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Publication Date

2026-05-29

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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Atomistic Design of Ultra-Wide Bandgap Surfaces and Heterostructures

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Materials Science and Engineering

by

Hector Gomez

June 2026

Dissertation Committee:

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University of California, Riverside

Acknowledgments

This dissertation would not have been possible without the guidance, support, and generosity of many people, and I am grateful to all of them. Much of this work was carried out during the COVID-19 pandemic, and the collaboration and mentorship that sustained it happened largely over Zoom.

I am deeply grateful to Dr. Mahesh Neupane, whose encouragement brought me into this doctoral program and connected me with the research group in which this work was carried out. I first met him in 2019, when he hosted me at ARL-West through the DoD HBCU/MI Research Program. That experience directly influenced my decision to pursue a doctorate at UCR. His scientific expertise shaped this work in fundamental ways, and our regular meetings throughout the pandemic pushed me to think more critically.

Professor Michael Groves at California State University, Fullerton, has been one of the most influential people in my research career. He welcomed me into his research group when I was struggling as an undergraduate student in 2018 and saw possibilities in me before I could see them myself. He never stopped opening doors for me. He encouraged me to apply to the DoD HBCU/MI Research Program and helped me gain admission to this doctoral program. We continued our collaboration throughout the pandemic, and several of the publications underlying this dissertation grew from that partnership. Whenever I hit a wall, he was the person I turned to. I could not have gotten here without him.

I would also like to thank Professor Roger Lake for providing the research environment in which this work was carried out and for giving me the freedom and resources to pursue it. His support made this dissertation possible.

I thank Professor Jianlin Liu for serving on my proposal and doctoral committees and for the productive collaboration with his group, the results of which are presented in Chapter 8.

Several colleagues and labmates made this work easier and more enjoyable. Jenille Cruz, a collaborator from Professor Groves's group at California State University, Fullerton, has worked with me since my undergraduate years and continued to collaborate with me during my doctoral research on diamond surfaces. From Professor Lake's group, Topojit Debnath generously shared his expertise in phonon calculations and helped me implement the methodology correctly. Sohee Kwon taught me a great deal about running VASP calculations efficiently and was a patient and knowledgeable resource throughout my time in the group. I also greatly appreciated Yuhang Liu and In Jun Park, whose support with coursework and routine questions made my time in the lab easier.

I also thank the Bartels group at the University of California, Riverside, for a productive collaboration, the results of which are presented in Chapter 7.

I am also grateful to Dr. Mihai Negoita and Dr. Robert Kaplar at Sandia National Laboratories for their guidance and support during my internship. Their mentorship introduced me to semiconductor device modeling and deepened my understanding of ultra-wide-bandgap power devices. The results of this work are presented in Appendix C.

This work was supported by the GAANN Fellowship in Materials Science and Engineering (Award #P200A210031). The computational work would not have been possible without the resources provided by the Center for Computational and Applied Mathematics at California

State University, Fullerton; the Department of Defense High Performance Computing Modernization Program (HPCMP); and the Texas Advanced Computing Center (TACC) at the University of Texas at Austin. Access to TACC was made possible through the ACCESS program (allocation DMR130081), which is supported by National Science Foundation grants Nos. 2138259, 2138286, 2138307, 2137603, and 2138296.

Finally, I want to thank my family and especially my mother, whose love and sacrifice brought me further than either of us could have imagined. My father, despite his own struggles, made sure I had what I needed when it mattered most. I am also grateful to Megan, Art, and Erlinda Marentes for their warmth and generosity and for always making space for me. Whether we were watching movies or just sitting around and talking, their home was always open, and that time away from work was a welcome distraction.

*To my mother,
who drove me to the bus stop before dawn
every morning for years
so I would not miss it.*

ABSTRACT OF THE DISSERTATION

Atomistic Design of Ultra-Wide Bandgap Surfaces and Heterostructures

by

Hector Gomez

Doctor of Philosophy, Graduate Program in Materials Science and Engineering

University of California, Riverside, June 2026

Dr. Roger K. Lake, Co-Chairperson

Dr. Mahesh R. Neupane, Co-Chairperson

The intrinsic properties of ultra-wide-bandgap semiconductors are exceptional. Diamond alone combines a bandgap of 5.47 eV, a theoretical breakdown field exceeding 10 MV/cm, and a thermal conductivity unmatched by any other semiconductor material. Whether these properties translate into working devices is determined not only by the bulk crystal but also by the atomic and electronic structure of its surface. This dissertation establishes, through first-principles calculations, how atomic-scale bonding at surfaces and interfaces governs the electronic properties that cannot be understood from the bulk structure alone.

The diamond (100) surface reconstructs without an activation barrier, driving a metallic-to-semiconducting transition. In contrast, the diamond (111) surface admits a secondary pathway through a previously unidentified metastable intermediate, with the final reconstructed surface remaining semi-metallic. These reconstructed surfaces serve as the structural and electronic references for all subsequent termination studies.

Surface-termination chemistry controls the electron affinity and, therefore, the viability of transfer doping. The identity, geometry, and coverage of H- and O-terminating species each modulate the electron affinity. On the (100) surface, oxidized group-IV terminations shift the electron affinity toward positive values and recover bulk-like bandgaps, enabling normally-off device operation with thermal stability that hydrogen termination cannot provide. On the (111) surface, however, oxidized group-IV terminations yield thermally robust surfaces but do not achieve complete structural or electronic passivation.

For TMD/GaN heterostructures, thermodynamic analysis informed by electron microscopy reveals covalent interfacial bonding rather than purely van der Waals interfaces. The MoS_2/GaN heterostructure exhibits a type-I band alignment, whereas the NbS_2/GaN interface remains metallic. For h-BN growth on $\text{Ni}(111)$, substitutional oxygen incorporation impedes rather than promotes monolayer synthesis by severely restricting adatom diffusion. In every system examined, the surface is where the physics is decided.

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Chapter 1

Introduction

1.1 Semiconductor Materials Beyond Silicon

Silicon is one of the defining materials of the modern technological era. Its abundance in the Earth's crust, processability, and stable native oxide have enabled the large-scale manufacture of integrated circuits [1]. This manufacturing maturity supports modern computing, communication, sensing, and power-control technologies. Despite this technological success, silicon has a relatively narrow bandgap ($E_g = 1.12$ eV), which limits its performance in high-voltage, high-power, and high-temperature devices [2, 3]. Wide-bandgap (WBG) semiconductors such as 4H-SiC and GaN have addressed many of these limitations and are now commercially deployed in power conversion and radio-frequency amplification [4]. However, as semiconductor devices are pushed toward higher voltage, higher power density, higher operating frequency, and higher temperature, the limits of established WBG materials become increasingly important. This has motivated interest in ultra-wide-bandgap (UWBG) semiconductors, whose bandgaps exceed that of GaN ($E_g > 3.4$ eV) [5]. In parallel, two-dimensional materials such as h-BN have emerged as a complementary class of wide-bandgap materials with distinct device roles [6]. Figure 1.1 summarizes this materials sequence, from mature Si technology through WBG semiconductors to emerging UWBG

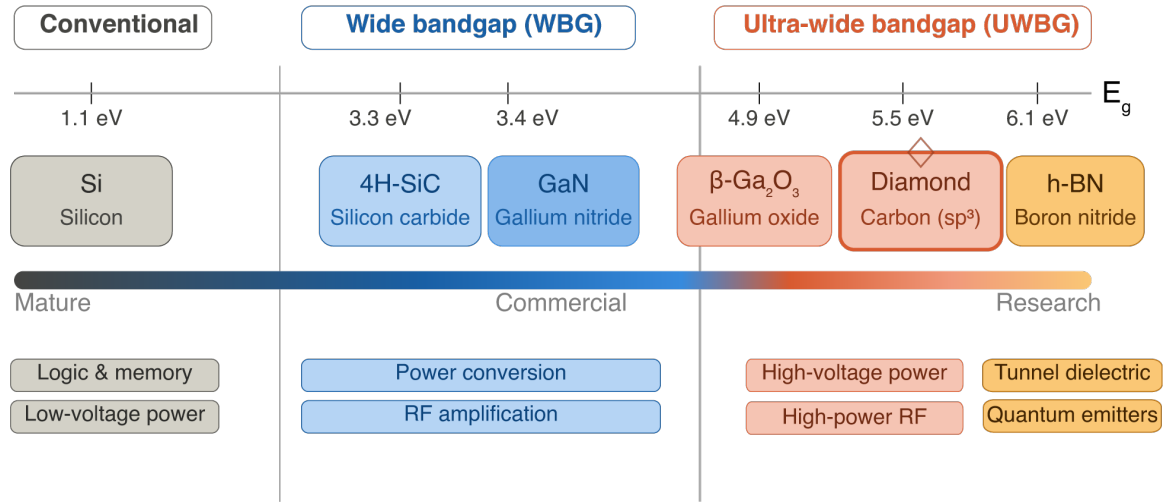
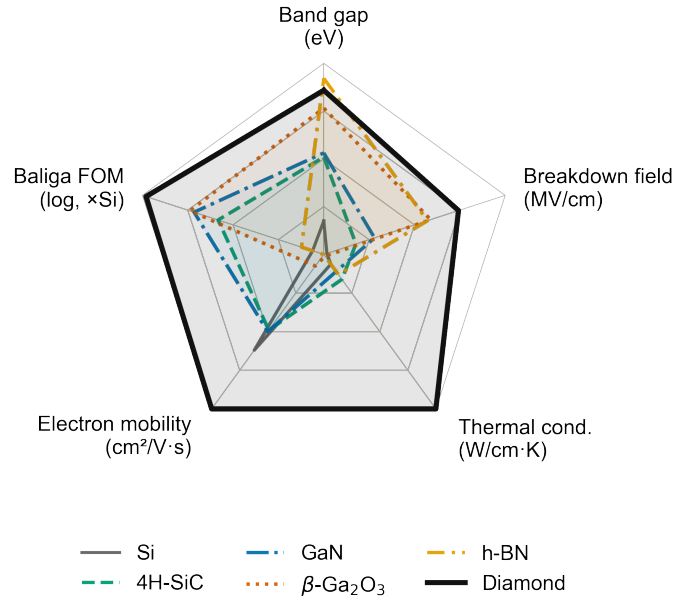


Figure 1.1: Schematic progression of semiconductor materials from conventional Si through wide-bandgap (WBG) semiconductors to ultra-wide-bandgap (UWBG). Materials are arranged by representative bandgap, with typical device roles indicated below each class. The lower bar indicates the qualitative transition from mature, high-volume Si manufacturing to emerging UWBG materials development.

materials. The sequence is organized by representative bandgaps and by the device roles associated with each material class. Whereas Fig. 1.1 emphasizes the bandgap sequence and technology landscape, Fig. 1.2 compares representative conventional, WBG, and UWBG semiconductors across key device-relevant material properties. Within the UWBG class, diamond exhibits exceptional intrinsic properties relative to technologically mature WBG materials such as GaN. Diamond is therefore well suited for semiconductor devices that must operate at high power, high frequency, or elevated temperature. At the same time, the usefulness of these intrinsic properties depends on more than the bulk crystal. In practical devices and growth environments, surfaces, interfaces, and local bonding configurations often determine the electronic structure and materials behavior that can actually be realized [7].



Tsao et al. (2018), Cassabois (2016), Hattori (2016). BFOM log-scaled.

Figure 1.2: Comparison of key material properties relevant to power semiconductor applications, normalized to the maximum value among the materials shown. The Baliga figure of merit, $BFOM = \epsilon \mu E_C^3$, is plotted on a logarithmic scale. Material parameters and BFOM values are taken from [8, 9, 10]; Si and 4H-SiC are included as reference semiconductors. Mobility values for β -Ga₂O₃ are estimates.

1.2 Diamond as a Semiconductor

The origin of these properties lies in the bonding of the crystal itself. Diamond is an allotrope of carbon in which each atom is tetrahedrally coordinated through sp^3 -hybridized bonds, forming a rigid three-dimensional covalent network. This bonding arrangement is responsible for diamond's exceptional hardness and chemical inertness, but it also gives rise to a set of electronic and thermal properties that make diamond an attractive semiconductor. The strong overlap of neighboring sp^3 orbitals produces a wide separation between bonding and antibonding states, resulting in an indirect bandgap of approximately 5.5 eV, as shown in Fig. 1.3. The same rigid bond network transmits atomic vibrations with exceptional efficiency, yielding a thermal conductivity exceeding $2200 \text{ W m}^{-1} \text{ K}^{-1}$ [11]. The wide bandgap and strong bonding also produce a hole mobility above $2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a critical breakdown field surpassing 10 MV cm^{-1} [12], placing diamond among the most promising semiconductors for high-power and high-temperature electronics.

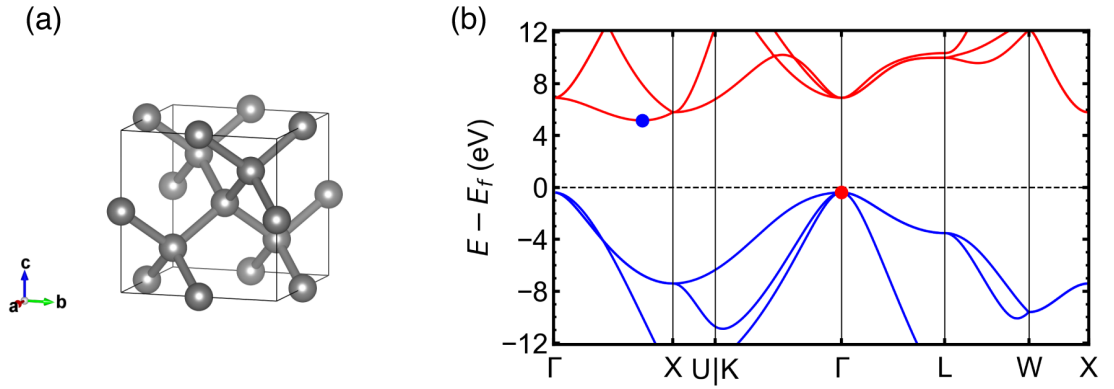


Figure 1.3: (a) Unit cell and (b) band structure of bulk diamond calculated using the HSE06 functional. The indirect bandgap (E_g) is estimated as 5.53 eV.

Diamond is therefore a leading material for next-generation high-power and high-frequency electronics, particularly as device requirements increasingly exceed the limits of conventional semi-

conductors [13]. Realizing these intrinsic advantages in practical devices remains challenging. Diamond wafers, for example, remain limited in size, and the cost and reproducibility of chemical vapor deposition growth continue to present barriers to manufacturing scale-up [14]. More fundamentally, diamond is difficult to dope. The rigid sp^3 bonding network tends to place substitutional impurity states deep within the bandgap, where thermal energy at room temperature is insufficient for efficient carrier ionization. Boron is the most effective p-type dopant in diamond, but its activation energy of 0.37 eV is more than an order of magnitude larger than the thermal energy at room temperature ($k_B T \approx 0.026$ eV) [15]. Unlike shallow dopants in silicon (Fig. 1.4), which ionize almost completely at room temperature, boron's large activation energy causes incomplete ionization in diamond [16, 17].

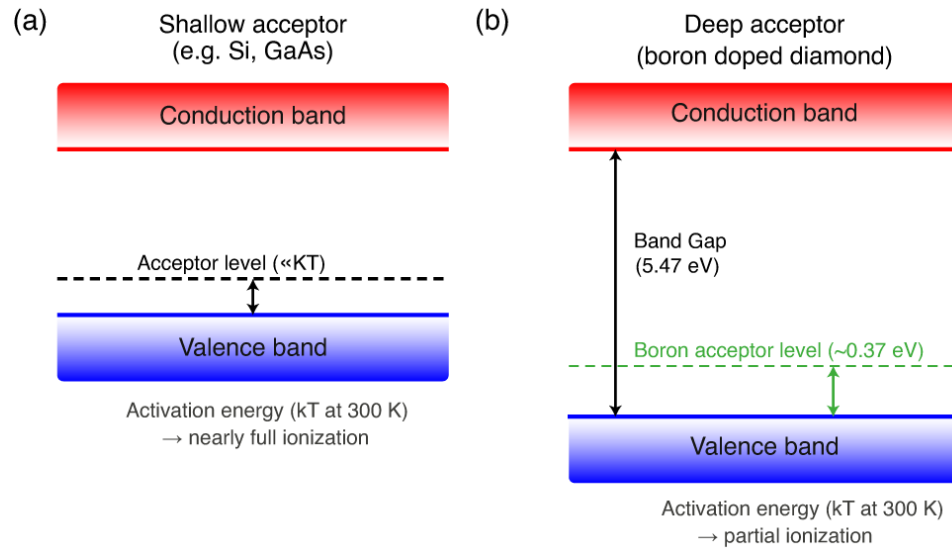


Figure 1.4: Schematic band diagrams comparing (a) a shallow acceptor in a conventional semiconductor such as Si, where the activation energy is much less than $k_B T$ at 300 K and ionization is nearly complete, and (b) the deep boron acceptor in diamond, where the activation energy of 0.37 eV greatly exceeds $k_B T \approx 0.026$ eV, resulting in only partial ionization of dopants at room temperature.

For p-type diamond in particular, the incomplete ionization of boron means that the device-relevant carrier density in surface-channel devices is often governed by the surface rather than by the bulk [18]. This surface sensitivity motivates the broader scope of this dissertation, where atomic-scale bonding at surfaces and interfaces determines the electronic properties and growth outcomes examined here.

1.3 Surface Transfer Doping and Electron Affinity

Surface transfer doping provides a practical route to high carrier densities in diamond without relying on bulk dopant ionization. In this mechanism, charge is exchanged spontaneously between the diamond surface and an adsorbed acceptor layer. When energetically accessible empty acceptor states lie below the diamond valence-band maximum, electrons transfer from the occupied valence band into those states, leaving a two-dimensional hole gas (2DHG) confined near the surface [19, 20, 21]. For molecular acceptors, the relevant acceptor state is typically the lowest unoccupied molecular orbital (LUMO). This surface-induced channel forms the basis of p-channel diamond field-effect transistors. The achievable 2DHG density depends on the energetic offset between the acceptor states and the diamond valence-band maximum, which is governed by the surface electron affinity, surface dipole, and interface electrostatics [20].

Surface termination, therefore, provides the principal atomistic design variable for controlling transfer-doping efficiency. The electron affinity, defined as $\chi = E_{\text{vac}} - E_{\text{CBM}}$, is determined by the surface dipole established by the terminating species, as illustrated in Fig. 1.5.

Hydrogen termination produces a $\text{C}^{\delta-}-\text{H}^{\delta+}$ surface dipole that lowers the vacuum level relative to the bulk bands, yielding a negative electron affinity (NEA) of -1.3 eV [19]. In this

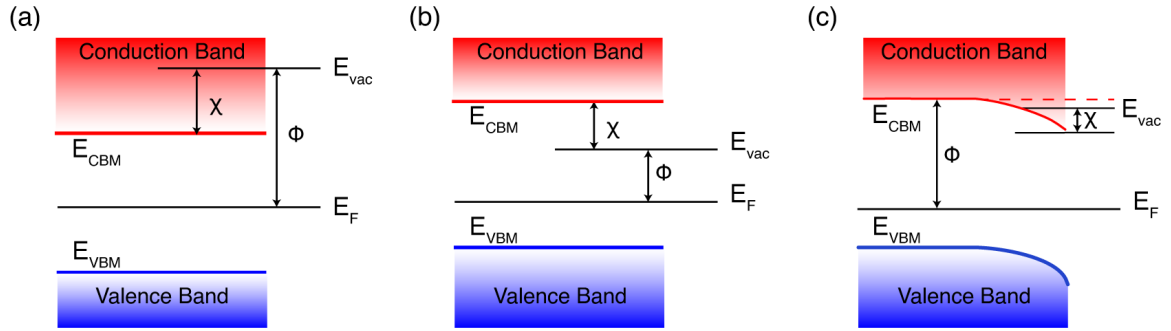


Figure 1.5: Schematic band diagrams illustrating positive electron affinity, true negative electron affinity, and effective negative electron affinity at a semiconductor surface. Φ denotes the work function and E_F the Fermi level. Adapted from [22, 23].

configuration, the valence-band maximum lies in favorable alignment with empty states of surface acceptors, including the lowest unoccupied molecular orbitals (LUMOs) of molecular acceptors, enabling the high hole densities observed in hydrogen-terminated diamond transistors [24, 25]. Although ALD Al_2O_3 passivation improves the thermal durability of the 2DHG [26] and has enabled device operation at temperatures up to 400 °C [27], hydrogen-terminated surfaces remain sensitive to the surrounding environment and to high-temperature processing. Oxygen termination offers improved thermal stability but reverses the surface dipole, raising the vacuum level relative to the bulk bands and producing a positive electron affinity (PEA) [28], as illustrated in Fig. 1.6. The

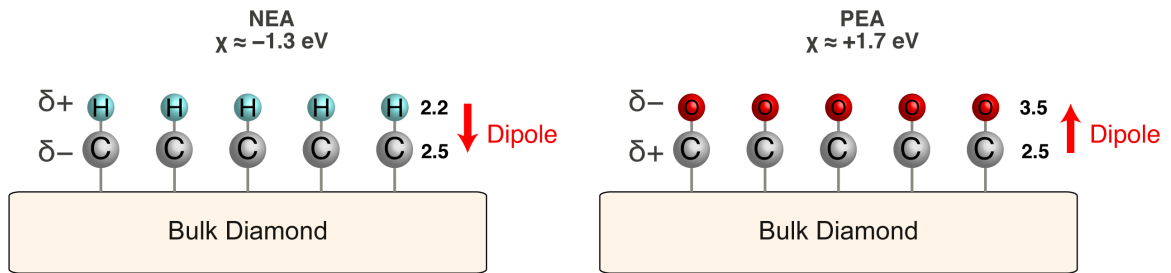


Figure 1.6: Surface dipole orientation for hydrogen- and oxygen-terminated diamond. The $\text{C}^{\delta-}-\text{H}^{\delta+}$ bond dipole points inward, lowering the vacuum level and favoring negative electron affinity (NEA), whereas the $\text{C}^{\delta+}-\text{O}^{\delta-}$ bond dipole points outward, raising the vacuum level and favoring positive electron affinity (PEA). Electronegativity values are indicated.

magnitude of this PEA depends on the local bonding configuration, and surfaces under ambient conditions typically exhibit coexisting bonding species rather than a single well-defined termination [29, 30, 31]. Hydrogen and oxygen terminations therefore represent opposite limits. Hydrogen provides favorable electronic alignment for surface transfer doping but is limited in thermal stability, whereas oxygen provides improved stability but generally exhibits an electron affinity that is less favorable for spontaneous surface transfer doping. The relationship between surface electron affinity, acceptor alignment, and 2DHG formation is summarized in Fig. 1.7.

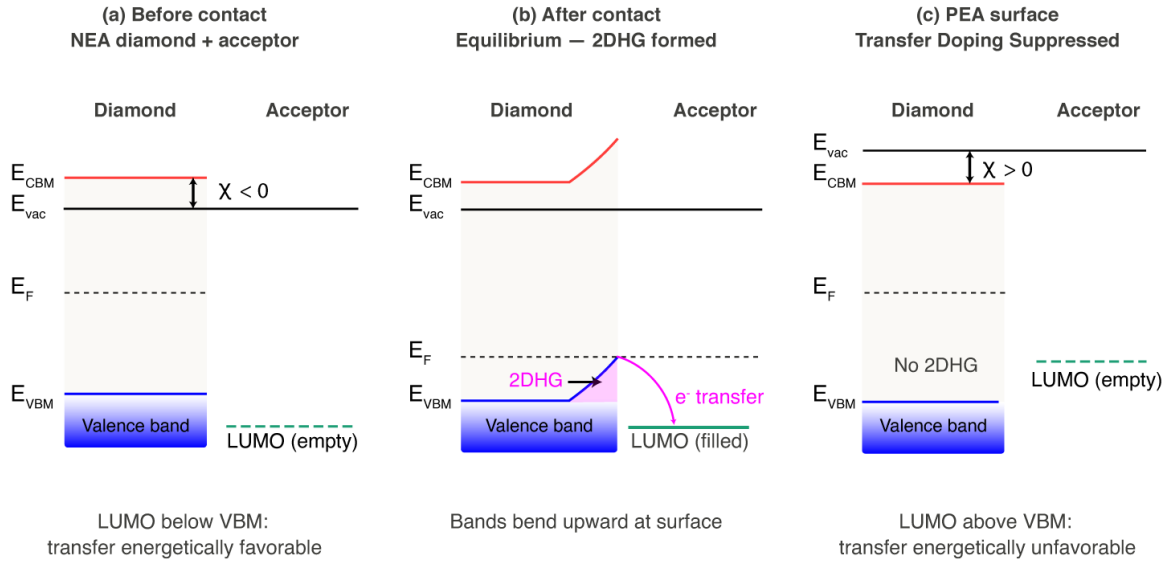


Figure 1.7: Schematic band diagrams illustrating surface transfer doping on diamond in the presence of a molecular acceptor. (a) For a surface with favorable acceptor–valence-band alignment, the acceptor LUMO lies below the diamond valence-band maximum, making electron transfer energetically favorable. (b) Following charge transfer, band bending brings the valence-band maximum close to the Fermi level, forming a two-dimensional hole gas (2DHG) near the surface. (c) For a surface with unfavorable acceptor–valence-band alignment, the acceptor LUMO lies above the valence-band maximum, suppressing electron transfer and 2DHG formation.

Before considering group-IV terminations, it is useful to establish how conventional hydrogen and oxygen terminations modify the diamond (100) surface. The (100) orientation is commonly employed in device implementations and provides a well-defined reference for evaluating

how surface bonding and coverage control electron affinity and transfer-doping-relevant band alignment. Group-IV terminations offer a route between these two limits.

1.4 Group-IV Terminated Diamond

The bare diamond (100) surface reconstructs into a (2×1) phase in which surface carbon atoms form dimers [32, 33]. Silicon and germanium adatoms deposited by vacuum deposition and high-temperature annealing produce a (3×1) dimer–monomer reconstruction [34, 35]. In this structure, the adatoms bridge pairs of surface carbon atoms in an ether-like geometry and preserve a comparable NEA to the hydrogen-terminated surface.

Although these terminations are thermally stable, the group-IV adatoms retain dangling-bond character that can serve as reactive sites for atmospheric oxidation. Oxidation of group-IV terminated surfaces is therefore a structurally defining step for real device operation as illustrated for the Si-terminated case in Fig. 1.8. Upon atmospheric exposure, group-IV adatoms react with oxygen to form C–X–O bonding configurations (X = Si, Ge) that retain the surface reconstruction [36] and exhibit enhanced thermal stability and favorable electron affinity. These oxidized configurations define the channel interface beneath the gate dielectric in p-channel MOSFETs [37, 38]. Because surface transfer doping depends on the energetic alignment between the diamond bands and external acceptor states, oxidation can change not only the chemical structure of the buried interface but also the equilibrium charge state of the channel. Hydrogen-terminated diamond devices are normally-on, meaning a 2DHG is present at zero gate bias, which poses a safety risk in power-switching applications. The oxidized C–Si–O surface has a higher, and in some cases positive, electron affinity relative to H-terminated diamond, suppressing spontaneous 2DHG formation

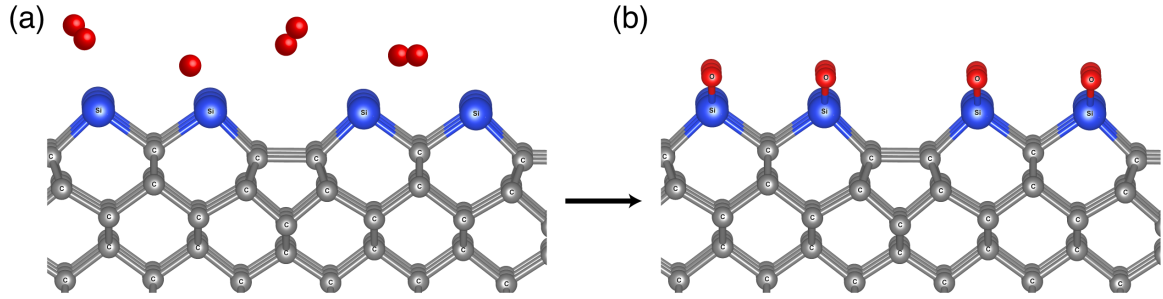


Figure 1.8: Schematic illustration of the oxidation of the Si-terminated diamond (100) surface. Panel (a) shows the non-oxidized surface exposed to molecular oxygen, with Si adatoms (blue) bridging pairs of surface carbon atoms. Panel (b) shows the oxidized surface, where oxygen atoms bind to the Si adatoms to form C–Si–O bonding configurations. Carbon, silicon, and oxygen atoms are shown in gray, blue, and red, respectively.

and yielding the normally-off operation preferred for power devices [38]. In these devices, a hole channel can instead be accumulated electrostatically under negative gate bias, with the oxidized C–Si–O layer defining the buried diamond/dielectric interface. The central question this dissertation addresses for group-IV terminated diamond is therefore which oxidized bonding configurations are thermodynamically accessible and what electron affinities they yield.

For the (111) orientation, normally-off operation has been demonstrated experimentally using an oxidized Si-terminated diamond surface with an ALD Al_2O_3 gate dielectric [38]. The proposed device interface contains an oxidized C–Si–O bonding network beneath the gate stack, as illustrated in Fig. 1.9. The (111) surface is of comparable practical interest to the (100) surface because it supports a higher density of surface atoms per unit area. The resulting dipole moment per unit area can produce a 2DHG sheet density approximately twice that achievable on the (100) surface under equivalent transfer-doping conditions [38, 39]. The (111) surface is also structurally more complex than the (100) surface. The clean surface favors a (2×1) Pandey chain reconstruction

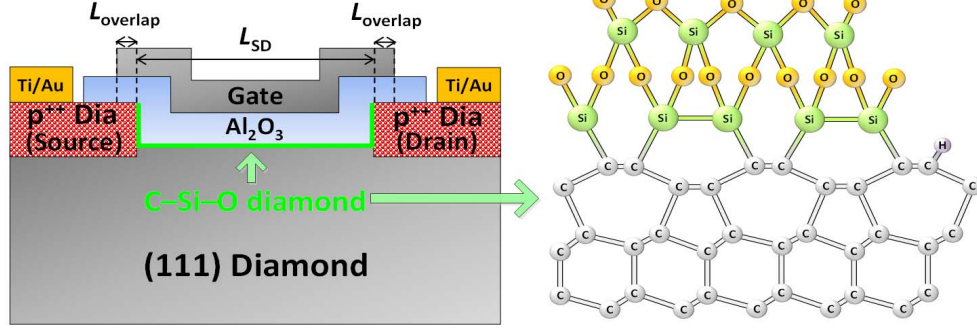


Figure 1.9: Schematic of a normally-off MOSFET based on an oxidized Si-terminated diamond (111) surface with an ALD Al_2O_3 gate dielectric and the proposed oxidized C–Si–O interfacial bonding motif. Reprinted from Ref. [38]. © 2022 IEEE.

stabilized by delocalized π bonding [32]. Silicon deposition on this surface yields a $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase at low coverage and a (2×2) phase at full coverage [40].

Germanium termination provides a chemically analogous group-IV surface system and is considered alongside silicon to determine how the terminating species affects oxidation, structural stability, and electronic properties. The combination of moderate electron affinity, thermal robustness, and compatibility with oxide gate stacks makes group-IV terminated diamond surfaces promising candidates for thermally stable p-channel field-effect devices.

1.5 TMD/GaN Mixed-Dimensional Heterostructures

The same structure-selection principle extends to mixed-dimensional TMD/GaN heterostructures. Gallium nitride is among the most widely deployed wide-bandgap semiconductors, with established applications in high-electron-mobility transistors and radio-frequency power amplifiers [41]. As a substrate for two-dimensional overlayers, GaN presents an interfacial bonding problem analogous to the group-IV terminated diamond surfaces studied here.

The integration of atomically thin transition metal dichalcogenide (TMD) overlayers with GaN has attracted interest as a route to new device functionalities that exploit the properties of both materials. TMDs are layered materials with the general formula MX_2 , where M is a transition metal and X is a chalcogen, and can exhibit semiconducting, metallic, or superconducting behavior depending on composition. Their atomically thin geometry reduces the lattice-matching constraints

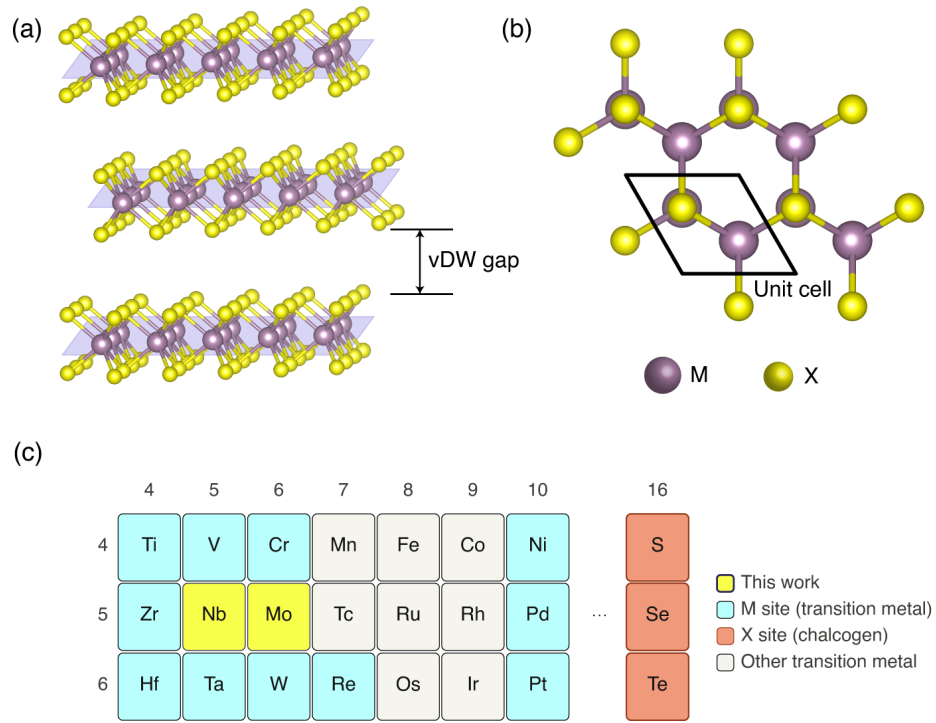


Figure 1.10: Crystal structure of MX_2 transition metal dichalcogenides. (a) Side view of the layered bulk structure depicting the X-M-X bonding configuration. Each layer is separated by a van der Waals (vdW) gap. (b) Top view of a single MX_2 layer with the primitive unit cell shown. (c) Periodic table highlighting the transition metal (M) and chalcogen (X) sites considered in this work, with Nb and Mo indicated as the systems studied here.

associated with conventional epitaxial growth. MoS_2/GaN and NbS_2/GaN provide a useful pair for examining how lattice mismatch shapes interfacial structure and electronic properties under comparable growth conditions, with respective mismatches of 0.9% and 3.8% [42, 43, 44].

Recent experimental work has shown that the MoS₂/GaN interface departs from the prior physisorbed van der Waals model [45], with transmission electron microscopy revealing a compact Ga–Mo separation of 2.8 ± 0.5 Å. This reduced interfacial separation is difficult to reconcile with a purely physisorbed interface and motivates consideration of covalent interfacial bonding, as illustrated in Fig. 1.11. The thermodynamic conditions under which this covalently bonded interface

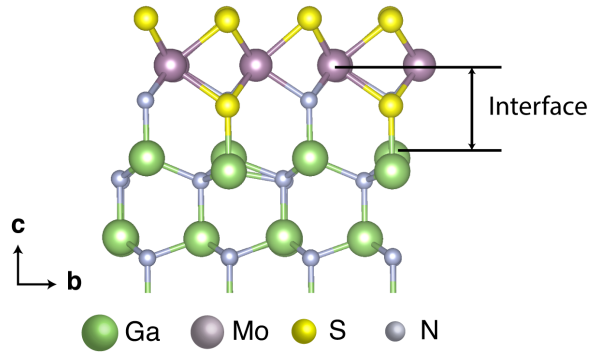


Figure 1.11: Schematic side-view structural model of the MoS₂/GaN interface, showing the compact separation between the Mo and Ga layers at the interface. The small Ga–Mo distance suggests covalent interfacial bonding.

forms, and the extent to which the resulting interfacial bonding governs charge transfer, have not been established from first principles and are addressed in a dedicated chapter of this dissertation.

1.6 h-BN Growth on Ni(111)

The same principle applies to the synthesis of two-dimensional materials. Whereas the TMD/GaN chapter examines how interfacial bonding modifies the electronic properties of a mixed-dimensional heterostructure, the h-BN/Ni(111) study examines how substrate chemistry modifies the growth pathway itself. Hexagonal boron nitride grown by molecular beam epitaxy on Ni(111) substrates provides a controlled platform for studying how substrate chemistry affects monolayer

h-BN synthesis. During pretreatment with boron-containing precursors, oxygen becomes incorporated into the Ni(111) substrate as substitutional defects [46], as illustrated in Fig. 1.12. As in the

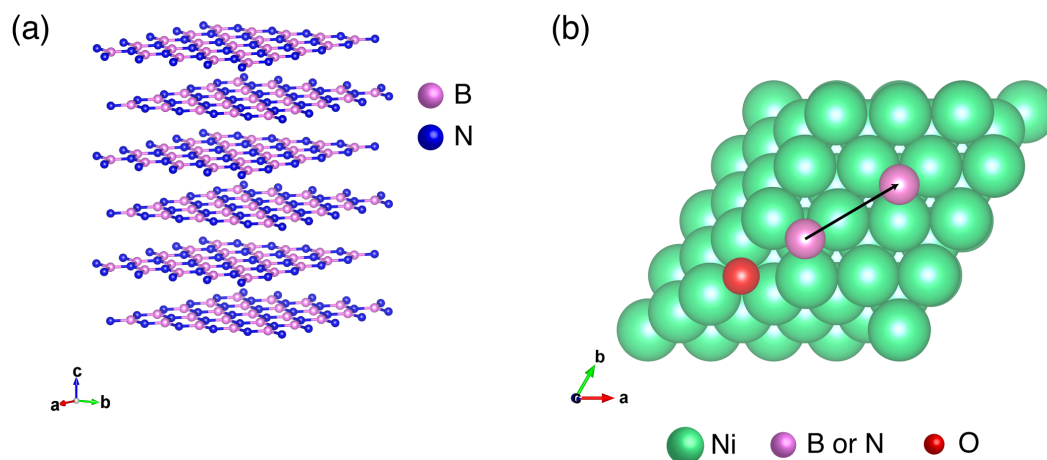


Figure 1.12: (a) Side view of the layered bulk h-BN structure showing the stacked B–N monolayers separated by van der Waals gaps. (b) Top view of the Ni(111) surface with a substitutional oxygen atom (red) and a B or N adatom (magenta) on an HCP site, with the diffusion pathway indicated by the arrow. Ni, B/N, and O atoms are shown in green, magenta, and red, respectively.

oxidized diamond and TMD/GaN systems, the realistic substrate structure under experimental conditions governs the growth outcome. First-principles calculations are used here to determine how substitutional oxygen modifies the adsorption and diffusion energetics of B and N adatoms on the Ni(111) surface, and whether this incorporation promotes or impedes h-BN monolayer synthesis.

1.7 Aims of This Investigation

This dissertation uses first-principles calculations to determine how chemically realistic surface and interface structures govern electronic properties and synthesis pathways in wide- and ultra-wide-bandgap semiconductors and related materials systems. This work addresses three related problems: the control of diamond surface electronic properties through termination and ox-

idation, interfacial bonding in TMD/GaN heterostructures, and the influence of oxygen defects on h-BN growth on Ni(111). The six principal aims are:

1. Establish the relative stability, reconstruction behavior, and electronic structures of bare diamond (100) and (111) surfaces as reference states for termination studies.
2. Determine how the coverage and local bonding configurations of hydrogen- and oxygen-containing terminations on diamond (100) control surface stability, electron affinity, and electronic structure relevant to surface transfer doping.
3. Identify the thermodynamically favorable oxidized bonding configurations of Si- and Ge-terminated diamond (100) surfaces and determine their electronic structures and electron affinities.
4. Identify thermodynamically favorable oxidized configurations of Si- and Ge-terminated diamond (111) surfaces, assess their dynamical stability and thermal robustness, and evaluate their electron affinities and implications for normally-off p-channel device interfaces.
5. Determine the thermodynamically favored interfacial stoichiometries of MoS₂/GaN and NbS₂/GaN under experimental growth conditions and characterize the resulting interfacial bonding and electronic structures.
6. Determine how substitutional oxygen in Ni(111) modifies the adsorption and diffusion energetics of B and N adatoms and assess whether oxygen incorporation promotes or impedes h-BN monolayer growth.

The remainder of this dissertation is organized as follows. Chapter 2 presents the theoretical and computational methods used throughout the dissertation. Chapters 3–6 examine diamond

surfaces in sequence. Chapter 3 establishes the bare diamond (100) and (111) surface reconstructions as reference structures. Chapter 4 examines hydrogen and oxygen terminations on diamond (100). Chapters 5 and 6 investigate oxidized Si- and Ge-terminated diamond (100) and (111) surfaces, respectively. Chapter 7 addresses MoS_2/GaN and NbS_2/GaN heterostructures. Chapter 8 investigates the effect of substitutional oxygen in Ni(111) on the growth of h-BN monolayers. Appendix C discusses a related study using technology computer-aided design (TCAD) simulations.

Chapter 2

Methodology

2.1 Density Functional Theory

The many-electron Schrödinger equation for a system of N interacting electrons cannot be solved directly for systems of more than a few electrons because the many-body wavefunction depends on the coordinates of all electrons and the computational cost grows exponentially with N (Eq. 2.1). Written in Hartree atomic units, the equation is

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \left[-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi = E\Psi. \quad (2.1)$$

Density functional theory (DFT) circumvents this scaling by replacing the many-electron wavefunction with the electron density, $n(\mathbf{r})$, as the central variable. The benefit of DFT is that, rather than attempting to determine $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ directly, it reformulates the ground-state many-body problem in terms of a scalar field that depends only on three spatial coordinates. The dimensionality of this density is independent of the total number of electrons, although its integral gives the total electron number. The theoretical foundation for this reformulation is given by the two Hohenberg–Kohn theorems [47]. The first theorem establishes that the ground-state density uniquely deter-

mines the external potential and therefore all ground-state properties of the system. The second theorem proves that the true ground-state density minimizes the total energy functional, providing a variational principle analogous to that used in wavefunction-based methods. These results show that the ground-state energy and observables are, in principle, functionals of $n(\mathbf{r})$. In practice, the Kohn–Sham formulation maps the interacting many-electron system onto an auxiliary system of non-interacting electrons chosen to reproduce the same ground-state density [48]. This mapping converts the many-body problem into a set of single-particle equations that can be solved self-consistently (Eq. 2.2),

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (2.2)$$

where v_{ext} is the electron–ion potential describing the attraction between electrons and nuclei, v_{H} is the Hartree potential describing the mean-field electron–electron repulsion, and $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}[n]/\delta n(\mathbf{r})$ is the exchange–correlation potential, which captures many-body quantum effects beyond the mean field, including exchange and electron correlation. The electron density is constructed from the Kohn–Sham orbitals as

$$n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2, \quad (2.3)$$

where f_i is the occupation of state i . This density is fed back into the effective potential, and the cycle is repeated until the input and output densities converge to within the criteria specified in Section 2.4. If the exact exchange–correlation functional were known, the Kohn–Sham scheme would yield the exact ground-state density and energy, but in practice it must be approximated, and

the quality of this approximation is the primary determinant of accuracy for the properties calculated here. For periodic systems the Kohn–Sham orbitals satisfy Bloch’s theorem,

$$\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (2.4)$$

where $u_{n\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. The periodic part is expanded in a plane-wave basis,

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (2.5)$$

where $\mathbf{G}$ are reciprocal lattice vectors, and the expansion is truncated at a kinetic energy cutoff E_{cut} such that $\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}$, converged independently for each system as described in Section 2.4. Core-valence interactions are treated using the projector-augmented wave (PAW) method [49, 50], which retains all-electron accuracy near the nuclei while preserving the efficiency of smooth pseudo-wavefunctions expanded in a plane-wave basis. Brillouin zone integrals are evaluated over discrete Γ -centered Monkhorst–Pack meshes [51] with densities converged independently for each system, as detailed in Section 2.4.

2.2 Exchange-Correlation Functionals

Because the Kohn–Sham equations recast the interacting many-electron problem into an effective single-particle form, the central approximation in DFT is the exchange-correlation potential, v_{xc} . The simplest widely used approximation is the local density approximation (LDA). In LDA, the exchange-correlation energy at each point is approximated using the electron density at

that point, treating the local environment as a uniform electron gas. For example, the LDA exchange energy is

$$E_x^{\text{LDA}} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int n(\mathbf{r})^{4/3} d\mathbf{r}, \quad (2.6)$$

where the prefactor and the 4/3 exponent follow from the analytic exchange energy of the uniform electron gas [48]. Beyond LDA, generalized gradient approximation (GGA) functionals incorporate

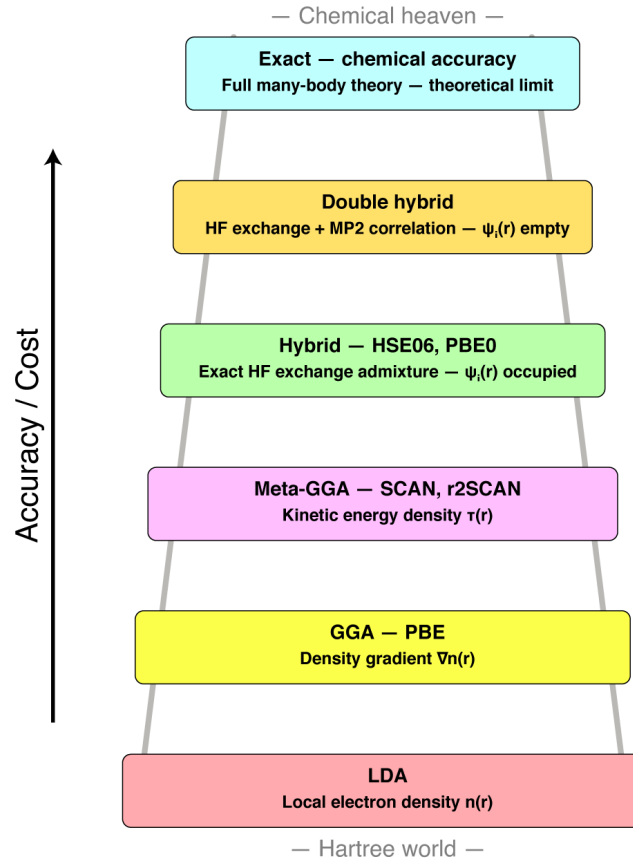


Figure 2.1: Jacob’s ladder of DFT exchange-correlation functionals, illustrating the hierarchy from LDA at the base to increasingly nonlocal approximations at higher rungs. Each rung incorporates additional information about the electronic structure at increased computational cost.

both the electron density and its gradient, $\nabla n(\mathbf{r})$, thereby accounting for spatial variations in the

density. The Perdew–Burke–Ernzerhof (PBE) functional [52] is one of the most widely used GGA functionals in computational materials science. Its exchange component can be written as

$$E_x^{\text{PBE}} = \int n(\mathbf{r}) \epsilon_x^{\text{LDA}}(n) F_x(s) d\mathbf{r}, \quad (2.7)$$

where $\epsilon_x^{\text{LDA}}(n)$ is the LDA exchange energy density and $F_x(s)$ is an enhancement factor that depends on the reduced density gradient. The reduced gradient is defined as

$$s = \frac{|\nabla n|}{2k_F n}, \quad (2.8)$$

where $k_F = (3\pi^2 n)^{1/3}$ is the local Fermi wavevector. In the uniform-density limit, $s = 0$, the enhancement factor satisfies $F_x(0) = 1$, and the PBE exchange expression reduces to the LDA exchange form. Although semi-local functionals such as PBE are computationally efficient, they systematically underestimate band gaps by up to 40% because of self-interaction error and the absence of the derivative discontinuity in the exchange-correlation potential. This limitation is particularly important for electronic-structure quantities such as band offsets, electron affinities, and surface states. Hybrid functionals partially address this problem by mixing a fraction of exact Hartree–Fock exchange with semi-local exchange. This reduces the self-interaction error and generally improves the description of band gaps and band-edge positions. The Heyd–Scuseria–Ernzerhof hybrid functional HSE06 [53] uses a screened hybrid form in which the Coulomb interaction is separated into short-range and long-range components,

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\mu) + (1 - \alpha) E_x^{\text{PBE,SR}}(\mu) + E_x^{\text{PBE,LR}}(\mu) + E_c^{\text{PBE}}, \quad (2.9)$$

where SR and LR denote short-range and long-range contributions, respectively. Here, α is the fraction of short-range exact exchange, and μ is the range-separation screening parameter. The standard HSE06 parameters are $\alpha = 0.25$ and $\mu = 0.20 \text{ \AA}^{-1}$. For the diamond surface calculations in this dissertation, a modified exact exchange fraction of $\alpha = 0.30$ was used while retaining $\mu = 0.20 \text{ \AA}^{-1}$. The HSE06* parameters were validated against bulk diamond using a systematic scan of α and μ , as summarized in Table 2.1. This modified functional with the revised exchange fraction produces the experimental band gap of diamond within 1%, and is referred to as HSE06* throughout this dissertation. For systems in which van der Waals dispersion interactions contribute

Table 2.1: Converged screening and exact-exchange parameters for the bulk diamond band gap using the HSE06 functional. Bold values indicate the parameter combination adopted in this work.

