequence of the increased mass density of the near interface oxide. In the SiC the NO spontaneously cleaved in the interface structures, which was shown to be physical from calculations in bulk 4H-SiC hence potentially being the nitrogen incorporation and extra oxidation observed post NO anneal in the SiC of the devices under examination.

Finally, an a-face surface of 4H-SiC was relaxed to show the formation of C-C double bonds which can either be seen as precursors to C-cluster defects or the full saturation of the dangling C bond meaning that the oxide on the a-face could be less strained than at the Si-face. The next chapter brings together the conclusions from all 4 content chapters and makes assertions about the devices as a whole with the work that could be done on such systems in the future.
Chapter 8

Summary and Future work

8.1 Summary

In this thesis a combined DFT and classical MD approach has been used to study the interactions of NH$_3$ and NO with crystalline and amorphous a-SiO$_2$. The objective of the thesis was to show how the NO and NH$_3$ molecules behave during the anneal and to give an atomic level picture of the anneal process.

In chapter 4 the interactions of NO with a pristine a-SiO$_2$ network was probed. The results show that in the neutral charge state the NO molecule has repulsive steric interactions with the network. On relaxation the NO molecule would reside in a cage like structure. The free space in the a-SiO$_2$ was then examined using a Voronoi-Dulaunay analysis and showed that there is a correlation between the orientation of the long axis of the molecule and cage. If these axes are aligned then the incorporation energy is lower than if they are mis-aligned. In the negative charge state, the NO molecule relaxes to a point much closer to the a-SiO$_2$ network than in the neutral charge state. The negative charge is stabilised by the network in two ways, if there is a O-Si-O bond angle greater than 119° then the NO molecule will widen that angle and site above the Si site. In all other cases there is a flattening of the SiO$_4$ tetrahedra with the N of the NO sitting next to the Si atom of the tetrahedra.

When looking at the diffusion of the NO molecule through the a-SiO$_2$ network, the NEB method in DFT was used to measure the barrier for migration through different rings sizes. This part of the study showed that the larger the ring the
lower the migration barrier in both the neutral and negative charge states. This is attributed to the increase in steric crowding felt by the molecule as the ring size decreases. There is also an increase in the barriers in the negative charge state, this is attributed to the extra electrostatic interaction in the negative charge state.

Chapter 5 looks at the interactions of NH$_3$ with crystalline and amorphous SiO$_2$ systems. First the interactions of the NH$_3$ atom with a crystalline surface were probed. It shows that the adsorption of the NH$_3$ molecule onto the surface, via H bonding, depends on the orientation of the molecule with respect to the surface of a-SiO$_2$. If the N of the NH$_3$ molecule is pointed towards the surface there is a much higher probability for the molecules to adsorb on the surface compared to if the N is facing away. The barriers for migration of NH$_x$ (x=1-3) were probed for ingress into the $\alpha$-cristobalite, this showed that the smaller fragments have a lower ingress barrier than the larger ones. All of these calculations were done one a fully hydroxylated surface the interactions of the NH$_3$ on a partially hydroxylated surface were also probed. This shows that there is barrier-less abstraction of H onto dangling O bonds.

After this the interactions of the NH$_3$ molecule was probed on an amorphous surface using classical molecular dynamics. This showed that there is three things that happen on the surface when the temperature is raised to 1500K. First, despite the high barrier for migration into the crystalline surface, the whole molecule can penetrate the amorphous surface. This is due to the variety of ring sizes available on the amorphous surface compared to the crystalline surface. Secondly, there is nitridation of the surface and formation of water molecules at strained sites on the surface, giving an atomic level picture of the nitridation shown in XPS measurements. Finally the molecule spends a considerable amount of time on the surface hopping between between silanol groups.

Finally, the interaction of the NH fragment was probed in the bulk of a-SiO$_2$. This study shows that this fragment can incorporate into the network in the, singlet multiplicity, at bonds greater than 1.64 Å leading to the nitroxy bridge defect that can trap both electrons and holes. The NH fragment can also form interstitials, this
happens the majority of the time in the singlet multiplicity and on all occasions in the triplet multiplicity. In the amorphous phase, the NH$_3$ can also break the network to nitridate the a-SiO$_2$ network and forming a defect akin to the Hydroxyl E$'$ centre.

In chapter 6, the defects of a-SiO$_2$ were examined. First, we looked at the defects without NO and NH$_3$ fragments. For the IET, there was a decrease in the precursor angle for spontaneous electron trapping in the systems, going from 132° to 120°. For the Hydroxyl E$'$ centre, the negative-U behaviour was seen in a significant number of the 288 sites sampled in this study. This was not seen in earlier work due to it being a limited sample. On nitridation the 0/-1 levels of all of the defects move deeper into the band gap of a-SiO$_2$. This is compared to the leakage current measurements done on differently annealed SiC/a-SiO$_2$ devices which show much lower current densities in NO annealed devices than in devices annealed in N$_2$.