Diamond	AEXX (α)					
HFSCREEN (μ)	0.15	0.2	0.25	0.3	0.35	0.4
0.15	4.909	5.175	5.444	5.715	5.987	6.262
0.2	4.817	5.053	5.290	5.530	5.771	6.014
0.25	4.737	4.946	5.157	5.369	5.583	5.798
0.3	4.668	4.853	5.040	5.227	5.417	5.607
0.35	4.606	4.770	4.936	5.103	5.271	5.440

non-negligibly to binding energies or interlayer separations, the DFT-D3 dispersion correction with Becke–Johnson damping [54] was included as an additive correction to the DFT total energy.

2.3 Computational Implementation

All calculations in this dissertation were performed using either the Grid-based Projector-Augmented Wave (GPAW) code [55, 56], interfaced with the Atomic Simulation Environment (ASE) [57], or the Vienna Ab initio Simulation Package (VASP) [58, 59]. Both codes implement the projector-augmented wave (PAW) formalism described above, although they employ distinct

PAW datasets, numerical representations, and implementation details. VASP calculations were performed using a plane-wave basis, whereas GPAW calculations used either real-space grids or localized atomic-orbital basis sets, as specified in the corresponding results chapters. Selected structural results were cross-validated between the two codes and, where available, against experimental data [32].

2.4 Convergence Parameters

Plane-wave cutoff energies and Brillouin-zone sampling densities were converged independently for each surface or interface system. Total energies were monitored until changes with respect to the relevant convergence parameter were below 1 meV/atom. Because GPAW and VASP use distinct PAW implementations and numerical representations, cutoff energies are not directly transferable between the two codes. System-specific k -point meshes, cutoff energies, and additional convergence data are provided in the corresponding results chapters.

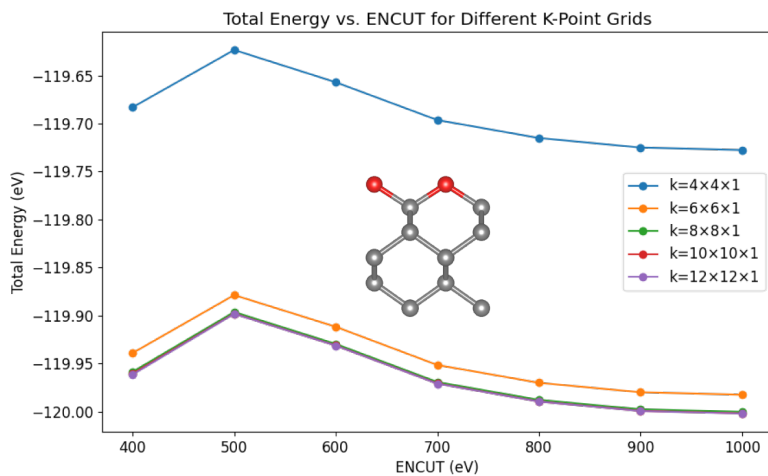


Figure 2.2: Convergence test for the O-terminated diamond (100) surface.

2.5 Surface and Interface Slab Models

Diamond surfaces were modeled using symmetric periodic slabs in which the crystal was cleaved along the desired crystallographic orientation. A vacuum region of at least 12 Å was introduced along the surface normal to reduce interactions between periodic images. For symmetric slabs, both exposed faces carry the same surface termination. This construction eliminates artificial dipoles perpendicular to the surface and allows the electrostatic potential to converge to equivalent vacuum plateaus on both sides of the slab. Such a well-defined vacuum reference is required for accurate electron affinity calculations. TMD/GaN heterostructure slabs were modeled using asymmetric geometries because of the polarity of the GaN surface. For these systems, the bottom face of the GaN slab was passivated using fractional pseudo-hydrogen atoms to remove artificial surface states. The top surface retained the physically relevant interface or surface termination. System-specific slab thicknesses, supercell dimensions, vacuum spacings, and k -point meshes are given in the corresponding results chapters.

2.5.1 Electron Localization Function

The electron localization function (ELF), introduced by Becke and Edgecombe [60], was used to characterize the spatial localization of electrons and the bonding character of selected surface structures. ELF is a dimensionless scalar field, commonly written as $\text{ELF}(\mathbf{r})$, that ranges from 0 to 1. It provides a real-space measure of electron localization based on the same-spin conditional pair probability, and can be used to identify regions associated with atomic cores, covalent bonds, lone pairs, and delocalized metallic-like bonding [61]. High ELF values indicate strong electron localization. In particular, regions with $\text{ELF}(\mathbf{r}) \gtrsim 0.7$ are typically associated with localized electron

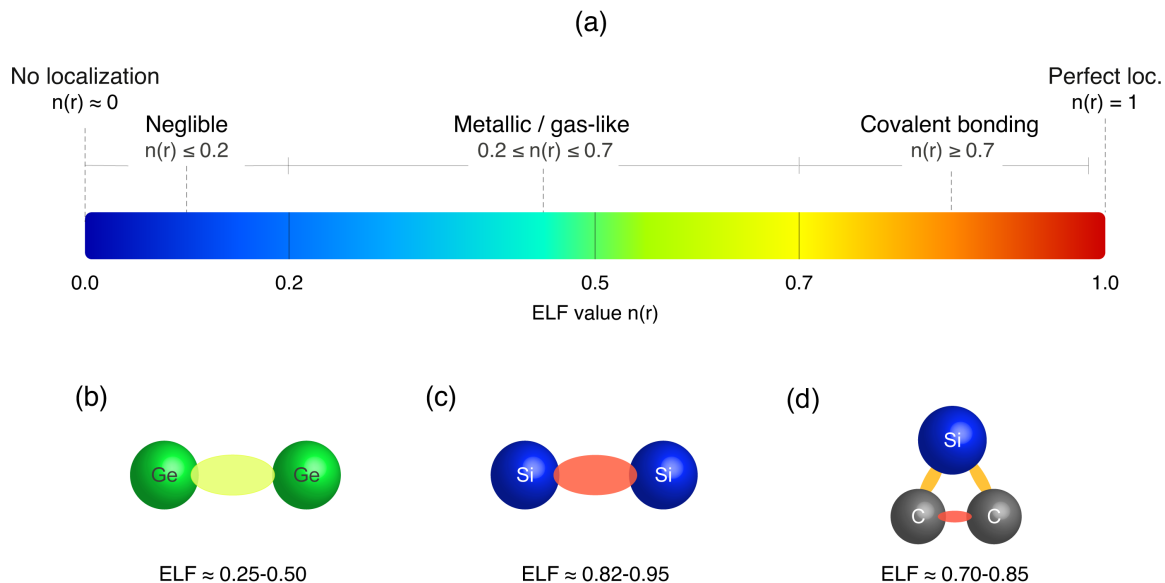


Figure 2.3: ELF colormap and bonding interpretation scale. Panels (b)–(d) show representative bonding configurations from the group-IV-terminated diamond surfaces analyzed in Chapter 5.

pairs, as found in covalent bonds or lone-pair-like states [61]. Values near $\text{ELF}(\mathbf{r}) = 0.5$ correspond to behavior similar to a homogeneous electron gas and are commonly associated with more delocalized, metallic-like bonding. Values approaching zero indicate low electron localization relative to the homogeneous electron-gas reference. ELF isosurfaces and planar projections were computed from VASP output and visualized using VESTA [62].

2.5.2 Electron Affinity and Potential Alignment

The electron affinity, χ , was determined using a slab electrostatic-potential alignment method. In this approach, the planar-averaged electrostatic potential along the surface normal is used to align the bulk diamond band-edge positions to the bulk-like region of the surface slab. To reduce atomic-scale oscillations, the planar-averaged electrostatic potential was further averaged over a length scale corresponding to the bulk interlayer spacing. The planar-averaged electrostatic potential was obtained using VASPKIT 1.5.1 [63] with option 426 - Planar Average Potential,

which reads the LOCPOT file written by VASP. Alternatively, the LOCPOT file was read and averaged using custom Python scripts, which allowed direct control over the bulk-like averaging window. The vacuum level, E_{vac} , was extracted from the flat plateau of the macroscopic electrostatic potential in the vacuum region, as shown in Fig. 2.4.

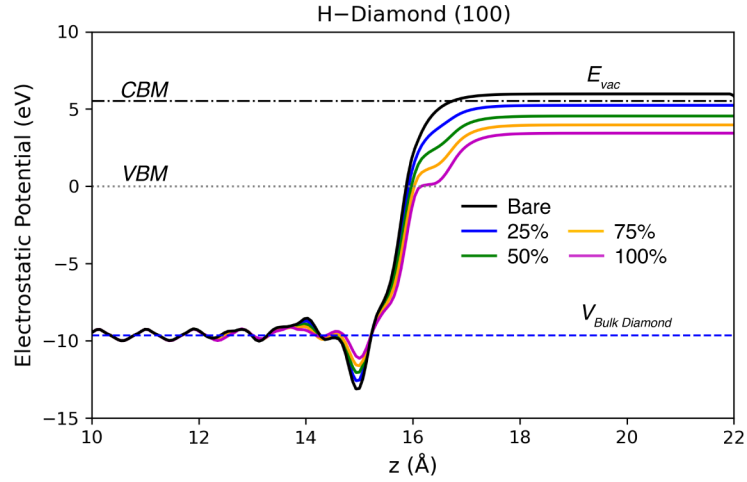


Figure 2.4: Electrostatic-potential alignment for bare and H-terminated diamond (100) surfaces with 25–100% hydrogen coverage.

The electron affinity was calculated as

$$\chi = E_{\text{vac}} - E_{\text{CBM}}^{\text{surf}} = E_{\text{vac}} - (V_{\text{surf}} + \Delta E_{\text{VBM}}^{\text{bulk}} + E_g^{\text{bulk}}), \quad (2.10)$$

where $E_{\text{CBM}}^{\text{surf}}$ is the conduction-band minimum of the surface slab on the aligned energy scale. Here, V_{surf} is the average electrostatic potential in the bulk-like interior of the slab, $\Delta E_{\text{VBM}}^{\text{bulk}}$ is the signed offset between the bulk diamond valence-band maximum and the average bulk electrostatic potential, and E_g^{bulk} is the bulk diamond band gap. The bulk valence-band offset is defined as

$$\Delta E_{\text{VBM}}^{\text{bulk}} = E_{\text{VBM}}^{\text{bulk}} - \bar{V}_{\text{bulk}}, \quad (2.11)$$

where $E_{\text{VBM}}^{\text{bulk}}$ is the valence-band maximum of bulk diamond and $\bar{V}_{\text{bulk}}$ is the average electrostatic potential of the bulk diamond reference. The absolute energy zero in VASP is arbitrary, so raw eigenvalues from separate bulk and slab calculations cannot be compared directly. Instead, the bulk band-edge offset is computed relative to the average electrostatic potential within the same bulk calculation, where both quantities share the same internal VASP reference. With the average bulk electrostatic potential used as the reference, $\Delta E_{\text{VBM}}^{\text{bulk}}$ is numerically equal to the bulk diamond VBM relative to that potential. For the diamond reference used here, $\Delta E_{\text{VBM}}^{\text{bulk}} \approx -9.65$ eV. The bulk conduction-band minimum is then obtained by adding the bulk diamond band gap, $E_g^{\text{bulk}} = 5.53$ eV. Thus, the slab conduction-band minimum is evaluated as

$$E_{\text{CBM}}^{\text{surf}} = V_{\text{surf}} + \Delta E_{\text{VBM}}^{\text{bulk}} + E_g^{\text{bulk}}. \quad (2.12)$$

In practice, V_{surf} was obtained by identifying a region near the middle of the slab where the macroscopic electrostatic potential exhibits bulk-like periodic behavior. This region was chosen away from both the surface termination and the flat vacuum plateau. The same bulk offset, $\Delta E_{\text{VBM}}^{\text{bulk}}$, and bulk band gap, E_g^{bulk} , were then applied to all surface configurations of the same material. This procedure places the vacuum level and bulk-referenced band edges on a common energy scale across different terminations and coverages. Negative values of χ correspond to negative electron affinity, whereas positive values correspond to positive electron affinity. The slab potential-alignment method is more reliable than estimating electron affinity directly from the slab band structure or slab PDOS because the band edges are referenced to an independently computed bulk diamond electronic structure. This approach follows the established potential-alignment procedure [64].

2.5.3 Surface Thermodynamics and Chemical Potentials

The thermodynamic stability of competing surface configurations cannot be assessed from total DFT energies alone because surfaces can exchange atoms with external chemical reservoirs. The relevant quantity is therefore a grand-canonical surface free energy. For a symmetric slab exposing two equivalent surfaces, the surface formation energy per unit area is

$$E_{\text{surf}} = \frac{1}{2A} \left(E_{\text{total}} - \sum_i N_i \mu_i \right), \quad (2.13)$$

where E_{total} is the total DFT energy of the slab, N_i is the number of atoms of species i , μ_i is the corresponding chemical potential, and A is the surface unit-cell area. The factor of 1/2 accounts for the two equivalent surfaces exposed by the symmetric slab. Chemical potentials for solid-phase species were taken as the DFT total energy per atom of the corresponding bulk crystal. For each gas-phase species i , the chemical potential was evaluated as

$$\mu_i(T, p) = E_i^{\text{DFT}} + \Delta H_i(T) - T \Delta S_i(T) + k_B T \ln \left(\frac{p}{p_0} \right), \quad (2.14)$$

where E_i^{DFT} is the DFT total energy of the isolated molecule and $p_0 = 1$ atm. The temperature-dependent enthalpy and entropy corrections were evaluated using the NIST Shomate equations,

$$H(T) - H_{298} = At + \frac{B}{2}t^2 + \frac{C}{3}t^3 + \frac{D}{4}t^4 - \frac{E}{t} + F - H, \quad (2.15)$$

$$S(T) = A \ln t + Bt + \frac{C}{2}t^2 + \frac{D}{3}t^3 - \frac{E}{2t^2} + G, \quad (2.16)$$

where $t = T/1000$ and A – H are species-specific Shomate coefficients taken from the NIST-JANAF thermochemical tables [65]. The tabulated enthalpy and entropy values were converted to consistent energy units before being combined with the DFT molecular energies. An example set of coefficients for gas-phase H_2 is given in Table 2.2. Finite-temperature effects on the surface were

Table 2.2: NIST Shomate equation coefficients for H_2 [65].

Coefficient	298–1000 K	1000–2500 K	2500–6000 K
A	33.066178	18.563083	43.413560
B	-11.363417	12.257357	-4.293079
C	11.432816	-2.859786	1.272428
D	-2.772874	0.268238	-0.096876
E	-0.158558	1.977990	-20.533862
F	-9.980797	-1.147438	-38.515158
G	172.707974	156.288133	162.081354
H	0.0	0.0	0.0

incorporated by adding harmonic vibrational free-energy corrections for the adsorbed species,

$$G_{\text{surf}} = \frac{1}{2A} \left[E_{\text{total}} - \sum_i N_i \mu_i + G(T) \right], \quad (2.17)$$

where $G(T)$ is the vibrational free-energy correction for the adsorbed species. To evaluate $G(T)$, a static DFT calculation was first performed with the surface atoms fixed and only the adsorbate atoms allowed to relax. A finite-displacement frequency calculation was then performed at the Γ point using VASP. The resulting vibrational frequencies were post-processed using the Catalysis-ElectroChem Kit in VASPKIT 1.5.1. Specifically, function 501 - Thermal Corrections for Adsorbate was used to evaluate the harmonic vibrational partition function and return $G(T)$ directly. This approach neglects translational contributions for adsorbed species, which is appropriate for chemisorbed atoms that are bound to the surface. Each inequivalent adsorbate atom was dis-

placed in the positive and negative directions along each Cartesian coordinate using $N_{\text{FREE}} = 2$. The corresponding finite-difference forces were used to construct the harmonic vibrational modes. Only zone-center modes were sampled, so phonon dispersion across the Brillouin zone was neglected. The inclusion of zero-point and finite-temperature vibrational corrections improves upon a purely static treatment. However, the Γ -point adsorbate-frequency approach is less complete than a full phonon calculation and was not used to assess dynamical stability. It nevertheless provides a first-order estimate of the vibrational free-energy correction for comparing relative surface formation energies.

For the Si- and Ge-terminated diamond (100) surfaces [66], both the gas-phase chemical-potential corrections from the Shomate equations and the Γ -point adsorbate vibrational correction $G(T)$ were applied. For the Si- and Ge-terminated diamond (111) surfaces, the full harmonic vibrational free energy $F_{\text{vib}}(T)$ from Brillouin-zone phonon calculations was used instead of the Γ -point adsorbate correction, as described in Section 2.6.1.

For TMD/GaN heterostructures, the asymmetric slab geometry requires a different reference without the prefactor of $1/2$. The interfacial stability was therefore evaluated using a grand-canonical interface formation energy. Vibrational free-energy corrections were not applied to the TMD/GaN heterostructures because the large supercell sizes make phonon calculations computationally prohibitive. The interface formation energy was defined as

$$E_{\text{form}} = \frac{1}{A} [E_{\text{slab}} - (E_{\text{clean}}^{\text{GaN}} + E_{\text{pristine}}^{\text{TMD}}) - \Delta N_{\text{N}}\mu_{\text{N}} - \Delta N_{\text{S}}\mu_{\text{S}}], \quad (2.18)$$

where E_{slab} is the total DFT energy of the combined TMD/GaN heterostructure, $E_{\text{clean}}^{\text{GaN}}$ is the energy of the bare GaN reference slab, and $E_{\text{pristine}}^{\text{TMD}}$ is the energy of the pristine TMD monolayer. Here,

ΔN_N and ΔN_S are the changes in N and S atom count relative to the reference slabs, and A is the interface unit-cell area. The nitrogen and sulfur chemical potentials were referenced to the NH_3/H_2 and $\text{H}_2\text{S}/\text{H}_2$ gas-phase equilibria,



such that

$$\mu_N = \mu(\text{NH}_3, T, p_{\text{NH}_3}) - \frac{3}{2}\mu(\text{H}_2, T, p_{\text{H}_2}), \quad (2.21)$$

$$\mu_S = \mu(\text{H}_2\text{S}, T, p_{\text{H}_2\text{S}}) - \mu(\text{H}_2, T, p_{\text{H}_2}). \quad (2.22)$$

System-specific chemical-potential values, partial pressures, and vibrational correction details are given in the corresponding results chapters.

2.6 Dynamical and Kinetic Methods

2.6.1 Phonons

The vibrational modes of a periodic solid arise from the collective motion of atoms about their equilibrium positions. These modes determine the dynamical stability of surface phases and contribute to their finite-temperature free energies. As shown in Fig. 2.5, vibrational properties were computed within the harmonic approximation using the finite-displacement method. In this approach, each inequivalent atom is displaced by $\pm 0.01 \text{ \AA}$ along each Cartesian direction, and the resulting forces on all atoms are computed from DFT. The interatomic force constants obtained

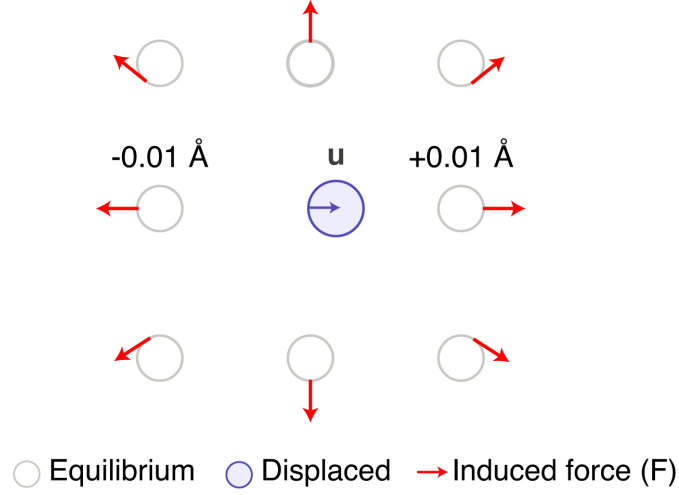


Figure 2.5: Finite-displacement method for phonon calculations. Each inequivalent atom is displaced by $\pm 0.01 \text{ \AA}$ along $\hat{x}$, $\hat{y}$, and $\hat{z}$ in turn, and the induced forces on all atoms are computed from DFT. Forces from positive and negative displacements are combined to construct the harmonic interatomic force constants.

from these displacements are used to construct the dynamical matrix,

$$D_{\alpha\beta}(I, J; \mathbf{q}) = \frac{1}{\sqrt{M_I M_J}} \sum_{\mathbf{R}} \Phi_{I\alpha, J\beta}(\mathbf{R}) e^{i\mathbf{q} \cdot \mathbf{R}}, \quad (2.23)$$

where M_I and M_J are the masses of atoms I and J , $\Phi_{I\alpha, J\beta}(\mathbf{R})$ is the interatomic force constant relating the displacement of atom J along direction β in unit cell $\mathbf{R}$ to the force on atom I along direction α , and the sum runs over lattice vectors $\mathbf{R}$. The eigenvalues of the dynamical matrix give the squared phonon frequencies, $\omega_{\mathbf{q}\nu}^2$, at wavevector $\mathbf{q}$ and branch ν . Imaginary frequencies therefore signal a mechanical instability of the assumed structure. Full Brillouin-zone phonon calculations

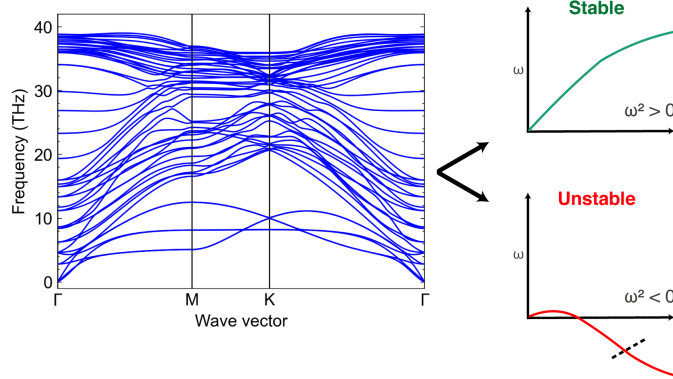


Figure 2.6: Phonon dispersion and stability-screening criteria. All-real frequencies, corresponding to $\omega^2 > 0$, indicate dynamical stability, whereas imaginary frequencies, corresponding to $\omega^2 < 0$, indicate that the structure lies at a saddle point rather than a local minimum.

were performed using Phonopy [67, 68]. These calculations were used both to screen the dynamical stability of each structure and to compute the harmonic vibrational free energy,

$$F_{\text{vib}}(T) = \frac{1}{2} \sum_{\mathbf{q}\nu} \hbar \omega_{\mathbf{q}\nu} + k_B T \sum_{\mathbf{q}\nu} \ln \left[1 - e^{-\hbar \omega_{\mathbf{q}\nu} / k_B T} \right]. \quad (2.24)$$

The first term is the zero-point energy, and the second term is the finite-temperature vibrational entropy contribution. Here, $\omega_{\mathbf{q}\nu}$ is the phonon frequency at wavevector $\mathbf{q}$ and branch ν , $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and T is the temperature.

2.6.2 Ab Initio Molecular Dynamics

Ab initio molecular dynamics (AIMD) simulations were performed within the canonical (NVT) ensemble, in which the number of atoms and simulation-cell volume are fixed while temperature is maintained by a Nosé–Hoover thermostat [69, 70]. Unlike classical molecular dynamics,

which propagates atomic trajectories using a pre-fitted force field, AIMD computes forces at each timestep directly from the DFT total energy $E[\rho]$, so that the equations of motion,

$$m_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E[\rho] - \xi m_I \dot{\mathbf{R}}_I, \quad (2.25)$$

are solved on the instantaneous electronic ground state at every step. Here m_I and $\mathbf{R}_I$ are the mass and position of atom I , and ξ is the thermostat friction coefficient that drives the system toward the target temperature in a time-averaged sense without direct velocity rescaling. A timestep of 1 fs was used throughout, short enough to resolve the fastest vibrational modes in the simulated systems. For example, the Si–O stretching mode near 1478 cm^{-1} in the oxidized Si-terminated diamond surface has a period of approximately 23 fs, corresponding to roughly 20 integration steps per cycle. All AIMD calculations used $2 \times 2 \times 1$ supercells to allow surface reconstruction and adsorbate rearrangement beyond the primitive unit cell. The Nosé–Hoover thermostat mass parameter SMASS was selected from the characteristic vibrational timescale of each system following the procedure described in Appendix A. For the oxidized Si-terminated diamond surface, $\text{SMASS} = 0.1$ was adopted, consistent with a DOS-weighted mean phonon frequency of 24.7 THz. A schematic of the NVT AIMD workflow is shown in Fig. 2.7.

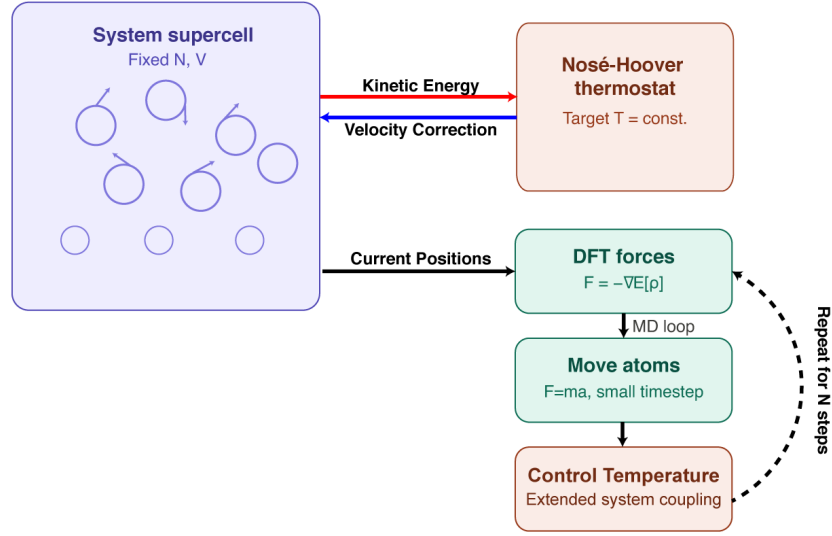


Figure 2.7: Schematic of the NVT AIMD workflow. The supercell has fixed N and V and is coupled to a Nosé–Hoover thermostat, which exchanges kinetic energy with the ionic degrees of freedom to maintain the target temperature T_0 in a time-averaged sense. At each timestep, DFT forces are computed from the instantaneous electronic ground state, and atomic positions and velocities are propagated using the thermostat-coupled equations of motion.

2.6.3 Minimum-Energy Pathways

Identifying stable surface configurations does not by itself establish whether transitions between them are kinetically accessible. The nudged elastic band (NEB) method [71] addresses this problem by representing a transition pathway as a discrete chain of atomic configurations, or images, connecting known initial and final states. Each image is optimized perpendicular to the path, while spring forces between neighboring images maintain spacing along the path and prevent the chain from collapsing toward the endpoints. The total force on image i is decomposed as

$$\mathbf{F}_i = \mathbf{F}_i^\perp + \mathbf{F}_i^{\parallel, \text{spring}}, \quad (2.26)$$

where $\mathbf{F}_i^\perp$ is the true DFT force projected perpendicular to the band,

$$\mathbf{F}_i^\perp = -\nabla E(\mathbf{R}_i) + [\nabla E(\mathbf{R}_i) \cdot \hat{\mathbf{t}}_i] \hat{\mathbf{t}}_i, \quad (2.27)$$

and $\mathbf{F}_i^{\parallel, \text{spring}}$ is the spring force acting parallel to the band,

$$\mathbf{F}_i^{\parallel, \text{spring}} = k(|\mathbf{R}_{i+1} - \mathbf{R}_i| - |\mathbf{R}_i - \mathbf{R}_{i-1}|) \hat{\mathbf{t}}_i. \quad (2.28)$$

Here, k is the spring constant, $\mathbf{R}_i$ is the position vector of image i , and $\hat{\mathbf{t}}_i$ is the unit tangent to the band at image i . This force decomposition allows the DFT forces to drive each image toward the minimum-energy path, while the spring forces preserve the distribution of images along the reaction coordinate. The highest-energy image along the converged path approximates the transition state, and the energy difference between this image and the initial state gives the activation barrier.

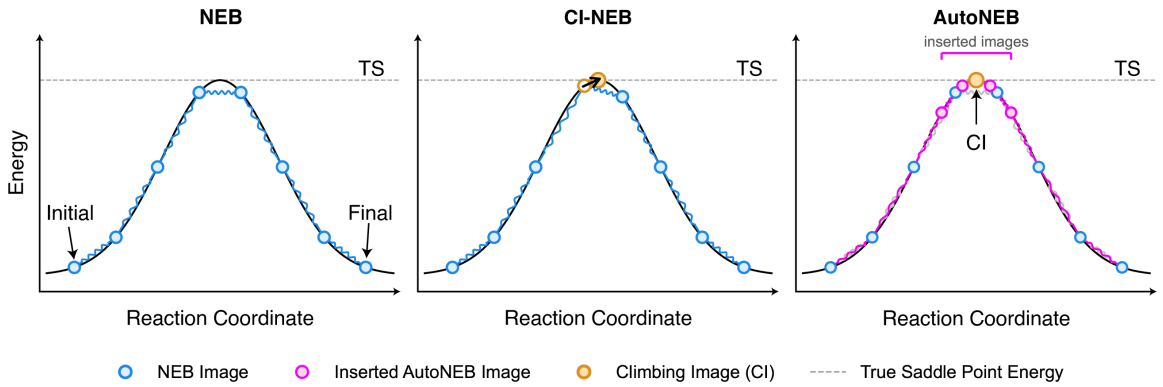


Figure 2.8: Schematic comparison of NEB, CI-NEB, and AutoNEB. In standard NEB, images are distributed evenly along the pathway, and the highest-energy image can underestimate the activation barrier. CI-NEB removes the spring force from the highest-energy image and drives it uphill along the band, allowing it to converge to the saddle point. AutoNEB adaptively inserts images in regions of large geometric or energetic separation before a final CI-NEB refinement, concentrating resolution where it is most needed.

Climbing-Image Nudged Elastic Band

In the climbing-image variant (CI-NEB) [71], the highest-energy image is released from the spring constraint and instead experiences a modified force that drives it uphill along the band. This modification causes the climbing image to converge toward a first-order saddle point on the potential-energy surface. CI-NEB therefore provides a more accurate estimate of the activation barrier than standard NEB without requiring a separate saddle-point search. In VASP, CI-NEB calculations were performed using the VTST toolkit [72].

Automated Nudged Elastic Band

The AutoNEB algorithm [73] extends the NEB method by focusing computational effort on regions of the pathway that require higher resolution. Starting from a small number of images, AutoNEB iteratively inserts new images into the largest geometric or energetic gaps along the band. This procedure first converges a coarse pathway and then refines the region around the apparent energy maximum. Once the maximum number of images is reached, a final CI-NEB calculation is used to locate the saddle point. This strategy can require fewer force evaluations than a uniformly sampled NEB calculation because images are concentrated where additional resolution is most useful [73].

2.7 Electronic Structure Analysis

2.7.1 Band-Structure Calculations

Band structures were calculated to characterize the metallic, semiconducting, or semimetallic character of each surface or interface configuration and to identify surface- or interface-derived

states near the band edges. For each structure, a self-consistent calculation was first performed using a converged Brillouin-zone sampling mesh. Band eigenvalues were then evaluated along high-symmetry paths of the corresponding bulk, surface, or interface Brillouin zone. The specific high-symmetry paths used for each crystallographic orientation and supercell geometry are given in the corresponding results chapters.

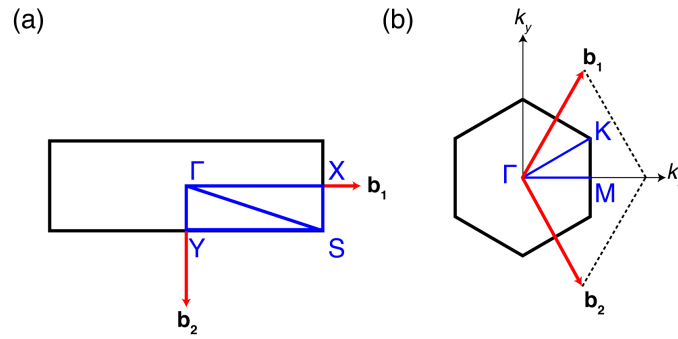


Figure 2.9: High-symmetry paths used for slab band-structure calculations in this dissertation. (a) Rectangular surface Brillouin-zone path Γ -X-S-Y- Γ . (b) Hexagonal surface Brillouin-zone path Γ -M-K- Γ . The paths are shown schematically because the absolute reciprocal-space dimensions depend on the surface or interface supercell.

For the diamond reconstruction calculations, PBE band structures were used to track the electronic phase transformation between ideal, intermediate, and reconstructed surfaces. Because semilocal functionals underestimate the diamond band gap, these PBE band structures were interpreted qualitatively, primarily to distinguish metallic, semiconducting, and semimetallic behavior. For terminated diamond surfaces, HSE06* band structures were used to obtain a more accurate description of band-edge positions and surface-derived states. In other cases, PBE band structures were combined with HSE06* density-of-states calculations, as specified in the corresponding results chapters.

For hybrid-functional band structures, the exact-exchange contribution was evaluated using the converged HSE06* electronic structure. Where necessary, zero-weight high-symmetry k points were added to the converged weighted k -point mesh so that eigenvalues along the band path could be obtained without changing the underlying Brillouin-zone integration. The Fermi level was set to zero in the plotted band structures unless otherwise specified. Band structures were post-processed using VASPKIT [63], SUMO [74], and custom Python scripts, depending on the system and plotting requirements.

2.7.2 Density of States and Local Density of States

Once the Kohn–Sham equations have been solved, the resulting eigenvalues and eigenfunctions can be analyzed through band structures, density of states, and real-space projections. The density of states (DOS) describes the number of available electronic states at a given energy. A large DOS at a given energy indicates that many electronic states are clustered in that energy range, whereas an energy range with zero DOS corresponds to a band gap. In practice, the DOS is computed by summing the Kohn–Sham eigenvalues over the Brillouin zone,

$$g(E) = \frac{1}{\Omega_{\text{BZ}}} \sum_n \int_{\text{BZ}} \delta(E - \epsilon_{n\mathbf{k}}) d\mathbf{k}. \quad (2.29)$$

For numerical evaluation, the discrete eigenvalues are typically broadened to produce a smooth energy-resolved spectrum. The DOS can be further decomposed by atom and orbital character to obtain the projected density of states (PDOS). The PDOS identifies the atomic and orbital contributions to electronic states at specific energies, such as whether band-edge states are primarily derived from carbon p orbitals or from adsorbate-derived states. This decomposition is central to under-

standing how surface chemistry modifies the electronic structure relevant to electron emission. The

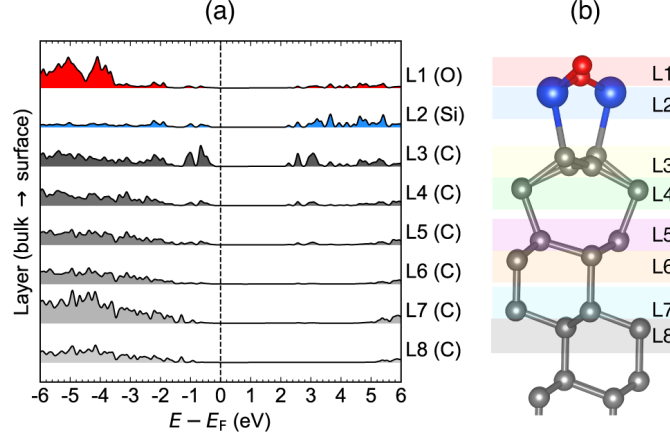


Figure 2.10: HSE06* atom layer-resolved projected density of states for the oxidized Si-terminated diamond (111) surface.

local density of states (LDOS) extends this analysis by resolving the electronic states in real space. Rather than describing only the number of states at a given energy, the LDOS identifies where those states are spatially localized,

$$\rho(\mathbf{r}, E) = \sum_{n\mathbf{k}} |\phi_{n\mathbf{k}}(\mathbf{r})|^2 \delta(E - \varepsilon_{n\mathbf{k}}). \quad (2.30)$$

For slab calculations, the LDOS is most usefully expressed as a planar average by integrating $\rho(\mathbf{r}, E)$ over the plane perpendicular to the surface normal z ,

$$\bar{\rho}(z, E) = \frac{1}{A} \int_A \rho(\mathbf{r}, E) dx dy. \quad (2.31)$$

The planar-averaged LDOS shows how the electronic structure evolves from the bulk-like interior of the slab to the surface and into the vacuum. This representation makes it possible to identify electronic states that are localized at the surface, including dangling-bond states and adsorbate-induced

states, rather than bulk states that extend into the surface region. Alternatively, the full spatial dis-

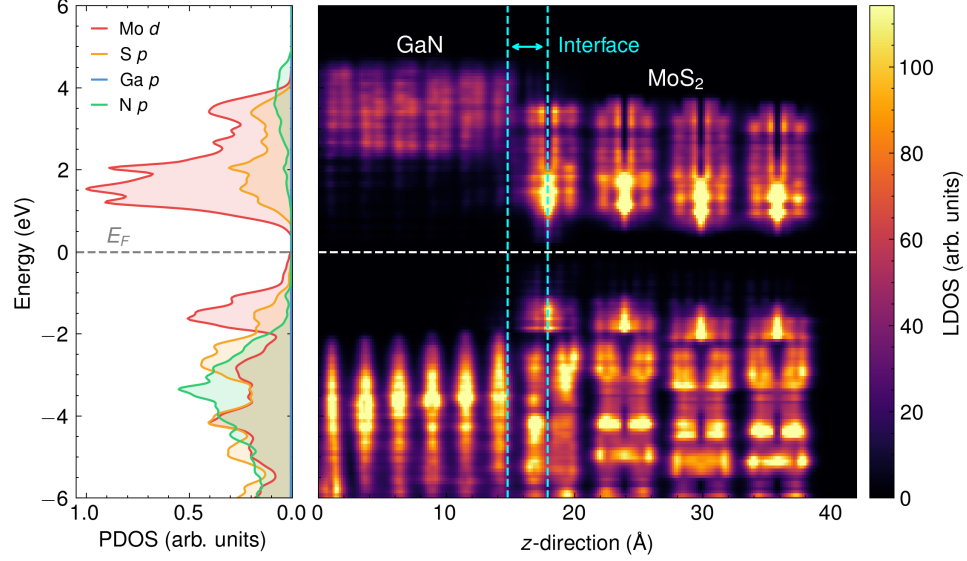


Figure 2.11: Orbital-projected density of states and layer-resolved local density of states for the Ga-3N1S MoS₂/GaN heterostructure, shown here as an example of the LDOS analysis employed in this dissertation. The interface region is delimited by the vertical cyan lines. Full discussion is given in Chapter 7.

tribution $\rho(\mathbf{r}, E)$ can be visualized directly as a real-space charge-density map. This approach is used in Chapter 7 to resolve the electronic reconstruction at the MoS₂/GaN interface. DOS, PDOS, and LDOS quantities computed at the PBE level were obtained using the tetrahedron method with Blöchl corrections [75] for accurate integration near band edges. For hybrid-functional HSE06* calculations of diamond, where use of the tetrahedron method is computationally prohibitive, Gaussian smearing with $\sigma = 0.05$ eV was used instead. All quantities were post-processed using VASPKIT and custom Python scripts.

2.7.3 Charge Density Difference and Bader Analysis

The charge-density difference (CDD) was used to provide a complementary real-space description of charge redistribution induced by adsorption or interface formation. The CDD is defined as

$$\Delta\rho(\mathbf{r}) = \rho_{\text{total}}(\mathbf{r}) - \rho_{\text{sub}}(\mathbf{r}) - \rho_{\text{ads}}(\mathbf{r}), \quad (2.32)$$

where ρ_{total} is the electron density of the combined system, and ρ_{sub} and ρ_{ads} are the electron densities of the isolated substrate and adsorbate, respectively, computed using the same atomic positions as in the combined structure. Positive values of $\Delta\rho$ correspond to electron accumulation, whereas negative values correspond to electron depletion relative to the non-interacting reference. CDD isosurfaces were generated from the VASP charge-density files using custom Python scripts and visualized with VESTA. Quantitative charge transfer was evaluated using Bader charge analysis [76, 77, 78]. In this approach, the electron density is partitioned into atomic basins bounded by zero-flux surfaces, where the component of the density gradient normal to the surface vanishes. The charge associated with each atom is obtained by integrating the electron density within its corresponding Bader volume. Atomic charge transfer was defined as the difference between the integrated Bader electron count and the valence electron count of the corresponding neutral atom. Positive values indicate electron accumulation, whereas negative values indicate electron depletion. Bader analysis was performed using the `bader` code applied to the VASP charge density.

Chapter 3

Structural Phase Transition in Diamond (100) and (111) Surfaces

Portions of this chapter are adapted from: H. Gomez, M. N. Groves, and M. R. Neupane, “Study of the Structural Phase Transition in Diamond (100) and (111) Surfaces,” Carbon Trends 3, 100033 (2021), doi: 10.1016/j.cartre.2021.100033. Published under the Creative Commons Attribution 4.0 International License (CC BY 4.0), <https://creativecommons.org/licenses/by/4.0/>.

3.1 Introduction

The exceptional physical properties of diamond position it as one of the most promising materials for next-generation semiconductor devices. As an ultra-wide-bandgap (UWBG) material with a bandgap of ~ 5.5 eV, diamond offers unmatched radiation hardness and thermal stability in harsh operating environments [79, 80]. Its superior thermal conductivity and carrier mobilities place it ahead of competing wide-bandgap semiconductors such as SiC, GaN, and Ga_2O_3 in demanding high-power and radio-frequency (RF) device applications [11]. Beyond power electronics, diamond

surfaces play a central role in quantum information science, where near-surface nitrogen-vacancy (NV) centers serve as solid-state qubits whose coherence properties are directly sensitive to the surface morphology and adsorbed chemical species [81, 82]. The geometry of diamond microfluidic channels, relevant to NV-based biosensing, similarly depends on the structural character of the exposed surface [83].

Lab-grown diamond is predominantly synthesized by chemical vapor deposition (CVD) [84, 85], and the (100) and (111) surface orientations are the most technologically relevant, exhibiting distinct structural, electronic, and optical properties [86, 87, 88]. Both surfaces reconstruct following cleavage from the bulk substrate, and understanding the nature and pathway of these reconstructions is a prerequisite for any predictive model of surface termination chemistry or device performance.

The C(100) surface is well established to undergo an immediate reconstruction into the (2×1) dimer-row π -bonded geometry, producing a semiconducting surface without a measurable activation barrier [88]. The C(111) surface presents a more complex picture. After cleavage it initially retains a (1×1) bulk-like periodicity, but upon modest heating undergoes a (2×1) reconstruction in which the surface unit vector along the x -direction doubles during structural relaxation. Theoretical and experimental consensus identifies the resulting geometry as the Pandey Chain Model (PCM), in which delocalized π -bonded chains run parallel to the surface [89, 90]. Experimental studies have primarily characterized the reconstructed C(111) surface using C 1s core-level spectra and LEED measurements, which connect the observed surface structure to dimerized carbon atoms at the surface. On the theoretical side, Vanderbilt and Louie compared several candidate reconstructions and identified the PCM as the most stable configuration relative to metastable alternatives such as the Haneman buckling, Chadi, and Seiwatz models [91]. Subsequent studies using

semiempirical, tight-binding, molecular-dynamics, and density-functional approaches have refined the structural picture, but a direct comparison of the C(100) and C(111) reconstruction pathways remained lacking.

A significant fraction of recent computational studies on diamond (111) have adopted the ideal unreconstructed (1×1) surface for simplicity, bypassing the experimentally observed reconstruction entirely. This approximation has been employed in systematic searches for metallic electrode candidates [92], investigations of boron doping effects [93], studies of substitutional dopant behavior under oxygen termination [94], and analyses of hydrogen- and nitrogen-terminated surfaces for quantum sensing [95]. While each of these contributions offers valuable insight, conclusions drawn from the ideal surface geometry are necessarily weakened when the experimentally realized reconstructed geometry differs in ways that alter accessible bonding configurations, surface dipoles, and electronic structure. The subsequent chapters of this dissertation reveal that the geometry of the reconstruction significantly and intricately influences the termination chemistry and electron affinity of group-IV terminated diamond surfaces. This emphasizes the importance of establishing a carefully validated reconstructed reference state.

This chapter addresses that need by presenting a comprehensive first-principles study of the reconstruction mechanisms and accompanying electronic phase transitions in both C(100) and C(111), treated within the same computational framework. Using the grid-based projector augmented wave (GPAW) density functional theory code [55, 56] and the AutoNEB method [96] for transition-state determination, we establish structure-property relationships across the full phase transition from the as-cleaved bulk-like geometry to the thermodynamically stable reconstructed surface. Direct comparison of the two orientations within a unified computational setup allows the distinct reconstruction pathways, activation barriers, and electronic transformations to be placed on

a common footing for the first time. The reconstructed geometries and electronic baselines derived here serve as the validated starting points for all subsequent termination studies presented in this dissertation.

3.2 Computational Methods

All calculations were performed using the GPAW DFT code [55, 56] interfaced with ASE [57], with the PBE exchange-correlation functional [52], as described in Chapter 2. A plane-wave cutoff of 500 eV and a Γ -centered $6 \times 6 \times 1$ Monkhorst-Pack k -point grid [51] were used for all calculations. Ionic positions were relaxed until forces fell below 0.02 eV/Å.

For C(100), a 20-layer slab containing 40 atoms was used, with the four central layers constrained to bulk positions and the top and bottom seven layers free to relax. For C(111), a 14-layer slab containing 28 atoms was used, with the top and bottom five layers unconstrained. Both slab thicknesses are consistent with prior studies demonstrating that at least eight layers are required to correctly model these systems [91, 97, 98, 99]. The (2×1) unit cell was used throughout, as it is the smallest cell that accommodates the experimentally observed reconstruction and is computationally feasible for the NEB pathway calculations. Further confidence in the surface model was established by verifying the total energy difference between the bulk and PCM (2×1) surfaces against prior theoretical results [100]. Band structures for the initial and final states were additionally cross-validated against VASP calculations [101].

Reconstruction pathways were determined using the AutoNEB method, with a single climbing image CI-NEB step applied (Section 2.6.3). The AutoNEB algorithm is an extension of the elementary NEB method that effectively locates transition states by focusing computational

resources on less-resolved regions along the minimum energy pathway [96, 71, 102]. The code initializes a pathway with a user-designated number of images and then iteratively adds and relaxes more images until a second predetermined total number of images is reached. A converged rough pathway results, and once the region around the saddle point is resolved, a climbing image is used to converge the transition state [96]. Between 8 and 10 images were produced per AutoNEB calculation, and once the pathway was resolved enough to generate a reliable transition state guess, one image was used in the CI-NEB calculation to determine the transition state.

Bond rotation in the simulated model was also taken into consideration during the NEB calculations. For the C(111) case in particular, a brute-force approach was used to manually generate all possible versions of the intermediate and PCM surface reconstructions in the (2×1) cell and interpolate images between them and the unreconstructed surface. Representative cases involving major reconstructions were evaluated with the AutoNEB, including pathways where surface carbon atoms transition over other surface carbon atoms and pathways that avoided major rearrangements of atoms on the surface. In all cases where significant reconstructions occurred, the barriers were found to be prohibitively high, and only the cases involving minor reconstructions resulted in the lowest barriers reported in this chapter.

3.3 Results and Discussion

3.3.1 C(100): Structural Properties

Structural optimization of the ideal (2×1) C(100) surface yields the well-known dimer-row π -bonded geometry [88], in which pairs of surface carbon atoms form π -bonds, reducing the nearest-neighbor surface C–C distance from the bulk value to 1.38 Å. This is in good agreement with

prior theoretical values of 1.36–1.38 Å reported by Kern et al. [88], Kress et al. [103], and Zheng and Smith [104], and differs substantially from the value of 1.66 Å reported by Gavrilenko [105]. The computed structural parameters are summarized in Table 3.1 and illustrated in Fig. 3.1.

As reconstruction proceeds, the topmost carbon layer aggregates into pentagonal rings and minor fluctuations in bond lengths of 0.10–0.20 Å occur in the second layer, consistent with prior theoretical studies [106, 103, 104]. The surface formation energy is defined as:

$$E_{\text{surf-form}} = \frac{E_{\text{surf}} - N\varepsilon}{2A} \quad (3.1)$$

where E_{surf} is the total energy of the surface slab, N is the total number of atoms, $\varepsilon = E_{\text{bulk}}/N_{\text{bulk}}$ is the cohesive energy per atom, and A is the surface area. The total energy difference relative to the bulk is -5.89 eV (-0.16 eV/atom), confirming that the (2×1) reconstruction is strongly favored. The reduction in atomic spacing between surface carbons, with $d_{11}(\text{C-C})$ decreasing by 1.14 Å and $d_{12}(\text{C-C})$ by 0.18 Å relative to the ideal surface, drives this stabilization.

Table 3.1: Structural parameters of the reconstructed C(100) surface compared to published theoretical data. d_{ij} denotes the vertical distance between layers i and j , and Δ_{ij} denotes the buckling amplitude. All values in Å. Adapted from Ref. [32] under CC BY 4.0.

Structural Parameter	This Work	Kress ^a	Zheng & Smith ^b	Gavrilenko ^c
$\Delta_{1,y}$	1.38	1.37	1.38	1.66
$d_{12,y}$	0.48	0.48	0.59	0.67
$d_{12,\perp}$	0.68	0.59	0.67	0.68
$d_{23,\perp}$	0.80	0.80	0.80	1.01
$d_{34,\perp}$	0.95	0.95	0.94	0.87
$d_{45,\perp}$	0.97	0.96	0.94	0.92
$\Delta_{3,\perp}$	0.26	0.26	0.25	<0.01
$\Delta_{4,\perp}$	0.16	0.14	0.15	0.06

^a Kress et al. [103] ^b Zheng & Smith [104] ^c Gavrilenko [105]

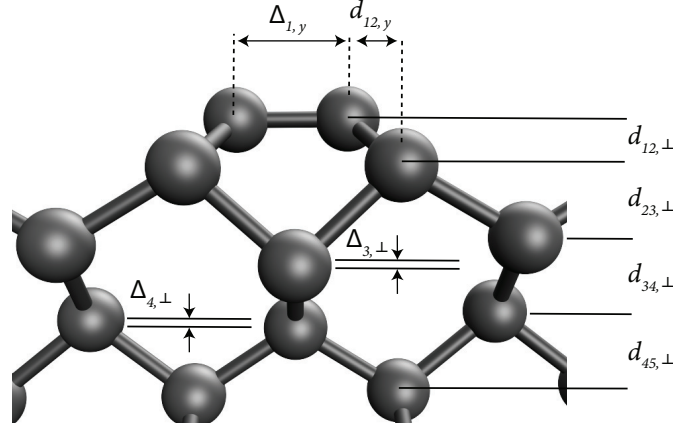


Figure 3.1: Side-view structural analysis of the reconstructed (2×1) C(100) surface. d_{ij} denotes the vertical distance between substrate layers and Δ_{ij} the buckling amplitude. The majority of the slab retains bulk-like geometry below the uppermost reconstructed layers. Adapted from Ref. [32] under CC BY 4.0.

3.3.2 C(111): Structural Properties

The reconstructed C(111) surface adopts the Pandey chain model geometry, in which de-localized π -bonded chains run parallel to the surface [90]. The reconstruction creates buckling in the first two surface layers, with the remaining layers retaining bulk-like positions. The computed structural parameters are compared to LEED measurements [89] and prior AIMPRO calculations [106] in Table 3.2 and illustrated in Fig. 3.2.

Most structural parameters agree with the LEED data to within 4%, with the exception of $d_{\Delta 2}$, which is approximately 15% smaller than the experimental value. This discrepancy is attributed to the constraint imposed on the central layers, which affects the nearest-neighbor geometry of the subsurface atoms. Comparison with the prior DFT-LDA calculations of Kern et al. [88] yields deviations below 3%. The total energy difference between the PCM and bulk-like surfaces is -1.76 eV (-0.08 eV/atom), and the surface formation energy $E_{\text{surf-form}} = -0.14$ eV confirms that the PCM reconstruction is strongly favored, consistent with experiment [89, 90].

During the NEB calculations described below, a previously unreported metastable intermediate was identified along the C(111) reconstruction pathway. This intermediate is structurally distinct from both the bulk-like and PCM surfaces. It has an interlayer spacing of $d_{12} = 1.49 \text{ \AA}$, defined as the vertical separation between the first and second atomic layers, and $d_{\Delta 1} = 0.43 \text{ \AA}$, which describes the vertical distortion associated with the first-layer reconstruction. Relative to the PCM geometry, these values correspond to deviations of approximately $+5\%$ and -46% , respectively. In the intermediate, each surface carbon in the first layer is bonded to one carbon in-plane and two atoms below the surface plane, whereas in the PCM each surface carbon is bonded to two carbons in-plane and one below the plane. The total energy difference of the intermediate relative to the ideal surface is -0.30 eV , corresponding to approximately -0.01 eV/atom . This places the intermediate between the ideal surface and the PCM on the energy landscape and suggests that it may be experimentally accessible under non-equilibrium preparation conditions. Because of its superficial similarity to previously proposed C(111) reconstructions, the Chadi model was reconstructed explicitly for comparison. The resulting bond lengths and atomic orientations differ substantially from those of the intermediate identified here, confirming that the intermediate is not a Chadi-type variant.

3.3.3 Electronic Properties

Kohn-Sham band structures were calculated for the ideal and reconstructed (2×1) C(100) and C(111) surfaces and for the C(111) intermediate. It should be noted that PBE band gaps are underestimated by approximately 40% relative to experiment [107]; the band structures presented here are used to characterize the metallic or semiconducting nature of each phase and to track the

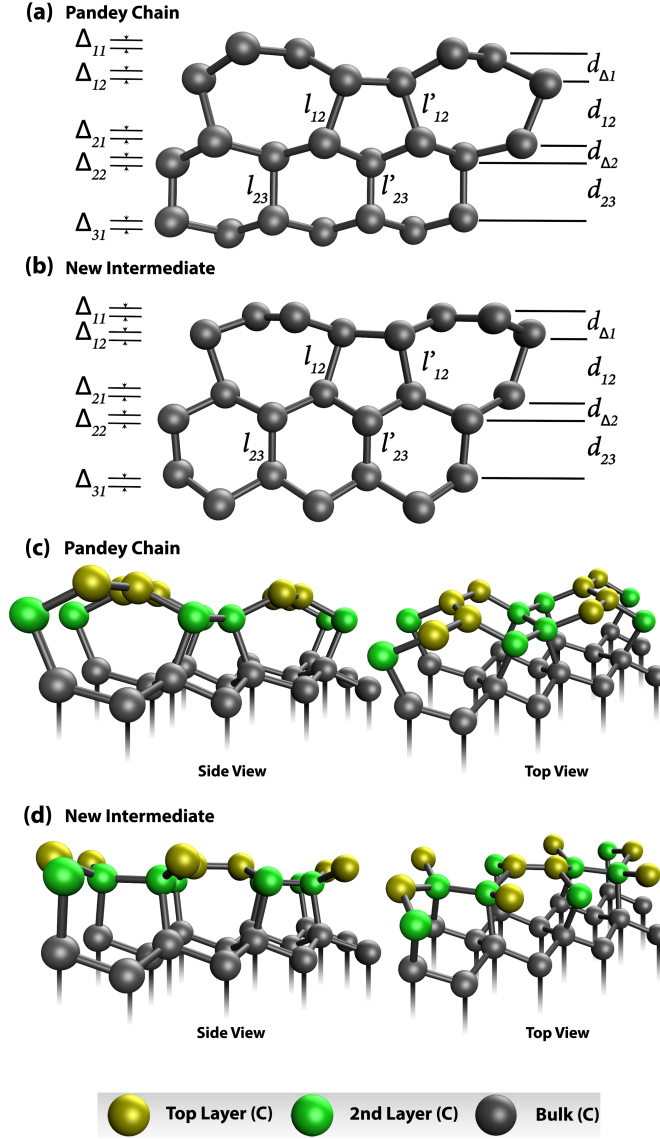


Figure 3.2: Side-view structural analysis of the (2×1) C(111) surface. (a) Reconstructed PCM geometry. (b) Newly identified metastable intermediate. (c) Depth analysis of the PCM, with surface chain atoms highlighted. (d) Depth analysis of the intermediate. Yellow and green spheres denote first- and second-layer surface atoms respectively. Tabulated structural parameters are given in Table 3.2. Adapted from Ref. [32] under CC BY 4.0.

Table 3.2: Structural parameters of the reconstructed C(111) PCM surface and the newly identified intermediate, compared to LEED measurements [89] and AIMPRO calculations [106]. d_{ij} denotes the vertical distance between layers, Δ_{ij} the buckling amplitude, l_{ij} the bond length between layers, and l'_{ij} the asymmetric bond length. All values in Å. Adapted from Ref. [32] under CC BY 4.0.

Structural Parameter	PCM (This Work)	Intermediate (This Work)	Walter (LEED) ^a	Sque (AIMPRO) ^b
d_{12}	1.55	1.49	1.55	1.52
d_{23}	1.49	1.74	1.55	1.42
$d_{\Delta 1}$	0.69	0.43	0.68	0.69
$d_{\Delta 2}$	0.44	0.49	0.51	0.40
Δ_{11}	0.01	0.01	0.01	0.01
Δ_{12}	0.01	0.02	0.01	0.01
Δ_{21}	0.03	<0.01	0.02	0.03
Δ_{22}	0.16	0.06	0.18	0.18
Δ_{31}	~ 0	~ 0	0.08	0.07
l_{12}	1.63	1.74	1.62	1.63
l'_{12}	1.65	1.59	1.64	1.60
l_{23}	1.65	1.69	1.61	1.60
l'_{23}	1.49	1.53	1.49	1.49

^a Walter et al. [89] ^b Sque et al. [106]

electronic phase transformation accompanying reconstruction, rather than to report quantitative gap values. Hybrid functional band structures for the termination studies in subsequent chapters are presented using HSE06* as described in Chapter 2.

For C(100), the ideal surface is metallic, with surface bands crossing the Fermi level and electron sharing between the top and bottom surface states (Fig. 3.3a), consistent with prior calculations [103]. Reconstruction drives a significant band splitting throughout the Brillouin zone, opening an indirect band gap of 1.46 eV (Fig. 3.3b). This metallic-to-semiconducting transition results from the breaking of out-of-plane degeneracy by the surface dimer formation.

For C(111), the ideal surface is similarly metallic, with bonding and antibonding states straddling the Fermi level (Fig. 3.3c). The newly identified intermediate retains metallic character, with surface bands at the onset of splitting (Fig. 3.3d). The reconstructed PCM surface exhibits a partial gap along the X- Γ -Y-S path in the Brillouin zone, with a maximum gap of 1.77 eV at

the Γ -point (Fig. 3.3e). At the symmetry point S, the Fermi level intersects residual surface bands with small splitting, which Sque et al. [106] attribute to dimerization of the upper chain in the PCM. The C(111) reconstruction therefore produces a metallic-to-semi-metallic transformation, in contrast to the full metallic-to-semiconducting transition observed for C(100). This difference in the reconstructed electronic character of the two surfaces has direct consequences for their behavior upon group-IV termination, as discussed in Chapters 5 and 6.

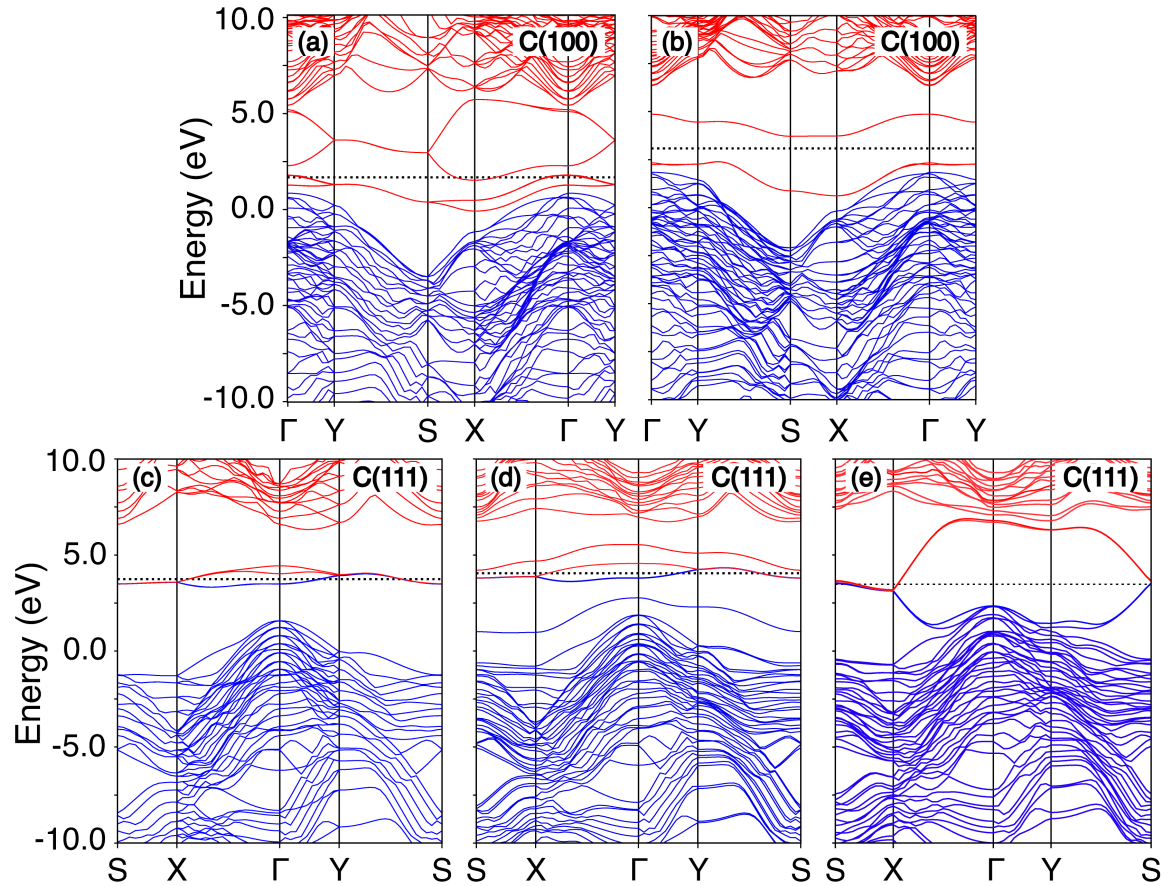


Figure 3.3: Kohn-Sham electronic band structures for (a) ideal C(100), (b) reconstructed C(100), (c) ideal C(111), (d) C(111) intermediate, and (e) reconstructed C(111) (PCM). The Fermi level is set to zero in all panels. Band gaps are underestimated relative to experiment owing to the use of the PBE functional; quantitative electronic properties of terminated surfaces are reported using HSE06* in subsequent chapters. Adapted from Ref. [32] under CC BY 4.0.

3.3.4 Reconstruction Pathways

Having established the structural and electronic properties of the ideal, intermediate, and reconstructed surfaces, the minimum energy pathways for the (2×1) reconstructions were determined using the AutoNEB method.

For C(100), no intermediates or transition states were found along the reconstruction pathway (Fig. 3.4a). The phase transition proceeds smoothly and without barrier from the ideal surface to the reconstructed dimer geometry, consistent with the absence of an activation barrier reported in the literature [88] and with the strongly exoergic energy difference of -5.89 eV.

For C(111), all distinct arrangements of the intermediate and PCM structures in the (2×1) unit cell were enumerated and the most facile transition pathways identified from a total of 48 possible combinations. Two distinct pathways were identified, shown as the primary (solid) and secondary (dashed) routes in Fig. 3.4b.

In the primary pathway, the ideal surface reconstructs directly to the PCM without passing through the intermediate, with no activation barrier and a monotonically decreasing energy profile terminating at $\Delta E = -1.76$ eV. This result contrasts with the 0.32 eV barrier reported by Petrini and Larsson [108], a discrepancy that is attributed to differences in the transition state search methodology: the linear synchronous transit approach used in that study does not guarantee identification of the minimum energy pathway, whereas the AutoNEB method employed here adaptively refines the pathway to minimize the energy along the reaction coordinate.

In the secondary pathway, the ideal surface first passes through the metastable intermediate via a barrier of 0.11 eV. From the intermediate, the system may either overcome a subsequent barrier of 0.44 eV to reach the PCM, or reverse with a barrier of only 0.11 eV and proceed via

the primary pathway. The much lower reverse barrier makes it considerably more probable that the system escapes the intermediate and reconstructs via the barrierless primary route rather than proceeding to the PCM directly from the intermediate.

The existence of the secondary pathway and the metastable intermediate suggests that the C(111) reconstruction landscape is more complex than previously appreciated. The intermediate, with its total energy of -0.30 eV relative to the ideal surface, lies in a shallow local minimum that may be accessible under non-equilibrium preparation conditions. This finding is relevant to the interpretation of XPS and LEED measurements on Si-terminated C(111) surfaces, where multiple surface reconstructions have been observed following Si deposition [40], as discussed in Chapter 6.

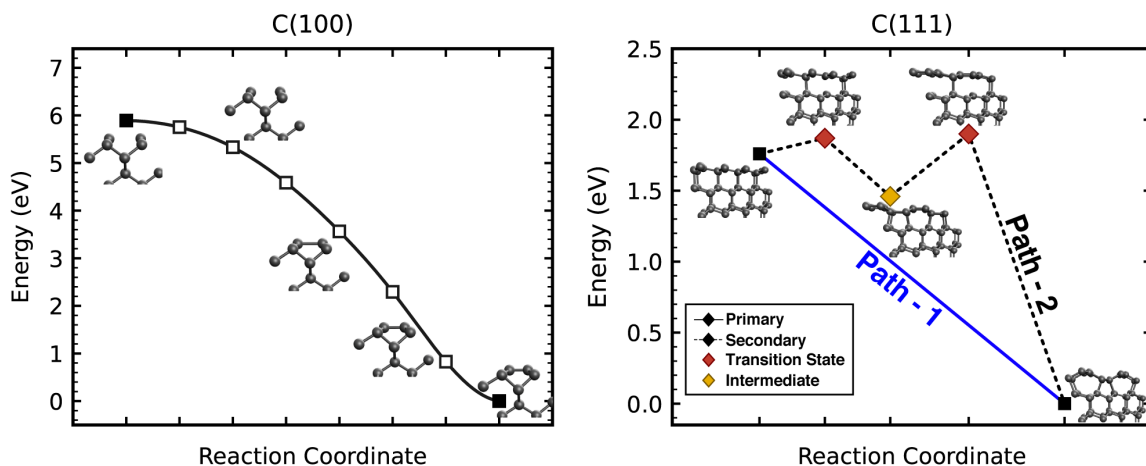


Figure 3.4: Minimum energy pathways for the reconstruction of (a) C(100) and (b) C(111) from the ideal bulk-like surface to the fully reconstructed phase, calculated using the AutoNEB method [96]. For C(111), the primary pathway (solid line) proceeds directly from the ideal surface to the PCM without a barrier, while the secondary pathway (dashed line) passes through the metastable intermediate with barriers of 0.11 eV and 0.44 eV as indicated. Transition states and the intermediate are marked by red and gold symbols respectively. Adapted from Ref. [32] under CC BY 4.0.

3.4 Conclusion

The reconstruction mechanisms and electronic phase transformations of the C(100) and C(111) diamond surfaces have been established using DFT and the AutoNEB method. For C(100), the (2×1) dimer reconstruction proceeds without an activation barrier, with a total energy gain of -5.89 eV (-0.16 eV/atom) relative to the ideal surface, and is accompanied by a metallic-to-semiconducting electronic phase transition with a PBE band gap of 1.46 eV. For C(111), the PCM reconstruction is similarly barrierless along the minimum energy pathway, with a total energy gain of -1.76 eV (-0.08 eV/atom), and produces a metallic-to-semi-metallic transition with a partial gap of 1.77 eV at the Γ -point. A previously unreported metastable intermediate was identified along a secondary C(111) reconstruction pathway, lying -0.30 eV below the ideal surface and structurally distinct from the PCM.

These results serve two purposes within the broader context of this dissertation. First, they provide validated structural baselines for the bare C(100) and C(111) surfaces against which the effect of H, O, Si, and Ge terminations can be assessed in Chapters 4–6. Second, they demonstrate that the C(111) reconstruction landscape is more complex than C(100), with a secondary pathway and a metastable intermediate that may be accessed under non-equilibrium conditions. This complexity is directly relevant to the formation of group-IV terminated C(111) phases, where multiple LEED patterns observed following Si deposition [40] suggest that the reconstruction geometry of the substrate plays an active role in determining which termination phases are kinetically accessible.

Chapter 4

Structural and Electronic Properties of H- and O-Functionalized Diamond (100) with Variable Coverage

*Portions of this chapter are adapted from: J. Cruz, H. Gomez, M. N. Groves, and M. R. Neupane, “Structural and electronic properties of H- and O-functionalized diamond (100) with variable coverage,” Carbon Trends **21**, 100580 (2025), doi: 10.1016/j.cartre.2025.100580. Published under the Creative Commons Attribution 4.0 International License (CC BY 4.0). The surface structural configurations and adsorption energetics reported therein were obtained in collaboration with J. Cruz, with whom the author shares co-first authorship. The HSE06* band-structure calculations and electron-affinity determinations presented here were performed by the author.*

4.1 Introduction

Chapter 3 established that the bare diamond (100) surface reconstructs barrierlessly into the (2×1) dimer-row geometry. This chapter builds on that reconstructed reference by examining

how H- and O-containing adsorbates modify the structural and electronic properties of diamond (100) surfaces as a function of coverage.

Diamond is an ultra-wide-bandgap semiconductor characterized by high thermal conductivity, exceptional carrier mobility, and a substantial breakdown field. These attributes enable operation under intense electric fields, thereby ensuring efficient heat dissipation and rapid switching [109, 110]. Motivated by these advantages, diamond is actively researched for applications in field-effect transistors (FETs), power amplifiers, energy converters, sensing devices, and quantum technologies [111, 112, 113].

Despite its potential, diamond faces significant challenges in electronic applications. A central limitation is the absence of a reliable doping mechanism that can transition diamond from an insulator to a semiconductor. Substitutional doping is largely ineffective because the strong sp^3 bonding network yields high dopant activation energies that require substantial external energy to activate sufficient mobile carriers [24]. This limitation hinders conventional transistor operation, prompting exploration of surface transfer doping as an alternative route to induce p-type surface conductivity in intrinsic diamond.

Here, first-principles calculations are employed to investigate how mixed H- and O-containing adsorbates influence the structural and electronic properties of diamond (100) surfaces. The calculations reveal that variations in surface termination and coverage govern structural stability, band gap, and electron affinity. These results clarify how adsorbate composition and coverage modulate both stability and electronic behavior, establishing a framework for the interpretation of mixed H/O surface effects. In the context of this dissertation, the results also provide the H/O reference baseline against which the group-IV terminated surfaces studied in subsequent chapters are assessed.

In surface transfer doping, electrons are transferred from the diamond valence band to adjacent acceptor states with sufficiently high electron affinities. This charge transfer produces a two-dimensional hole gas (2DHG) near the surface, and the efficiency of this process depends on the alignment between the surface valence-band maximum (VBM) and the acceptor level [114, 115, 116]. A variety of molecular, oxide, and ionic species have been shown to induce p-type conductivity on diamond by enhancing hole density through surface charge transfer [21, 117, 118, 119, 120, 121]. In particular, MoO₃ on oxidized Si-terminated diamond induced p-type transfer doping, where passivation of surface trap states improved the VBM–acceptor level alignment and promoted 2DHG formation [122].

Among various surface terminations, H-terminated diamond is of particular importance because its low ionization potential and negative electron affinity (NEA) create favorable conditions for surface transfer doping via molecular adsorption at room temperature [19]. Owing to this sensitivity, O-containing adsorbates can significantly modify its carrier density and mobility. For example, introducing less than 2.2% oxygen coverage increases the carrier density by three orders of magnitude compared with a pristine H-terminated surface [123]. When exposed to air and subsequently annealed, H-terminated (100) surfaces also develop surface conductivity, with SA-LEED measurements revealing approximately 23% coverage by randomly distributed oxygen species [124]. These findings illustrate the pronounced influence of oxygen adsorption on the electronic properties of H-terminated diamond, even at modest coverage levels.

Building on these observations, subsequent studies have examined the structural stability of specific oxygen terminations. In particular, first-principles calculations showed that ether terminations (O_{ether}) become more stable than ketone (O_{ketone}), hydroxyl (OH), or H-terminated configurations once the coverage exceeds approximately 67% [30]. A complementary experimental study

further revealed that surface chemistry and stability are strongly dependent on the hydrogenation conditions, with both the surface orientation and hydrogen arrangement influencing the achievable coverage densities [125].

Partial oxygen coverage is also associated with variations in device-relevant properties. O-terminated surfaces have been shown to enhance the sensitivity of gas sensors at room temperature, an effect linked to the presence of O-containing species such as the terminations examined in this work [126]. These results indicate that surfaces often regarded as H-terminated may exhibit coexisting H- and O-containing species with variable coverage [31], thereby influencing both electronic stability and the performance of near-surface nitrogen-vacancy (NV) centers [127].

Exposing diamond to thermally activated O₂ produces a range of oxygenated species on its surface [128], with the configuration and adsorbate composition strongly dependent on treatment conditions such as triacid cleaning or oxygen annealing [129]. Hydrogen and hydroxyl species originating from dissociated water are also commonly present on clean diamond at room temperature, where they produce an NEA that enhances the electron-emission efficiency of field emitters and the sensitivity of ion-selective FETs [130]. Surface orientation further influences oxygenation behavior. Oxygenated (110) and (111) surfaces exhibit distinct species distributions [131], and theoretical analysis shows that both orientation and preparation methods govern surface reactivity [132].

Despite significant progress, the influence of specific adsorbate types and coverages on the electronic properties of diamond is not fully understood. Although previous studies have identified the binding configurations of H- and O-based species, these structural motifs are not always directly correlated with their electronic properties [30, 31]. Recent theoretical studies have shown that the bonding character of oxygen with surface carbon atoms and the relative stability of competing oxygen configurations strongly affect surface conductivity. Oxygen-carbon bonding was found

to modify the conductivity of H-terminated diamond [133], and several nearly isoenergetic half-monolayer oxygen arrangements suggest that multiple mixed-termination motifs may coexist and remain semiconducting without gap states [134].

4.2 Computational Methods

Density functional theory (DFT) calculations were performed using GPAW [135, 136, 55, 137] in combination with the Atomic Simulation Environment (ASE) [57] to generate and relax candidate surface structures using pre-established workflows. Adsorption energies were obtained at the Perdew–Burke–Ernzerhof (PBE) level [52] using a $3 \times 6 \times 1$ Monkhorst–Pack $\mathbf{k}$ -point mesh [51], a 500 eV plane-wave cutoff, and a force-convergence threshold of 0.02 eV/Å. Electronic-property calculations were carried out with the Vienna *Ab initio* Simulation Package (VASP) [138] to take advantage of its robust implementation of hybrid functionals. To facilitate this, all favorable structures determined with GPAW were subsequently re-optimized using VASP with identical PBE settings, and all electronic properties were then evaluated using VASP. The equilibrium lattice constants derived from the GPAW and VASP codes showed a discrepancy of less than 0.2%, confirming consistency between the two codes [139].

The diamond (100) surface was modeled using a (2×1) reconstruction expanded into a (4×2) supercell (Fig. 4.1). Structural relaxations were performed using asymmetric slabs, where the top five carbon layers were allowed to relax, while the remaining layers were fixed to bulk positions. A 20 Å vacuum region was included along the surface normal to suppress spurious interactions. Dipole corrections in GPAW were applied following the method of Neugebauer and Scheffler [140]. Representative adsorption structures are shown in Fig. 4.1(c) and (d).

For band-structure calculations, 10-layer inversion-symmetric slabs were used in VASP, with the central two layers constrained to bulk positions to preserve mirror symmetry. Convergence tests confirmed that the band gap was converged within 0.05 eV at this thickness, consistent with previous theoretical investigations [132, 134, 141]. Because extending hybrid-functional calculations to slabs thicker than ten layers is computationally prohibitive, band-gap evaluations were restricted to this thickness.

To achieve accurate vacuum alignment, electron-affinity calculations employed 16-layer asymmetric slabs, ensuring convergence of the ionization energy with respect to the bulk reference.

Surface terminations were introduced in the (4×2) supercell, providing eight adsorption sites on the top layer. Terminations with H, OH, O_{ketone}, and O_{ether} were assessed at 25, 50, 75, and 100% coverage. For mixed terminations, the lowest-energy configuration of each oxygen species was determined at a given coverage, with the remaining sites terminated by hydrogen. Because bonding in these systems is primarily covalent, van der Waals corrections were not included. The optimized models reproduced known structural features such as the surface dimer bond length (approximately 1.38 Å) and vertical subsurface spacing ($d_{C_S-C_B} \approx 1.51$ Å), consistent with previous reports [32, 142, 143, 144].

After verifying that the relaxed slabs reproduced the known structural features, the stability of each termination was evaluated through adsorption energetics. The average adsorption energy per adsorbate was calculated as

$$E_{\text{ads}} = \frac{1}{\sum_i n_i} \left(E_T - E_S - \sum_i n_i E_i \right), \quad (4.1)$$

where E_T is the total energy of the terminated surface, E_S is the energy of the bare surface, n_i is the number of adsorbates of type i , and E_i is the reference energy of an isolated atom or molecule in its spin-polarized ground state.

To obtain reliable band-gap and electron-affinity values, the hybrid functional HSE06* with a mixing parameter of 0.30 was employed, consistent with previous work [145]. Hybrid functionals provide accurate band gaps, in contrast to generalized-gradient-approximation functionals such as PBE, which underestimate the band gap and misalign electron affinities [146]. Band structures were calculated using a Γ -centered $2 \times 3 \times 1$ $\mathbf{k}$ -point mesh, chosen to ensure convergence while remaining computationally feasible for large supercells.

The electron affinities (χ) of the diamond surfaces were determined using the slab-alignment method,

$$\chi = E_{\text{vac}} - E_{\text{CBM}}^{\text{surf}} = E_{\text{vac}} - (V_{\text{surf}} + \Delta E_{\text{VBM}}^{\text{bulk}} + E_g^{\text{bulk}}), \quad (4.2)$$

where E_{vac} is the energy of the vacuum level from the slab potential, V_{surf} is the average electrostatic potential in the slab interior, $\Delta E_{\text{VBM}}^{\text{bulk}}$ is the energy offset between the bulk valence-band maximum and the average bulk potential (9.65 eV), and E_g^{bulk} is the HSE06* bulk diamond band gap (5.53 eV). This approach follows established conventions [64, 147], ensuring a uniform absolute reference across all surface terminations.

4.3 Results and Discussion

4.3.1 Coverage-Dependent Structural Properties

The structural properties of reactive diamond surfaces, particularly those oriented along the (100) plane, are strongly influenced by surface adsorption. To systematically evaluate the effects

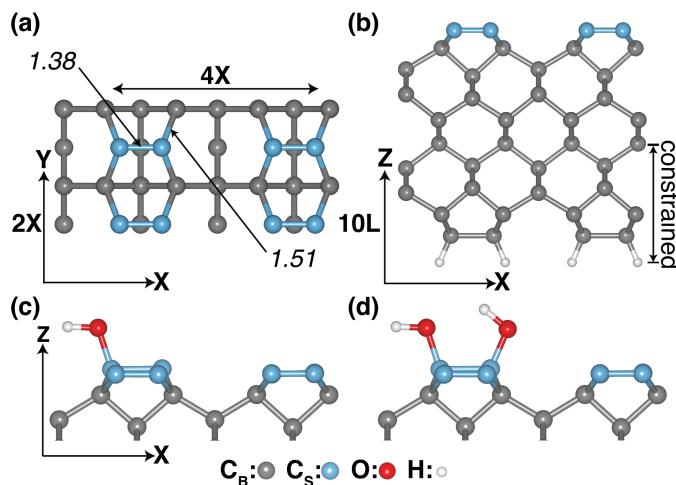


Figure 4.1: Top- and side-view structures of a (4×2) non-terminated diamond (100) surface with bottom-layer hydrogen passivation. Panels (c) and (d) show the top three layers with 12.5% and 25% hydroxyl coverages, respectively. Gray spheres represent bulk carbon atoms (C_B), blue spheres represent surface carbon atoms (C_S), red spheres represent oxygen atoms (O), and white spheres represent hydrogen atoms (H). Reproduced from [29] under CC BY 4.0.

of surface adsorbates and their coverage, the concentrations of H- and O-containing species on the reconstructed diamond (100) surface were varied from 25% to 100%. Although similar coverage-dependent effects have been documented for diamond surfaces [106, 30, 141], the calculations were conducted to validate and benchmark the structural trends specific to the surface terminations examined in this study. Representative structures and the trends relevant to the present discussion are summarized below.

Adsorbate Configurations and Steric Effects

Across all coverages, the H, OH, and O_{ketone} terminations favored pairwise adsorption, whereas O_{ether} tended to adopt more dispersed or row-like configurations. This preference arises from steric constraints that drive O-containing species to maximize separation across available sites. The contrast was most pronounced at intermediate coverages, where limited surface sites enhanced

steric effects and dictated spatial organization. To quantify these effects, the O–O distances were examined using the van der Waals radius of oxygen (1.52 Å) as the steric threshold [148]. Dispersing oxygen pairs across the surface reduced steric hindrance and was energetically favorable, most notably for O_{ketone} . Calculations in larger (8×4) cells reinforced the preference for complete columns over rows and the energetic benefit of dispersed oxygen pairs, with energy gains of up to 2 eV.

Guided by the principle that adsorbate atoms tend to disperse maximally, the (4×2) slab is sufficient to capture the surface adsorbate arrangement at 25% and 50% coverages. However, an (8×4) or larger diamond surface may be required to identify the lowest-energy configuration of the adsorbates at 75% coverage. These findings reveal the steric and geometric factors governing oxygen functionalization of diamond surfaces.

Steric hindrance plays a crucial role in determining the spatial arrangement of adsorbates, especially for O-containing species such as O_{ether} and O_{ketone} . Across various coverages, dispersed configurations are generally preferred over aggregation, as they maximize interatomic separation and minimize repulsive interactions. However, for hydroxyl terminations, an additional degree of freedom arises from the orientation of the hydrogen atoms within each hydroxyl group. This effect is discussed in the following section.

Hydroxyl Orientation and Local Interactions

As discussed above, steric interactions strongly influence the arrangement of adsorbates. Two primary factors govern the preferred orientation of hydroxyl groups: (1) steric effects, which favor arrangements with greater spatial freedom, and (2) the potential for hydrogen bonding between

neighboring hydroxyl groups. Several candidate configurations were evaluated, and the most stable configurations were identified by comparing their total adsorption energies.

Fig. 4.2 illustrates two representative configurations at 100% OH coverage. In the OH-X configuration, hydrogen atoms are aligned along the x direction, parallel to $[110]$, whereas in the OH-Y configuration, they align along the y direction, parallel to $[\bar{1}10]$. OH-Y is marginally more stable, with an adsorption energy of -4.52 eV compared with -4.47 eV for OH-X. This subtle yet consistent difference highlights the role of orientation in modulating steric repulsion and hydrogen bonding.

Both configurations exhibit mean O–O separations of approximately 2.5 Å, with OH-Y showing slightly larger spacing than OH-X. The C–O–H bond angles closely match the gas-phase methanol value [149], confirming that the surface OH geometries are realistic.

Although the geometric differences are subtle, the hydrogen orientation noticeably affects local H–O interactions. In OH-X, steric hindrance displaces some hydrogen atoms outward, resulting in an average H–O separation of 1.73 Å. In contrast, OH-Y maintains a shorter separation of 1.63 Å, indicative of stronger interactions and slightly enhanced stability. Thus, alignment along the y direction reduces steric hindrance and stabilizes the surface, making OH-Y consistently the most favorable orientation.

The structural preference for OH-Y thus carries direct consequences for the electronic structure, as examined in the following section.

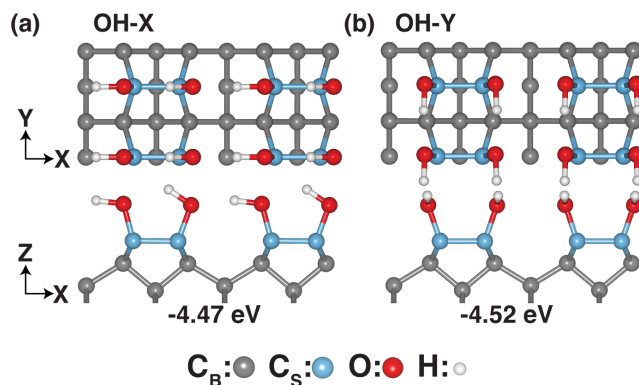


Figure 4.2: Top-view (xy -plane) and side-view (xz -plane) profiles of 100% OH-covered (4×2) diamond (100) surfaces and the respective adsorption energies, with (a) hydrogen atoms pointing along the y direction (OH-Y) and (b) along the x direction (OH-X). Gray spheres represent bulk carbon atoms (C_B), blue spheres represent surface carbon atoms (C_S), red spheres represent oxygen atoms (O), and white spheres represent hydrogen atoms (H). Reproduced from [29] under CC BY 4.0.

Adsorption Energetics Across Surface Coverages

To understand how surface coverage influences stability, the adsorption energies of the H, OH, O_{ketone} , and O_{ether} terminations were computed across varying coverages. The adsorption energies reveal distinct differences among the four adsorbates, with O_{ether} exhibiting the largest variation with coverage, while H shows the least. Overall, O-containing terminations are more stable than H terminations, with hydroxyl species being more favorable than hydrogen, consistent with previous studies [106, 150, 151, 152]. This trend reflects the less favorable reference state of OH, as the formation of H_2O releases more energy than that of H_2 .

The coverage dependence of these adsorption energies is summarized in Fig. 4.3. In general, for H, OH, and O_{ketone} , E_{ads} becomes less favorable as the coverage increases. Conversely, O_{ether} exhibits a non-monotonic pattern, gaining stability at 50% coverage, losing stability at 75% coverage, and regaining stability at full coverage. This crossover between O_{ketone} and O_{ether} aligns with a previous study [30], highlighting the combined influence of chemistry and coverage fraction

on surface energetics. The approximately 67% crossover threshold was reported in that prior study; the present calculations sample 25%, 50%, 75%, and 100% coverage.

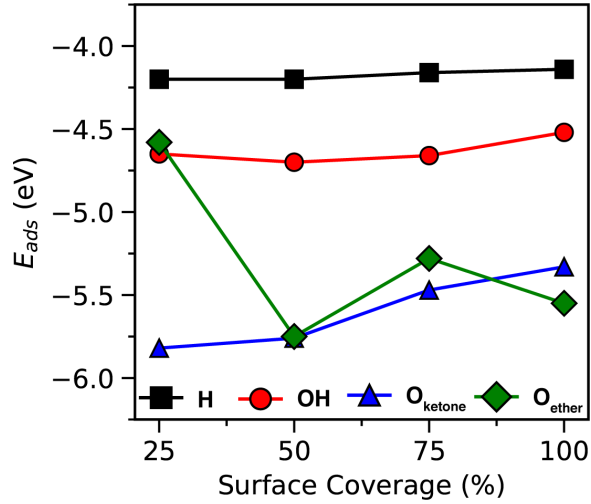


Figure 4.3: Adsorption energies (E_{ads}) as a function of surface coverage for H, OH, O_{ketone}, and O_{ether} terminations on diamond (100) surfaces. Reproduced from [29] under CC BY 4.0.

4.3.2 Coverage-Dependent Band-Gap Evolution

To examine the relationship between the surface structure and electronic properties, the electronic band structures were computed for all considered coverage levels using the HSE06* functional. Hybrid functionals correct the systematic band-gap underestimation inherent to semi-local methods and produce results consistent with experiment. The HSE06* calculations presented here form the basis of this analysis. The following sections detail the observed trends in band dispersion, gap evolution, and surface-state formation across different adsorbates and coverages.

Band-Gap Dependence on Hydroxyl Orientation

As established above, OH-Y is structurally more favorable than OH-X. Here, the electronic consequences of this orientation are examined, as shown in the band structures in Fig. 4.4. In both cases, the surfaces remain insulating with direct gaps at Γ , but the magnitude of the gap differs significantly. Specifically, OH-Y exhibits a band gap of 5.46 eV, compared with 5.08 eV for OH-X, corresponding to an approximately 7% smaller gap in the latter, which arises from a downward shift of the conduction-band minimum. This comparison demonstrates how the orientation of hydroxyl groups can directly influence band-edge alignment. The OH-Y gap is effectively bulk-like, differing from the HSE06* bulk value of 5.53 eV by only 0.07 eV, well within the expected ± 0.26 eV accuracy of the method [153, 154].

Beyond the difference in gap magnitude, OH-Y also maintains a higher conduction onset and reduced valence-band dispersion along Γ -Y compared with OH-X. These variations originate from differences in surface dipole alignment and orbital overlap, which directly affect carrier-injection barriers and effective masses. The band-gap and dispersion trends are consistent with the higher electron affinity of OH-Y relative to OH-X (Table 4.1), indicating that hydroxyl orientation governs both band alignment and vacuum-level positioning while directly linking the structural preference to the resulting electronic properties.

Band-Gap Trends Across Surface Coverages

Surface coverage density plays a critical role in modulating the electronic properties of diamond. In the systems considered here, the surface is modeled as a mixture of terminated and bare sites. Thus, increasing the coverage corresponds to the progressive replacement of bare surface

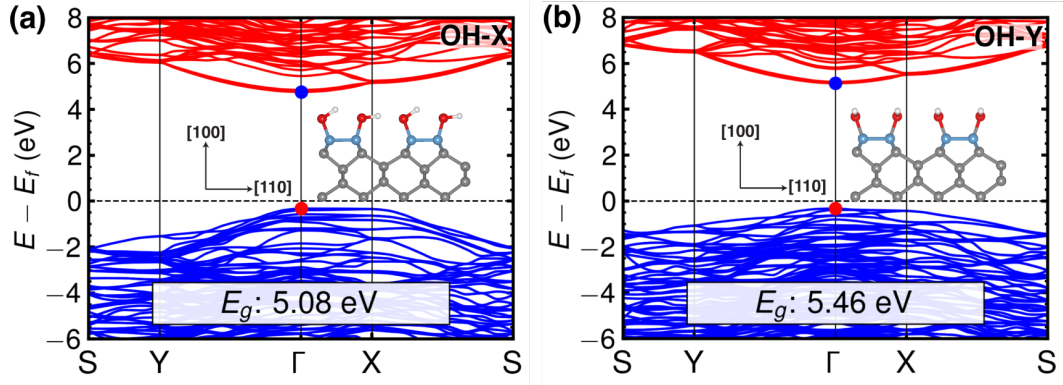


Figure 4.4: Calculated band structures using the HSE06* functional for the fully OH-terminated (100) surface with (a) OH-X, where H is oriented along $[110]$ in-plane and parallel to the dimer/chain axis, and (b) OH-Y, where H is oriented along $[\bar{1}10]$ in-plane and perpendicular to x . Adapted from [29] under CC BY 4.0.

atoms with H- or O-containing groups. This patchwise coverage alters the orbital interactions and local dipole alignment, thereby shifting the band gap. The dependence of the band gap on surface coverage is summarized in Fig. 4.5. As the fraction of terminated sites increases, the character of the electronic states evolves in distinct ways, depending on the adsorbate. Bare regions are gradually replaced by hydrogen or hydroxyl groups, and the band edges shift predictably, reflecting the progressive passivation of dangling bonds. In contrast, oxygenated species introduce more complex interactions that depend not only on coverage but also on bonding configuration.

The H- and OH-terminated surfaces exhibit smooth, monotonic increases in the band gap with coverage. This reflects the stabilizing effect of dense passivation, which eliminates the mid-gap states and gradually restores bulk-like dispersion. In contrast, the O-containing terminations exhibit strongly non-monotonic behavior. For O_{ketone} [Fig. 4.6(a)], the gap widens to 3.81 eV at 50% coverage but then decreases to 2.47 eV at full coverage. For O_{ether} [Fig. 4.6(b)], the fluctuations are even stronger, with the band gap alternating between narrow and wide regimes. These oscillations arise from variations at the conduction-band edge, which is highly sensitive to oxygen

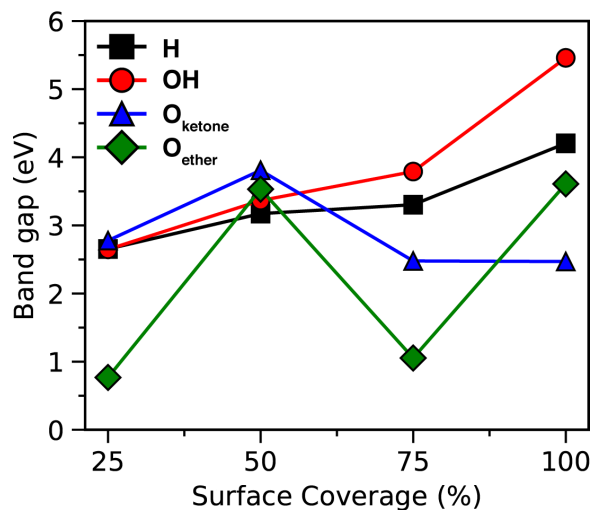


Figure 4.5: HSE06* band-gap values as a function of surface coverage for H, OH, O_{ketone}, and O_{ether} terminations. Reproduced from [29] under CC BY 4.0.

coordination and orbital overlap. Flat conduction-band features are particularly pronounced at 25% and 75% O_{ether} coverage, where incomplete bonding produces localized states that suppress the gap. These flat conduction-band features indicate highly localized states that may possess lower carrier mobilities and may influence conductive pathways.

For all adsorbates, the valence-band states are relatively insensitive to surface coverage, whereas variations in the conduction-band edge dominate the observed gap trends. The O_{ketone} surfaces [Fig. 4.6(a)] exhibit moderate sensitivity, with flat features that persist even at 100% coverage and maintain a narrower gap than in the H- or OH-terminated cases. O_{ether} surfaces [Fig. 4.6(b)] are far more sensitive, with strongly localized conduction bands at 25% and 75% coverage, which resemble isolated surface bonds that collapse the gap. Once the surface is fully saturated at 100% coverage, these states reorganize into a bulk-like dispersion and the gap recovers.