Finally, chapter 7 discusses calculations in an interface system. Initially, the structures of the interface and bulk structures are compared. It is found that, at the interface, there is an increase in the variety of environments this is exemplified by a wider distribution for bond lengths and angles in the interface structures compared to the bulk structures. This was attributed to the mismatch in mass density between SiC and a-SiO$_2$ as the a-SiO$_2$ is squeezed into a much smaller space than in the bulk oxide. This is also the reason for the O vacancy having less Si-Si relaxation as the interface is approached. The NO interstitial was not found to spontaneously gain an electron in the interface structures. It does reside much closer to the network than in the bulk of a-SiO$_2$ but this is because the large voids present in the bulk structures are not present in the interface oxides. Finally, the surface relaxations of the a-face were discussed. It shows that on a clean a-face surface there is formation of C-C double bonds on the surface which could be the precursors for the formation of the C cluster defects theorised in those devices.

8.2 Learning outcomes

During the course of this PhD period many calculations have been done which, with the benefit of hindsight and experience, could have been avoided. In chapter 4 the
total number of calculations could have been brought down significantly by using the Voronoi-Dulaney method to identify the cages and then use DFT to model a much smaller number of NO atoms in each of the cages found. This would have also been true for the bulk calculations in chapter 5 too.

Another thing I would have done differently in the first two content chapters would be to make more use of ab-initio and classical MD. A small number of either type of calculation would have informed me of the movements and reactions of NO and NH$_3$ in a-SiO$_2$ within a-SiO$_2$ much better than doing the number of NEB calculations I did.

In chapter 6 I think an exercise of looking at the local structure of each defect (at least in the first sampled cell) would have been beneficial. This would have led to the finding some structural precursor leads to the lowest formation energy or the most problematic CTLs without having to do large sample sizes as was done.

I think a good way of summarising each of these learning outcomes is to say that I should have (and will in the future) think more deeply about the systems that I am looking at. This means that instead of formulating a problem and submitting many calculations, I should think about the wider factors (structure, electronics etc) that could affect the problem at hand.

Finally, a positive learning outcome would be that I have improved by programming skills (in bash, python and FORTRAN) beyond recognition and it has allowed me to more efficiently deal with the next set of problems that I have been tasked with. If I were to start again I would spend more time thinking about efficient algorithms to do some of the processes that I did by hand.

### 8.3 Future Work

There are two developments on the work done here that could be implemented in the future, the first would be calculating the barriers for forming the defects interacting with NO and NH$_x$ in chapter 6. This particularly needs to be understood for the O vacancy as there is a strong Si-Si interaction that needs to be overcome to the NO or NH$_x$ coordinated variant. For the Hydroxyl E' centre, there needs to be some bond
reorganisation in the system. The fragments of NH$_3$ also need to be coordinated to each of the defects to see if the levels change, as there is a large amount of N at the interface in the NH$_3$ annealed structures, along with barriers for the formation of these variants too.

The second element to refine and further analyse is the interface models looked at in chapter 7. The system requires the cell optimisation as it may have off-diagonal stress tensor terms that are causing the truncated relaxations seen for the O vacancy, this however is currently computationally unfeasible but may become easier in the future. Then a free space analysis could be done on these structures (as performed in chapter 4). This would allow for a quantitative comparison between the free space available in the interface structures compared to the bulk structures, hence giving a better argument to the increased density oxide. Finally, all the work presented in this thesis needs to be taken to an a-face interface structure. This would require the formation of a connection scheme and full interface here. All the calculations done in chapter 7 need to be done using a hybrid functional with a clear justification as to why that functional was used, this again is still computationally unfeasible but could become a facile task in the future.
Appendix A

Structural parameters of bulk $\text{a-SiO}_2$
models and raw data for NO +
Oxygen vacancy
Figure A.1: The O-Si-O bond angle distribution for the 30 cells used in this thesis

Figure A.2: The Si-O bond length distribution for the 30 cells used in this thesis
Figure A.3: The cage volume distribution for the 30 cells used in this thesis

Figure A.4: The ring size distribution for the 30 cells used in this thesis
<table>
<thead>
<tr>
<th></th>
<th>Neutral</th>
<th>Positive</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>detected</td>
<td>underdetected</td>
<td>minus ND DFT energy</td>
</tr>
<tr>
<td>1</td>
<td>0512.102926</td>
<td>-7109.17630</td>
<td>-7109.17596</td>
</tr>
<tr>
<td>2</td>
<td>0512.102917</td>
<td>-7109.17570</td>
<td>-7109.17516</td>
</tr>
<tr>
<td>3</td>
<td>0512.102908</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>4</td>
<td>0512.102899</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>5</td>
<td>0512.102890</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>6</td>
<td>0512.102881</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>7</td>
<td>0512.102872</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>8</td>
<td>0512.102863</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>9</td>
<td>0512.102854</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>10</td>
<td>0512.102845</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>11</td>
<td>0512.102836</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>12</td>
<td>0512.102827</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>13</td>
<td>0512.102818</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>14</td>
<td>0512.102809</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>15</td>
<td>0512.102790</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>16</td>
<td>0512.102781</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>17</td>
<td>0512.102772</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>18</td>
<td>0512.102763</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
<tr>
<td>19</td>
<td>0512.102754</td>
<td>-7109.17610</td>
<td>-7109.17566</td>
</tr>
<tr>
<td>20</td>
<td>0512.102745</td>
<td>-7109.17570</td>
<td>-7109.17526</td>
</tr>
</tbody>
</table>
Bibliography