Although these results are consistent with localized conduction states forming at intermediate fractions, the oscillatory behavior at 25% and 75% coverage may partly reflect the finite-size

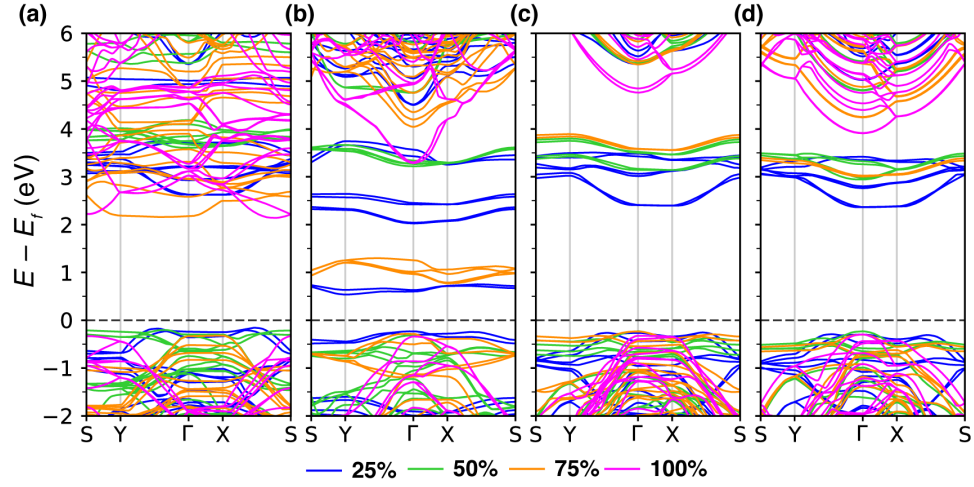


Figure 4.6: Band structures of (a) O_{ketone} , (b) O_{ether} , (c) OH, and (d) H-terminated diamond (100) surfaces calculated using the HSE06* functional. Colored lines represent different surface coverages: 25% (orange), 50% (green), 75% (blue), and 100% (magenta). Reproduced from [29] under CC BY 4.0.

sampling of the (4×2) supercell. Larger supercells are required to fully separate the intrinsic bonding effects from the possible cell-size artifacts.

The electronic properties of diamond (100) thus depend strongly on both adsorbate chemistry and surface density. O-containing terminations, and O_{ether} in particular, produce the strongest coverage-dependent modulation of band edges, with localized states emerging at intermediate densities. This sensitivity offers a pathway to deliberately tune electronic properties through controlled partial coverage, but it may also affect device reliability, as O_{ether} fractions near 25% and 75% can suppress the band gap, introduce possible leakage pathways, and reduce the expected breakdown strength.

4.3.3 Mixed Adsorbates

Surface Stability

To model the mixed adsorbates, the most favorable structures of OH, O_{ketone}, and O_{ether} with surface coverages of 25%, 50%, and 75%, respectively, were selected. Hydrogen atoms were then placed at the remaining non-terminated surface sites of carbon atoms to create mixed H/O-terminated configurations. The corresponding E_{ads} values are shown in Fig. 4.7. Compared with the 100% H-terminated surface, the mixed-terminated configurations are more energetically favorable. The system becomes significantly more stable when hydrogen atoms are replaced with O-containing species, indicating that complete surface oxygenation is thermodynamically preferred. Nevertheless, experimental studies show that diamond surfaces are rarely fully oxygenated after treatment and instead exhibit a mixture of H- and O-containing phases [125, 31]. This persistence of mixed terminations suggests that factors beyond thermodynamic driving forces, such as kinetic limitations, constrain the extent of the surface conversion.

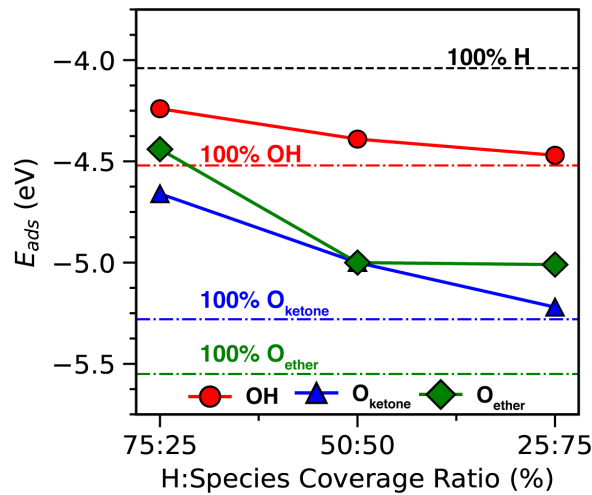


Figure 4.7: Adsorption energies for mixed H:OH, H:O_{ketone}, and H:O_{ether} terminations on diamond (100) surfaces across varying coverages. Reproduced from [29] under CC BY 4.0.

To further explore this process, E_{ads} of the mixed O_{ketone} adsorbates with varying H:O coverage ratios was calculated, as shown in Fig. 4.8. Small energy differences of 0.05–0.12 eV are observed between neighboring mixed O_{ketone} configurations, indicating locally less favorable intermediate states. For example, in the 50H:50 O_{ketone} case, a 2.4% energy difference is observed when the coverage is altered to 25H:62.5 O_{ketone} . These values represent relative thermodynamic metastability rather than explicit activation barriers, but they suggest that the progression toward full oxygenation is energetically uneven. Prior studies show that substituting surface hydrogen with oxygen typically involves breaking C–H bonds, followed by hydrogen migration across the surface [155, 156, 157]. Although kinetic barriers were not computed directly, these earlier results support the interpretation that both thermodynamic penalties and kinetic constraints hinder complete surface conversion under experimental conditions.

Thus, in systems with mixed H/O terminations, fully oxygenated surfaces may not form because of the complex kinetics involved in replacing hydrogen with O-containing groups, particularly under experimental conditions where H termination is required for diamond growth [158].

Passivating the bare adsorption sites with hydrogen leads to a systematic reduction in the spacing between neighboring O-containing adsorbates. In the 25% O_{ketone} configuration, the O–O spacing decreases from 3.12 Å to 3.00 Å in the 75H:25 O_{ketone} surface. A similar effect is observed at higher coverage, where the 50% O_{ketone} surface has an O–O spacing of 3.00 Å, which further decreases to 2.91 Å in the 50H:50 O_{ketone} configuration.

The mixed-termination surfaces also exhibit a modest anisotropy of approximately 0.03 Å between interatomic distances along the rows and columns. At high adsorbate coverage, steric repulsion between neighboring species becomes significant, leading to reduced thermodynamic stability.

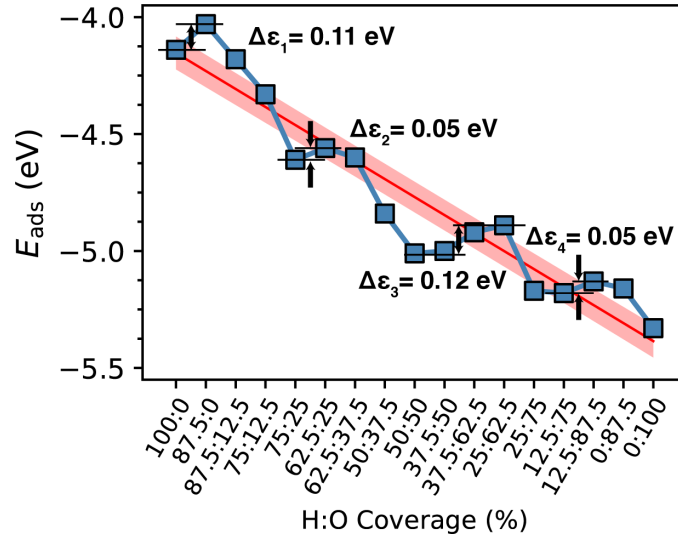


Figure 4.8: Adsorption energies of mixed $\text{H}:\text{O}_{\text{ketone}}$ adsorbed surfaces with different surface coverage ratios of hydrogen and oxygen species. The solid line represents the linear regression fit for all mixed $\text{H}:\text{O}_{\text{ketone}}$ cases. The highlighted region provides a visual guide, illustrating the deviations from the linear trend associated with progressive oxygen incorporation. Reproduced from [29] under CC BY 4.0.

This trend is consistent with the homogeneous cases, where shorter adsorbate–adsorbate separations correlate with increased steric hindrance and structural destabilization.

Prior studies have shown that O-containing species enhance the conductivity of diamond surfaces [123, 133], which typically exhibit heterogeneous composition and partial coverage [31]. The present results show that surface coverage and mixed adsorbates substantially influence the thermodynamic stability of these systems, motivating an examination of how mixed terminations affect the electronic structure.

Electronic Properties

Fig. 4.9(a)–(c) presents the computed band structures of diamond (100) surfaces with mixed hydrogen and hydroxyl coverage. Incorporating hydroxyl groups into an H-terminated sur-

face preserves the ultra-wide band gap while introducing subtle variations that depend on the H:OH ratio. Reducing the hydroxyl fraction narrows the gap but maintains values above that of the fully H-terminated surface. The 50H:50OH surface lies between these two limits and shows that a balanced mixture sustains a gap comparable to that of the OH-rich regime. At a high hydroxyl content, the 25H:75OH surface reaches 5.39 eV, slightly lower than that of the fully OH-terminated case (5.46 eV). Two of the three mixed terminations are direct-gap semiconductors at Γ , while the 25H:75OH configuration exhibits an indirect band gap. H/OH mixing thus consistently maintains band gaps above 4.5 eV, implying that surfaces exposed to humid environments, which are expected to acquire mixed H/OH coverage, would retain insulating properties favorable for high-field electronic operation.

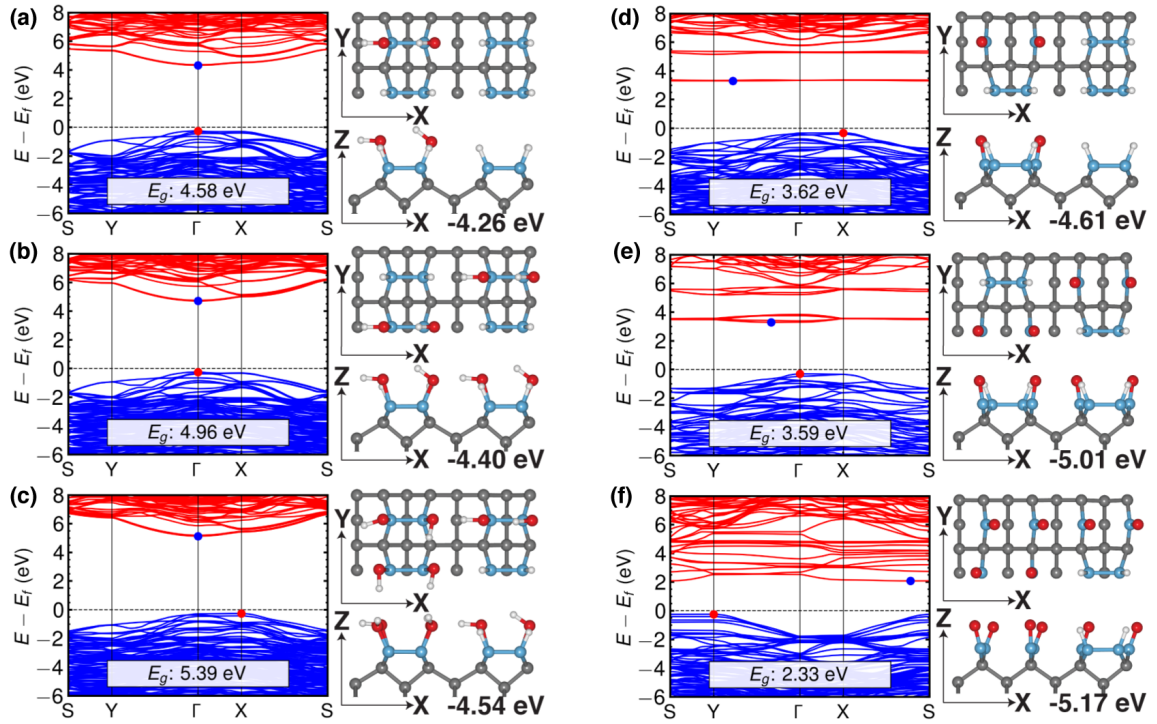


Figure 4.9: HSE06* band structures, top-view (xy -plane) profiles, and side-view (xz -plane) profiles for diamond (100) surfaces with mixed terminations: (a) 75H:25OH, (b) 50H:50OH, (c) 25H:75OH, (d) 75H:25 O_{ketone} , (e) 50H:50 O_{ketone} , and (f) 25H:75 O_{ketone} . Reproduced from [29] under CC BY 4.0.

Although the hydroxyl groups preserve the wide-gap character of the surface, carbonyl bonding is far more disruptive. Fig. 4.9(d)–(f) shows that mixed H: O_{ketone} surfaces exhibit a distinctly different trend. Increasing the hydrogen fraction and reducing the oxygen fraction shifts the conduction-band minimum upward, widening the gap to 3.62 eV for 75H:25 O_{ketone} and 3.59 eV for 50H:50 O_{ketone} . At high O_{ketone} coverage, as exemplified by the 25H:75 O_{ketone} surface, flat conduction bands emerge near the Fermi level. These features reduce the band gap to 2.33 eV and indicate the formation of localized surface states.

The bands near the conduction-band edge remain flat across all coverages, reinforcing the presence of localized surface states. All three surfaces are indirect-gap semiconductors. These

results suggest that O_{ketone} -poor surfaces may possess very large effective masses and limited carrier mobility, whereas greater O_{ketone} coverage can mitigate these effects. Device contacts formed on O_{ketone} -rich surfaces may therefore experience higher contact resistance, even if some hydrogen coverage is preserved. The strong tendency of O_{ketone} groups to localize conduction states also has implications beyond contacts, as charge instabilities near the surface are known to degrade the performance of NV centers used in quantum sensors and quantum communication devices [127].

While O_{ketone} groups tend to localize conduction states and reduce the band gap, O_{ether} bonding produces the opposite effect. The H: O_{ether} surfaces shown in Fig. 4.10 reveal that increasing O_{ether} coverage drives a transition from semiconducting to metallic behavior. At low O_{ether} content, the 75H:25 O_{ether} configuration remains semiconducting, with an indirect gap of 4.94 eV. At intermediate coverage, the 50H:50 O_{ether} surface exhibits the second-largest gap among all the mixed cases (5.08 eV), with a direct transition at S . At high O_{ether} content, as in the 25H:75 O_{ether} surface, partially filled bands cross the Fermi level, forming metallic conduction channels that reduce the insulating reliability of the surface.

From a device perspective, the O_{ether} system presents two limiting cases: (1) high O_{ether} coverage with low H content promotes metallic conduction, which may be advantageous for contact formation, whereas (2) low O_{ether} coverage with high H content yields a wide band gap, suggesting improved insulation and reduced leakage in high-field applications.

As summarized in Fig. 4.11, the mixed H:OH surfaces remain close to the pure OH reference and consistently preserve ultra-wide band gaps. This stability indicates that OH-rich surfaces are favorable for maintaining dielectric reliability and suppressing leakage, even under partial-coverage conditions. In contrast, the H: O_{ketone} mixtures narrow the gap when the oxygen coverage

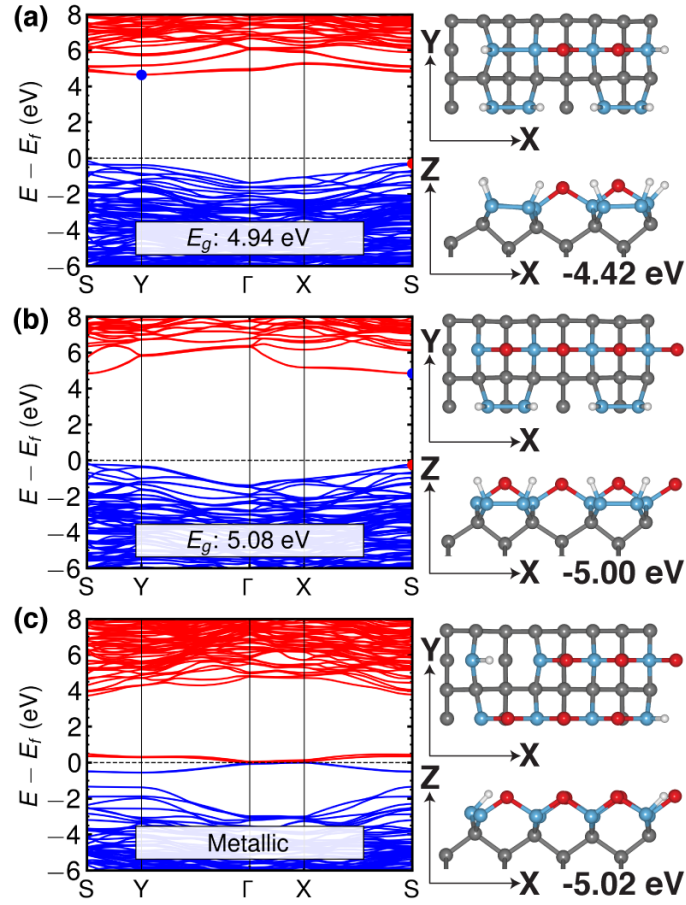


Figure 4.10: Band structures, top-view xy -plane profiles, and side-view xz -plane profiles for mixed-terminated diamond (100) surfaces featuring (a) 75H:25 O_{ether} , (b) 50H:50 O_{ether} , and (c) 25H:75 O_{ether} . Reproduced from [29] under CC BY 4.0.

exceeds 50%. Such narrowing reflects the emergence of localized conduction-band states that increase effective mass, reduce mobility, and lead to higher contact resistance in device applications. The $H:O_{\text{ether}}$ mixtures exhibit the most pronounced tunability. At 25H:75 O_{ether} , the surfaces become metallic with conduction pathways opening at the Fermi level, whereas at 50H:50 O_{ether} , they retain wide band gaps of approximately 5 eV, consistent with insulating behavior.

Thus, OH-rich surfaces preserve wide band gaps that favor stable operation, O_{ketone} narrows the gap and increases carrier-injection barriers, and O_{ether} enables tunability between metallic

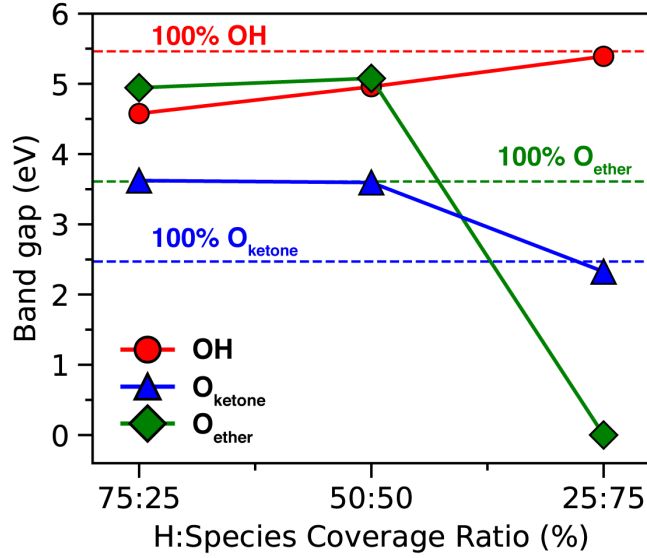


Figure 4.11: Band-gap values for H:OH, H:O_{ketone}, and H:O_{ether} mixed-terminated diamond (100) surfaces. Red, green, and blue dash-dotted lines mark the HSE06* gaps for fully covered OH, O_{ketone}, and O_{ether}, respectively. Reproduced from [29] under CC BY 4.0.

and insulating regimes depending on the coverage ratio. Earlier studies have demonstrated the role of oxygen groups in tailoring diamond surface chemistry and conductivity for applications such as quantum devices and gas sensors [126, 31]. Expanding on these insights, the analysis reveals that heterogeneous O-containing adsorbate configurations dictate thermodynamic stability and carrier dynamics.

Electron Affinity

Electron affinity (χ) plays a central role in determining carrier injection across metal–diamond interfaces by governing the alignment of the band edges in relation to the vacuum level. When χ is negative, the conduction-band minimum lies above the vacuum level, which lowers the hole-injection barrier (ϕ_{Bp}) and favors ohmic contact formation. Conversely, positive χ values increase ϕ_{Bp} and contact resistance, thereby diminishing the carrier-injection efficiency [159]. To

assess how surface chemistry modifies this behavior, χ was computed for both pure and mixed terminations using the slab-alignment method. The results are summarized in Table 4.1.

Table 4.1: Electron affinity (χ) of mixed-terminated diamond (100) surfaces. The Pure (%) column provides the fraction of the surface terminated by the indicated species alone, whereas the Mixed (H:O %) column specifies the relative H:O coverage ratio. All values are referenced to the average bulk potential in diamond. Data from [29].

Species	Pure (%)	χ (eV)	Mixed (H:O %)	χ (eV)
Bare	–	0.45	–	–
H	25	–0.29	–	–
	50	–0.98	–	–
	75	–1.56	–	–
	100	–2.09	–	–
Ether	25	1.35	75:25	–0.82
	50	1.70	50:50	0.45
	75	2.04	25:75	–
	100	2.48	–	–
Ketone	25	1.78	75:25	–0.11
	50	2.77	50:50	1.60
	75	3.24	25:75	2.63
	100	3.62	–	–
OH	25	0.14	75:25	–1.61
	50	–0.30	50:50	–1.26
	75	–0.39	25:75	–0.88
OH-X	100	–0.83	–	–
OH-Y	100	–0.72	–	–

In the simplest case, the reconstructed (2×1) bare surface exhibits a χ of approximately 0.5 eV, in agreement with both experiment and theory [64, 160]. As expected, H-terminated surfaces remain firmly in the NEA regime across all coverage levels, consistent with theoretical predictions that yield strongly negative values. These reference cases serve as the foundation for investigating the influence of hydroxyl and oxidized terminations on electron affinity.

Using these reference cases as a basis, O-containing terminations generally shift χ toward more positive values as the oxygen fraction increases. Pure O-terminated surfaces exhibit positive

electron affinities (PEAs) at all coverages for both motifs, with the fully oxidized O_{ether} and O_{ketone} surfaces reaching approximately 2.5 eV and approximately 3.6 eV, respectively. In contrast, mixed H/O terminations transition from NEA to PEA as the oxygen fraction exceeds 50%. At 75H:25O, O_{ether} remains within the NEA regime ($\chi = -0.82$ eV), while O_{ketone} lies near the boundary at $\chi = -0.11$ eV. These results suggest that increasing oxidation drives χ positive and promotes injection-limited behavior.

In comparison, hydroxyl terminations generally yield modest NEAs clustered near the NEA–PEA boundary for pure coverages below 75%, where orientation effects introduce systematic shifts. At full coverage, OH-X consistently produces more negative values than OH-Y, reflecting the influence of hydrogen orientation. Mixed H:OH configurations drive χ further negative, producing values comparable to those of the H-terminated surface. These trends arise from the orientation of surface dipoles, where outward-pointing dipoles generate a positive surface charge that produces an NEA [161].

Because oxygen increases χ while hydrogen partially compensates, hydroxyl groups represent an intermediate case, consistent with the bulk- and surface-corrected results reported by Sque et al. for fully hydroxylated dimers [106]. By contrast, earlier PBE studies predicted substantially more negative values below -2 eV for hydroxylated surfaces [130, 147]. These discrepancies most likely stem from limited structural detail in earlier studies, since the exchange-correlation functional and the bulk-alignment procedure were similar across works. This limitation affects the treatment of local dipoles and likely explains why earlier calculations predicted more negative values. Overall, the variation emphasizes that the χ of OH-terminated diamond is highly sensitive to orientation and coverage, which determine whether local dipoles reinforce or cancel one another.

Because the ideal hole-barrier height is directly tied to the ionization energy, $\phi_{Bp}^{\text{ideal}} = I - \Phi_m$, changes in surface termination can shift ϕ_{Bp}^{ideal} by several electronvolts and thereby influence whether a metal–diamond junction approaches ohmic or injection-limited behavior. Explicit interfacial effects, including Fermi-level pinning and metal-induced gap states, are beyond the scope of this study.

Implications for Contacts and Surface Conductivity

The trends in electron affinity carry direct implications for carrier injection and surface transport. H- and OH-terminated surfaces retain negative or near-zero affinities, which lower ϕ_{Bp} against high work-function metals and facilitate efficient hole injection. By contrast, oxygenated terminations increase χ and elevate ϕ_{Bp} , with O_{ether} producing intermediate barriers and O_{ketone} driving the largest. In this context, mixed H/O terminations play an important role by moderating the increase in ϕ_{Bp} , since OH-rich surfaces preserve NEA conditions across all coverages and thereby suppress injection-limited transport.

Beyond contact resistance, termination chemistry also dictates transfer doping and the stability of the 2DHG. Specifically, OH-rich surfaces with robust NEAs promote adsorption of acceptor molecules and stabilize the 2DHG, thereby sustaining high surface conductivity. This effect underpins the operation of FETs and chemical sensors based on hydrogenated diamond, where reliable 2DHG formation ensures stable p-type conduction even under ambient conditions. Conversely, O_{ketone} -dominated surfaces with large positive affinities inhibit charge transfer and disrupt the 2DHG, reducing conductivity and suppressing p-type behavior. Such characteristics limit their utility in electronic and sensing applications.

More broadly, these surface-dependent trends help explain long-standing experimental observations. Notably, strong Fermi-level pinning [159, 162] can be rationalized by the coexistence of OH, O_{ether}, and O_{ketone} groups [28], which generate a broad spectrum of surface states that are consistent with experimental pinning behavior.

In the context of this dissertation, these H/O-terminated surfaces provide the reference baseline for the group-IV terminated diamond surfaces examined in the following chapters. The motivation for pursuing Si- and Ge-terminated diamond is that H termination is thermally fragile, while oxygen termination suppresses favorable transfer-doping conditions. The following chapter examines whether Si- and Ge-terminated (100) surfaces provide a more thermally stable route to favorable electron affinities after atmospheric oxidation [36].

4.4 Conclusion

In this work, the effects of H- and O-containing adsorbates on the structural and electronic properties of diamond (100) surfaces were examined. First, oxygenated terminations emerged as more stable than hydrogenated ones, with O_{ketone} favored at partial coverage and O_{ether} stabilized at full coverage. Second, although complete oxygenation is thermodynamically preferred, its realization is tempered by kinetic barriers, underscoring the complexity of practical surface preparation. Third, surface passivation universally removed mid-gap states, yet the evolution of the band gap and electron affinity depended sensitively on chemistry and coverage: H and OH preserved wide gaps and negative affinities, whereas O_{ether} and O_{ketone} introduced non-monotonic trends and strong positive affinities at high coverage. Finally, mixed terminations extended this tunability, bridging semiconducting and metallic regimes.

Termination chemistry and coverage jointly determine the stability and electronic structure of diamond (100) surfaces. These findings provide guiding principles for tailoring diamond (100) surfaces to lower contact resistance in high-power electronics, enhance sensitivity in chemical sensors, and stabilize charge states in quantum devices based on near-surface NV centers. They also establish the quantitative H/O reference baseline used to assess the group-IV terminated diamond surfaces examined in the following chapters.

Chapter 5

Investigation of Oxidized Si- and Ge-Terminated Diamond (100) Surfaces

*The work presented in this chapter is reprinted in part from H. Gomez, J. Cruz, C. Milne, T. Debnath, A. G. Birdwell, E. J. Garratt, B. B. Pate, S. Rudin, D. A. Ruzmetov, J. D. Weil, P. B. Shah, T. G. Ivanov, R. K. Lake, M. N. Groves, and M. R. Neupane, “First-principles investigation of oxidized Si- and Ge-terminated diamond (100) surfaces,” J. Chem. Phys. **161**, 064702 (2024), with the permission of AIP Publishing.*

5.1 Introduction

Chapter 4 established the H/O termination limit for diamond (100), showing that electron affinity depends not only on the chemical identity of the adsorbate but also on the bonding motif and fractional coverage. Hydrogen-rich and mixed H/OH surfaces can retain NEA, whereas oxygen-rich ether and ketone surfaces shift the surface into PEA. Because this crossover depends strongly on how oxygen bonds to the reconstructed surface, the surface structure under realistic conditions must be known before transfer-doping behavior can be predicted. Hydrogen termination provides favor-

able electronic alignment for 2DHG formation, but the hydrogen-terminated surface is thermally and chemically limited under processing conditions. Oxygen termination is more robust, but it reverses the surface dipole and suppresses spontaneous transfer doping. A useful alternative must therefore preserve favorable band alignment while avoiding the instability of hydrogen termination.

Several classes of diamond (100) terminations have been explored with this goal in mind, including group I–IV elements, first-row transition metals, and metal oxides [163, 164, 165]. Silicon and germanium are especially relevant because they form ordered terminations on diamond (100) and produce thermally stable (3×1) reconstructed surfaces [34, 36]. This reconstruction differs from the H- and O-terminated reference surfaces of Chapter 4 in both periodicity and coverage. Si and Ge coverages typically fall near 57–69%, below the 70–100% range accessible for H- and O-terminated surfaces, a reduction attributed mainly to steric interactions between neighboring group-IV adatoms [34]. Even at this lower coverage, both terminations retain an NEA, though with a smaller magnitude than H-terminated diamond.

The ordered group-IV surfaces therefore address only part of the H/O tradeoff, improving robustness while leaving the exposed Si and Ge bonds chemically active. Oxygen is the most relevant atmospheric reactant in this context, and intentional oxidation of the (3×1) surfaces using O_2 and H_2O has been demonstrated experimentally [36]. After oxidation, the surfaces can retain the (3×1) reconstruction, but the added oxygen modifies both stability and electronic structure through changes in the local bonding environment. Oxidized Si-terminated diamond has been studied for surface transfer doping [166] and as an interfacial layer in Al_2O_3/SiO_2 capacitors and field-effect transistors [167]. Fei et al. and Ota et al. used Si- and Si–O-terminated diamond to fabricate MOS-FETs in which *p*-type conductivity and 2DHG formation were attributed to charge transfer across the C–Si–O interface [168, 169].

Despite this experimental progress, the atomic structure of the oxidized interface remains unresolved. Surface oxidation can drive oxygen migration at dangling-bond sites, changing the local bond ordering from C–Si–O to C–O–Si with consequent changes in surface reactivity, band alignment, and electron affinity. Related studies on Al-, B-, and Sc-terminated diamond have explored analogous strategies in which an oxidized surface is coupled to an electropositive atom [165, 170, 171, 172, 164]. Since Si and Ge are also electropositive, similar bonding motifs may stabilize the group-IV surface while preserving useful band alignment. Ota et al. linked a threshold-voltage shift to a change from C–O–Si to C–Si–O bonding [169], an interpretation that relied on conceptual atomistic models rather than a systematic first-principles treatment. Prior theory also left an important structural gap, since earlier calculations used a (2×1) surface cell [173] that does not represent the experimentally observed (3×1) reconstruction.

This chapter uses the experimentally observed (3×1) diamond (100) reconstruction as the structural basis for examining group-IV termination chemistry. It asks whether non-oxidized Si- and Ge-terminated surfaces preserve the NEA favorable for surface transfer doping, whether oxidation is thermodynamically favored, and how C–X–O versus C–O–X bond ordering controls the band gap and electron affinity, where X denotes Si or Ge. These results define the diamond (100) group-IV benchmark for comparison with the reconstructed diamond (111) surfaces examined in Chapter 6.

5.2 Computational Methods

The calculations in this chapter follow the general procedures described in Chapter 2, and only the details specific to the Si- and Ge-terminated diamond (100) systems are summarized here.

The initial structure search for the (3×1) diamond (100) surfaces was performed with GPAW using the PBE functional [52] within the Atomic Simulation Environment [57, 56, 55], which provides reliable structural trends at comparatively low computational cost. The resulting structures were then refined in VASP [58, 59] using PAW pseudopotentials [49, 50], with VASP used for all final structural and electronic-property calculations.

The initial Si- and Ge-terminated surface models were constructed from the LEED-derived structures reported by Schenk et al. and Sear et al. [34, 35]. A 12-layer, 36-atom diamond slab was used to allow reconstruction along the x direction, with lattice parameters $a = 7.572 \text{ \AA}$ and $b = 2.524 \text{ \AA}$ and a minimum vacuum thickness of $12 \text{ \AA}$ along the surface normal. The four central carbon layers were constrained to bulk-like positions while all other atoms were allowed to relax, and Si and Ge atoms were added symmetrically to both slab surfaces to preserve inversion symmetry and avoid artificial dipoles. The 12-layer slab thickness follows prior convergence criteria for diamond surface calculations, which indicate that at least eight layers are needed to recover bulk-like behavior [91, 174, 175, 176]. Layer-resolved projected densities of states confirmed that bulk-like electronic character was recovered by the fourth carbon layer, so that the terminating species primarily affected the near-surface region. These calculations were performed in GPAW using a localized atomic-orbital basis with double-zeta polarization [177].

Several oxidized and non-oxidized Si- and Ge-terminated configurations were examined, with the oxidation sequence varied to identify both stable and metastable bonding motifs, including C–X–O and C–O–X bonding sequences where X denotes Si or Ge. All structural relaxations were continued until residual forces were below $1 \text{ meV/\AA}$. The (3×1) surfaces used a $3 \times 10 \times 1$ Monkhorst–Pack k -point mesh [51] for structural calculations, while reference (2×1) and (1×1) surfaces were evaluated using $8 \times 8 \times 1$ meshes. A plane-wave cutoff of 900 eV was used for all

VASP calculations, with nonspherical contributions inside the PAW spheres included during relaxation and spin polarization included where required.

Electronic band structures were computed using PBE to identify surface-state character and band dispersion, while hybrid-functional total densities of states were computed using HSE06* on a refined $5 \times 10 \times 1$ mesh. The HSE06* parameters were validated against bulk diamond through a systematic scan of the exact-exchange fraction α and screening parameter μ , as summarized in Table 2.1. The parameters $\alpha = 0.30$ and $\mu = 0.20$ give a bulk diamond band gap of 5.53 eV and are used for all hybrid-functional density-of-states calculations in this chapter.

Electron affinities were recomputed using the electrostatic potential-alignment method described in Chapter 2, providing a common absolute energy reference across all surface terminations studied in this dissertation. The absolute values reported here therefore differ from those in Ref. [66], though the structural stability trends, bonding assignments, and relative ordering of the surfaces are unchanged.

Surface formation energies were computed as

$$E_{\text{surf}} = \frac{1}{2A} \left(E_{\text{total}} - \sum_i N_i \mu_i \right), \quad (5.1)$$

where E_{total} is the total energy of the slab, A is the surface area, N_i is the number of atoms of species i , and μ_i is the corresponding chemical potential. The factor of two accounts for the two equivalent surfaces in the symmetric slab, and the solid-state chemical potentials were taken from the total energies per atom of bulk diamond, bulk Si, and bulk Ge, giving $\mu_{\text{C}}^{\text{bulk}} = -9.10$ eV, $\mu_{\text{Si}}^{\text{bulk}} = -5.41$ eV, and $\mu_{\text{Ge}}^{\text{bulk}} = -4.51$ eV.

Gas-phase H and O chemical potentials were corrected using experimental zero-point energy and entropy terms from the NIST database, since semilocal DFT does not accurately describe the total energies of gas-phase molecules. The temperature-dependent gas-phase chemical potentials were evaluated as

$$\mu_{\text{H}}^{(\text{g})} = \frac{1}{2} \left(E_{\text{H}_2}^{\text{DFT}} + E_{\text{ZPE}}^{\text{Exp}} - TS^{\text{Exp}} \right), \quad (5.2)$$

and

$$\mu_{\text{O}}^{(\text{g})} = \frac{1}{2} \left(E_{\text{O}_2}^{\text{DFT}} + E_{\text{ZPE}}^{\text{Exp}} - TS^{\text{Exp}} \right), \quad (5.3)$$

with DFT molecular reference energies of $E_{\text{H}_2}^{\text{DFT}} = -6.78$ eV and $E_{\text{O}_2}^{\text{DFT}} = -9.86$ eV, corresponding to single-atom values of $E_{\text{H}}^{(\text{g})} = -3.39$ eV and $E_{\text{O}}^{(\text{g})} = -4.93$ eV.

Gibbs free-energy corrections were applied to account for vibrational and entropic contributions absent from standard DFT total energies. The corrected surface free energy was computed as

$$G_{\text{surf}} = \frac{1}{2A} \left[E_{\text{total}} - \sum_i N_i \mu_i + G(T) \right], \quad (5.4)$$

where

$$G(T) = H(T) - TS, \quad (5.5)$$

and

$$H(T) = U(T) \approx \int_0^T C_p dT \approx E_{\text{ZPE}} + \Delta U. \quad (5.6)$$

The entropy and internal energy were approximated using only vibrational contributions, since translational and rotational degrees of freedom are negligible for surface-bound adsorbates,

$$S \approx S_{\text{vib}}, \quad (5.7)$$

$$U \approx E_{\text{vib}}. \quad (5.8)$$

The zero-point energy was evaluated as

$$E_{\text{ZPE}} = \frac{1}{2} \sum_i^{n_{\text{ads}}} h \omega_i^{\text{ads}}, \quad (5.9)$$

where the index i runs over the adsorbate vibrational modes, ω_i^{ads} is the frequency of mode i , and ΔU is the finite-temperature vibrational contribution to the internal energy beyond the zero-point energy.

Vibrational frequencies were calculated at the Γ point using finite differences. Adsorbed atoms were displaced by $\pm 0.015 \text{ \AA}$ along the $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions while the carbon atoms were held fixed. All $3N$ vibrational degrees of freedom of the adsorbed atoms were included, where N is the number of adsorbate atoms, and imaginary frequencies were excluded from the zero-point-energy sum. An electronic convergence threshold of $\text{EDIFF} = 1 \times 10^{-7} \text{ eV}$ was used for these calculations, and thermodynamic post-processing was performed using VASPKIT [63].

5.3 Non-Oxidized Si- and Ge-Terminated Diamond (100)

Chapter 4 showed that electron affinity on diamond (100) is sensitive to termination coverage and bonding motif. The first question for group-IV termination is therefore structural. Before

oxidation is considered, the stable non-oxidized Si- and Ge-terminated reference surfaces must be identified using the experimentally observed reconstruction. This section establishes that reference by comparing the accessible non-oxidized (3×1) configurations, their coverage-dependent stability, and their electronic properties.

5.3.1 Structural Motifs and Coverage

In situ annealing of Si or Ge adlayers on reconstructed diamond (100) produces a (3×1) surface, as observed experimentally [34, 35]. This periodicity arises from a dimer–monomer pattern in the surface unit cell. For the lowest-energy structures, Si and Ge occupy approximately 0.33 monolayer per surface carbon site, giving an overall coverage of approximately 0.66 ML.

Two bonding motifs are accessible depending on the position of the group-IV atom relative to the upper carbon layer. In the ether configuration [Fig. 5.1(a)], four-coordinated Si or Ge atoms bridge two surface carbon atoms and form C–Si–C or C–Ge–C units. In the ketone configu-

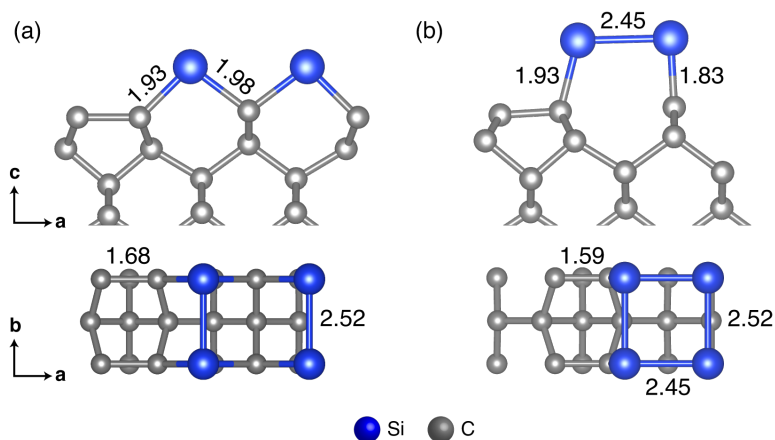


Figure 5.1: Representative non-oxidized (3×1) group-IV terminated diamond (100) surfaces showing (a) the ether configuration and (b) the ketone configuration. Top and bottom panels correspond to side and top views, respectively. Gray and blue spheres represent C and Si atoms, respectively; the Ge-terminated surfaces adopt analogous configurations.

ration [Fig. 5.1(b)], each group-IV atom bonds to one surface carbon atom, one in-plane group-IV neighbor, and two group-IV atoms in adjacent cells. The ether configuration is stable for both Si- and Ge-terminated diamond, whereas the ketone configuration is stable only for Si; attempts to form the Ge ketone structure instead produced Ge_2 dimer formation, consistent with the weaker Ge–C bond relative to its Si–C counterpart. Introducing Si or Ge elongates the reconstructed surface C–C dimer bond by 16–20% relative to the bare surface, increasing from 1.38 Å on bare diamond (100) to 1.68 Å and 1.63 Å for the Si- and Ge-terminated ether surfaces, respectively, consistent with prior calculations [173]. The lateral spacing between adjacent group-IV atoms along the (010) direction is 2.52 Å, in agreement with experimental and theoretical values [173, 178, 35, 179]. Detailed structural parameters are provided in Appendix B.

5.3.2 Surface Stability and Coverage

The relative stability of the non-oxidized bonding motifs and their dependence on coverage were assessed through the surface formation energy E_{surf} , which provides a common thermodynamic basis for comparing configurations across the accessible coverage range. As shown in Fig. 5.2, both Si- and Ge-terminated diamond exhibit a strong reduction in surface energy as coverage approaches 0.66 ML, at which point the ether configuration emerges as the lowest-energy structure. Beyond this coverage, steric interactions between neighboring group-IV adatoms become increasingly unfavorable, driving the surface energy upward.

For Si termination, the 1 ML structure is approximately 37% higher in energy than the 0.66 ML ether surface, yet remains approximately 8% lower in energy than the bare surface, indicating that full monolayer coverage is energetically accessible but not preferred. The 87 meV

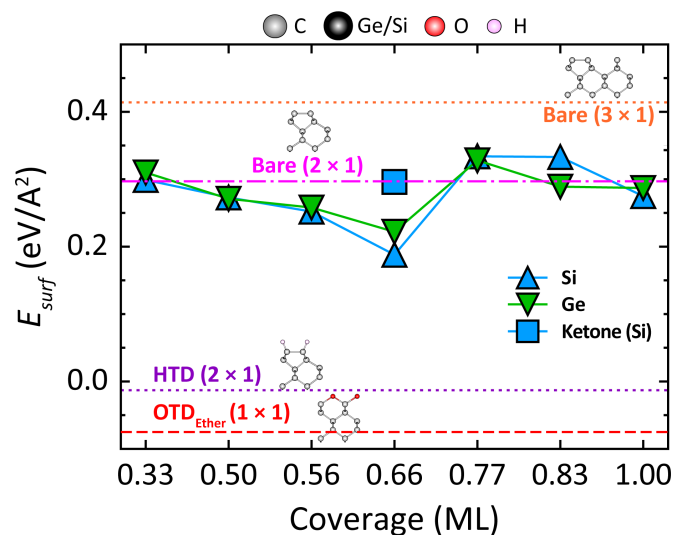


Figure 5.2: Surface formation energies without thermal corrections as a function of coverage density for Si- and Ge-terminated diamond (100) surfaces. The bare surface, H-terminated diamond, and O-terminated ether surface are shown as horizontal reference lines. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

separation between these two configurations is of the same order as $k_B T$ at 673 K, suggesting that the 1 ML phase may nonetheless be accessible under selected preparation conditions. The Si ketone structure lies slightly above the ether at 0.66 ML and is therefore best interpreted as a metastable intermediate rather than the preferred configuration. For Ge termination, experiment gives a coverage of 0.63 ± 0.06 ML, consistent with an incomplete ether structure [35], and the calculated 0.56 ML structure within a (3×3) cell is only 15% less stable than the 0.66 ML ether surface. This close energetic competition supports the experimental interpretation that steric hindrance limits the attainable Ge coverage rather than any thermodynamic preference for lower coverage. The 0.66 ML ether surface therefore emerges as the most appropriate non-oxidized reference structure for the oxidation studies that follow.

5.3.3 Finite-Temperature Stability

Static DFT total energies do not account for vibrational or entropic contributions, which can shift the relative stability of surface configurations at the temperatures relevant to diamond processing and device operation. Gibbs free-energy corrections were therefore applied to assess whether the stability ordering established at zero temperature is preserved across the 300–800 K range, with the corrected surface free energy G_{surf} providing a more physically meaningful comparison under realistic conditions. The vibrational contributions of bonded Si and Ge species are substantially smaller than those of H and O adsorbates, with zero-point energies of 0.03–0.06 eV for the group-IV terminations compared with values on the order of 0.3–0.4 eV for C–H and C–O bonded surfaces. This reduction arises from the larger atomic masses and longer bond lengths of Si and Ge, and its effect on the relative stability ordering is examined in Fig. 5.3.

At room temperature, the relative G_{surf} ordering remains consistent with the zero-temperature DFT results. H-terminated diamond is the most stable surface between 300 and 650 K in this comparison. Above this range, the entropic contribution from the C–O–C vibrational modes of the O-terminated ether reference drives a crossover in stability. This behavior is consistent with experimental observations that C–H bonds desorb at elevated temperatures [19, 7]. Above approximately 650 K, the calculated stability order, from least stable to most stable, is Ge-terminated diamond < Si-terminated diamond < H-terminated diamond < O-terminated ether diamond.

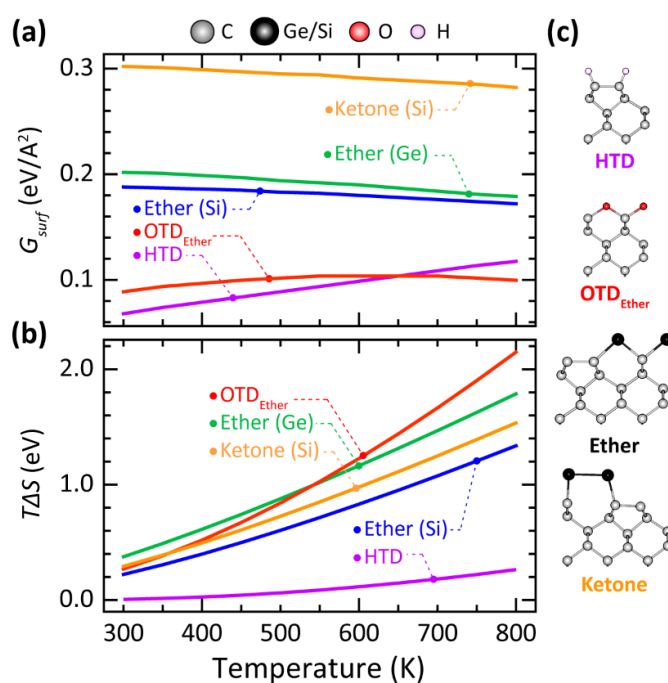


Figure 5.3: (a) Surface formation energies with Gibbs free-energy corrections (G_{surf}) and (b) relative entropic contribution ($T\Delta S$) between 300 and 800 K. Smaller G_{surf} values indicate thermodynamically stable surfaces. Side profiles of the terminations are shown in (c). Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

5.3.4 Electronic Properties of the Non-Oxidized Surfaces

The non-oxidized Si- and Ge-terminated ether surfaces both retain negative electron affinity and exhibit narrow indirect band gaps whose origins lie in surface-derived states rather than in the bulk diamond bands. This is confirmed by the atom-projected band structures in Fig. 5.4, which show that states near both band edges carry substantial group-IV character, establishing the surface termination as the direct source of the reduced gap. The charge-density difference and electron localization function panels of the same figure reveal the bonding mechanism underlying this behavior. Si and Ge donate charge to the neighboring surface carbon atoms, leaving the group-IV sites electron deficient and the C–Si and C–Ge bonds with pronounced covalent character. Bader analysis quantifies this redistribution, giving a charge accumulation of approximately $0.2\text{--}0.5e$ on the surface carbon atoms for the Si-terminated surface and a transfer of approximately $0.57e$ from Ge to surface carbon in the Ge case, slightly less than the $0.59e$ found for Si and consistent with the somewhat weaker Ge–C interaction.

HSE06* calculations give indirect band gaps of 0.76 eV and 0.72 eV for the Si- and Ge-terminated ether surfaces, respectively, with the Si value falling within $\pm 5\%$ of the experimentally measured gap of approximately 0.8 eV [178]. The Fermi level lies closer to the conduction-band edge in the Ge case, contrasting with the more *p*-type character reported for Si-terminated diamond and consistent with the slightly reduced charge transfer between Ge and the surface carbon atoms. Electrostatic-potential alignment yields electron affinities of $\chi = -0.86$ eV and $\chi = -0.74$ eV for the Si- and Ge-terminated surfaces, respectively, confirming that both terminations retain negative electron affinity favorable for surface transfer doping, though with a smaller NEA magnitude than H-terminated diamond. The electron-deficient character of the group-IV sites identified above also

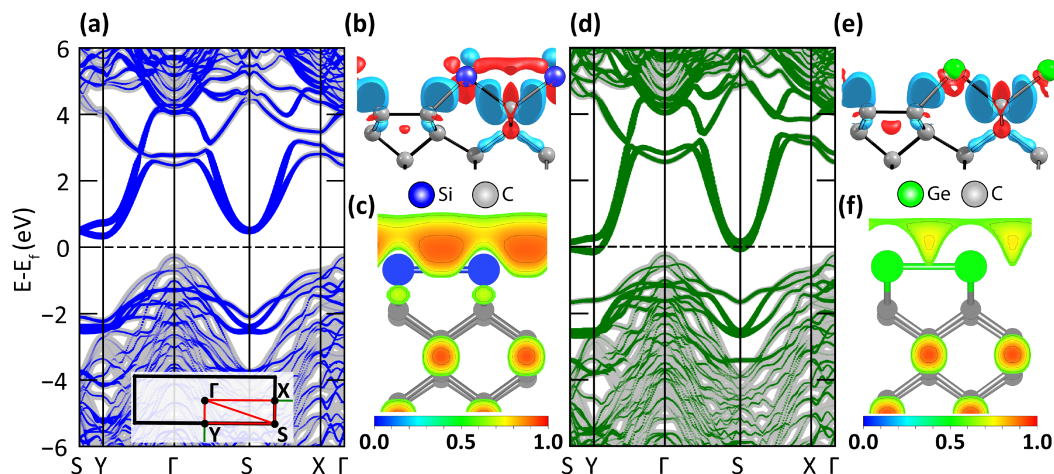


Figure 5.4: Atom-projected band structures, charge-density difference, and electron localization function for non-oxidized (3×1) group-IV terminated diamond (100) surfaces. Panels (a–c) show the Si-terminated ether surface, and panels (d–f) show the Ge-terminated ether surface. The projected band structures identify the group-IV contribution to the surface-derived band-edge states. The charge-density difference shows charge redistribution upon group-IV termination, and the electron localization function shows the corresponding bonding character. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

provides a natural explanation for the susceptibility of these surfaces to atmospheric oxidation, and it is the oxidized configurations that define the device-relevant interface examined in the sections that follow. Additional data is provided in Appendix B.

5.4 Oxidized Si- and Ge-Terminated Diamond (100)

Although the non-oxidized group-IV surfaces retain NEA, their exposed Si and Ge bonds leave them chemically active, and the central question becomes whether oxidation can stabilize these surfaces while preserving favorable electronic alignment. This section addresses that question by comparing the accessible oxidized bonding motifs, their thermodynamic stability, and their resulting electronic properties.

5.4.1 Oxidized Bonding Motifs

Since Si and Ge each possess four valence electrons and adopt tetrahedral bonding configurations, each group-IV atom on the 0.66 ML (3×1) surface can coordinate with oxygen in several distinct ways, and the relevant question is not only how much oxygen is incorporated but also how its placement within the surface bonding network affects the resulting structure and electronic properties. The two principal oxidized motifs identified in this study are shown in Fig. 5.5. In the O_{Ether}

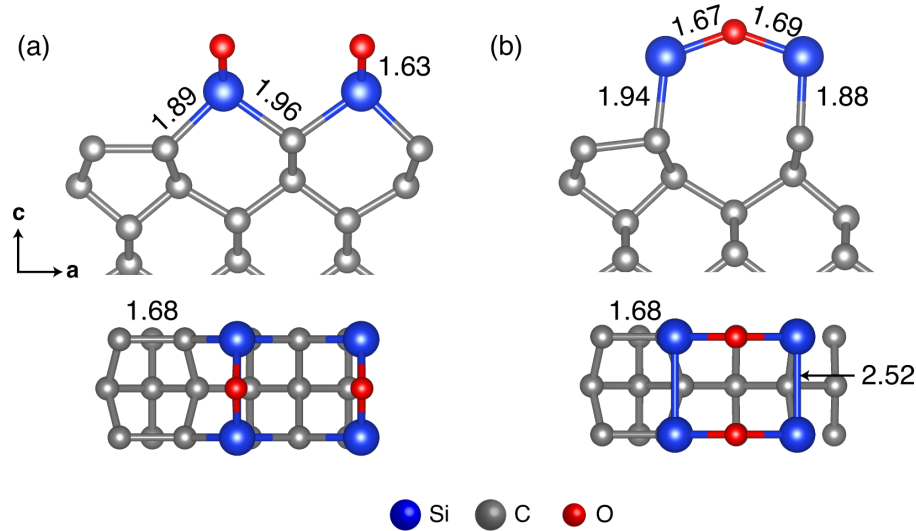


Figure 5.5: Representative relaxed atomic structures of the principal oxidized (a) O_{Ether} and (b) O_{Ketone} (3×1) group-IV terminated diamond (100) surfaces.

configuration [Fig. 5.5(a)], each group-IV adatom is coordinated by two bridging oxygen atoms in a bonding environment reminiscent of bulk SiO_2 and GeO_2 , with Si–O and Ge–O bond lengths of 1.63 and 1.76 Å, respectively, consistent with reported bulk values [180, 181]. Complete oxidation in this geometry also disrupts the lateral Si–Si and Ge–Ge bonding present in the non-oxidized ether surfaces, and the detailed bonding diagnostics are provided in Appendix B. In the O_{Ketone} configuration [Fig. 5.5(b)], oxygen is inserted between adjacent Si–Si or Ge–Ge bonds in the ke-

tone geometry, producing Si–O–Si and Ge–O–Ge bond angles of 140.5° and 134.5° , respectively, consistent with experimental values reported for SiO₂ and GeO₂ compounds [181, 182].

Additional ether-derived configurations were examined to determine whether alternative oxygen placements or O–O bonding arrangements could compete energetically with the O_{Ether} endpoint, and these are shown in Fig. 5.6. In the OB_{Ether} configuration [Fig. 5.6(a)], a single oxygen

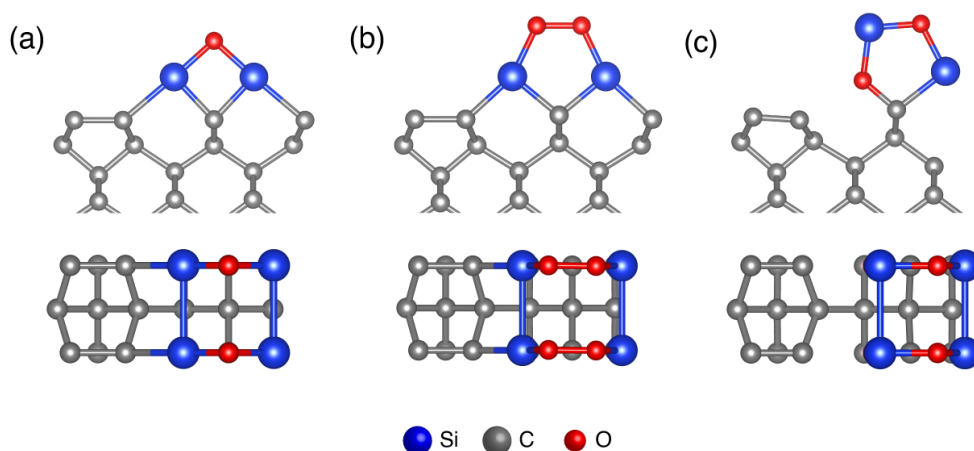


Figure 5.6: Representative alternate oxidized ether configurations for group-IV terminated (3×1) diamond (100) surfaces. (a) OB_{Ether}, (b) PB_{Ether}, and (c) canted. Top and bottom panels correspond to side and top views, respectively. Gray, blue, and red spheres represent C, group-IV, and O atoms, respectively.

atom bridges adjacent group-IV atoms along the (100) plane, forming Si–O–Si or Ge–O–Ge linkages that shorten the group-IV separation to 2.62 Å for Si and 2.82 Å for Ge, compared with 3.16 and 3.23 Å on the corresponding non-oxidized ether surfaces. The PB_{Ether} configuration [Fig. 5.6(b)] introduces a peroxy bridge between neighboring group-IV atoms, while the canted configuration [Fig. 5.6(c)] rotates the oxidized bonding network away from the regular ether orientation; both are chemically plausible given that atmospheric oxidation may produce multiple local oxygen bonding environments simultaneously. Within the calculated stability hierarchy, however, the regular

O_{Ether} geometry remains the preferred fully oxidized endpoint, as established in the thermodynamic analysis that follows.

5.4.2 Thermodynamic Stability of Oxidized Surfaces

The thermodynamic stability of the oxidized Si- and Ge-terminated surfaces was evaluated from 300 to 800 K using Gibbs free-energy corrections, as shown in Fig. 5.7. For Si termination, partial oxidation substantially lowers G_{surf} relative to the non-oxidized surface. Under ambient conditions, OB_{Ether} and O_{Ketone} reduce G_{surf} by approximately 25% and 49%, respectively, making O_{Ketone} the most stable partially oxidized Si configuration. For Ge termination, the stabilization is weaker. OB_{Ether} lowers G_{surf} by only about 6%, while O_{Ketone} remains metastable and is favored only below approximately 400 K.

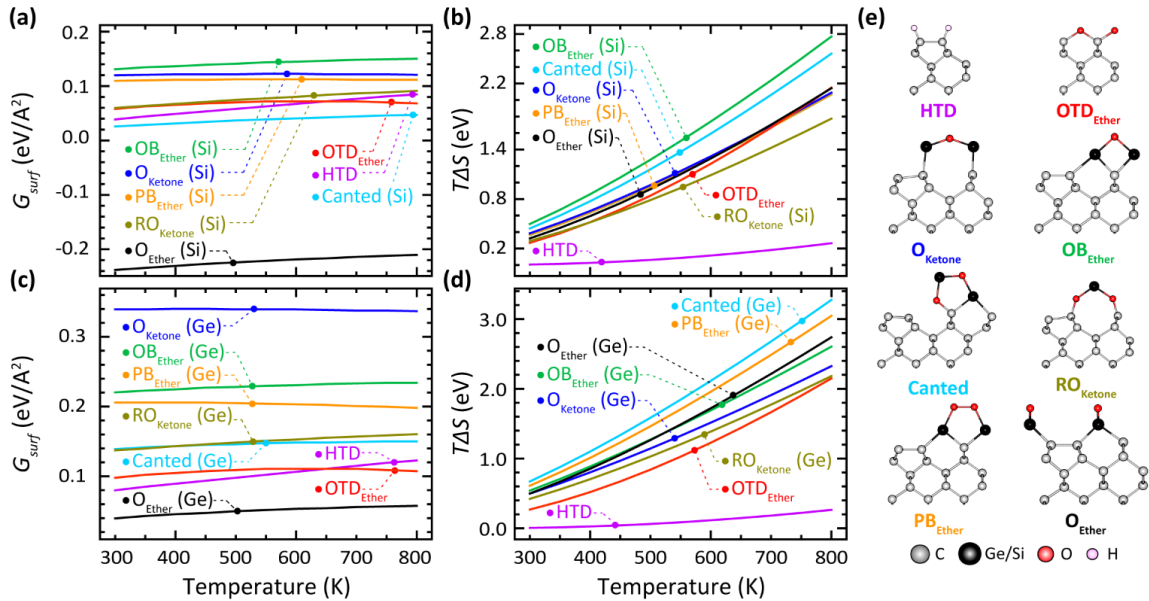


Figure 5.7: G_{surf} and relative entropic contribution ($T\Delta S$) for (3×1) Si (a, b) and Ge (c, d) surfaces from 300 to 800 K. Side profiles of the terminations are shown in (e). Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

At full oxidation, O_{Ether} is the most stable structure for both terminations across the full temperature range. For Si, this configuration is approximately 4–5 times more stable than the H-terminated and O-terminated ether references. This stabilization reflects the stronger Si–O bond and the more complete saturation of surface dangling bonds. For Ge, the stabilization is more modest, and the O_{Ether} stability is closer to that of the reference surfaces. Among the fully oxidized two-oxygen configurations, the stability order is O_{Ether} , followed by the canted and PB_{Ether} geometries. This ordering indicates that the 0.66 ML ether surface strongly favors complete dangling-bond saturation through regular C–X–O bonding. The entropic contributions increase with temperature for all oxidized configurations. The most stable O_{Ether} surfaces show moderate vibrational contributions, consistent with rigid structures dominated by enthalpic stabilization. Less stable configurations, including the canted and PB_{Ether} surfaces, show larger vibrational contributions. This trend is more pronounced for Ge than for Si and is consistent with the lower overall stability of the Ge-terminated oxidized surfaces.

5.4.3 Electronic Structure and Electron Affinity

Oxidation is expected to passivate dangling-bond-derived surface states and modify the band edges of the group-IV terminated diamond (100) surfaces. The projected band structures and charge-density differences in Fig. 5.8 show how this occurs for the principal O_{Ether} and O_{Ketone} configurations, with oxidation changing the character of the band-edge states through hybridization among surface C, group-IV, and O orbitals in both cases.

For O_{Ether} with Si, complete dangling-bond saturation through the regular C–Si–O ordering produces a PBE band gap of 3.27 eV, approximately five times larger than the non-oxidized

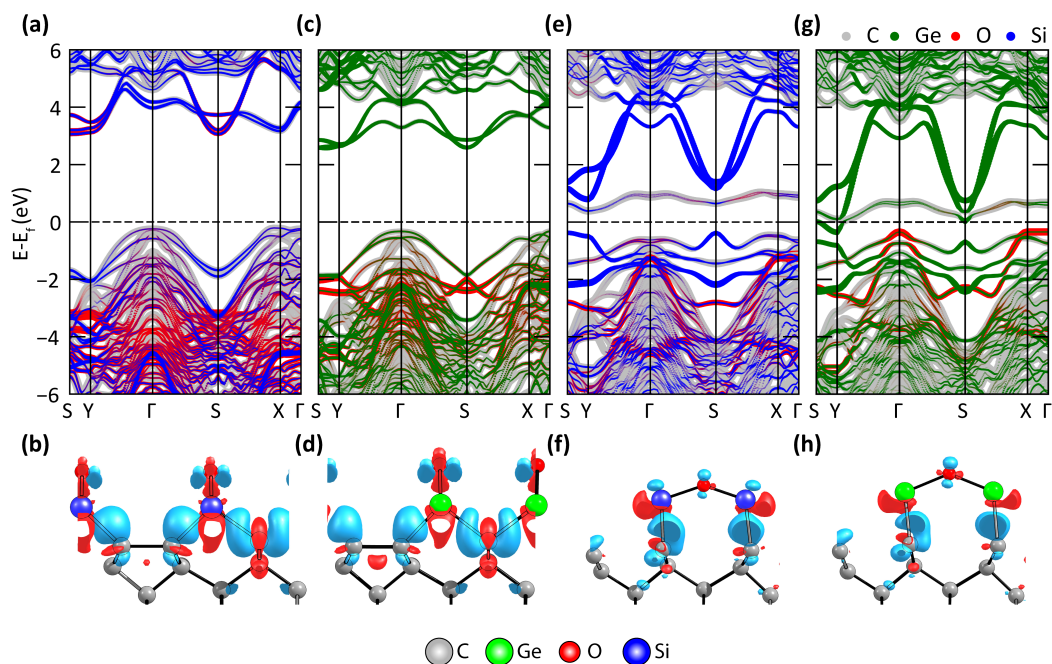


Figure 5.8: Atom-projected band structures and charge-density differences for the principal oxidized group-IV terminated diamond (100) surfaces. Panels (a,b) and (c,d) show O_{Ether} with Si and Ge, respectively. Panels (e,f) and (g,h) show O_{Ketone} with Si and Ge, respectively. The projected band structures identify the group-IV and oxygen contributions to the surface-derived band-edge states, while the charge-density differences show the redistribution of charge induced by oxidation. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

Si-terminated ether surface, with HSE06* increasing this value to 4.61 eV in agreement with a recent theoretical study [183]. The conduction-band minimum and valence-band maximum occur at the S and Γ points, respectively, with dispersive band edges composed primarily of hybridized Si and C states and smaller O contributions near the Fermi level. Bader analysis of the charge-density difference shows that oxidation drives charge redistribution from the Si atoms toward both surface C and terminating O atoms, with accumulation of approximately $0.28\text{--}0.57e$ on surface C and approximately $0.93e$ on O, strengthening the surface C–Si interaction while establishing a polar Si–O bonding environment. The 98 meV offset between V_{surf} and V_{bulk} , shown in the electrostatic-potential alignment in Appendix B, reflects the potential lineup associated with the C–Si–O termination. The relatively small offset is consistent with the reduced channel carrier density reported for C–Si–O-based MOSFETs [169]. The oxidized Ge-terminated ether surface shows similar features, with an HSE06* indirect gap of 3.94 eV and Ge–O hybridized states appearing approximately 2 eV below the Fermi level. Bader analysis gives approximately $1.02\text{--}1.1e$ accumulated on O, with surface C atoms gaining approximately $0.23\text{--}0.57e$, and the stronger charge localization around O relative to the Si case is consistent with the weaker Ge–C bond.

The O_{Ketone} configurations differ fundamentally from the O_{Ether} case, as oxidation opens a gap in surfaces that are metallic before oxidation. For O_{Ketone} with Si, HSE06* gives a gap of 1.65 eV, more than twice the PBE value of 0.77 eV, with a non-dispersive unoccupied flat band near the conduction-band minimum composed mainly of hybridized O, Si, and surface C states. Bader analysis gives approximately $1.5\text{--}1.6e$ transferred from Si to O. For O_{Ketone} with Ge, HSE06* gives a smaller indirect gap of 1.09 eV, with O bands that hybridize strongly with the first carbon layer and remain localized near the surface; the charge transfer from Ge to O is approximately $1.2e$, smaller than in the Si case and consistent with weaker covalent bonding. A notable feature of both O_{Ketone}

surfaces is the presence of semi-flat bands near the band edges, originating from dangling bonds on the surface carbon dimer and from hybridized O, group-IV, and surface C orbitals. Although non-dispersive unoccupied bands can act as electron trapping sites, the occupied dispersive states near the valence-band edge also distort the bulk-like parabolicity, increasing the hole effective mass and potentially reducing hole mobility in device applications. Additional passivation of the remaining surface dangling bonds may therefore improve current density and surface conductivity, consistent with recently reported oxidized Si-terminated normally-off MOSFETs [169].

A broader comparison of PBE and HSE06* total densities of states across all diamond (100) surfaces is shown in Fig. 5.9, summarizing the band-gap evolution from the non-oxidized through fully oxidized configurations. The non-oxidized ether surfaces retain narrow gaps below 1 eV, while the fully oxidized O_{Ether} surfaces recover large gaps approaching the bulk diamond value, confirming that complete oxidation in the C–X–O ordering effectively passivates the surface-derived states.

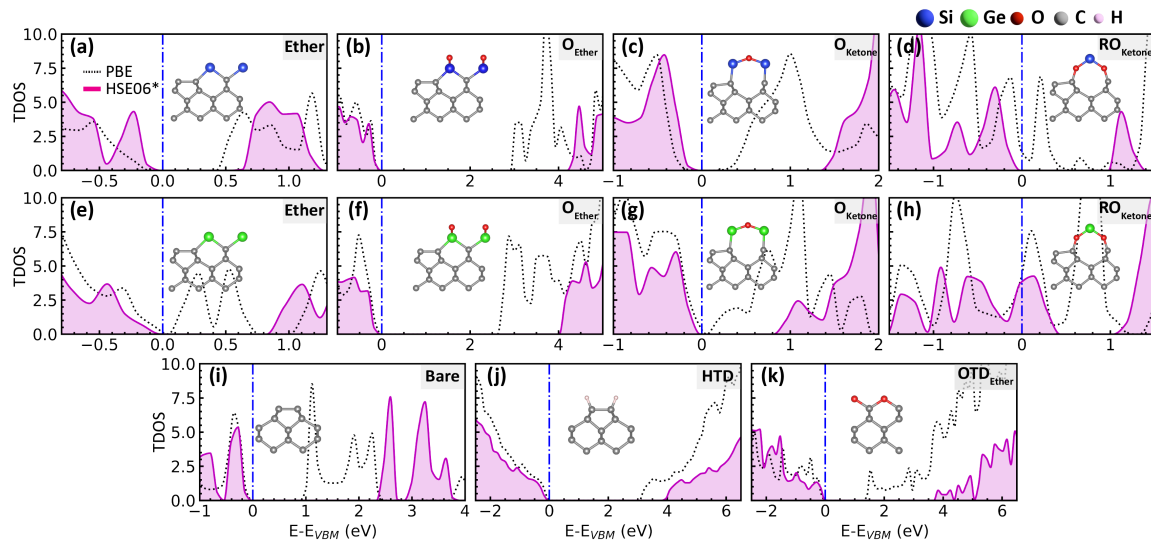


Figure 5.9: TDOS comparison for Si-terminated (a–d) and Ge-terminated (e–h) diamond surfaces showing the effect of oxidation on the fundamental band gap. Reference bare, H-terminated diamond, and O-terminated ether diamond surfaces are shown in (i–k). Dotted and solid lines represent PBE and HSE06* TDOS, respectively. The VBM is set to zero. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

The same oxidation that restores large band gaps also shifts the surface dipole, and electrostatic-potential alignment shows that the fully oxidized O_{Ether} surfaces move into the PEA regime, with updated aligned values of $\chi = +0.63$ eV for Si and $\chi = +1.80$ eV for Ge. Oxidation therefore improves structural stability and suppresses surface-derived gap states at the cost of removing the spontaneous transfer-doping advantage of the non-oxidized group-IV surfaces.

The reversed ordered ketone configuration provides a direct test of the C–O–X bond ordering proposed in device interpretations [169]. Outward migration of the group-IV atom from the oxidized ketone surface produces a C–O–X–O–C sequence, denoted RO_{Ketone}, which is more stable than the regular oxidized ketone surface but remains less stable than O_{Ether} across the full temperature range. The atom-projected band structures and charge-density differences for this configuration are shown in Fig. 5.10. For Si, RO_{Ketone} retains NEA with $\chi = -0.77$ eV and an HSE06*

gap of approximately 1 eV, while for Ge, HSE06* predicts a metallic surface with no resolvable gap, rendering the electron affinity undefined and limiting its suitability as a device interface.

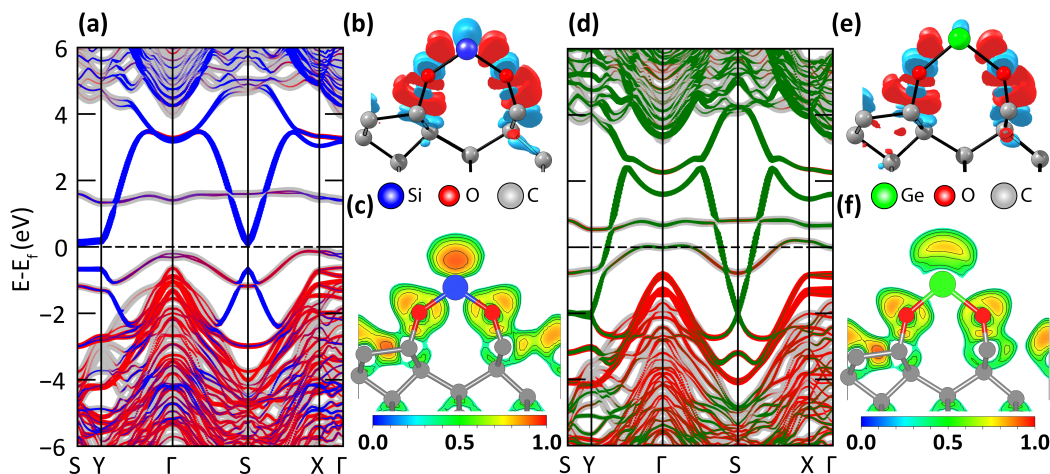


Figure 5.10: Atom-projected band structures, charge-density differences, and electron localization functions for the $\text{RO}_{\text{Ketone}}$ configuration of group-IV terminated diamond (100) surfaces. Panels (a–c) show the Si-terminated surface and panels (d–f) show the Ge-terminated surface. The projected band structures identify the Si (blue) and O (red), and Ge (green) and O (red) contributions to the surface-derived band-edge states, respectively. The charge-density differences and electron localization functions show the charge redistribution and bonding character induced by the reversed C–O–X bond ordering. The dashed line indicates the Fermi level. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

The electron affinities for the principal configurations are summarized in Table 5.1, computed using the electrostatic-potential alignment procedure described in Chapter 2 and illustrated in Fig. 5.11. The absolute values reported here were recomputed using the thesis-wide alignment procedure and therefore supersede those in Ref. [66], though the structural stability trends, bonding assignments, and relative ordering of the surfaces remain unchanged.

Table 5.1: HSE06* electron affinities of the Si- and Ge-terminated diamond (100) surfaces computed using the electrostatic-potential alignment procedure described in Chapter 2. Typical literature values for calculated [64, 147, 173, 184] (column marked with $\dagger$) and experimentally obtained [35, 178] (column marked with $\ddagger$) electron affinities are given for comparison.

Reconstruction	Surface	Electron affinity (eV)		
		This work	Theory †	Expt. ‡
(2×1)	H	-2.09	-2.07	-1.30
(3×1)	Ether (Si)	-0.86	-0.80	-0.86
(3×1)	Ether (Ge)	-0.74	-0.85	-0.71
(3×1)	O _{Ether} (Si)	+0.63	+0.62	+0.74
(3×1)	O _{Ether} (Ge)	+1.80	—	—
(3×1)	RO _{Ketone} (Si)	-0.77	—	—

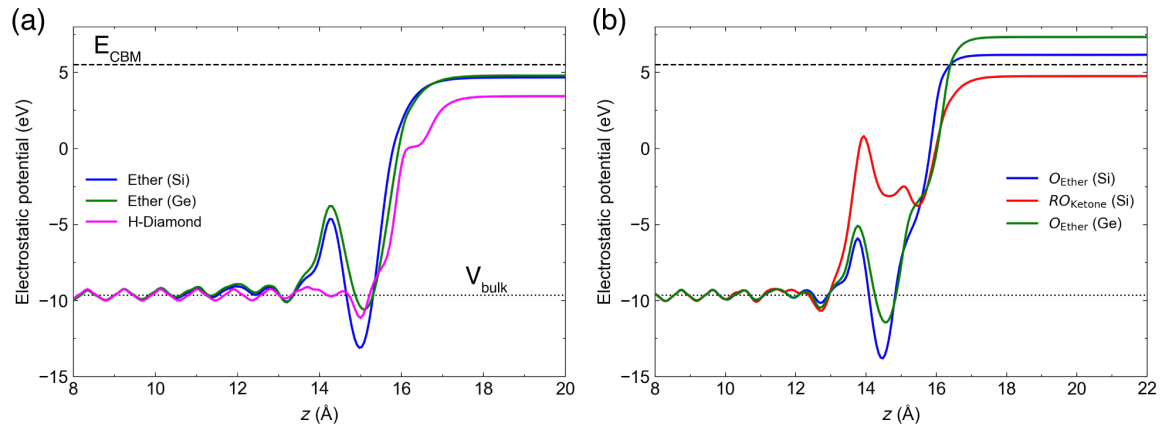


Figure 5.11: Aligned electrostatic potentials for (a) non-oxidized and (b) oxidized group-IV terminated diamond (100) surfaces. The dashed and dotted lines indicate E_{CBM} and V_{bulk} , respectively, defining the common reference used to determine electron affinities.

5.5 Conclusion

This chapter has examined the structural and electronic properties of non-oxidized and oxidized (3×1) Si- and Ge-terminated diamond (100) surfaces, with the central finding that oxidation state and bond ordering govern the interface electronic properties rather than the group-IV element alone. Among the non-oxidized motifs, the ether geometry is thermodynamically favored for both Si and Ge while the ketone is stable only for Si, and both ether surfaces retain negative electron affinity with values near -0.8 eV, confirming that non-oxidized group-IV termination preserves electron affinities favorable for surface transfer doping on diamond (100). Charge-transfer analysis identifies the electron-deficient group-IV sites as natural reaction centers for atmospheric oxygen, and oxidation is found to increase surface stability while producing bond-order-dependent electronic properties. The fully oxidized O_{Ether} configuration is the most stable endpoint for both terminations, restoring band gaps above 3.9 eV by saturating the surface dangling bonds through a regular C–X–O ordering, but shifting the electron affinity into positive values of $+0.63$ eV and $+1.80$ eV for Si and Ge, respectively. The reversed C–O–X ordering provides a contrasting limit in which NEA is retained for Si at $\chi = -0.77$ eV but at the cost of reduced thermodynamic stability and trap-like features near the band edges, while for Ge this configuration remains electronically unfavorable. Chapter 6 examines whether this balance is altered on the reconstructed diamond (111) surface, where a different reconstruction geometry, distinct oxidation pathways, and higher dipole density per unit area offer new opportunities for tuning the transfer-doping-relevant band alignment.

Chapter 6

Phase Stability and Electron Affinity of Oxidized Group-IV Terminated Diamond (111)

The work presented in this chapter is being prepared for publication.

6.1 Introduction

Chapters 4 and 5 established the electron affinities for H/O- and group-IV terminated diamond (100). On the (100) surface, non-oxidized Si- and Ge-terminated ether configurations retain NEA with $\chi \approx -0.8$ eV, while full oxidation in the C–X–O ordering shifts the affinity positive, and only the reversed C–O–X ordering recovers NEA for Si at $\chi = -0.77$ eV. The central question left open by those results is whether the same bond-ordering dependence governs the (111) surface, and whether the higher dipole density of (111) alters the balance between stability, electronic passivation, and transfer-doping-compatible band alignment. The diamond (111) surface is of particular

interest for transfer doping because its higher dipole density can yield a 2DHG sheet density approximately twice that of diamond (100) [38, 39]. However, the (111) surface reconstructs into the (2×1) Pandey-chain geometry [90], which differs fundamentally from the dimer-row reconstruction of (100) and constrains the accessible group-IV bonding motifs. Silicon termination has emerged as a thermally stable alternative to hydrogen termination on the (100) surface [34]. The oxidized Si-terminated (100) surface retains its structure to 1200 °C, and the oxidized Ge-terminated (100) surface is recoverable by annealing to 700 °C [36], both representing substantial improvements over H-terminated diamond. A well-ordered Si-terminated diamond (111) surface can be fabricated by Si deposition and vacuum annealing [40], although the Pandey-chain reconstruction complicates the formation of well-defined group-IV terminated phases. Following Si deposition, $(\sqrt{3} \times \sqrt{3})$ and (2×2) LEED patterns have been observed, and subsequent ambient exposure drives spontaneous oxidation [40, 122].

One experimentally relevant preparation route involves brief atmospheric exposure followed by vacuum annealing at 450 °C, which removes surface contamination while preserving the oxidized C–Si–O interface and provides a direct experimental reference for the thermodynamic stability window examined in this chapter [122]. XPS analysis reveals a heterogeneous C–Si–O interface in which regions of the bare (2×1) reconstruction coexist with carbon atoms forming single and multiple C–Si bonds.

A recent theoretical study identified stable C–Si–O configurations with electron affinities of 0.70–1.32 eV [184], but those models were constructed from the ideal unreconstructed surface. Prior theoretical work has also predicted silicene and germanene overlayers on the unreconstructed diamond (111) surface [185]. The role of the Pandey-chain reconstruction in constraining accessible oxidized geometries and electronic properties therefore remains unresolved. The

analogous question for Ge-terminated diamond (111) has received less attention than for the (100) surface [35, 36, 66]. This chapter uses first-principles calculations to identify oxidized endpoints accessible from the Pandey-chain reconstructed diamond (111) surface, assess their thermodynamic and finite-temperature stability, and evaluate their suitability for surface-transfer-doped device applications.

6.2 Computational Methods

All calculations follow the general first-principles methods described in Chapter 2, and only details specific to the diamond (111) group-IV systems are summarized here. Diamond (111) surfaces were modeled using symmetric 14-layer slabs, with at least 15 Å of vacuum separating periodic images and the central four carbon layers fixed to bulk geometry [186]. A 600 eV plane-wave cutoff and Γ -centered Monkhorst–Pack k-mesh [51] equivalent to $12 \times 12 \times 1$ for the primitive surface cell were used, scaled accordingly for all supercells. Given the sensitivity of phonon calculations to the quality of the force constants, ionic positions were relaxed until forces fell below 10^{-3} eV/Å with an electronic convergence threshold of 10^{-7} eV. Electronic band structures and electron affinities were computed using the HSE06* hybrid functional with the electrostatic alignment procedure described in Chapter 2, using a bulk diamond reference potential of 9.65 eV and band gap of 5.53 eV [29, 66].

Dynamical stability was assessed using the finite-displacement method as implemented in Phonopy [67, 68], with 0.01 Å displacements in $2 \times 2 \times 1$ supercells. This extends the Gibbs correction approach of Chapter 5 by including the full phonon dispersion rather than Γ -point vibrational

frequencies alone. The resulting force constants were used to identify unstable vibrational modes, and the harmonic vibrational free energy was evaluated as

$$F_{\text{vib}}(T) = \frac{1}{2} \sum_{\mathbf{q}\nu} \hbar \omega_{\mathbf{q}\nu} + k_{\text{B}} T \sum_{\mathbf{q}\nu} \ln \left[1 - e^{-\hbar \omega_{\mathbf{q}\nu} / k_{\text{B}} T} \right], \quad (6.1)$$

where $\omega_{\mathbf{q}\nu}$ is the phonon frequency at wavevector $\mathbf{q}$ and branch index ν , with the first and second terms giving the zero-point and finite-temperature vibrational contributions, respectively. Candidate structures at each coverage were screened sequentially: configurations exhibiting imaginary phonon modes were discarded, and the remaining structures were subjected to ab initio molecular dynamics (AIMD) to assess finite-temperature stability. AIMD simulations were performed in the NVT ensemble at 300 K and 723 K using a Nosé–Hoover thermostat [69, 70], a 1 fs timestep, and 5 ps trajectories, with $2 \times 2 \times 1$ supercells sampled at the Γ point, consistent with the ambient exposure and annealing conditions reported experimentally [122]. A single minimum-energy pathway calculation was performed using the climbing-image nudged elastic band (CI-NEB) method [71] with eight intermediate images to resolve the transformation barrier from the linear (2×1) oxygenated intermediate to the reconstructed (2×2) PCM–Si₂O₂ phase.

The relative thermodynamic stability of competing surface terminations was evaluated using the updated surface Gibbs free energy

$$G_{\text{surf}}(T, P) = \frac{1}{2A} \left[E_{\text{slab}} + F_{\text{vib}}(T) - \sum_i N_i \mu_i \right], \quad (6.2)$$

where A is the area of one surface face, the factor of two accounts for the two equivalent surfaces of the symmetric slab, E_{slab} is the DFT total energy, and N_i and μ_i are the number and chemical

potential of species i , respectively. The C, Si, Ge, and O chemical potentials were referenced to bulk diamond, bulk Si, bulk Ge, and molecular O₂, respectively, consistent with the conventions of Chapter 5.

The oxygen chemical potential was written as

$$\mu_{\text{O}}(T, P) = \frac{1}{2} \left[E_{\text{O}_2}^{\text{DFT}} + \Delta\mu_{\text{O}_2}^{\circ}(T, P^0) + k_{\text{B}}T \ln \left(\frac{P}{P^0} \right) \right], \quad (6.3)$$

where $\Delta\mu_{\text{O}_2}^{\circ}(T, P^0)$ includes enthalpic and entropic corrections from JANAF thermochemical tables [65], and a +0.643 eV correction was applied to the PBE O₂ binding energy following Wang *et al.* [187]. The Si and Ge chemical potentials were fixed at their respective bulk PBE reference values ($\Delta\mu_{\text{Si}} = \Delta\mu_{\text{Ge}} = 0$), representing Si- and Ge-rich conditions. Surface phase diagrams were computed over oxygen chemical potentials corresponding to ambient oxygen pressure ($p_{\text{O}_2} = 0.21$ atm) and UHV conditions ($p_{\text{O}_2} = 5 \times 10^{-14}$ – 5×10^{-10} atm), consistent with experimental deposition environments [122].

6.3 Results and Discussion

6.3.1 Group-IV Terminated Surfaces

The clean diamond (111) surface reconstructs into the Pandey-chain geometry, which is energetically favored over the unreconstructed (1×1) surface [90, 186]. Two high-symmetry adsorption sites are considered on this surface. The first is a bridge site spanning adjacent chain atoms, denoted *epoxy*. The second is an on-top site above a surface chain atom, denoted *ketone*. Hereafter, the Pandey-chain reconstructed surface is referred to as the Pandey-chain model (PCM).

Adsorbate coverages are reported relative to the ideal diamond (111) surface density, with 1 ML corresponding to one adsorbate per surface carbon atom.

Following adatom deposition on the (2×1) PCM surface, Si stabilizes both the *epoxy* and *ketone* configurations, whereas Ge stabilizes only the *epoxy* configuration. In the *epoxy* geometry [Fig. 6.1(a)], each adatom bridges two adjacent PCM carbon atoms at 0.5 ML coverage. This geometry forms two X–C bonds ($X = \text{Si, Ge}$), with bond lengths of 2.04 Å for Si and 2.17 Å for Ge, while retaining an outward-facing dangling bond directed toward the vacuum. In the *ketone* configuration [Fig. 6.1(b)], each Si atom occupies an on-top site above a single chain carbon atom at 1 ML coverage. This structure preserves the PCM backbone and forms Si–Si bonds of 2.52 Å between adjacent adatoms. Schenk et al. proposed that the surface evolves from Si trimers into a rhombohedral Si layer on diamond (111), in apparent agreement with the rhombic silicene-like structure predicted by Xu et al. [185, 40]. The Si *ketone* structure considered here is therefore closely related to this experimentally motivated full-monolayer Si configuration. Conversely, the analogous *ketone* arrangement for Ge undergoes partial desorption during relaxation and is not considered further.

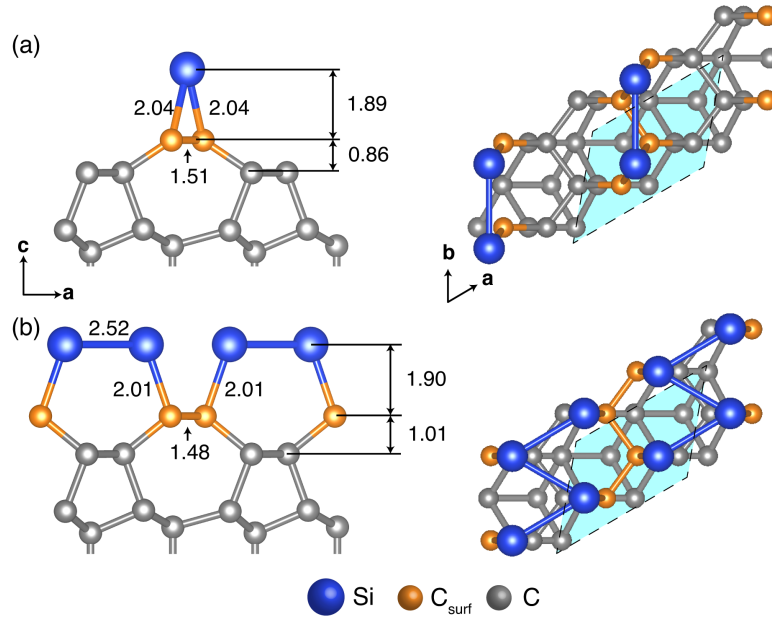


Figure 6.1: Relaxed structural configurations of group-IV adatoms on the PCM diamond (111) surface. (a) *Epoxy* bridge-site adsorption at 0.5 ML coverage. (b) *Ketone* on-top adsorption at 1 ML coverage. The structures are shown for Si. Ge adopts the same *epoxy* motif but does not stabilize in the *ketone* configuration. The blue region depicts the (2×1) primitive cell. Blue, orange, and gray spheres represent Si, surface-chain C, and subsurface C atoms, respectively.

Electronic Properties

The electronic structures of the non-oxidized PCM surfaces are shown in Fig. 6.2. The Si *epoxy* configuration is a narrow-gap surface, with Si-derived occupied and unoccupied surface states separated by only 0.15 eV [Fig. 6.2(a)]. By contrast, changing the local Si bonding to the *ketone* configuration closes this gap. The Si *ketone* configuration exhibits two-dimensional metallic character [185], with Si-derived surface states crossing E_F [Fig. 6.2(b)]. This 1 ML Si configuration is relevant to the experimentally prepared Si-terminated diamond (111) surface reported by Schenk et al., for which a negative electron affinity of -0.76 eV was measured at full monolayer Si coverage [40]. In contrast, the Ge *epoxy* surface retains a finite surface-state gap of 0.93 eV between Ge-derived occupied and unoccupied surface bands [Fig. 6.2(c)].

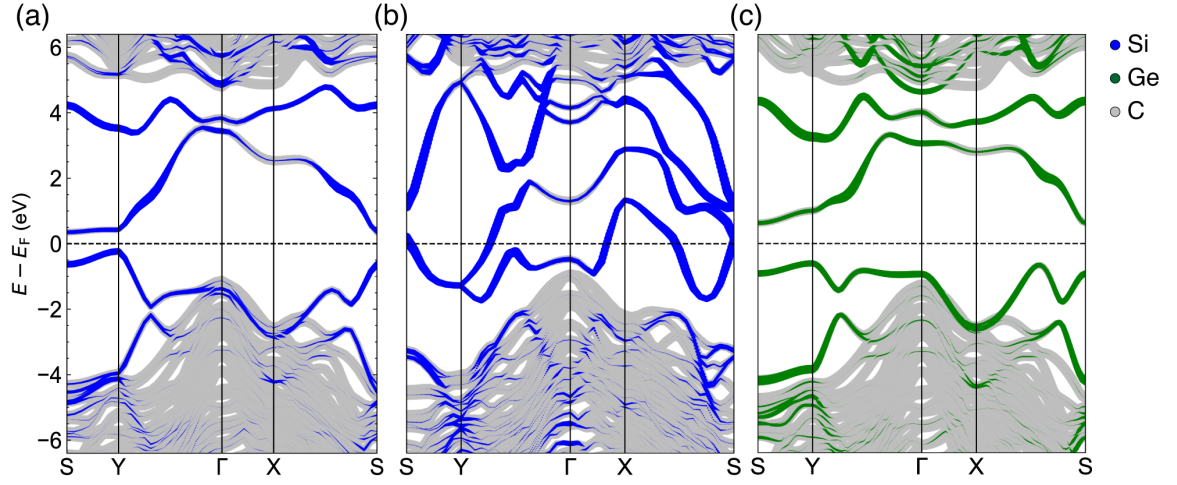


Figure 6.2: Atom-projected HSE06* band structures of the non-oxidized PCM surfaces: (a) Si *epoxy* (0.5 ML) and (b) *ketone* (1 ML), and (c) Ge *epoxy* (0.5 ML). Blue, green, and gray circles represent Si-, Ge-, and C-projected states, respectively, with circle size proportional to the projection weight.

Following the band-structure analysis, Fig. 6.3 shows the planar-averaged electrostatic potentials for the non-oxidized Si- and Ge-terminated PCM configurations. The bulk-like oscillations in the slab interior are consistent across the three surfaces, confirming that the potentials can be aligned to the same bulk reference. Near the surface region at $z \approx 18 \text{ \AA}$, the Si *ketone* configuration shows the largest perturbation in the electrostatic potential. This distinct profile is consistent with its different Si bonding environment and with the Si-derived metallic surface bands shown in Fig. 6.2(b). The Si and Ge *epoxy* configurations show more gradual changes across the surface dipole region. After alignment to the bulk diamond reference, both *epoxy* surfaces place the vacuum level below the bulk-referenced conduction-band minimum, corresponding to negative electron affinities. The Si *epoxy* surface yields an electron affinity of -0.40 eV , whereas the Ge *epoxy* surface yields a more negative value of -1.16 eV . For comparison, the electron affinities of the hydrogen-terminated and bare PCM surfaces are listed with the full set of values in Table 6.1.

These results show that the electron affinity is determined by the net vacuum-level shift after bulk alignment, rather than by the depth of any single local feature in the surface potential profile.

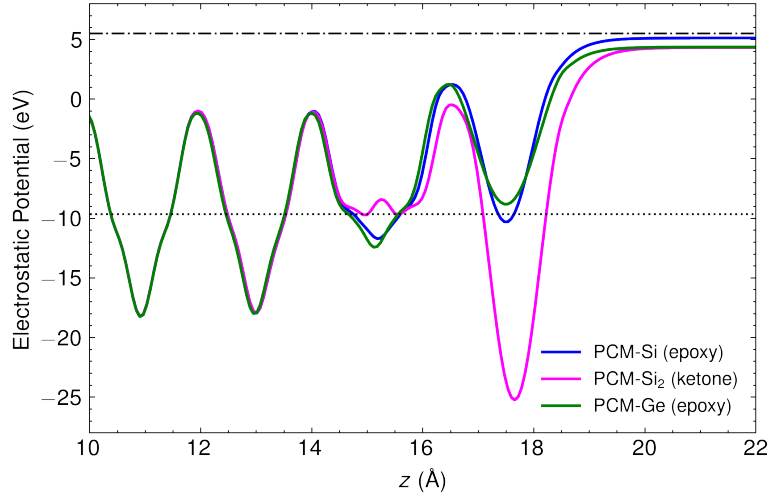


Figure 6.3: Planar-averaged electrostatic potentials for the non-oxidized Si- and Ge-terminated PCM diamond (111) surfaces. The dash-dotted and dotted lines indicate the bulk-referenced conduction-band minimum and bulk diamond average electrostatic potential, respectively.

6.3.2 Oxidized Group-IV Terminated Surfaces

Structural and Thermodynamic Properties

The lack of electronic passivation in the non-oxidized phases motivates an investigation of oxidized group-IV terminations. Schenk et al. [40] identified a Pandey-chain-derived backbone as the relevant structural motif for Si-terminated diamond (111), and subsequent XPS measurements confirmed Si–C bonding consistent with this structure after ambient oxidation [122]. The oxidation pathway analysis is therefore restricted to PCM-derived structures, since the Pandey-chain reconstruction defines the experimentally prepared starting geometry. Structures derived from the ideal unreconstructed (1×1) surface [184] represent a distinct pathway requiring collective reconstruc-

tion of the diamond surface, rather than local oxidation of the deposited group-IV adlayer. They are therefore included only as thermodynamic references.

PCM-derived oxidized structures were first screened using phonon calculations and finite-temperature AIMD. Three oxidized phases pass phonon screening and remain intact during 300 K AIMD: PCM-Si₂O₂, PCM-Si₄O₃, and PCM-Ge₂O. In each case, the underlying PCM surface is retained, while unstable higher-coverage phases relieve adsorbate-layer strain through soft phonon modes, reconstruction during AIMD, or oxide desorption.

The screening results in Fig. 6.4 show why more complete oxidation is not generally stabilized on the PCM surface. For Si, two classes of high-coverage motifs fail the screening: μ_3 configurations [Fig. 6.4(a,c)], in which O bridges three adjacent Si sites analogously to the Ideal-Si₄O₄ phase reported previously [184], and peroxy-bridged structures [Fig. 6.4(b,d)]. The μ_3 configurations exhibit imaginary phonon modes, while the peroxy-bridged structures pass phonon screening but reconstruct during AIMD, indicating that full oxygen incorporation overconstrains the PCM-supported Si-O adsorbate layer even though the underlying Pandey-chain surface remains intact. The higher-coverage exception is PCM-Si₄O₃ at 0.75 ML O coverage, where the mixed μ_3 -peroxy motif distributes oxygen coordination over inequivalent Si sites, allowing the adsorbate layer to relax without complete reconstruction. For Ge, oxygen coverages beyond 0.25 ML drive GeO and GeO₂ desorption during AIMD, indicating that additional oxygen is accommodated more readily by forming volatile Ge-O species than by extending the adsorbate layer.

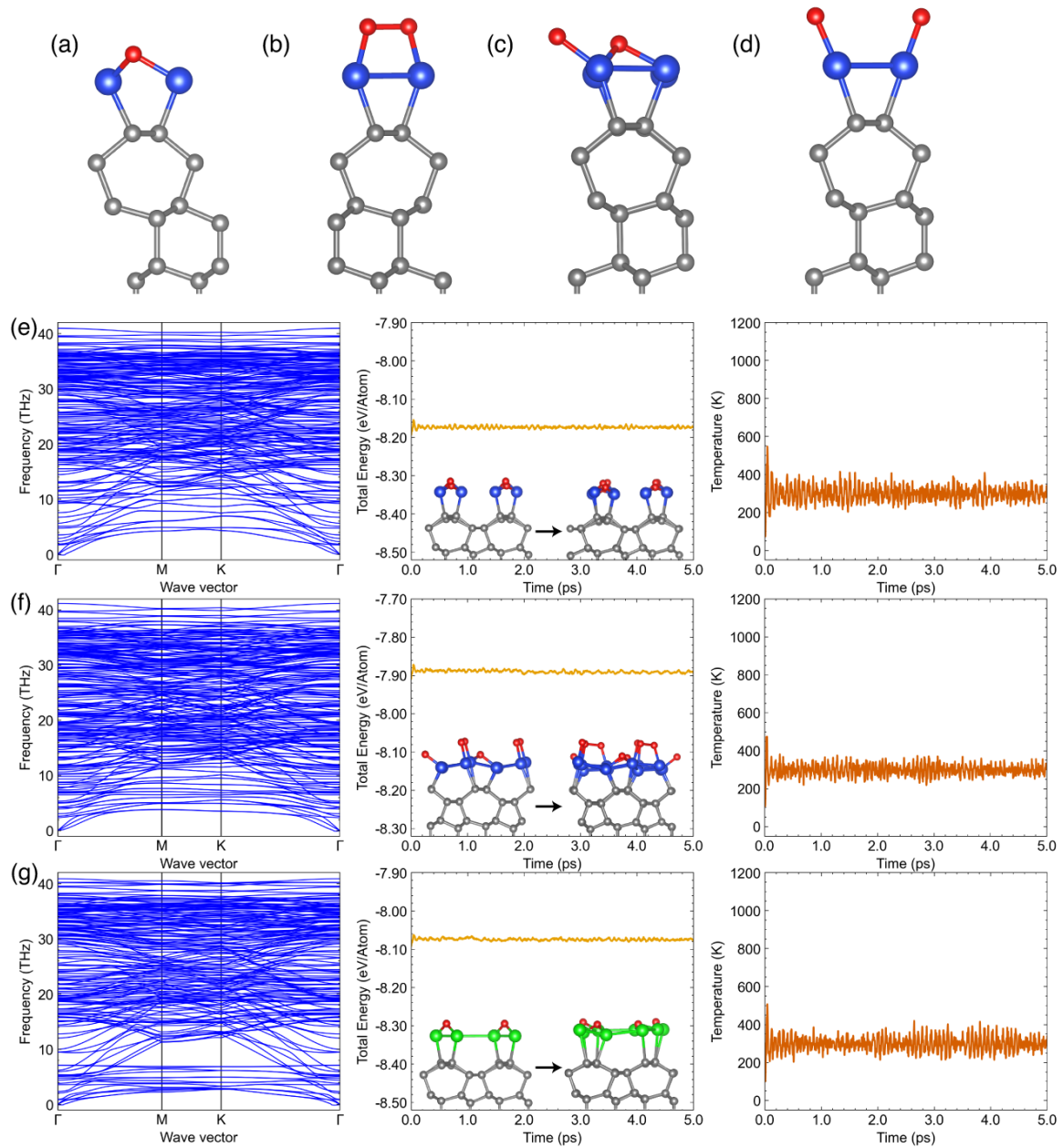


Figure 6.4: Stability screening of oxidized PCM diamond (111) surfaces. Panels (a) and (c) show unstable μ_3 configurations with imaginary phonon modes. Panels (b) and (d) show peroxy-bridged structures that reconstruct during AIMD. Panels (e)–(g) show the phonon dispersions and 300 K AIMD results for the stable PCM–Si₂O₂, PCM–Si₄O₃, and PCM–Ge₂O phases, respectively. Initial and final AIMD configurations are shown as insets.

The relative thermodynamic stabilities of the three phases that pass the initial screening are compared in Fig. 6.5, with ideal unreconstructed structures included as references. Within this screened set, PCM-Si₂O₂ is the lowest-energy oxidized structure across the temperature and oxygen chemical-potential range considered, identifying it as the thermodynamic endpoint along the reconstructed oxidation pathway.

The corresponding relaxed geometries are shown in Fig. 6.6. PCM-Si₂O₂ disrupts the bridging C-Si-C motif of the non-oxidized *epoxy* precursor, forming a reconstructed (2 × 2) C-Si-O network in which O atoms bridge adjacent Si centers. PCM-Si₄O₃ similarly modifies the Si coordination, distributing oxygen over inequivalent sites through the mixed μ_3 -peroxy motif at

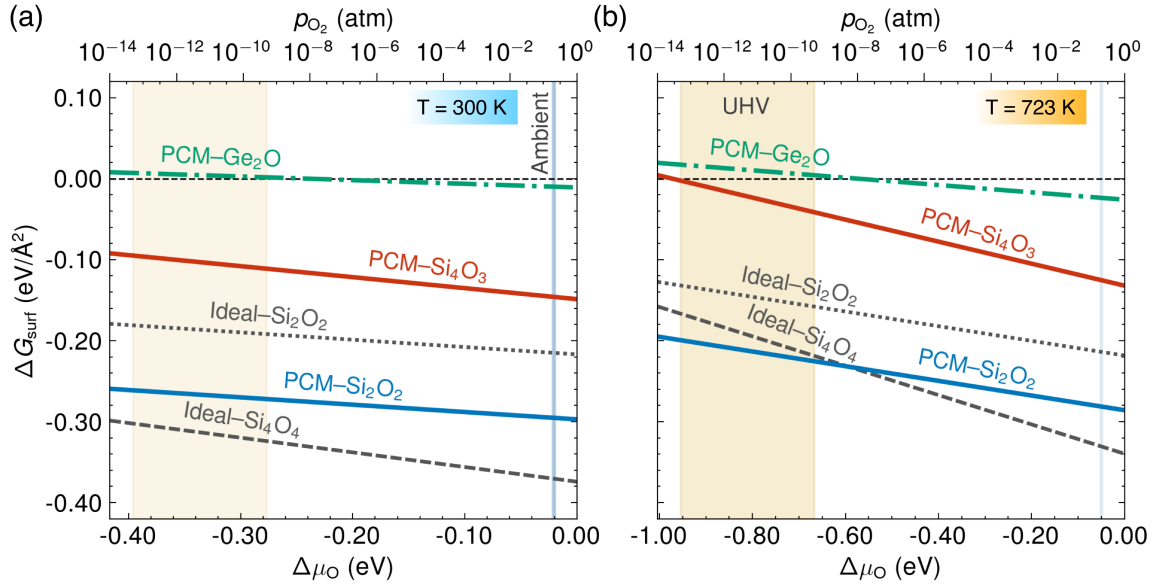


Figure 6.5: Surface free energies ΔG_{surf} as a function of oxygen chemical potential $\Delta\mu_{\text{O}}$ at (a) 300 K and (b) 723 K. Colored curves show PCM-derived phases that pass phonon and 300 K AIMD screening, while gray curves show ideal unreconstructed references. The upper axes give the corresponding oxygen partial pressure. Beige shading marks UHV conditions, and the blue line in (a) marks ambient conditions. The horizontal dashed line denotes the bare PCM reference.

0.75 ML coverage. By contrast, PCM-Ge₂O retains the *epoxy*-derived connectivity, with O atoms forming Ge–O–Ge bridges at 0.25 ML coverage.

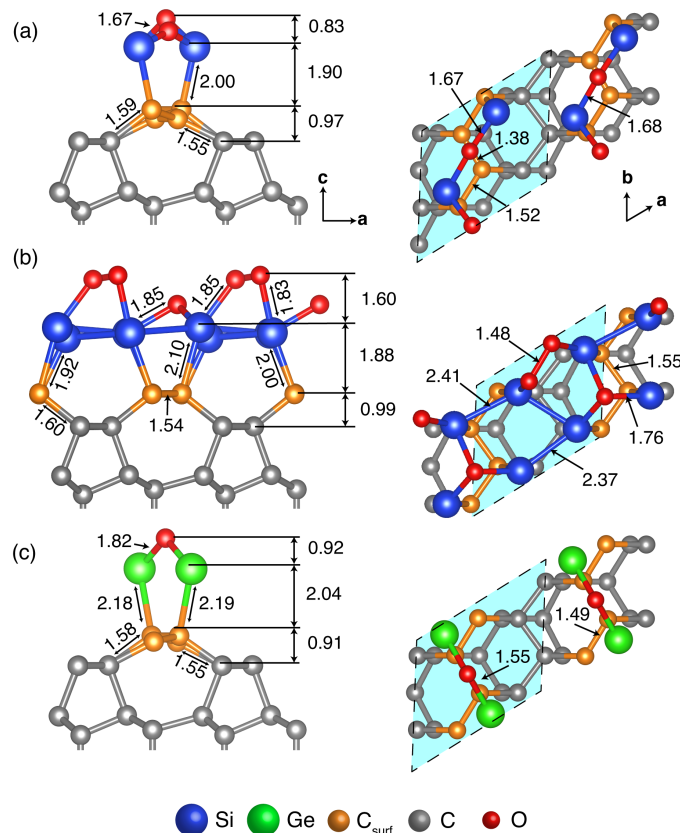


Figure 6.6: Relaxed structural configurations of oxidized PCM diamond (111) surfaces. (a) PCM-Si₂O₂ (*epoxy*, 0.5 ML O), (b) PCM-Si₄O₃ (*ketone-derived*, 0.75 ML O), and (c) PCM-Ge₂O (*epoxy*, 0.25 ML O), shown in side view and top view. Selected bond lengths are given in Å. The cyan region depicts the (2 × 2) surface unit cell. Blue, orange, gray, red, and green spheres represent Si, surface-chain C, subsurface C, O, and Ge atoms, respectively.

The formation of PCM-Si₂O₂ proceeds through a (2 × 1)-periodic oxygenated intermediate in which each O atom bridges a single Si–C pair, forming a linear C–Si–O chain structure. This intermediate is a local minimum on the potential-energy surface, and finite-temperature AIMD simulations show that it spontaneously reconstructs into the lower-strain (2 × 2) PCM-Si₂O₂ network. CI-NEB calculations quantify this transformation as low-barrier ($E_a = 0.25$ eV) and strongly

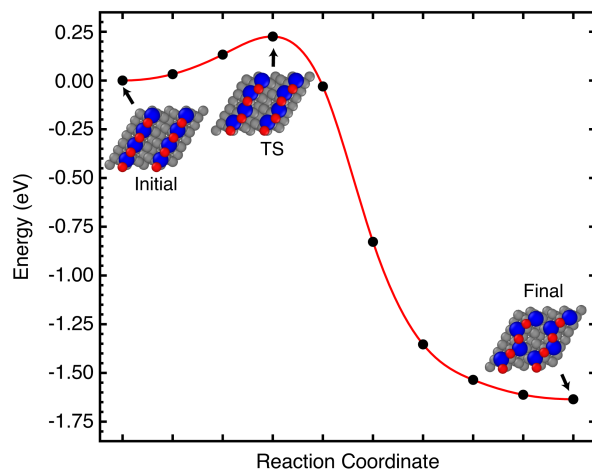


Figure 6.7: Minimum-energy pathway for the transformation from the linear (2×1) oxygenated intermediate to the reconstructed (2×2) PCM-Si₂O₂ phase on the Si-terminated surface, calculated using the CI-NEB method. The activation barrier is $E_a = 0.25$ eV and the reaction is exothermic by $\Delta E \approx -1.65$ eV. Insets show the geometries of the initial, transition, and final states along the path.

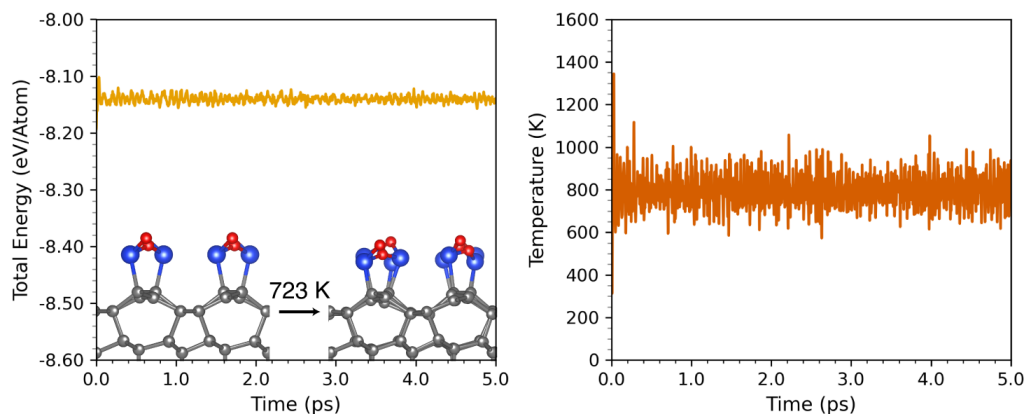


Figure 6.8: NVT AIMD total energy (left) and instantaneous temperature (right) for PCM-Si₂O₂ at 723 K over a 5 ps trajectory.

exothermic ($\Delta E \approx -1.65$ eV) (Fig. 6.7). Additional AIMD simulations at 723 K show negligible energy drift (Fig. 6.8), with the PCM-Si₂O₂ structure remaining intact over the 5 ps trajectory.

Electronic Properties

With the screened oxidized structures established, we next examine their electronic properties. Oxygen incorporation modifies the surface-state spectrum of the group-IV terminated PCM surfaces, with the strongest effect observed for the oxidized *epoxy* motif. Figure 6.9 compares the HSE06* atom-projected band structures of PCM-Si₂O₂, PCM-Si₄O₃, and PCM-Ge₂O. PCM-Si₂O₂ exhibits the largest gap among the three structures, with an indirect slab gap of 2.54 eV between the valence-band maximum at Γ and the conduction-band minimum at K. For this surface, O-derived states are concentrated in the deeper valence region, while Si-derived contributions are absent near E_F . This indicates that oxidation of the *epoxy* motif removes the Si-derived gap states present in the non-oxidized surface.

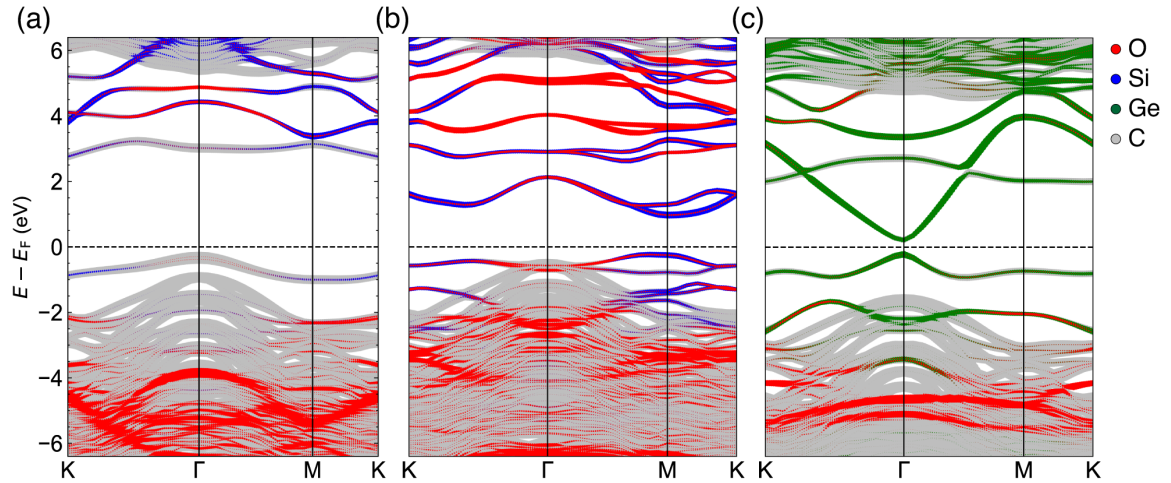


Figure 6.9: Atom-projected HSE06* band structures for (a) PCM-Si₂O₂, (b) PCM-Si₄O₃, and (c) PCM-Ge₂O. Red, blue, green, and gray projections indicate O-, Si-, Ge-, and C-derived states, respectively. The dashed horizontal line marks E_F .

PCM-Si₄O₃ has a smaller gap of 1.20 eV, with mixed Si- and O-derived surface bands appearing near the band edges and reducing the gap relative to PCM-Si₂O₂. These bands disperse across the Brillouin zone and are therefore associated with extended surface-derived states rather

than isolated flat defect levels. PCM-Ge₂O has the smallest gap of the three oxidized surfaces at 0.41 eV, and its band-edge states retain substantial Ge-derived character, showing that the Ge-O motif leaves group-IV-derived states closer to E_F than in PCM-Si₂O₂. Thus, the oxidized Si *epoxy* structure provides the clearest gapped electronic structure among the oxidized PCM surfaces considered here. The higher-coverage Si oxide and the oxidized Ge surface remain gapped, but their smaller gaps and group-IV-derived band-edge states indicate less complete removal of surface-derived states from the gap region.

The layer-resolved density of states in Fig. 6.10 further clarifies the character of the PCM-Si₂O₂ gap. The O-derived contribution from the outermost layer is concentrated mainly in the deeper valence region, and the Si-derived contribution from the second layer is weak near E_F . The states closest to the band edges are instead dominated by carbon layers near the surface. Thus, the oxidized *epoxy* structure suppresses Si-derived gap states, while the remaining band-edge states retain near-surface C character.

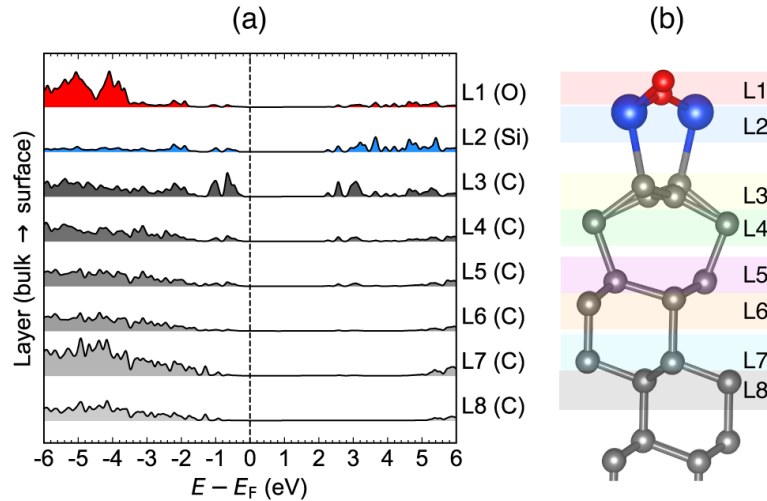


Figure 6.10: Layer-resolved projected density of states for PCM-Si₂O₂. The O-derived contribution from the outermost layer is concentrated mainly in the deeper valence region, while the states nearest the band edges are dominated by near-surface C layers. The Fermi level is set to zero.

The calculated electron affinity of PCM-Si₂O₂ is 0.49 eV (Table 6.1), slightly lower than the 0.63 eV obtained for the oxidized Si-terminated diamond (100) surface using the same electrostatic-potential alignment procedure. The corresponding planar-averaged electrostatic potentials and vacuum-level alignment are shown in Fig. 6.11. This indicates that PCM-Si₂O₂ retains a moderate positive electron affinity consistent with the oxidized Si-terminated diamond (100) surface. PCM-Si₄O₃ has a larger electron affinity of 0.92 eV, although its surface-state-dominated gap makes it a less favorable electronic endpoint than PCM-Si₂O₂. The band edges of PCM-Si₂O₂ retain near-surface C character arising from unpassivated and buckled surface carbon atoms, and these states may be relevant to the trap-state behavior reported for oxidized Si-terminated diamond (111) during MoO₃ transfer doping [122]. Thus, PCM-Si₂O₂ should be viewed as the cleanest oxidized Si-derived surface identified here, rather than as an ideal trap-free transfer-doping configuration.

For the Ge-terminated surface, PCM-Ge₂O yields an electron affinity of 0.39 eV, slightly lower than the Si oxides. From a vacuum-level alignment perspective, this moderate positive elec-

Table 6.1: Calculated electron affinities (eV) of clean, hydrogenated, group-IV terminated, and oxidized diamond (111) surfaces using the HSE06* functional. Typical literature values for calculated [64, 147] (column marked with †) and experimentally obtained [40] (column marked with ‡) electron affinities are given for comparison.

Reconstruction	Termination	Electron affinity (eV)		
		This work	Theory [†]	Expt. [‡]
(2 × 1)	Clean	+0.32	+0.32	+0.28
(2 × 1)	H	−2.15	−2.19	−
(2 × 1)	Si (<i>epoxy</i>)	−0.40	−	−
(2 × 1)	Si (<i>ketone</i>) ^a	−1.21	−	−0.76
(2 × 1)	Ge (<i>epoxy</i>)	−1.16	−	−
(2 × 2)	Si ₂ O ₂	+0.49	−	−
(2 × 2)	Si ₄ O ₃	+0.92	−	−
(2 × 2)	Ge ₂ O	+0.39	−	−

^aThe *ketone* configuration is metallic.

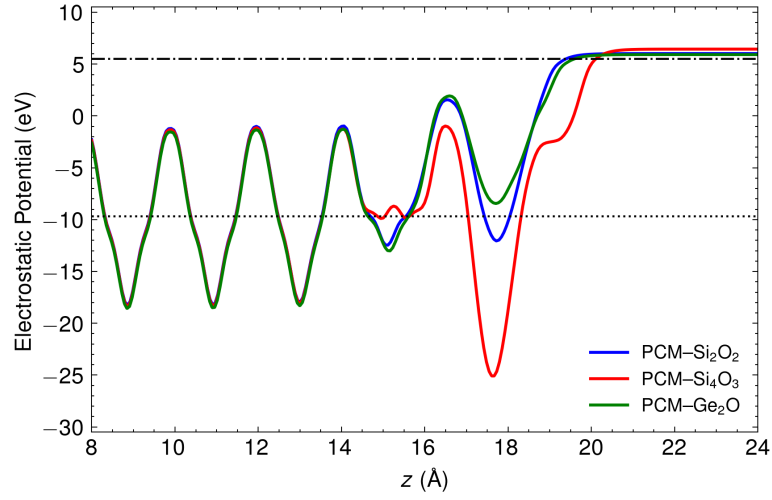


Figure 6.11: Planar-averaged electrostatic potentials for the oxidized Si- and Ge-terminated PCM diamond (111) surfaces. The vacuum levels are used to determine the electron affinities reported in Table 6.1.

tron affinity does not preclude surface transfer doping, although the resulting charge transfer depends on the acceptor alignment and the surface-state spectrum. However, the band structure shows a much smaller gap of 0.41 eV, with substantial Ge-derived character near the band edges. The cone-like dispersion near Γ confirms that these states are extended surface-derived bands rather than isolated defect levels, and their proximity to E_F makes the Ge-terminated oxide less favorable for forming a clean transfer-doped 2DHG. Thus, the Ge result reinforces the need to consider the band structure alongside the electron affinity when assessing oxidized group-IV terminations.

6.4 Conclusion

Density functional theory calculations were used to evaluate the thermodynamic stability, kinetic accessibility, and electronic structure of oxidized Si- and Ge-terminated diamond (111) surfaces derived from the experimentally observed Pandey-chain reconstruction. The results show that oxidation is strongly constrained by the reconstructed starting geometry. Consequently, the accessible oxidized phases are limited to PCM-derived structures based on the *epoxy* and *ketone* motifs, rather than the ideal unreconstructed structures considered as thermodynamic references.

For Si termination, PCM-Si₂O₂ is identified as the dominant kinetically accessible endpoint within the screened PCM-derived pathway. This phase forms through a low-barrier (2×1) to (2×2) reconstruction, is thermodynamically favorable across the oxygen chemical potentials considered, and remains intact during a 5 ps AIMD trajectory at 723 K. The predicted (2×2) periodicity is consistent with diffraction features reported after Si deposition and ambient exposure [122, 40]. Oxidation removes Si-derived gap states and opens an indirect slab gap of 2.54 eV while retaining an electron affinity of 0.49 eV. However, unlike the oxidized Si-terminated diamond (100) surface, the band edges retain near-surface C character from unpassivated and buckled surface carbon atoms. These states may be relevant to the trap-state behavior reported for oxidized Si-terminated diamond (111) during MoO₃ transfer doping [122]. Thus, PCM-Si₂O₂ is the most favorable oxidized Si-derived endpoint within the reconstruction-constrained (111) pathway, but it does not provide the same electronically clean surface obtained on diamond (100).

For Ge termination, volatile oxide formation limits the stable endpoint to PCM-Ge₂O. This surface has an electron affinity of 0.39 eV, which is lower than that obtained for oxidized Ge-terminated diamond (100). More importantly, PCM-Ge₂O retains only a small 0.41 eV gap,

with Ge-derived states near the band edges. This behavior contrasts with oxidized Ge-terminated diamond (100), where oxidation produces a much larger gap and a more electronically clean surface.

These results show that reconstruction-constrained oxidation favors Si over Ge as the more promising group-IV termination for diamond (111), although neither reconstructed pathway reproduces the favorable electronic structure obtained for oxidized group-IV terminated diamond (100).

Chapter 7

Thermodynamic Stability and Electronic Structure of TMD/GaN Interfaces

Portions of this chapter are based on unpublished work conducted in collaboration with L. Bartels and members of the Bartels group at the University of California, Riverside. This work is being prepared for publication. Cross-sectional TEM measurements and the unpublished UPS and XPS measurements discussed in this chapter were obtained by collaborators in the Bartels group. All DFT calculations presented in this chapter were performed by the author.

7.1 Introduction

The preceding chapters used first-principles thermodynamics to identify stable diamond surface structures under chemically realistic conditions. For diamond, this approach showed that the relevant electronic structure is determined by the termination or oxidation motif that is thermodynamically stable and compatible with the reconstructed surface. This chapter extends the same thermodynamic structure-selection approach from diamond surfaces to buried TMD/GaN interfaces, with the goal of identifying the atomic interface configurations of MoS₂/GaN and NbS₂/GaN

that are consistent with cross-sectional transmission electron microscopy (TEM) measurements. The TEM measurements establish the interfacial spacing and registry of the TMD overlayer relative to GaN, but they do not uniquely determine the interfacial stoichiometry or bonding arrangement. Grand-canonical first-principles calculations are therefore used to screen candidate interface structures against both thermodynamic stability and TEM-derived geometric constraints. Once the most likely interface configurations are identified, their bonding, finite-temperature stability, charge redistribution, and electronic structure are evaluated. The integration of two-dimensional transition metal dichalcogenide (TMD) overlayers with III-nitride semiconductors offers a route toward mixed-dimensional electronic and optoelectronic heterostructures [188, 189]. Among these systems, MoS₂/GaN is particularly attractive because the in-plane lattice constants of MoS₂ and wurtzite GaN differ by only 0.9% [42, 43]. By comparison, NbS₂ has a larger lattice constant, corresponding to a 3.8% mismatch with GaN [44]. These two systems therefore provide a useful comparison for determining how closely related TMD overlayers form distinct interfaces on the same semiconductor substrate.

Prior work has shown that interface preparation is a key variable in MoS₂/GaN heterostructures. In work from the Bartels group, Yang et al. demonstrated that optimized in situ surface preparation and ammonia treatment yield a clean nitrogen-terminated GaN surface, a well-ordered 2×2 interfacial reconstruction, and close adhesion of MoS₂ to GaN [190]. In a separate study, Zhang et al. showed that nitridation of the GaN surface can introduce an interfacial N-adatom layer that changes both the stable adsorption geometry and the electronic structure of monolayer MoS₂/GaN [191]. These studies motivate treating the interface not as a generic pristine van der Waals stack, but as a chemically sensitive structure shaped by pretreatment and growth conditions.

Recent experimental work from the Bartels group has further shown that GaN imposes epitaxial registry on sequentially grown TMD heterostructures, with orientational order propagating through the entire stack across materials of disparate lattice parameters and electronic characters. The DFT analysis in this chapter evaluates whether chemically coordinated TMD/GaN interfaces provide an atomic-level basis for anchoring the first TMD layer under realistic growth conditions. In this chapter, cross-sectional TEM measurements obtained through collaboration with the Bartels group at the University of California, Riverside establish the contrasting interface geometries of MoS₂/GaN and NbS₂/GaN. Grand-canonical DFT calculations are then used to identify the thermodynamically favored interfacial stoichiometries that are consistent with these TEM-derived constraints. The selected interface models are used to characterize the interfacial bonding, assess finite-temperature stability, and evaluate charge redistribution and electronic structure at the TMD/GaN interfaces.

7.2 Computational Methods

All DFT calculations follow the methodology described in Chapter 2. Calculations were performed using VASP with the PBE functional, a plane-wave cutoff of 520 eV, a Γ -centered $5 \times 5 \times 1$ k -mesh, and DFT-D3(BJ) dispersion corrections to account for van der Waals interactions. Structural relaxations were converged until residual forces fell below 10^{-3} eV/Å. GaN slab models were constructed as 2×2 supercells of wurtzite GaN with six GaN bilayers ($a = b = 6.378$ Å), with a vacuum region of at least 20 Å. Multiple GaN interface terminations were considered, including Ga- and N-terminated surfaces constructed from the (0001) and (000 $\bar{1}$) orientations. The non-interacting bottom surface was passivated with fractional pseudo-hydrogen atoms chosen ac-

cording to the electron-counting rule: $Z_H = 1.25$ for Ga dangling bonds and $Z_H = 0.75$ for N dangling bonds. Interface formation energies were evaluated using the grand-canonical approach described in Section 2.5.3, with nitrogen and sulfur chemical potentials referenced to the NH_3/H_2 and $\text{H}_2\text{S}/\text{H}_2$ gas-phase equilibria at $T = 1053 \text{ K}$ ($\approx 780^\circ\text{C}$). Experimentally motivated partial pressures of $p_{\text{NH}_3} = 1.3 \times 10^{-3} \text{ Torr}$ and $p_{\text{H}_2\text{S}} = 2.5 \times 10^{-3} \text{ Torr}$ were used, with a base chamber pressure of 10^{-6} Torr corresponding to the NH_3 -off and H_2S -off condition. Ab initio molecular dynamics simulations were performed at $T = 1053 \text{ K}$ for 8 ps using a Nosé–Hoover thermostat and a 1 fs timestep.

7.3 Experimental TEM Characterization

7.3.1 Contrasting Interface Structures in MoS_2/GaN and NbS_2/GaN

Cross-sectional TEM measurements, obtained through collaboration with the Bartels group at the University of California, Riverside, show that MoS_2/GaN and NbS_2/GaN form qualitatively different interfaces within the corresponding TMD heterostructure stacks. In the MoS_2/GaN heterostructure [Fig. 7.1(a)], the first MoS_2 layer is epitaxial to the GaN surface, and the overlying TMD layers remain aligned with the substrate-imposed registry. No misfit dislocations or lateral registry shifts are observed. The measured Ga–Mo vertical separation is $\Delta z(\text{Ga–Mo}_1) = 2.8 \pm 0.5 \text{ \AA}$. The Mo_1 – Mo_2 interlayer separation is $5.2 \pm 0.5 \text{ \AA}$, consistent with bulk-like MoS_2 layer spacing. The compact Ga–Mo separation indicates stronger interfacial coupling than expected for a weakly bound van der Waals junction.

By contrast, the NbS_2/GaN heterostructure exhibits a larger interfacial separation [Fig. 7.1(b)]. The measured Ga–Nb vertical separation for the first NbS_2 layer is $\Delta z(\text{Ga–Nb}_1) = 3.9 \pm 0.6 \text{ \AA}$. The

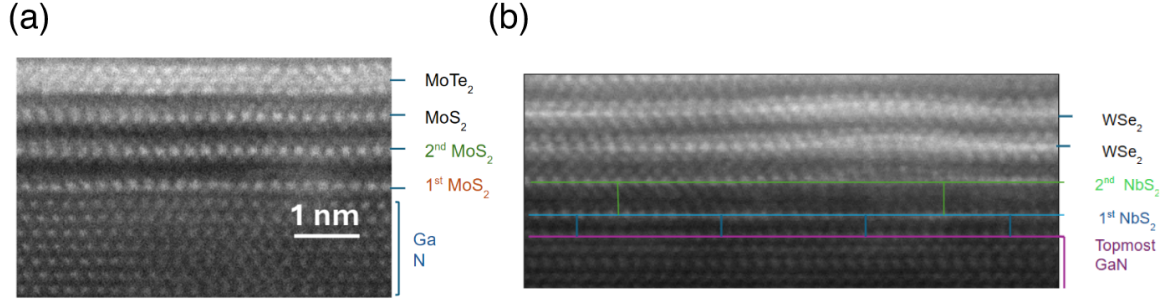


Figure 7.1: Cross-sectional TEM images of the TMD/GaN interfaces. (a) MoS₂/GaN interface within the MoTe₂/MoS₂/GaN heterostructure stack. The measured vertical separations are $\Delta z(\text{Ga}-\text{Mo}_1) = 2.8 \pm 0.5 \text{ \AA}$ and $\Delta z(\text{Mo}_1-\text{Mo}_2) = 5.2 \pm 0.5 \text{ \AA}$. (b) NbS₂/GaN interface within the MoTe₂/WSe₂/NbS₂/GaN heterostructure stack. The measured vertical separations are $\Delta z(\text{Ga}-\text{Nb}_1) = 3.9 \pm 0.6 \text{ \AA}$ and $\Delta z(\text{Nb}_1-\text{Nb}_2) = 6.1 \pm 0.6 \text{ \AA}$. Measurements were obtained through collaboration with the Bartels group, University of California, Riverside.

Nb₁-Nb₂ interlayer separation is $6.1 \pm 0.6 \text{ \AA}$, consistent with bulk-like NbS₂ layer spacing. Despite the larger interfacial separation and lattice mismatch, the NbS₂ layer remains laterally aligned with the GaN substrate. The preserved registry is consistent with interfacial anchoring of the first NbS₂ layer and propagation of the substrate-imposed orientation through the overlying TMD stack.

7.4 Results and Discussion

7.4.1 MoS₂/GaN Interface Model Screening Constrained by TEM

The MoS₂/GaN candidate set was generated from several GaN starting surfaces, shown schematically in Fig. 7.2. These include Ga-polar and N-polar GaN terminations, as well as a nitrogen-interlayer (NIL) configuration on Ga-polar GaN. The Ga-polar (0001) surface is systematically lower in energy than the N-polar (000 $\bar{1}$) surface across the full range of growth conditions considered [192], and is therefore the primary surface of interest. The N-polar termination was nonetheless included to assess whether N-polar intermixed configurations could satisfy the TEM-

derived geometric constraint. The NIL model was included because ammonia treatment precedes MoS₂ growth, and prior work by Zhang et al. showed that an interfacial N-adatom layer can modify the adsorption geometry and electronic structure of monolayer MoS₂/GaN [191].

Although the NIL configuration is metastable on the bare Ga-polar surface, it can be stabilized by the overlying MoS₂ layer and therefore provides a relevant starting point for interface screening. In this configuration, the N adatom layer forms a direct N–S bond rather than a pure van der Waals contact, and the interface is therefore covalently chemisorbed rather than physisorbed.

Four classes of interface configuration were considered for each starting surface. Pristine van der Waals structures place an intact MoS₂ layer directly on the GaN surface with no chemical modification. Intermixed structures replace one or more of the interfacial N atoms with S atoms from the MoS₂ bottom layer, forming direct Ga–S bonds at the interface. Exchange structures swap N and S atoms between the GaN surface and the MoS₂ bottom layer without net substitution. Substitutional structures replace interfacial N atoms with S atoms directly into the GaN lattice sites rather than at the interface layer.

The motivation for this screening is that the TEM-derived Ga–Mo spacing is too small to be explained by a pristine van der Waals stack. Even in an ideal registry, the expected separation between a terminal GaN surface layer and the first Mo plane of an intact MoS₂ layer would exceed the measured value if the layers were separated by a weak vdW gap. The compact spacing therefore suggests that the experimental interface involves interfacial reconstruction, chemical intermixing, or partial replacement of the nominal bottom S layer of MoS₂.

Using the plausible nitridated surfaces shown in Fig. 7.2(b) and (c) as starting points, pristine vdW, substitutional, exchange, and intermixed interface configurations were tested. Figure 7.3

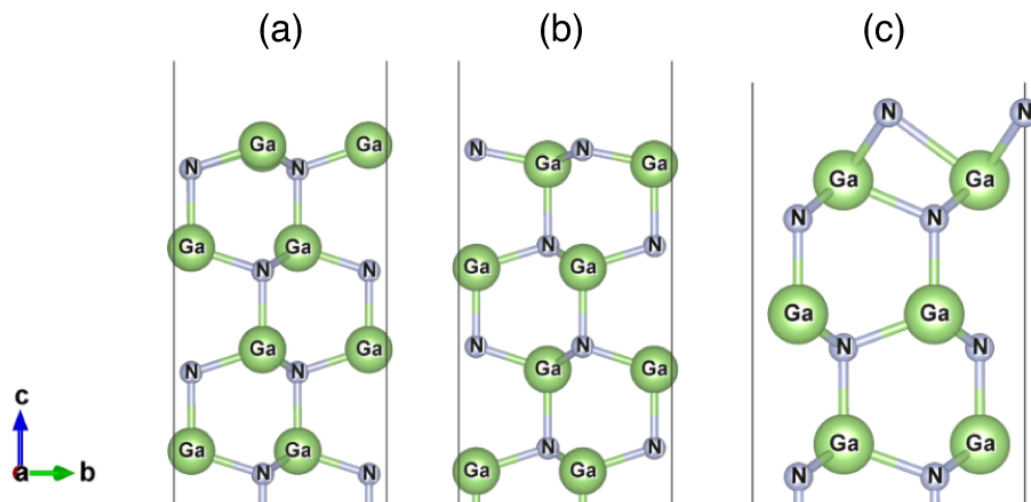


Figure 7.2: GaN starting surface configurations used to construct MoS₂/GaN interface candidates. The model set includes (a) Ga-polar (0001) GaN, (b) N-polar (000 $\bar{1}$) GaN, and (c) a nitrogen-interlayer (NIL) configuration on Ga-polar GaN. Nitrogen-containing starting configurations were included to represent possible effects of ammonia-treated growth conditions prior to MoS₂ deposition.

shows the Ga–Mo vertical separation for all screened models grouped by interfacial stoichiometry. Substitutional and exchange models relax to Ga–Mo separations of approximately 4.4–7.0 Å, well outside the TEM-derived window of 2.3–3.3 Å, and are therefore excluded from further consideration. The screening analysis below focuses on intermixed models, with pristine vdW structures retained only as reference configurations.

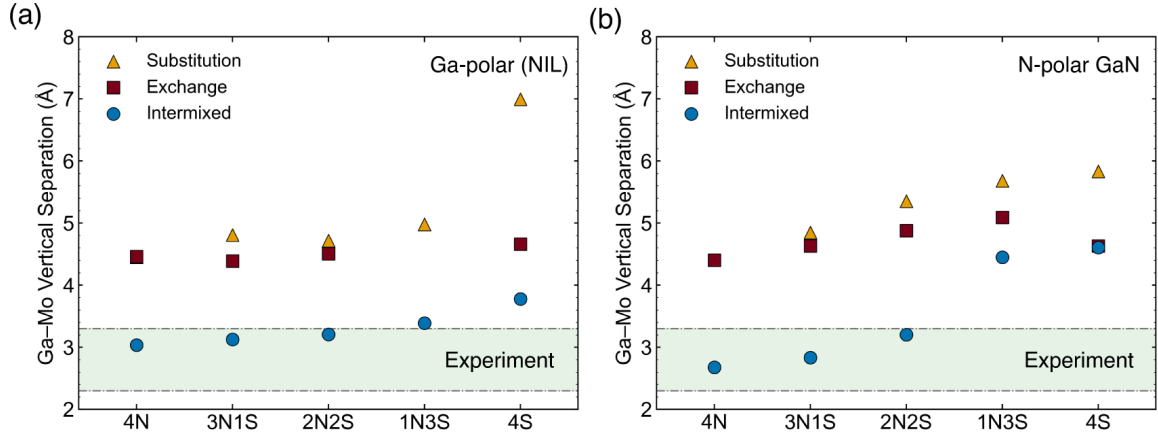


Figure 7.3: Ga–Mo vertical separations for the screened MoS₂/GaN interface models, grouped by interfacial stoichiometry for (a) NIL-GaN and (b) N-polar GaN. Blue circles, red squares, and gold triangles indicate intermixed, exchange, and substitutional configurations, respectively. The green shaded region indicates the TEM-consistent range of 2.3–3.3 Å, based on the measured Ga–Mo separation of 2.8 ± 0.5 Å. Exchange and substitutional configurations lie outside this range and are excluded from further analysis.

Figure 7.4 compares the surviving intermixed models in terms of grand-canonical interface formation energy and Ga–Mo vertical separation. Each model is labeled by its interfacial stoichiometry, where the prefix indicates polarity (Ga- or N-polar) and the suffix denotes the number of N and S atoms at the interface, for example Ga-3N1S refers to a Ga-polar intermixed structure with three interfacial N atoms and one S atom. The Ga-polar intermixed models are the only candidates satisfying both the TEM-derived geometric constraint and thermodynamic favorability under the reference growth conditions. Among these, Ga-3N1S, Ga-4N, and Ga-2N2S exhibit low formation energies with Ga–Mo separations of 3.13, 3.04, and 3.21 Å, respectively, placing them within the TEM-supported range. Ga-3N1S is the lowest-energy structure under the reference thermodynamic conditions and is therefore identified as the most likely interface configuration. The energetic ordering of the screened models is listed in Table 7.1.

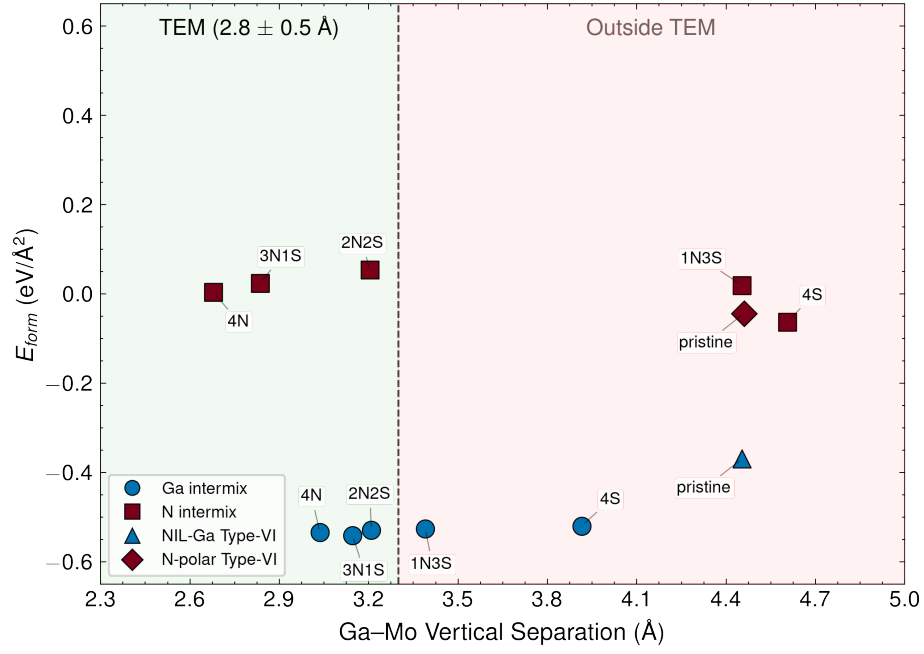


Figure 7.4: Grand-canonical interface formation energy E_{form} vs. Ga–Mo vertical separation for the screened MoS_2/GaN interface models. Blue circles denote Ga-polar intermixed structures, red squares denote N-polar intermixed structures, blue triangles denote Ga-polar pristine vdW reference structures, and red diamonds denote N-polar pristine vdW reference structures. The green shaded region marks the TEM-consistent range of $2.3\text{--}3.3\text{ \AA}$, based on the experimental interfacial spacing of $2.8 \pm 0.5\text{ \AA}$.

Table 7.1: Grand-canonical stability ranking of MoS_2/GaN interface models at $T = 1053\text{ K}$.

Rank	Structure	Interface type	E_{DFT} (eV)	Ga–Mo Δz (Å)	E_{form} (eV/Å ²)
1	Ga-3N1S	intermix	−391.7736	3.130	−0.5415
2	Ga-4N	intermix	−395.3541	3.036	−0.5340
3	Ga-2N2S	intermix	−387.4891	3.209	−0.5291
4	Ga-1N3S	intermix	−383.5587	3.390	−0.5268
5	Ga-4S	intermix	−378.9967	3.915	−0.5065
6	Ga-pristine	vdW	−407.9050	4.453	−0.3694
7	N-4S	intermix	−405.9927	4.606	−0.0629
8	N-pristine	vdW	−439.0535	4.460	−0.0437
9	N-4N	intermix	−419.0314	2.678	+0.0038
10	N-1N3S	intermix	−406.9496	4.453	+0.0191
11	N-3N1S	intermix	−414.4739	2.836	+0.0240
12	N-2N2S	intermix	−409.5855	3.204	+0.0535

7.4.2 Growth-Relevant Phase Stability of the MoS₂/GaN Interface

The three Ga-intermixed candidates that satisfy both the energetic and geometric criteria were evaluated across the full experimentally relevant chemical-potential space. Figure 7.5 shows the resulting phase diagram as a function of $\Delta\mu_N$ and $\Delta\mu_S$ at $T = 1053$ K.

Two stability fields emerge from the phase diagram: Ga-4N under N-rich, S-poor conditions and Ga-3N1S at elevated sulfur chemical potential. Operating points (1) and (2) correspond to the active nitridation step and the transition between nitridation and sulfurization. Introduction of H₂S at operating point (3) shifts the sulfur chemical potential into the 3N1S stability field. Under the final sulfurization conditions, Ga-3N1S is the most favorable interfacial stoichiometry and remains consistent with the TEM-derived Ga–Mo spacing.

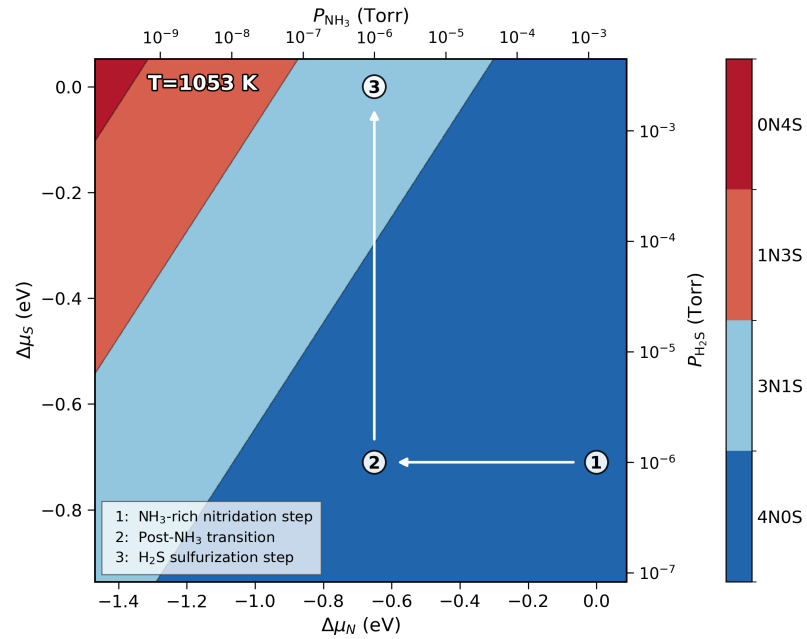


Figure 7.5: Grand-canonical phase diagram for Ga-polar MoS₂/GaN interface candidates at $T = 1053$ K. Top and right axes show NH₃ and H₂S partial pressures. Operating points: (1) NH₃ on, H₂S off; (2) both off; (3) NH₃ off, H₂S on.

7.4.3 Finite-Temperature Stability of the Ga-3N1S Interface

AIMD simulations were performed at $T = 1053$ K for 8 ps to assess the thermal stability of the Ga-3N1S MoS₂/GaN interface (Fig. 7.6). The interface remains structurally intact throughout the simulation, with no evidence of reconstruction, indicating stability at the growth temperature over the simulated timescale.

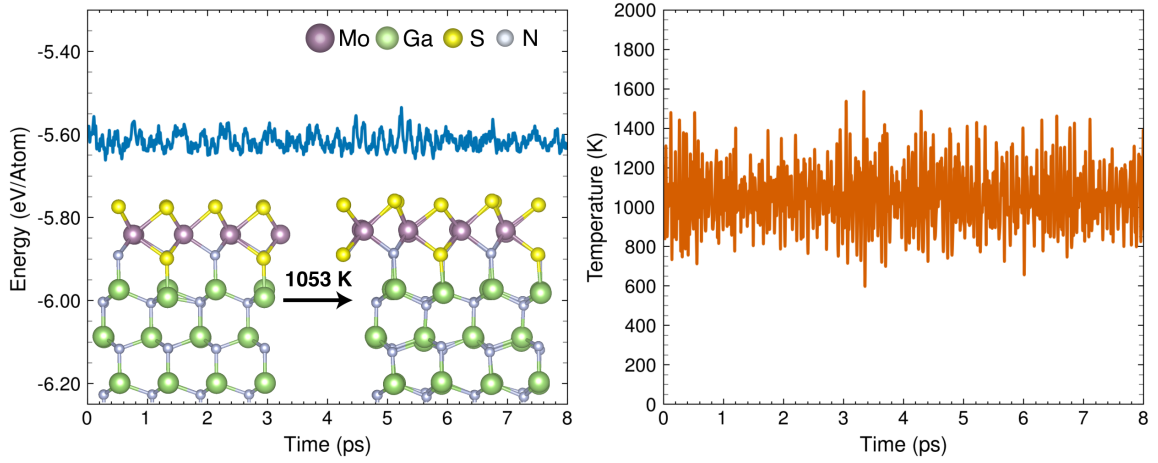


Figure 7.6: AIMD thermal stability test of the Ga-3N1S MoS₂/GaN interface at $T = 1053$ K over 8 ps. The interface remains structurally intact throughout the trajectory.

7.4.4 NbS₂/GaN Interface Screening and Comparison

For NbS₂/GaN, only intermixed and exchange structures were evaluated. Figure 7.7 shows the interface formation energy as a function of Ga–Nb vertical separation for the two structure classes. The TEM-derived reference spacing is 3.9 ± 0.6 Å.

The Ga-4S intermixed structure is both the lowest-energy candidate and consistent with the measured spacing. Its formation energy is approximately -0.64 eV/Å², and its Ga–Nb separa-

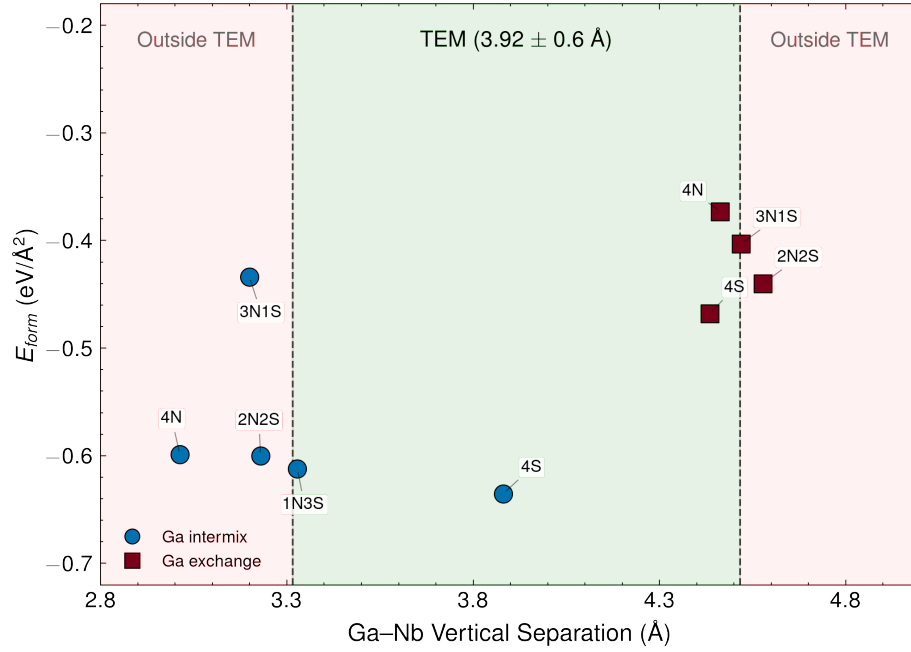


Figure 7.7: Ga–Nb vertical separation for NbS₂/GaN interface models under the final H₂S sulfuration condition. Circles: Ga-polar intermixed; Squares: Ga-polar exchange. The green region indicates the TEM-consistent range based on 3.9 ± 0.6 Å.

tion is 3.88 Å, in excellent agreement with TEM. Exchange structures are consistently less favorable and cluster at larger Ga–Nb separations of 4.4–4.9 Å. The energetic ordering is listed in Table 7.2.

Table 7.2: Grand-canonical stability ranking of NbS₂/GaN interface models at the chemical potential corresponding to the H₂S sulfurization step at $T = 1053$ K.

Rank	Structure	Interface type	E_{DFT} (eV)	Ga–Nb Δz (Å)	E_{form} (eV/Å ²)
1	Ga-4S	intermix	−382.032885	3.880	−0.6354
2	Ga-1N3S	intermix	−385.062298	3.328	−0.6122
3	Ga-2N2S	intermix	−388.488806	3.229	−0.6003
4	Ga-4N	intermix	−396.126279	3.013	−0.5987
5	Ga-4S	exchange	−409.876244	4.435	−0.4681
6	Ga-2N2S	exchange	−408.892189	4.577	−0.4402
7	Ga-3N1S	intermix	−386.471683	3.199	−0.4338
8	Ga-3N1S	exchange	−407.587271	4.519	−0.4032
9	Ga-4N	exchange	−406.528218	4.462	−0.3731

7.4.5 Growth-Relevant Phase Stability of the NbS₂/GaN Interface

The NbS₂/GaN interface was evaluated using the same grand-canonical structure-selection approach applied to MoS₂/GaN. The resulting NbS₂/GaN phase space is simpler than the MoS₂/GaN case. Although mixed N/S candidates were included in the screening, the ground-state phase diagram is controlled by the two end-member configurations, Ga-4N and Ga-4S. Figure 7.8 shows the resulting phase diagram as a function of $\Delta\mu_N$ and $\Delta\mu_S$ at $T = 1053$ K.

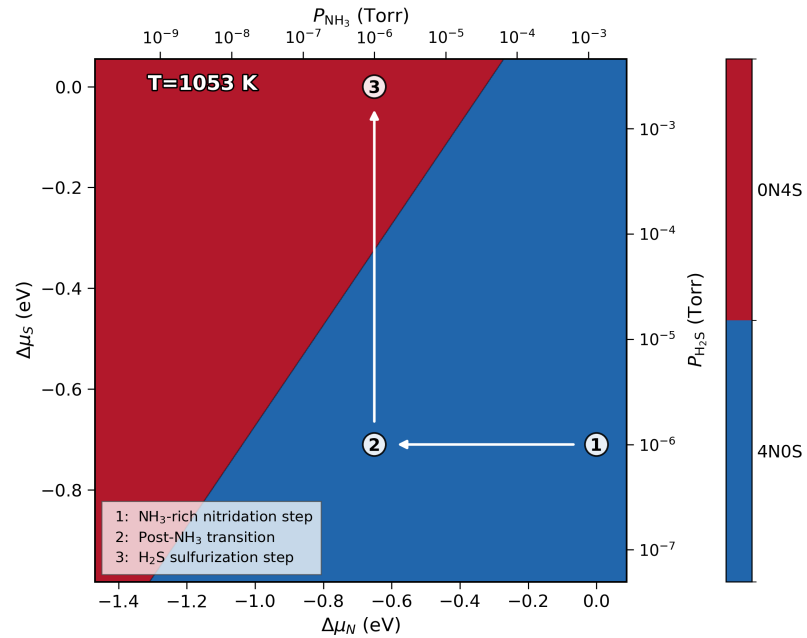


Figure 7.8: Grand-canonical phase diagram for Ga-polar NbS₂/GaN interface candidates at $T = 1053$ K. Top and right axes show NH₃ and H₂S partial pressures. The stable phase space is dominated by the end-member Ga-4N and Ga-4S configurations.

Under N-rich, S-poor conditions the Ga-4N interface is favored, while increasing the sulfur chemical potential stabilizes Ga-4S as the thermodynamically favored NbS₂/GaN stoichiometry under the final sulfurization conditions. This structure is consistent with the TEM-derived Ga–Nb spacing and is therefore identified as the most likely NbS₂/GaN interface configuration.

The key distinction between the two systems is the absolute interfacial separation: the favored MoS₂/GaN models lie near 3.0–3.2 Å, whereas the favored NbS₂/GaN interface sits near 3.9 Å. This larger separation is consistent with comparatively weaker interfacial coupling in NbS₂/GaN than in MoS₂/GaN. TEM measurements nevertheless show that substrate-imposed registry is preserved through the NbS₂-containing heterostructure stack.

7.4.6 Electronic Reconstruction at the MoS₂/GaN Interface

Charge-density-difference (CDD) analysis was used to characterize the electronic reconstruction associated with the selected Ga-3N1S interface. Figure 7.9 shows the cross-sectional CDD, the integrated charge-transfer profile, and the relaxed atomic structure of the Ga-3N1S MoS₂/GaN interface. The cross-sectional $\Delta\rho(x,z)$ map in Fig. 7.9(a) shows that charge redistribution is concentrated at the reconstructed interface. Electron depletion is localized near the GaN surface region, while electron accumulation appears on the MoS₂ side near the first Mo layer. The spatial separation between depletion and accumulation indicates an interfacial dipole associated with the reconstructed Ga-3N1S bonding environment. The planar-averaged CDD profile in Fig. 7.9(b) quantifies this redistribution along the surface normal. The largest positive and negative contributions occur within the interfacial region bounded by the topmost Ga layer and the first Mo plane. The running integral $\int \Delta\rho dz$ shows the net charge displacement across the interface and converges to zero away from the interface, confirming that the redistribution is spatially localized. Figure 7.9(c) shows the relaxed atomic structure corresponding to the CDD analysis. The compact Ga-3N1S geometry places the reconstructed interfacial layer directly between the GaN surface and the overlying MoS₂ layer, spanning approximately 3.13 Å. The relaxed structure shows direct interfacial coordination, while the charge-density map and integrated profile show that the associated charge redistribution is con-

fined to within a few angstroms of the MoS₂/GaN boundary. These results are consistent with a covalently reconstructed interface rather than a pristine van der Waals contact.

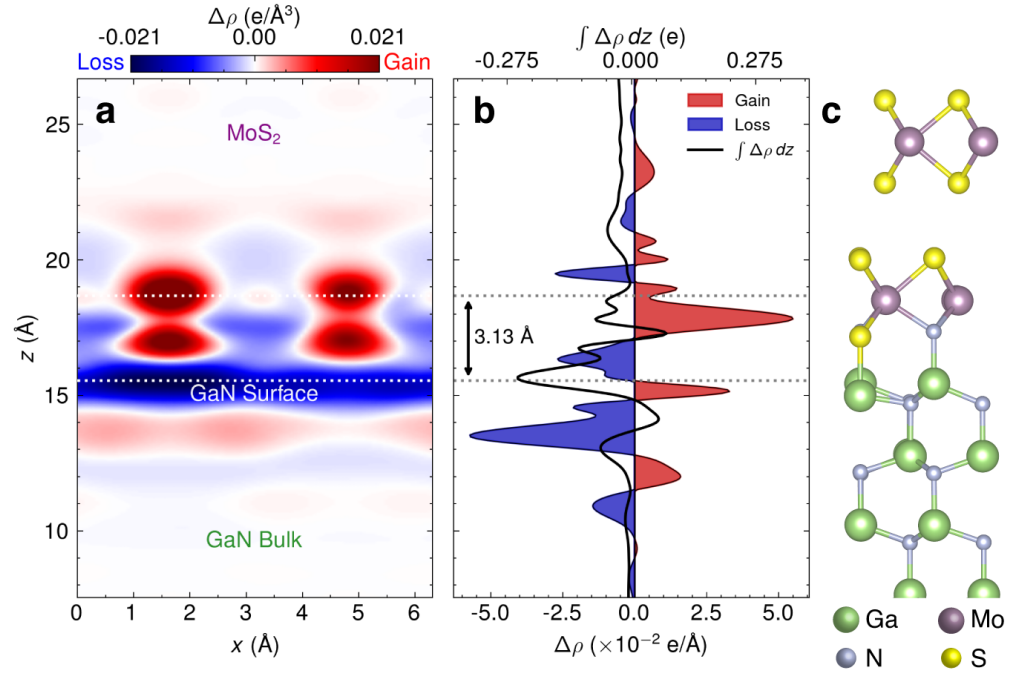


Figure 7.9: CDD analysis of the Ga-3N1S MoS₂/GaN interface. (a) Cross-sectional $\Delta\rho(x, z)$ map. (b) Planar-averaged $\Delta\rho(z)$ and integrated charge displacement $\int \Delta\rho dz$, with dashed gray lines marking the 3.13 $\text{\AA}$ interfacial region. (c) Relaxed atomic structure of the reconstructed interface.

The per-layer charge decomposition shown in Fig. 7.10 further resolves the charge redistribution by structural region, using a larger MoS₂ slab to confirm convergence of the charge transfer beyond the four-layer models used in the preceding figures. The interfacial layer shows the strongest charge redistribution, with substantial accumulation and depletion that largely offset one another. The resulting small net charge is consistent with a covalently bonded transition layer rather than a simple charge donor or acceptor. The GaN surface region shows a net negative charge, indicating electron loss to the interface. Subsequent MoS₂ layers show progressively smaller net charge, consistent with electrostatic screening away from the interface.

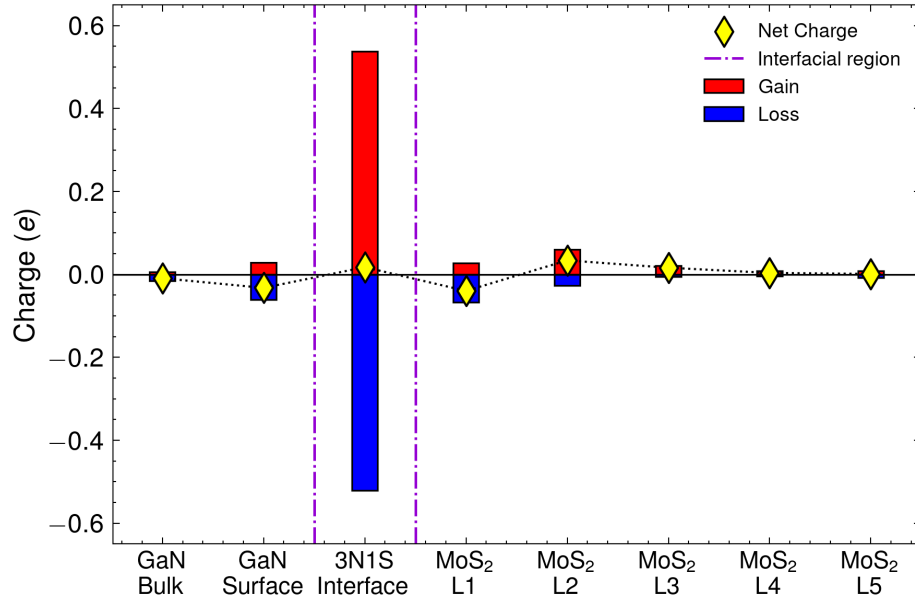


Figure 7.10: Per-layer charge transfer decomposition for the Ga-3N1S MoS₂/GaN interface. Red and blue bars denote charge accumulation (gain) and depletion (loss) within each region, respectively, and yellow diamonds connected by a dashed line indicate the net charge transfer. Purple dashed lines mark the boundaries of the covalent interfacial region between the topmost Ga and bottommost Mo atoms. The five overlying MoS₂ bilayers are labeled L1–L5.

The electrostatic potential alignment yields $\Delta V = V_{\text{MoS}_2} - V_{\text{GaN}} \approx -0.09$ eV, with the MoS₂ side lying slightly lower in potential than GaN. This negative step is consistent with the net electron transfer from GaN toward the MoS₂ side indicated by the CDD analysis, and its small magnitude reflects the dipolar character of the charge redistribution at the reconstructed interface. Applying the Kraut method [193] yields a valence band offset of -0.34 eV and a conduction band offset of $+0.16$ eV, corresponding to a type-I alignment in which the MoS₂ gap is nested within the GaN gap.

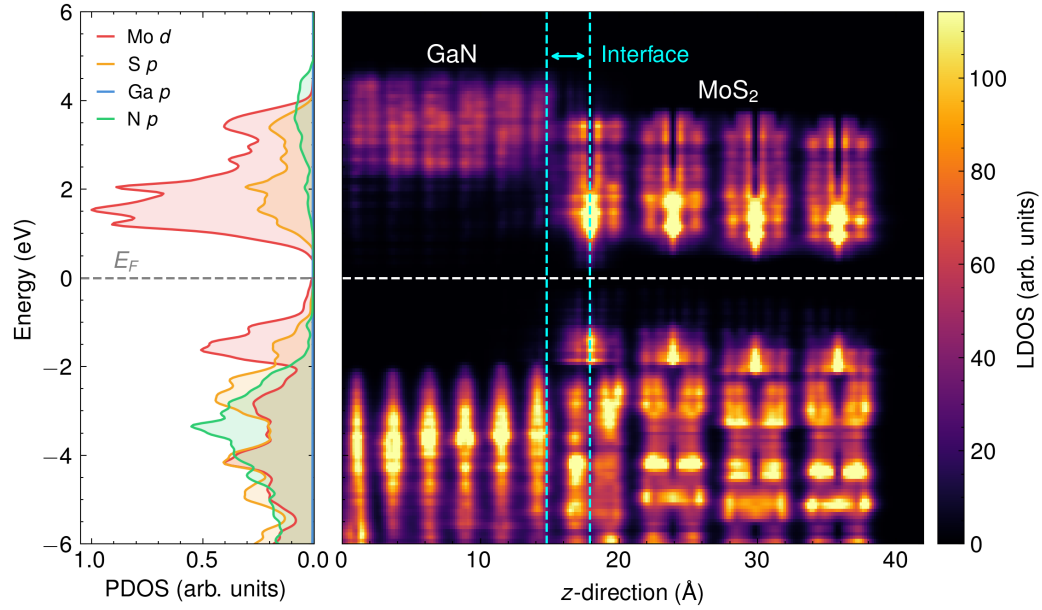


Figure 7.11: Orbital-projected DOS and layer-resolved LDOS for the Ga-3N1S MoS₂/GaN heterostructure. PDOS curves are normalized to the maximum of each species. Dashed lines mark the Fermi level and interface position.

7.4.7 Layer-Resolved Electronic Structure of the Ga-3N1S MoS₂/GaN Interface

Figure 7.11 shows the orbital-projected density of states alongside the layer-resolved local density of states for the Ga-3N1S MoS₂/GaN heterostructure. The bright features between +1.0 and +1.5 eV on the MoS₂ side of the interface are identified as Mo 4*d* conduction-band states. The GaN region shows negligible spectral weight between approximately −2.0 and +2.0 eV, consistent with its wide band gap. The Fermi level lies near the MoS₂ conduction-band edge, while the electrostatic-potential offset yields a type-I band alignment. The MoS₂ valence-band edge visible in the LDOS map shifts to lower energy with increasing distance from the interface, indicating that the interfacial MoS₂ layers exhibit a more p-type electronic environment relative to the bulk-like layers farther from the junction. This trend is consistent with unpublished UPS and XPS measurements from the Bartels group, which show a shift of the MoS₂ valence-band maximum to lower binding energy at

the GaN interface and a secondary Mo $3d$ spectral component that decreases with increasing MoS₂ thickness. These measurements indicate distinct interfacial and upper-layer Mo environments. The LDOS map also shows that the interface-induced spectral features closest to E_F are concentrated within the first two MoS₂ layers, with bulk-like character recovering progressively farther from the interface. The LDOS and CDD results indicate that the reconstructed Ga-3N1S interface produces localized charge redistribution associated with Mo $4d$ -derived states and reconstructed interfacial bonding. This localized redistribution should be distinguished from a spatially extended electron-accumulation layer in MoS₂. The electronic properties of the MoS₂/GaN junction are therefore sensitive to interfacial stoichiometry and change with the nitridation and sulfurization conditions used during growth.

7.4.8 Electronic Structure Comparison with the NbS₂/GaN Interface

The same CDD analysis was applied to the selected Ga-4S NbS₂/GaN interface to compare its electronic reconstruction with that of Ga-3N1S MoS₂/GaN. The CDD map in Fig. 7.12(a) shows that charge redistribution remains localized near the interface. However, the separation between the topmost Ga layer and the first Nb plane is 3.88 Å, larger than the 3.13 Å interfacial width obtained for Ga-3N1S MoS₂/GaN. This larger spacing is consistent with the TEM-measured separation and establishes that the selected NbS₂/GaN interface is less compact than the reconstructed MoS₂/GaN interface. The planar-averaged profile and running integral in Fig. 7.12(b) show that the charge displacement remains localized near the interface and returns toward zero away from the interfacial region. Thus, the selected NbS₂/GaN interface exhibits localized interfacial charge redistribution, but with a larger equilibrium separation than the MoS₂/GaN interface.

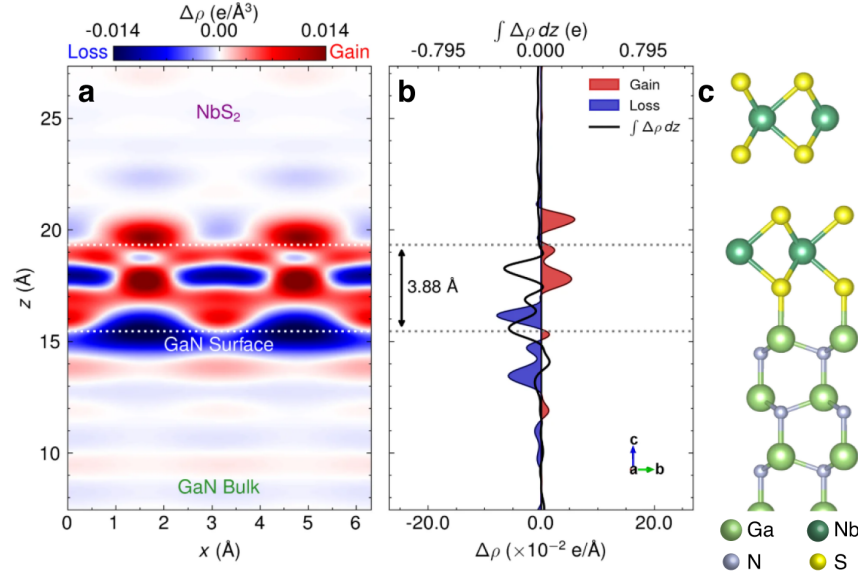


Figure 7.12: CDD analysis of the Ga-4S NbS₂/GaN interface. (a) Cross-sectional $\Delta\rho(x, z)$ map. (b) Planar-averaged $\Delta\rho(z)$ and integrated charge displacement $\int \Delta\rho dz$, with dashed gray lines marking the 3.88 Å interfacial region. (c) Relaxed atomic structure of the selected NbS₂/GaN interface.

The corresponding orbital-projected DOS and layer-resolved LDOS are shown in Fig. 7.13.

States near E_F are dominated by Nb d contributions on the NbS₂ side of the interface, while the GaN region shows little spectral weight near E_F . This indicates that the selected NbS₂/GaN interface largely retains the metallic electronic structure of the NbS₂ overlayer. In contrast to Ga-3N1S MoS₂/GaN, where charge redistribution and Mo-derived states are concentrated near the compact reconstructed interface, the Ga-4S NbS₂/GaN interface has a larger equilibrium separation and retains predominantly NbS₂-derived states near E_F . This comparison supports the structural and electronic distinction between the two selected interfaces. MoS₂/GaN forms a compact reconstructed interface, whereas NbS₂/GaN forms a larger-separation interface whose states near E_F remain primarily NbS₂-derived.

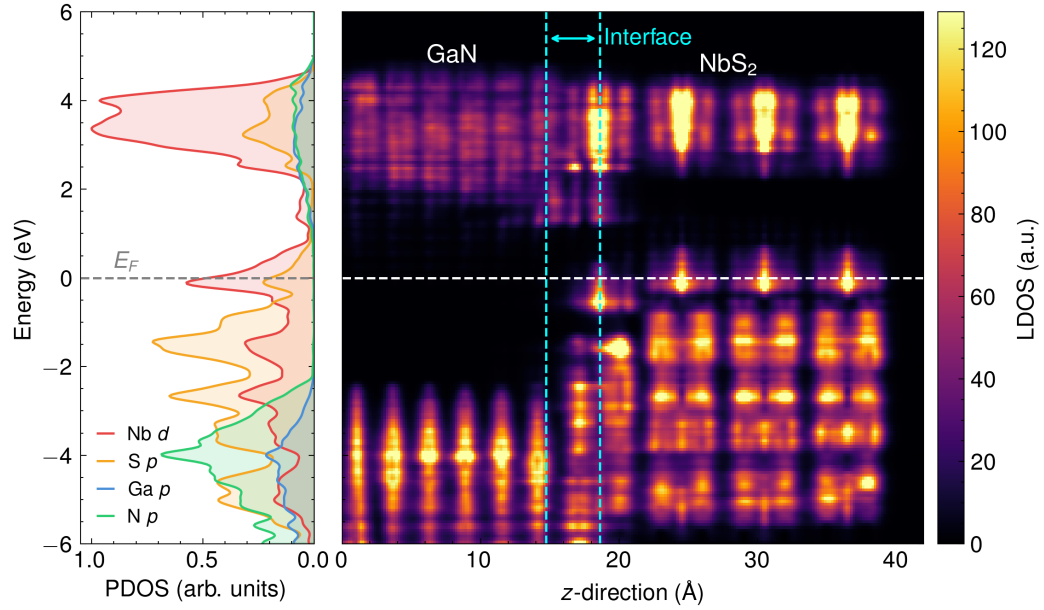


Figure 7.13: Orbital-projected DOS and layer-resolved LDOS for the selected Ga-4S NbS₂/GaN interface. The dashed horizontal line marks E_F , and the dashed cyan lines mark the interfacial region.

7.5 Conclusion

TEM measurements show that substrate-imposed registry is preserved through both TMD heterostructure stacks. First-principles thermodynamic screening identifies distinct atomic configurations at the underlying MoS₂/GaN and NbS₂/GaN interfaces. The favored MoS₂/GaN interface is compact and reconstructed, whereas the favored NbS₂/GaN interface has a larger equilibrium separation.

For MoS₂/GaN, TEM-constrained grand-canonical screening excludes pristine van der Waals models and identifies Ga-polar reconstructed interfaces as the only candidates that simultaneously satisfy the energetic and geometric constraints. Among these, Ga-3N1S is the most favorable structure under the final sulfurization conditions. AIMD supports the finite-temperature stability of this interface over the simulated timescale, and CDD analysis shows that it is electronically distinct

from a pristine van der Waals contact. Electron redistribution is tightly confined to the 3.13 Å interfacial region between the topmost Ga layer and the first Mo plane, with net charge transfer directed from the GaN slab toward the reconstructed interface and overlying MoS₂ stack. Layer-resolved LDOS and orbital-projected DOS further show that Mo 4*d*-derived states near the conduction-band edge are concentrated within the first two MoS₂ layers of the interface.

For NbS₂/GaN, the thermodynamically favored structure is likewise consistent with the experimentally measured spacing, but the selected interface remains centered near 3.9 Å, substantially farther out than the favored MoS₂/GaN structures. The corresponding LDOS shows that states near E_F remain primarily NbS₂-derived. The key distinction between the two systems is that the favored MoS₂/GaN interface is substantially more compact and undergoes stronger electronic reconstruction than the favored NbS₂/GaN interface. This comparison reinforces a central conclusion of this dissertation: the relevant electronic properties are governed by the chemically realistic interface selected under growth conditions rather than by an idealized van der Waals model. The chemically coordinated interface configurations identified here provide a plausible atomic-level basis for substrate-induced registry propagation through TMD heterostructure stacks. TEM measurements show that orientational order is maintained through the overlying TMD layers, while the DFT screening identifies stable TMD/GaN interface structures that are consistent with anchoring of the first TMD layer to the substrate.

Chapter 8

Investigation of the Effect of Oxygen Incorporation on Ni(111) Substrates During h-BN Growth

Reprinted from Y. Li, H. Gomez, J. Tran, Y. He, C. Shou, T. Yang, P. Wei, R. K. Lake, and J. Liu, “The role of oxygen incorporation in Ni (111) substrates on the growth of hexagonal boron nitride monolayers,” Nanotechnology 34, 505602 (2023). © IOP Publishing. Reproduced with permission. All rights reserved.

8.1 Introduction

The preceding chapters used first-principles calculations to show that chemically realistic surfaces and interfaces can differ substantially from idealized structural models. For diamond, oxidation and termination were constrained by the reconstructed surface geometry, which determined the stable bonding motifs and their electronic consequences. For TMD/GaN interfaces, TEM-constrained thermodynamic screening showed that the experimentally relevant interface is

selected by growth-dependent stoichiometry, registry, and interfacial reconstruction rather than by an ideal van der Waals stacking model. This chapter extends the same structure-property perspective to the growth of h-BN on transition-metal substrates.

Here, the focus shifts from the electronic properties of a completed surface or buried interface to the atomistic growth processes that determine whether a high-quality two-dimensional layer can form. Specifically, oxygen incorporation in Ni(111) is examined as a substrate modification that can alter the adsorption and diffusion of B and N adatoms during hexagonal boron nitride (h-BN) growth. First-principles calculations are used to evaluate whether oxygen-modified Ni(111) promotes or suppresses the surface mobility required for h-BN film formation.

Atomically thin h-BN is a material of significant interest owing to its outstanding properties, including a wide band gap of approximately 6 eV, high electric breakdown strength around 12 MV cm^{-1} , and exceptional thermal conductivity reaching approximately $600 \text{ W m}^{-1} \text{ K}^{-1}$ [46]. These attributes make h-BN an excellent candidate for various device applications. However, the growth of large-scale, high-quality h-BN monolayer films remains a substantial challenge [46, 194, 195]. Traditional exfoliation methods can produce high-quality 2D flakes, but they are often irregular and small. Techniques such as chemical vapor deposition (CVD), physical vapor deposition (PVD), and molecular beam epitaxy (MBE) can yield larger films, but growth conditions and substrate properties strongly influence defect density, domain size, and film continuity [194, 195, 196]. Substrate engineering has therefore been pursued as a route to improve the growth of high-quality h-BN monolayers.

A promising approach involves modifying the catalytic strength of transition-metal substrates through impurity incorporation. Previous work from the Liu group showed that carbon incorporation in Ni-based substrates can tune the adsorption and diffusion of B and N adatoms and

improve h-BN growth under selected conditions [194, 195]. This effect depends strongly on substrate orientation and impurity chemistry: carburization promotes h-BN growth on Ni(100), whereas growth on carburized Ni(111) is suppressed [195]. These results motivate examining whether oxygen incorporation in Ni(111), introduced during pretreatment using a boron source such as B_2O_3 , modifies the surface mobility of B and N adatoms in a favorable or unfavorable manner.

This chapter investigates the effect of oxygen incorporation on Ni(111) substrates during h-BN growth using first-principles calculations. By examining the adsorption and diffusion of isolated B and N adatoms on pristine and oxygen-incorporated Ni(111), this work identifies how oxygen modifies the surface energy landscape relevant to h-BN film formation. The results provide atomic-scale insight into whether oxygen incorporation improves or suppresses the catalytic conditions required for high-quality h-BN growth.

8.2 Computational Methods

All calculations follow the first-principles methodology described in Chapter 2. Only details specific to the oxygen-incorporated Ni(111) systems are summarized here. Calculations were performed using VASP with the PBE exchange-correlation functional and PAW pseudopotentials. A plane-wave cutoff of 600 eV and a $4 \times 4 \times 1$ k -point mesh were used for the Ni(111) slab calculations.

The pristine Ni(111) surface was modeled using a $4 \times 4 \times 4$ slab containing 64 Ni atoms. Oxygen-incorporated surfaces were constructed by replacing one or two Ni atoms with O atoms, corresponding to the 1O and 2O substitutional defect models. Substitutional oxygen was chosen to reflect the experimentally observed incorporation of oxygen into the Ni(111) substrate during MBE

pretreatment [46]. Interstitial oxygen configurations were also tested, but produced nonphysical diffusion profiles in the CI-NEB calculations (Fig. 8.1). The substitutional model was therefore adopted for all subsequent adsorption and diffusion calculations.

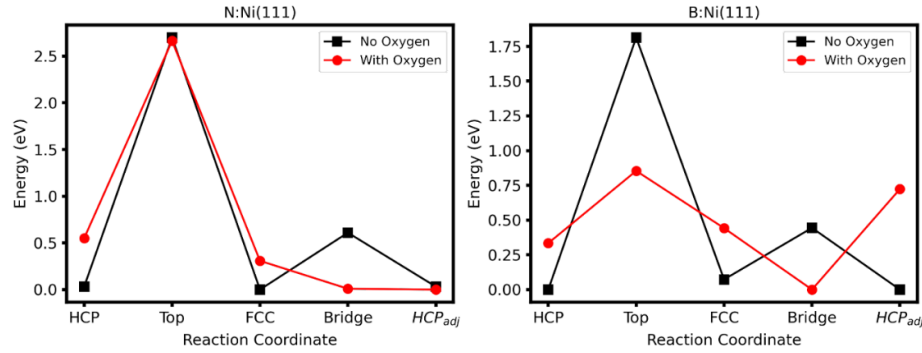


Figure 8.1: Comparison of CI-NEB diffusion barriers for B and N adatoms on Ni(111) with interstitial (top) and substitutional (bottom) oxygen configurations. Interstitial oxygen produced nonphysical barrier profiles, motivating the use of substitutional oxygen defects for the subsequent adsorption and diffusion calculations.

The bottom two Ni layers were fixed to approximate the bulk constraint, while the remaining atoms were free to relax. A linear dipole correction was applied along the surface normal to reduce artifacts from the asymmetric slab geometry.

Adsorption energies were calculated for isolated B and N adatoms placed at the HCP, FCC, top, bridge, and adjacent HCP sites on pristine and oxygen-incorporated Ni(111), as shown in Fig. 8.2. Diffusion barriers were evaluated using the climbing-image nudged elastic band (CI-NEB) method for B and N migration from an HCP site to an adjacent HCP site through the intermediate high-symmetry adsorption sites.

Adsorption energies were calculated as

$$E_{ads} = E_{B/N \text{ on the surface}} - E_{B/N} - E_{surf}, \quad (8.1)$$

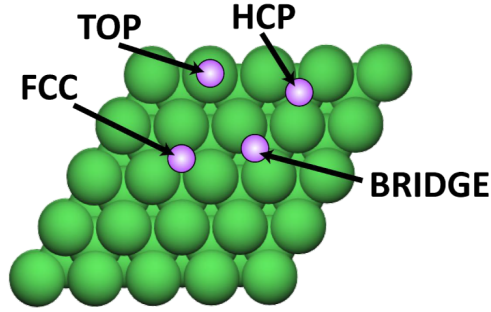


Figure 8.2: Adsorption sites considered for B and N adatoms on the Ni(111) surface.

where $E_{B/N}$ is the energy of the isolated B or N atom, E_{surf} is the energy of the corresponding Ni(111) surface without the adsorbate, and $E_{B/N \text{ on the surface}}$ is the total energy of the surface with the adsorbed B or N atom.

8.3 Results

Figure 8.3(a,b) shows the adsorption energies of B and N atoms on pristine and oxygen-incorporated Ni(111). With a single substitutional oxygen atom (1O), adsorption energies remain close to those of the pristine surface. The diffusion barriers, however, are modified. For B migration from an HCP site to an adjacent HCP site [Fig. 8.3(c)], barrier heights increase by 0.02 eV at the top site and 0.05 eV at the bridge site relative to the pristine surface, increases too small to significantly impede B mobility. For N migration [Fig. 8.3(d)], the corresponding increases are 0.27 eV and 0.35 eV, indicating that a single oxygen atom has a substantially more detrimental effect on N diffusion than on B diffusion.

With two substitutional oxygen atoms (2O), the adsorption energies become predominantly negative across all sites except the top site [Fig. 8.3(b)], and the diffusion barriers increase dramatically. For B on the 2O surface [Fig. 8.3(c)], the top-site barrier reaches 5.53 eV and the

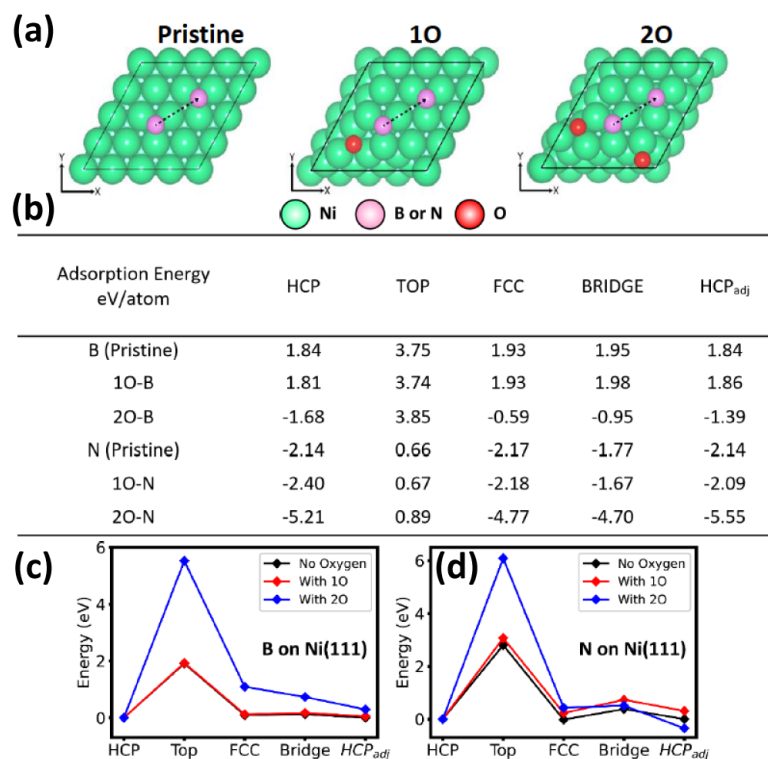


Figure 8.3: Calculated adsorption and diffusion energetics of B and N adatoms on pristine Ni(111) and Ni(111) surfaces containing one (1O) or two (2O) substitutional O atoms. (a) Top views of the pristine, 1O, and 2O substrates with a B or N adatom. The diffusion pathway between adjacent HCP sites is indicated. (b) DFT-calculated adsorption energies of B and N on the three substrates. Diffusion-energy profiles of (c) B and (d) N along the pathways shown in (a). Reprinted from Y. Li, H. Gomez, J. Tran, Y. He, C. Shou, T. Yang, P. Wei, R. K. Lake, and J. Liu, "The role of oxygen incorporation in Ni(111) substrates on the growth of hexagonal boron nitride monolayers," *Nanotechnology* **34**, 505602 (2023). © IOP Publishing. Reproduced with permission. All rights reserved.

bridge-site barrier 0.73 eV. For N [Fig. 8.3(d)], the corresponding barriers are 6.09 eV and 0.51 eV. Barriers of this magnitude effectively prohibit diffusion along this pathway, confining adatoms to the HCP sites. The combined effect of deeper adsorption wells and prohibitively large migration barriers indicates that h-BN growth is strongly suppressed on the oxygen-incorporated surface.

8.4 Conclusion

First-principles calculations show that oxygen incorporation in Ni(111) substrates impedes rather than promotes h-BN monolayer growth. A single substitutional oxygen atom introduces negligible barriers to B diffusion but substantially raises the migration barriers for N atoms. Two substitutional oxygen atoms produce adsorption wells deep enough to trap both B and N adatoms, with top-site barriers exceeding 5 eV that effectively prohibit diffusion. These results establish that oxygen incorporation restricts the surface mobility required for h-BN film formation and provide atomic-scale understanding of why substrate pretreatment conditions that introduce oxygen into Ni(111) are detrimental to high-quality monolayer synthesis.

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Appendix A

Nosé–Hoover Thermostat Mass Parameter

In this thesis, the AIMD calculations employ a $2 \times 2 \times 1$ supercell to allow for reconstruction and more degrees of freedom for the adsorbed atoms. The mass parameter of the Nosé–Hoover thermostat, controlled by the VASP tag `SMASS`, was selected from the characteristic vibrational timescale of each simulated system. For a target thermostat period τ , estimated from a representative phonon frequency, the corresponding thermostat mass was computed as

$$Q = \left(\frac{\tau}{2\pi}\right)^2 2N_{\text{DOF}} \cdot k_{\text{B}} T, \quad (\text{A.1})$$

where N_{DOF} is the number of mobile ionic degrees of freedom, k_{B} is the Boltzmann constant, and T is the target AIMD temperature. The value of Q was then converted to the dimensionless VASP `SMASS` parameter according to

$$\text{SMASS} = \frac{Q}{m_{\text{u}} L^2}, \quad (\text{A.2})$$

where m_u is the atomic mass unit and L is the length of the first lattice vector. This procedure allows the thermostat response to be adjusted for each material system according to its characteristic phonon spectrum, rather than using a single fixed thermostat mass across chemically distinct systems. As an example, for the oxidized Si-terminated diamond surface the phonon density of states spans 0–45.0 THz, with the DOS-weighted mean frequency at approximately 24.7 THz, as shown in Fig. A.1 and in the following equation,

$$\langle \nu \rangle = \frac{\sum_i \nu_i g(\nu_i)}{\sum_i g(\nu_i)} = \frac{(0.0)(0.021) + (0.1)(0.023) + \dots + (45.0)(0.000)}{0.021 + 0.023 + \dots + 0.000} = 24.7 \text{ THz} \quad (\text{A.3})$$

where ν_i is the phonon frequency at point i and $g(\nu_i)$ is the phonon density of states evaluated at ν_i . These values are taken from the `total_dos.dat` output from Phonopy, of which the first few lines are shown below:

The corresponding thermostat period is,

$$\tau = \frac{1000}{24.7 \text{ THz}} = 40.5 \text{ fs} \quad (\text{A.4})$$

For a $2 \times 2 \times 1$ simulation cell with $N_{\text{DOF}} = 240$, $T = 723 \text{ K}$, and $L = 10.097 \text{ \AA}$, this gives

$$\text{SMASS} = \frac{(40.5 \times 10^{-15} / 2\pi)^2 2(240)k_B(723)}{m_u(10.097 \times 10^{-10})^2} \approx 0.12, \quad (\text{A.5})$$

and a value of $\text{SMASS} = 0.1$ was adopted as a conservative round number close to this estimate.

The 1 fs timestep is justified separately by the highest frequency mode in the system at 1478 cm^{-1} ,


```
# Tetrahedron method
0.0000000000 0.0213178281
0.1000000000 0.0232276360
...
```

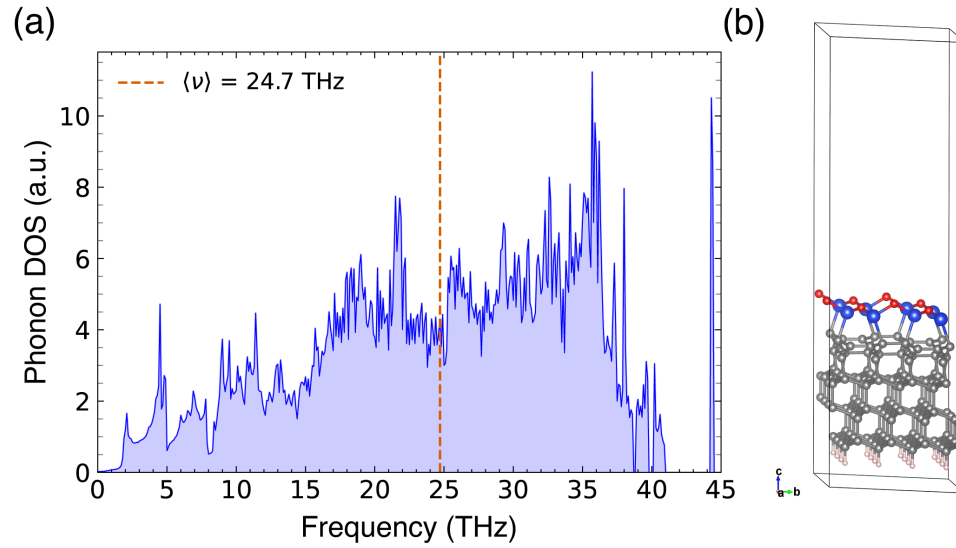


Figure A.1: Phonon density of states $g(\nu)$ for the oxidized Si-terminated diamond (111) surface in the (2×2) supercell used for AIMD simulations. The dashed vertical line marks the DOS-weighted mean frequency $\langle \nu \rangle = 24.7$ THz.

which has a vibrational period of approximately 23 fs, ensuring each oscillation cycle is resolved with around twenty integration steps.

Appendix B

Supplementary Data for Chapter 5

Structural Parameters

Figures B.1 and B.2 define the structural parameters used to characterize the non-oxidized and oxidized (3×1) group-IV terminated diamond (100) surfaces, respectively. The labeled distances include the group-IV adatom height above the surface carbon layer (d_{X1} , $d_{X1'}$), the lateral group-IV spacing (d_{XX}), the group-IV–oxygen bond length (d_{OX} , $d_{OX'}$), the interlayer spacings ($d_{12,\perp}$, $d_{23,\perp}$, $d_{34,\perp}$, $d_{45,\perp}$), and the surface carbon buckling amplitudes ($\Delta_{3,\perp}$, $\Delta_{4,\perp}$).

Tables B.1 and B.2 provide the complete structural parameters for the non-oxidized and oxidized (3×1) group-IV terminated diamond (100) surfaces, respectively, corresponding to the configurations illustrated in Figs. B.1 and B.2.

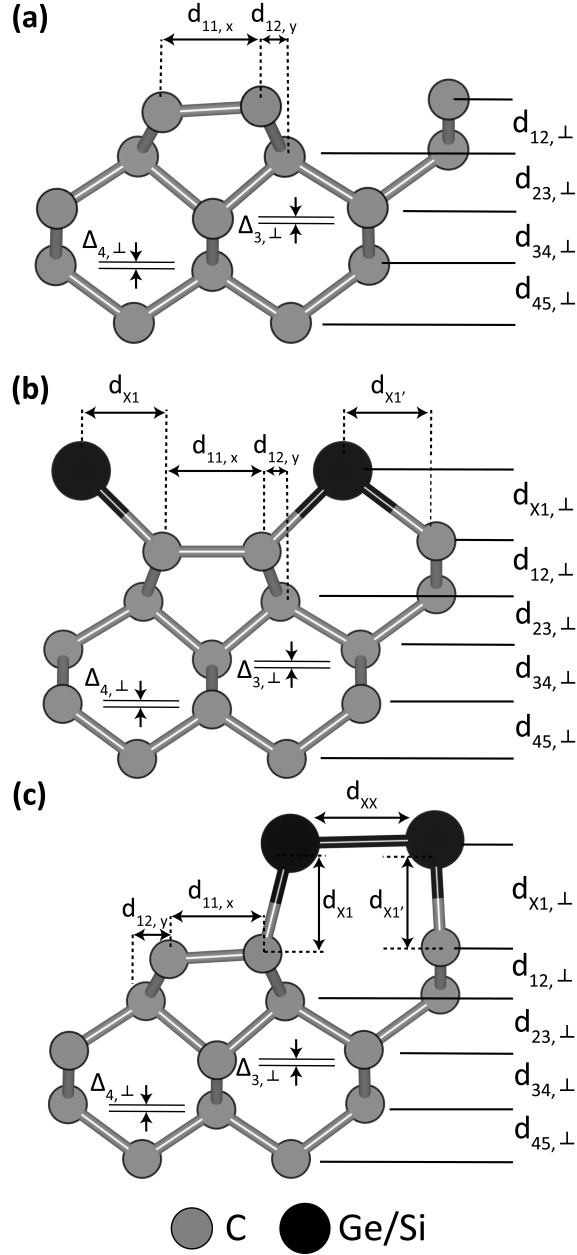


Figure B.1: Structural parameter definitions for the (3×1) group-IV terminated diamond (100) surfaces. (a) Bare reconstructed surface, (b) ether configuration, and (c) ketone configuration. Gray and black spheres represent C and group-IV (Si or Ge) atoms, respectively.

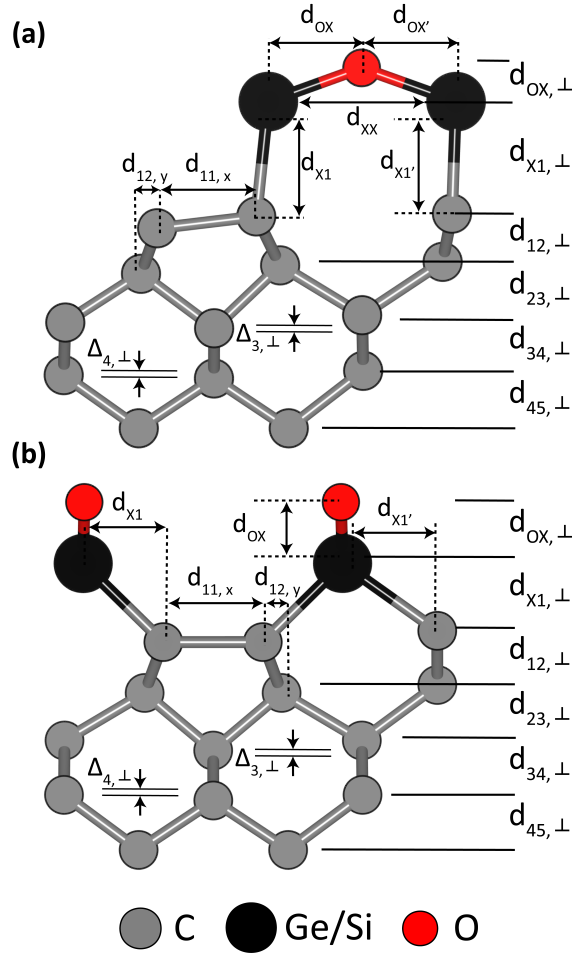


Figure B.2: Structural parameter definitions for the oxidized (3 × 1) group-IV terminated diamond (100) surfaces. (a) O_{Ketone} and (b) O_{Ether} configurations. Gray, black, and red spheres represent C, group-IV (Si or Ge), and O atoms, respectively.

Table B.1: A comparison of the structural data for the ether and ketone configurations with previously published theoretical data [*] for the reconstructed (3×1) SiTD and GeTD surfaces taken from Ref. [173]. The values of d_{ij} represent the distances between atoms in the respective directions, while Δ_{ij} denotes the buckling between atoms in the same layer, all expressed in units of Å.

Structural Parameter	Bare (2×1)	Ether (Si)	Ether (Si)*	Ether (Ge)	Ether (Ge)*	Ether (1×1 : O)	Ketone (1×1 : O)	Ketone (Si)	HTD (2×1 : H)
d_{XX}	–	3.16	–	3.23	–	2.52	2.50	2.45	2.49
d_{X1}	–	1.94	1.91	2.02	1.96	1.50	1.21	1.83	1.10
$d_{X1'}$	–	1.98	1.95	2.07	2.02	1.50	1.21	1.93	1.10
$d_{11,x}$	1.38	1.68	1.65	1.63	1.61	–	–	1.59	1.62
$d_{12,y}$	0.48	1.55	1.54	1.55	1.54	1.53	1.53	1.55	1.54
$d_{X1,\perp}$	–	1.19	1.16	1.36	1.24	0.81	1.21	1.82	1.02
$d_{12,\perp}$	0.68	0.72	0.71	0.83	0.67	0.87	0.87	0.81	0.81
$d_{23,\perp}$	0.80	0.81	0.79	0.80	0.77	0.90	0.92	0.94	0.80
$d_{34,\perp}$	0.95	0.75	0.71	0.92	0.70	0.90	0.89	0.92	0.92
$d_{45,\perp}$	0.97	0.93	–	0.93	–	0.87	0.87	0.93	0.96
$\Delta_{3,\perp}$	0.26	0.17	0.19	0.22	0.20	0.02	0.03	0.18	0.20
$\Delta_{4,\perp}$	0.16	0.10	0.12	0.10	0.13	0.04	0.04	0.10	0.14

Table B.2: Structural parameters of the oxidized (3×1) Si and Ge variants. Here, d_{ij} represents the distance between atoms, Δ_{ij} is the buckling amplitude between atoms within the same layer, and “X” denotes either Si or Ge atoms. All units are in angstroms ($\text{\AA}$).

Structural Parameter	O _{Ether} (Si)	O _{Ether} (Ge)	O _{Ketone} (Si)	O _{Ketone} (Ge)	RO _{Ketone} (Si)	RO _{Ketone} (Ge)
d_{OX}	1.62	1.74	1.67	1.80	2.01	1.83
$d_{\text{OX}'}$	–	–	1.65	1.81	1.65	1.92
d_{XX}	3.19	3.26	1.63	1.76	2.76	2.87
d_{X1}	1.89	1.98	1.88	2.06	–	–
$d_{\text{X1}'}$	1.96	2.06	1.94	1.98	–	–
d_{O1}	–	–	–	–	1.34	1.39
$d_{\text{O1}'}$	–	–	–	–	1.39	1.29
$d_{11,x}$	1.68	1.62	1.68	1.65	1.70	1.60
$d_{12,y}$	1.56	1.55	1.50	1.50	1.50	1.49
$d_{\text{OX},\perp}$	1.03	1.22	0.57	0.71	0.94	1.27
$d_{\text{X1},\perp}$	0.86	0.89	1.88	1.97	1.29	1.27
$d_{12,\perp}$	0.94	0.95	0.81	0.80	0.82	0.83
$d_{23,\perp}$	0.81	0.79	0.80	0.77	0.94	1.08
$d_{34,\perp}$	0.75	0.71	0.92	0.70	0.92	0.84
$d_{45,\perp}$	0.93	0.93	0.93	0.93	0.93	0.84
$\Delta_{3,\perp}$	0.17	0.19	0.22	0.20	0.18	0.18
$\Delta_{4,\perp}$	0.10	0.12	0.10	0.13	0.10	0.11

Electron Localization Functions

Figure B.3 shows the electron localization functions (ELF) for the oxidized ether and ketone configurations of the Si- and Ge-terminated diamond (100) surfaces. The ELF values, projected onto the (010) and (100) planes, characterize the bonding character of the surface configurations, with values near 1 indicating covalent bonding and values near 0.5 indicating metallic-like electron delocalization. For the O_{Ether} configurations, the ELF plots show a light-blue region between the Si and Ge atoms ($\text{ELF} \approx 0.25$), indicating a low probability of locating an electron pair between the group-IV atoms and confirming that the lateral Si–Si and Ge–Ge covalent bonds present on the non-oxidized surfaces are absent after full oxidation. For the O_{Ketone} configurations, the Si surface retains covalent bonds with both the oxygen and adjacent Si atoms, whereas the Ge–Ge bonds in the analogous Ge surface exhibit metallic character, consistent with the weaker Ge–C interaction and the lower thermodynamic stability of the Ge ketone configuration. These bonding differences between the Si and Ge oxidized surfaces are reflected in the surface formation energies discussed in Section 5.4.

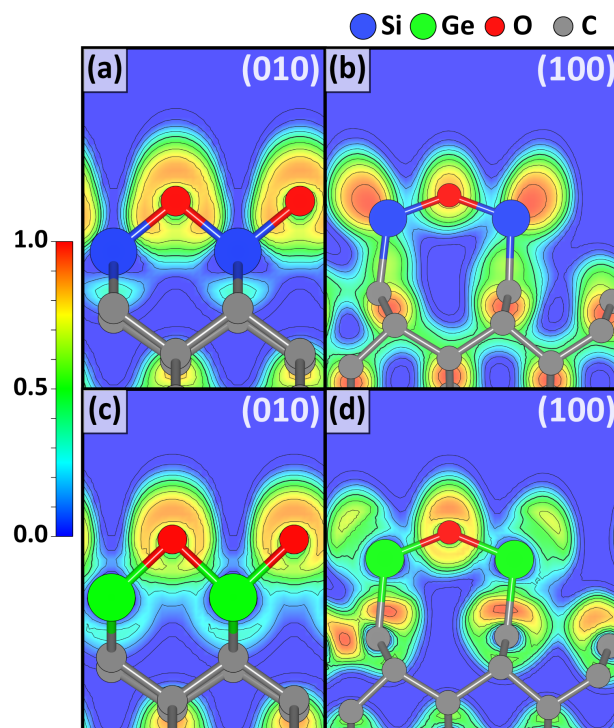


Figure B.3: Electron localization functions for oxidized (3×1) group-IV terminated diamond (100) surfaces projected onto the (010) and (100) planes. Panels (a,b) show O_{Ether} and O_{Ketone} with Si, respectively. Panels (c,d) show O_{Ether} and O_{Ketone} with Ge, respectively. ELF values range from 0 (fully delocalized) to 1 (fully localized). Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

Electrostatic Potential Alignment and Band Bending

Figure B.4 shows the electrostatic potential alignment used to determine the electron affinities reported in Table 5.1. The 98 meV offset between V_{surf} and V_{bulk} shown in the inset reflects the upward band bending at the C–Si–O interface, which is smaller than that of H-terminated diamond and consistent with the reduced channel carrier density observed in C–Si–O-based MOS-FETs [169].

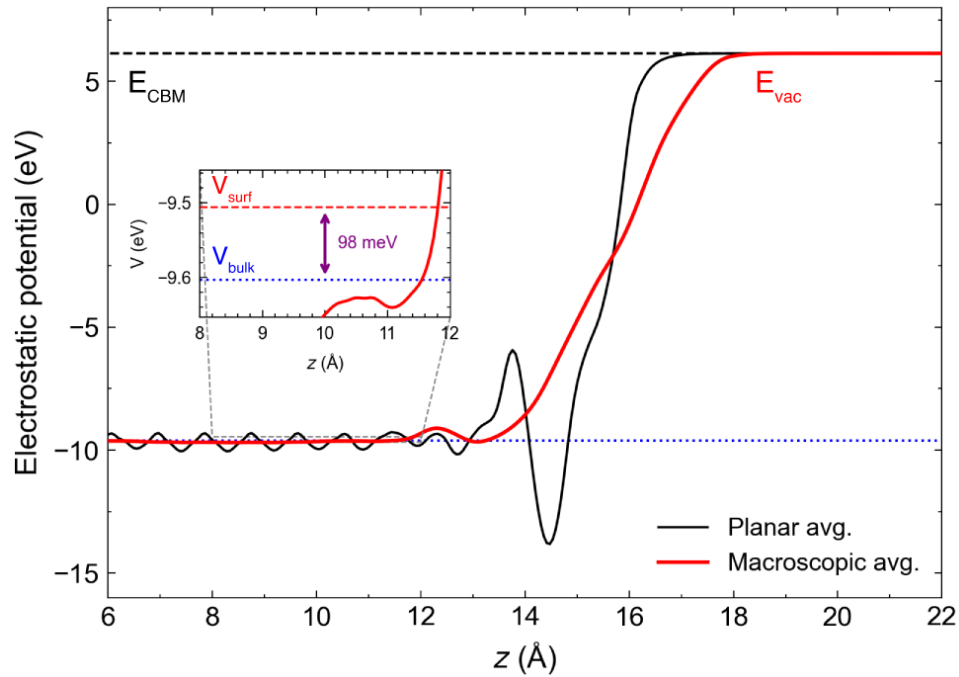


Figure B.4: Electrostatic potential alignment for the oxidized Si-terminated diamond (100) surface. The planar average (black) and macroscopic average (red) are plotted as a function of position along the surface normal z . The dashed line indicates E_{CBM} and the dotted line indicates V_{bulk} . The inset shows the 98 meV separation between V_{surf} and V_{bulk} , which reflects the upward band bending at the surface and defines the bulk reference used in the potential alignment procedure.

Layer-Resolved Projected Densities of States

Figures B.5 and B.6 show the layer-resolved projected densities of states for the Si- and Ge-terminated diamond (100) surfaces, respectively. Each panel shows the contribution from the group-IV adatom layer, oxygen (where present), and the first four carbon layers (L1–L4) below the surface. The recovery of bulk-like electronic character by the fourth carbon layer confirms that the terminating species primarily affect the near-surface region. The dashed magenta line indicates the Fermi level.

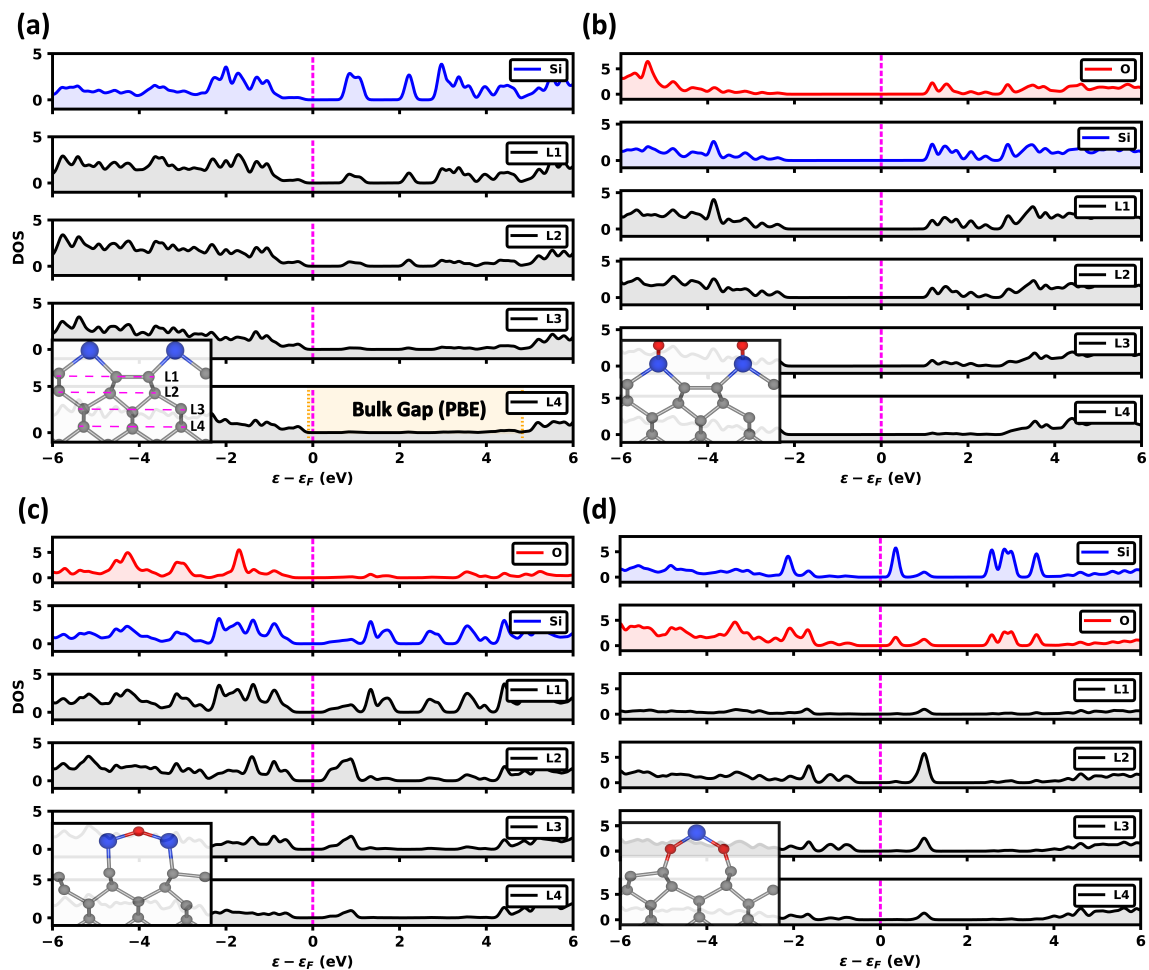


Figure B.5: Layer-resolved projected densities of states for Si-terminated diamond (100) surfaces. (a) Non-oxidized ether, (b) O_{Ether} , (c) O_{Ketone} , and (d) RO_{Ketone} configurations. Blue and red curves show Si and O contributions, respectively. Gray curves show carbon layer contributions L1–L4. The dashed magenta line indicates the Fermi level. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

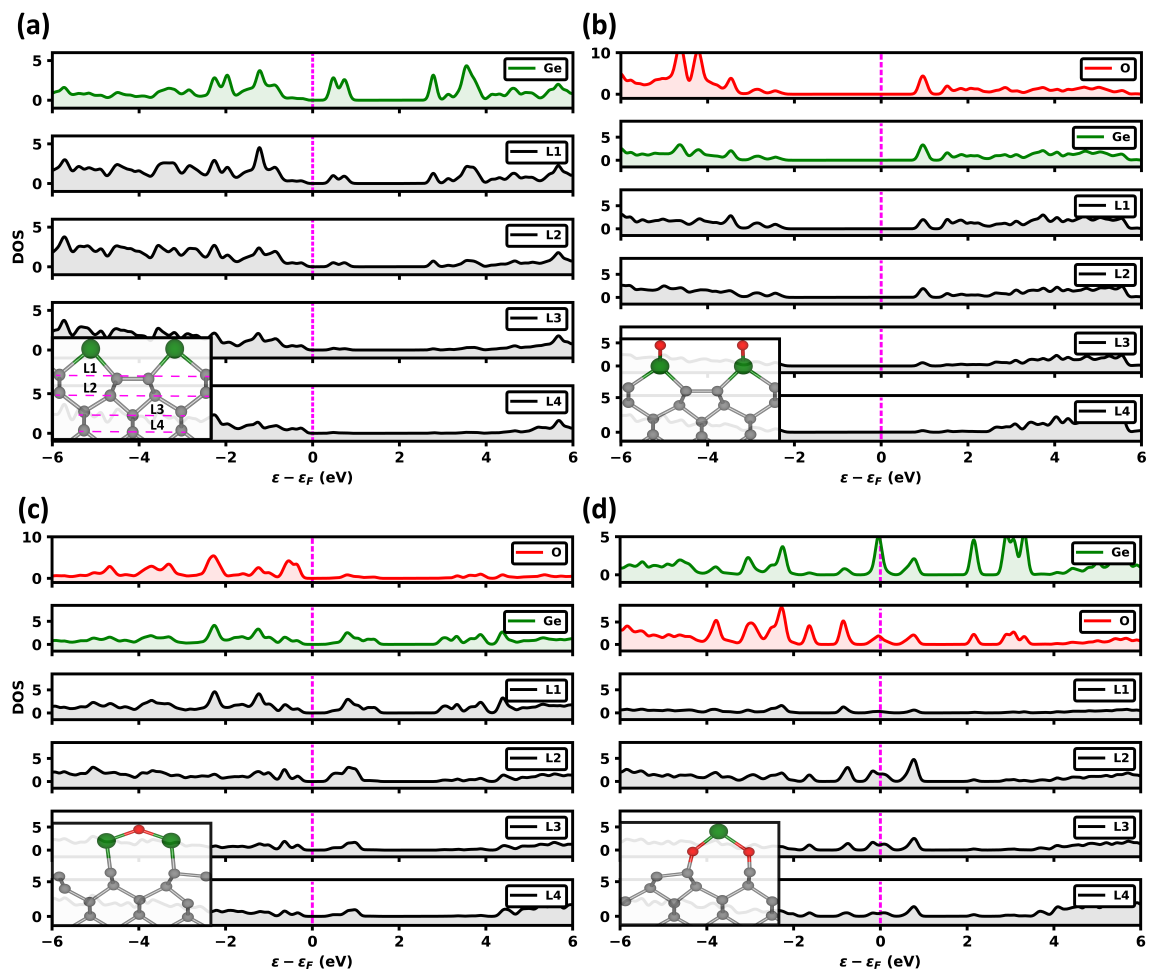


Figure B.6: Layer-resolved projected densities of states for Ge-terminated diamond (100) surfaces. (a) Non-oxidized ether, (b) O_{Ether} , (c) O_{Ketone} , and (d) RO_{Ketone} configurations. Green and red curves show Ge and O contributions, respectively. Gray curves show carbon layer contributions L1–L4. The dashed magenta line indicates the Fermi level. Reprinted with permission from H. Gomez *et al.*, J. Chem. Phys. **161**, 064702 (2024). Copyright 2024, AIP Publishing.

Appendix C

TCAD Study of a NiO/ β -Ga₂O₃

Heterojunction Diode

This study was conducted during the author's internship at Sandia National Laboratories under the mentorship of M. Negoita and with guidance from R. Kaplar. The work was carried out in connection with the ULTRA Energy Frontier Research Center. The TCAD simulations and analysis presented in this appendix were performed by the author.

C.1 Introduction

β -Ga₂O₃ has attracted interest for next-generation high-voltage power electronics owing to its ultra-wide bandgap of approximately 4.8 eV and high theoretical breakdown electric field exceeding 8 MV/cm, more than double that of SiC and GaN [197]. These properties translate to a far superior Baliga figure of merit relative to established wide-bandgap semiconductors. However, the absence of p-type doping capability in β -Ga₂O₃ remains a major limitation, precluding the bipolar device structures and junction-based edge termination schemes widely used in Si and SiC power electronics. One approach to address this limitation is to construct p-n heterojunctions using

an external p-type material. p-NiO is a particularly attractive candidate because it can be deposited by sputtering and forms a type-II band alignment with β -Ga₂O₃, which provides a high barrier height against carriers and suppresses reverse leakage current [198].

Technology Computer-Aided Design (TCAD) simulations were conducted using Silvaco commercial software to investigate the interfacial properties of a p-NiO/n-Ga₂O₃ heterojunction diode (HJD) and to assess the impact of doping concentration and interface trap density on power device performance. By optimizing these parameters, this study aimed to replicate and extend the experimental results [198], serving as a template for the informed design and fabrication of high-performance NiO/ β -Ga₂O₃ HJDs with enhanced electrical properties and breakdown voltage.

To accurately model the interfacial properties of the type-II heterojunction, the Daniels-son model described by Eq. C.1 was enabled and used in the TCAD simulations [199, 200]. The Danielsson equation assumes that recombination centers at the heterojunction mediate electron-hole recombination across the energy gap. A full derivation of the model is provided in Section C.4.

$$U_{\text{TAR}} = U_{\text{DAN}} = \frac{n_j^- p_j^+ - n_{j0}^- p_{j0}^+}{\frac{1}{c_n N_{jt}} (n_j^- + n_{j0}^- a_0) + \frac{1}{c_p N_{jt}} \left(p_j^+ + \frac{p_{j0}^+}{a_0} \right)} \quad (\text{C.1})$$

Figures C.1 and C.2 illustrate the vertical NiO/ β -Ga₂O₃ p-n diode model, which used a p-type NiO layer with a thickness of 0.2 μm on an 8 μm lightly doped β -Ga₂O₃ n-type drift layer.

These layers had doping concentrations of $1 \times 10^{16} \text{ cm}^{-3}$ and $1 \times 10^{19} \text{ cm}^{-3}$, respectively. Additionally, a bulk (001) β -Ga₂O₃ substrate with a thickness of 100 μm and a doping concentration of $2.6 \times 10^{18} \text{ cm}^{-3}$ was utilized. The total nominal device width was 125 μm . These parameters and

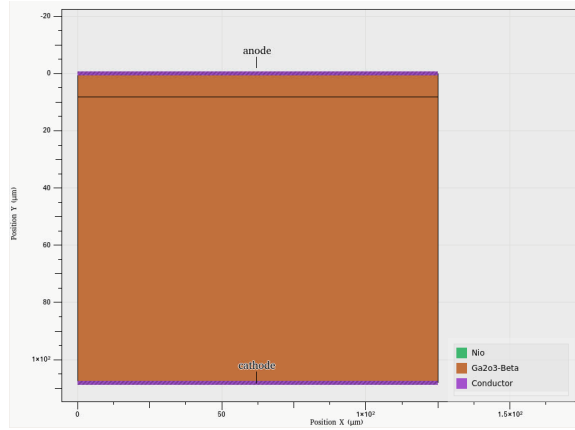


Figure C.1: TCAD device structure of the vertical NiO/β-Ga₂O₃ heterojunction p-n diode.

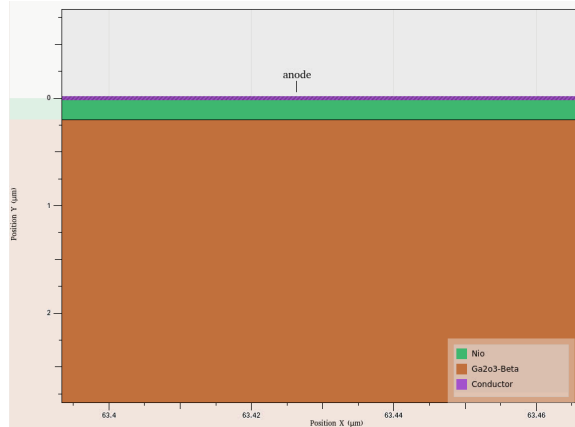


Figure C.2: Zoomed-in vertical NiO/β-Ga₂O₃ heterojunction p-n diode interface region.

geometry are consistent with those of Lu et al. [198], who fabricated a sputtered 1-kV NiO/ β -Ga₂O₃ p-n diode with a breakdown voltage of 1059 V.

C.2 Results

Figure C.3 presents a comparison of the forward I-V curves for the model with and without the Danielsson model (DNLS) enabled, alongside the experimental data of Lu et al. [198]. Without the DNLS model, the initial turn-on voltage was $\sim 40\%$ larger than the experimental value. Upon enabling the DNLS model with the default electron and hole recombination parameters and neutral traps ($v_{n,p} = 10^7$), the turn-on voltage decreased to ~ 2.1 V. However, by changing the trap type to acceptor in the DNLS model, the turn-on voltage was modified to a value consistent with literature [198], with electron and hole recombination rates increased to 10^{13} .

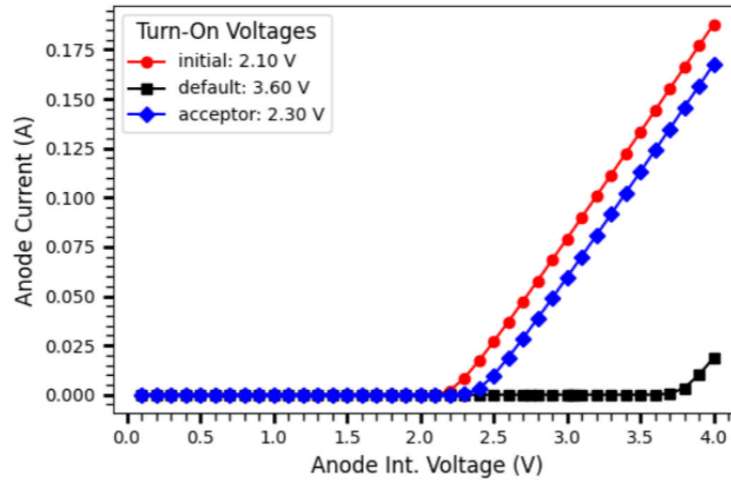


Figure C.3: Comparison of forward bias I-V curves for the vertical NiO/ β -Ga₂O₃ heterojunction p-n diode with and without the Danielsson model enabled. The inset shows the experimental data and estimated turn-on voltage from Lu et al. [198].

To further enhance the model with realistic conditions, bulk traps H1 ($E_V + 0.1$ eV), E2 ($E_C - 0.82$ eV), E2* ($E_C - 0.76$ eV), and E3 ($E_C - 1.11$ eV) were incorporated in the Ga₂O₃ material [201]. In the DNLS model, different energy levels for the traps were tested. Figure C.4 presents a comparison of the forward I-V curves for the model with varying parameters. As illustrated in

Fig. C.4(a), when the DNLS interface trap level relative to the equilibrium Fermi level is set to zero (DNLS.ET = 0), the model demonstrated a turn-on voltage of approximately 2.3 V, which aligns well with experimental data [198]. However, a shift in DNLS.ET of ± 0.2 eV resulted in a notable change in the turn-on voltage, varying between 2.1 V and 3.5 V. The concentrations of bulk traps E2, E2*, and E3 in Ga₂O₃ were modified between 10^{12} – 10^{16} cm⁻³, as shown in Figs. C.4(b)–(d). Interestingly, even with varying physical concentrations, the trap density did not influence the turn-on voltage; instead, it was reliant on the relative positioning of the Fermi level. One possible explanation is that the trap levels remain empty as the Fermi level moves away from the conduction band and do not contribute to carrier recombination or affect the turn-on voltage. In contrast, as they become filled when it is closer, the turn-on voltage is reduced as more electrons are readily available to fill the traps.

Furthermore, for the reverse bias, the Selberherr impact ionization model was implemented. The specific parameters used were based on the work of Ghosh et al. [202] for the (001) substrate along the *z*-direction. When reverse biased in equilibrium, the device exhibited a breakdown voltage of approximately 1171 V (Fig. C.5), which is about 10% greater than that reported by Lu et al. [198]. Similar to the forward bias, the additional trap levels had no effect on the breakdown voltage, even when the trap levels were filled. Additionally, no observable change was detected when switching between acceptor and donor trap levels at the interface.

C.3 Conclusion

In summary, this study employed TCAD simulations with Silvaco software to optimize doping concentration and interface trap density for p-NiO/n-Ga₂O₃ HJDs. The Danielsson model

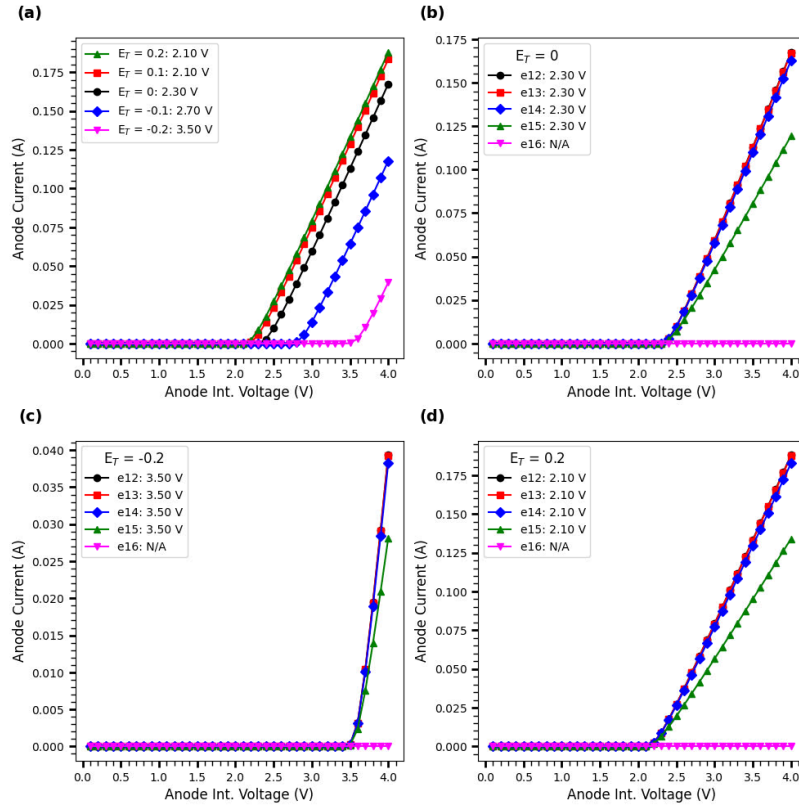


Figure C.4: Comparison of forward bias I-V curves for the vertical NiO/ β -Ga₂O₃ heterojunction p-n diode showing variations in (a) E_T values and (b)–(d) bulk trap density concentrations

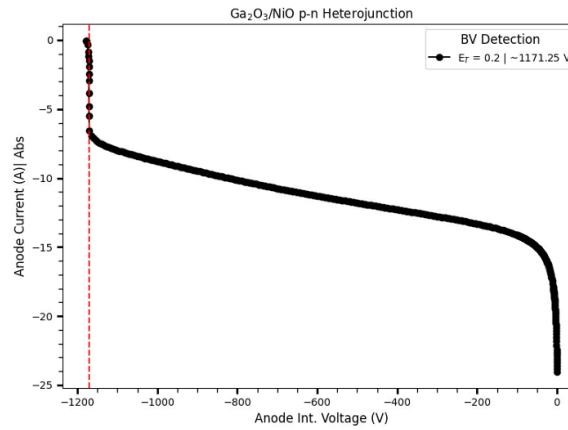


Figure C.5: Reverse I-V curve for the vertical NiO/ β -Ga₂O₃ heterojunction p-n diode with filled trap levels. Breakdown occurs at approximately 1171 V.

was used to characterize interfacial properties and the Selberherr impact ionization model was adopted for reverse bias, based on parameters from existing research. A reverse bias breakdown voltage of approximately 1171 V was observed, surpassing previous experimental results by 10% [198]. Key findings include the significant impact of the DNLS model and interface trap energy levels on the turn-on voltage, with the relative positioning of the Fermi level being more crucial than the trap concentration. These results suggest that device performance is stable across variations in trap conditions, providing guidance for the development of future NiO/ β -Ga₂O₃ HJDs.

C.4 Danielsson Model Derivation

To derive the Tunnel-Assisted Recombination (TAR) rate U_{TAR} starting from the given recombination rates for electrons and holes and the ratio.

1. Recombination Rates: The recombination rates for electrons (U_{Sn}) and holes (U_{Sp}) at the heterojunction are given by:

$$U_{Sn} = c_n n_j (N_{jt} - n_{jt}) - e_n n_{jt}$$

$$U_{Sp} = c_p p_j n_{jt} - e_p (N_{jt} - n_{jt})$$

2. Thermal Equilibrium: In thermal equilibrium, the recombination rates are zero, leading to:

$$e_n = c_n n_{j0} \left(\frac{N_{jt} - n_{jt0}}{n_{jt0}} \right) = c_n n_{j0} a_0$$

$$e_p = c_p p_{j0} \left(\frac{n_{jt0}}{N_{jt} - n_{jt0}} \right) = c_p p_{j0} \frac{1}{a_0}$$

where $a_0 = \frac{N_{jt} - n_{jt0}}{n_{jt0}}$ is the ratio of available electron states to available hole states.

3. Steady State: In steady state, the recombination rates for electrons and holes are equal:

$$U_{Sn} = U_{Sp}$$

This gives:

$$c_n n_j (N_{jt} - n_{jt}) + e_p (N_{jt} - n_{jt}) = c_p p_j n_{jt} + e_n n_{jt}$$

4. Express n_{jt} in Terms of N_{jt} : Solving for n_{jt} from the steady state equation:

$$\frac{n_{jt}}{N_{jt}} = \frac{c_n n_j + e_p}{c_n n_j + e_p + c_p p_j + e_n}$$

$$n_{jt} = N_{jt} \frac{c_n n_j + c_p p_{j0} \frac{1}{a_0}}{c_n n_j + c_p p_{j0} \frac{1}{a_0} + c_p p_j + c_n n_{j0} a_0}$$

5. Thermal equilibrium relations: Using $e_n = c_n n_{j0} a_0$ and $e_p = c_p p_{j0} \frac{1}{a_0}$:

$$n_{jt} = N_{jt} \frac{c_n n_j + c_p p_{j0} \frac{1}{a_0}}{c_n n_j + c_p p_{j0} \frac{1}{a_0} + c_p p_j + c_n n_{j0} a_0}$$

6. TAR Rate: Substituting n_{jt} into $U_{Sn} = c_n n_j (N_{jt} - n_{jt}) - e_n n_{jt}$:

$$U_{TAR} = \frac{c_n n_j N_{jt} (c_p p_j + c_n n_{j0} a_0) - c_n n_{j0} a_0 N_{jt} (c_n n_j + c_p p_{j0} \frac{1}{a_0})}{c_n n_j + c_p p_{j0} \frac{1}{a_0} + c_p p_j + c_n n_{j0} a_0}$$

$$U_{TAR} = \frac{c_n c_p N_{jt} (n_j p_j - n_{j0} p_{j0})}{c_n n_j + c_p p_{j0} \frac{1}{a_0} + c_p p_j + c_n n_{j0} a_0}$$

Grouping the denominator by c_n and c_p :

$$U_{TAR} = \frac{c_n c_p N_{jt} (n_j^- p_j^+ - n_{j0}^- p_{j0}^+)}{c_n (n_j^- + n_{j0}^- a_0) + c_p (p_j^+ + p_{j0}^+ \frac{1}{a_0})}$$

7. Final Expression:

$$U_{TAR} = \frac{n_j^- p_j^+ - n_{j0}^- p_{j0}^+}{\frac{1}{c_n N_{jt}} (n_j^- + n_{j0}^- a_0) + \frac{1}{c_p N_{jt}} (p_j^+ + p_{j0}^+ \frac{1}{a_0})}$$

This is the tunnel-assisted recombination rate as implemented in the Silvaco Victory Device simulator [200], following the model of Danielsson et al. [199].

C.5 Sensitivity Tests

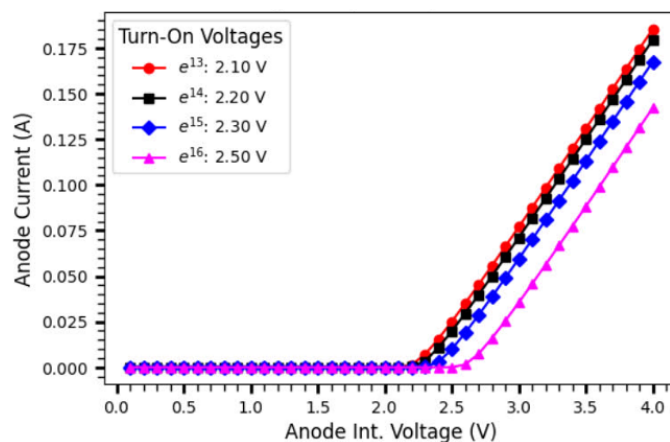


Figure C.6: Sensitivity test for the acceptor trap concentrations

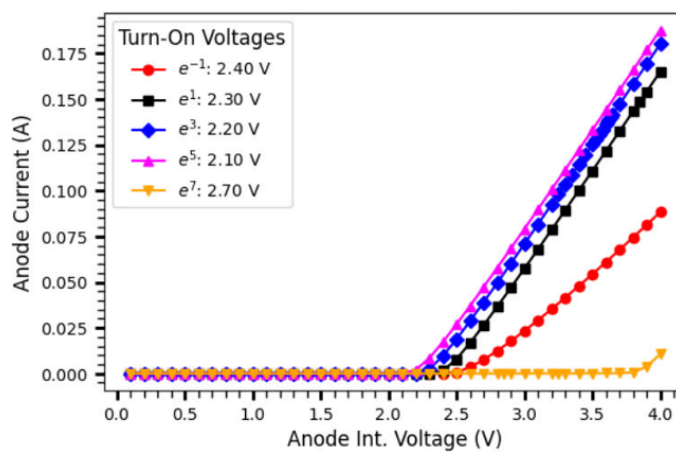


Figure C.7: Sensitivity test for the donor trap concentrations

C.5.1 DeckBuild Input Script

DeckBuild input script for the NiO/Ga₂O₃ heterojunction diode simulation.

```
set no_cores = 16
set dev_x    = 125.0
set sub_y    = 100.0
set drift_y  = 8.0
set p_y      = 0.2
set ND_sub   = 2.6e18
#set ND_drift = 4.0e16
set ND_drift = 1.0e16
set NA_p     = 1.0e19

go victorydevice simflags="-128 -p $no_cores"

MESH cylindrical

# x plane meshing
x.m l=0.0      s=12.5
x.m l=$dev_x s=12.5

# y mesh meshing
y.m l=0                      s=0.02
y.m l=$p_y                   s=0.005
y.m l=$p_y+$drift_y          s=0.01
y.m l=$p_y+$drift_y+$sub_y s=10.0

# p-layer
REGION number=1 user.material=nio          y.min=0          y.max=$p_y

# drift
REGION number=2 user.material=ga2o3-beta y.min=$p_y      y.max=$p_y+$drift_y

# substrate
REGION number=3 user.material=ga2o3-beta \
    y.min=$p_y+$drift_y y.max=$p_y+$drift_y+$sub_y

# electrodes
ELECTRODE name=cathode bottom
ELECTRODE name=anode    top

# doping
DOPING region=3 uniform n.type conc=$ND_sub
DOPING region=2 uniform n.type conc=$ND_drift
```



```
DOPING region=1 uniform p.type conc=$NA_p
```

```
INTERFACE intregion="1/2" hetero thermionic tunnel danielsson dnls.acc \  
    dnls.cn=1e-1 dnls.nt=1e15 dnls.cp=1e-1 dnls.et=0
```

Extract Data from DeckBuild

```
extract init infile="initial.str"  
extract start 2d.conc.file material="nio" impurity="Electron Conc" \  
    mat.occno=1 sigfigs=15 outfile="nio_only.csv"  
extract cont 2d.conc.file material="ga2o3-beta" impurity="Electron Conc" \  
    mat.occno=1 sigfigs=15 outfile="ga2o3_only.csv"  
quit
```

C.5.2 Python Analysis Scripts

Breakdown Voltage Detection

```
import pandas as pd  
import matplotlib.pyplot as plt  
import numpy as np  
  
def plot_csv_data(ax, file_path, legend_title):  
    data = pd.read_csv(file_path)  
    voltage_columns = [col for col in data.columns if 'Voltage' in col]  
    current_columns = [col for col in data.columns if 'Current' in col]  
    markers = ['o', 's', 'D', '^', 'v']  
    colors = ['black', 'red', 'blue', 'green', 'magenta']  
    plot_handles = []  
    breakdown_voltages = []  
  
    for i, (v_col, c_col) in enumerate(zip(voltage_columns, current_columns)):  
        legend_name = f'e{i + 12}'  
        marker = markers[i % len(markers)]  
        color = colors[i % len(colors)]  
        current_log = np.log10(np.abs(data[c_col]))  
        handle, = ax.plot(data[v_col], current_log, marker=marker,  
                           linestyle='--', color=color, label=legend_name,  
                           markersize=6)  
        plot_handles.append(handle)  
        voltage = data[v_col].values  
        current = data[c_col].values  
        current_diff = np.diff(current)
```

```

threshold = 0.05
constant_indices = np.where(np.abs(current_diff) < threshold)[0]
for idx in constant_indices:
    if idx + 1 < len(voltage):
        v_value = voltage[idx + 1]
        if -1175 < v_value < -1170:
            breakdown_voltages.append(v_value)

if breakdown_voltages:
    bv = max(breakdown_voltages)
    ax.axvline(bv, color='red', linestyle='--',
               label=f' ~{np.abs(bv):.2f} V')

ax.set_xlabel('Anode Int. Voltage (V)', fontsize=12)
ax.set_ylabel('Anode Current (A) | Abs', fontsize=12)
ax.tick_params(axis='both', which='major', labelsize=10, width=2, length=6)
ax.tick_params(axis='both', which='minor', labelsize=8, width=1, length=4)
ax.minorticks_on()
ax.legend(plot_handles + [handle],
          [f'E$T$ = 0.2 | ~{np.abs(bv):.2f} V'],
          title=legend_title, fontsize=10, title_fontsize=12,
          loc='upper right')

fig, ax = plt.subplots(figsize=(5, 5))
plot_csv_data(ax, 'hj_diode_traps_p2_e12_rvrse.csv', 'BV Detection')
plt.title(r'Ga$_{20}$$_{3}$$/NiO p-n Heterojunction')
plt.tight_layout()
plt.savefig('breakdown_voltage_hjd.png', dpi=300, bbox_inches='tight')
plt.show()

```

Turn-On Voltage Detection

```

import pandas as pd
import matplotlib.pyplot as plt
import numpy as np

def plot_csv_data(ax, file_path, legend_title):
    data = pd.read_csv(file_path)
    voltage_columns = [col for col in data.columns if 'Voltage' in col]
    current_columns = [col for col in data.columns if 'Current' in col]
    markers          = ['o', 's', 'D']
    custom_labels    = ['initial', 'default', 'acceptor']
    custom_colors    = ['red', 'black', 'blue']
    legend_labels    = []

```

```

plot_handles = []

for i, (v_col, c_col) in enumerate(zip(voltage_columns, current_columns)):
    legend_name = custom_labels[i] if i < len(custom_labels) else f'Extra {i+1}'
    color = custom_colors[i] if i < len(custom_colors) else 'gray'
    marker = markers[i] if i < len(markers) else 'o'
    handle, = ax.plot(data[v_col], data[c_col], marker=marker,
                      linestyle='-', color=color, label=legend_name,
                      markersize=6)
    voltage = data[v_col].values
    current = data[c_col].values
    turn_on_index = np.where(current > 1e-5)[0]
    if turn_on_index.size > 0:
        ton = voltage[turn_on_index[0]]
        legend_labels.append((legend_name, f'{legend_name}: {ton:.2f} V'))
    else:
        legend_labels.append((legend_name, f'{legend_name}: N/A'))
    plot_handles.append(handle)

ax.set_xlabel('Anode Int. Voltage (V)', fontsize=12)
ax.set_ylabel('Anode Current (A)', fontsize=12)
ax.tick_params(axis='both', which='major', labelsize=10, width=2, length=6)
ax.tick_params(axis='both', which='minor', labelsize=8, width=1, length=4)
ax.minorticks_on()
ax.legend(plot_handles, [l[1] for l in legend_labels],
          title=legend_title, fontsize=10, title_fontsize=12,
          loc='upper left')

fig, ax = plt.subplots(figsize=(6, 4))
plot_csv_data(ax, 'frwd_sweep_init_dnls.csv', 'Turn-On Voltages')
plt.tight_layout()
plt.savefig('anode_current_vs_voltage_frwd_sweep.png', dpi=300,
          bbox_inches='tight')
plt.show()

```

Conduction Band Energy Contour Plot

```

import numpy as np
import matplotlib.pyplot as plt
from scipy.interpolate import griddata

def read_data(file_path):
    data = np.loadtxt(file_path, delimiter=' ')
    return data[:, 0], data[:, 1], data[:, 2]

```

```

def create_contour_plot(x, y, z):
    xi = np.linspace(x.min(), x.max(), 300)
    yi = np.linspace(y.min(), y.max(), 300)
    xi, yi = np.meshgrid(xi, yi)
    zi = griddata((x, y), z, (xi, yi), method='cubic')
    plt.contourf(xi, yi, zi, levels=500, cmap='hsv', vmax=4.5, vmin=0)
    plt.colorbar(label='Conduction Band Energy (eV)')
    plt.xlabel(r'Position X ( $\mu\text{m}$ )')
    plt.ylabel(r'Position Y ( $\mu\text{m}$ )')
    plt.ylim(-0.01, 1)
    plt.gca().invert_yaxis()
    plt.axhline(y=0.2, linestyle='solid', color='k', linewidth=0.5)
    plt.axhline(y=8.2, linestyle='solid', color='k', linewidth=0.5)
    plt.fill_between(xi[0], -0.05, 0, color='none', edgecolor='k', hatch='///')
    plt.annotate('Anode', xy=(0.5, 1), xycoords='axes fraction',
                 xytext=(0.5, 1.1), textcoords='axes fraction',
                 arrowprops=dict(facecolor='black', shrink=0.05),
                 horizontalalignment='center', verticalalignment='center')
    plt.savefig('conduction_band_energy.png', format='png', dpi=300,
                bbox_inches='tight', pad_inches=0.1)
    plt.show()

if __name__ == '__main__':
    x, y, z = read_data('nio_ga2o3_cond.csv')
    create_contour_plot(x, y, z)

```

Acceptor/Donor Trap Concentration Comparison

```

import pandas as pd
import matplotlib.pyplot as plt
import numpy as np

def plot_csv_data(ax, file_path, legend_title):
    data = pd.read_csv(file_path)
    voltage_columns = [col for col in data.columns if 'Voltage' in col]
    current_columns = [col for col in data.columns if 'Current' in col]
    markers = ['o', 's', 'D', '~']
    custom_labels = [r'$e^{-13}$', r'$e^{-14}$', r'$e^{-15}$', r'$e^{-16}$']
    custom_colors = ['red', 'black', 'blue', 'magenta']
    legend_labels = []
    plot_handles = []

    for i, (v_col, c_col) in enumerate(zip(voltage_columns, current_columns)):

```

```

        legend_name = custom_labels[i] if i < len(custom_labels) else f'Extra {i+1}'
        color = custom_colors[i] if i < len(custom_colors) else 'gray'
        marker = markers[i] if i < len(markers) else 'o'
        handle, = ax.plot(data[v_col], data[c_col], marker=marker,
                           linestyle='-', color=color, label=legend_name,
                           markersize=6)
        voltage = data[v_col].values
        current = data[c_col].values
        turn_on_index = np.where(current > 1e-5)[0]
        if turn_on_index.size > 0:
            ton = voltage[turn_on_index[0]]
            legend_labels.append((legend_name, f'{legend_name}: {ton:.2f} V'))
        else:
            legend_labels.append((legend_name, f'{legend_name}: N/A'))
        plot_handles.append(handle)

    ax.set_xlabel('Anode Int. Voltage (V)', fontsize=12)
    ax.set_ylabel('Anode Current (A)', fontsize=12)
    ax.tick_params(axis='both', which='major', labelsize=10, width=2, length=6)
    ax.tick_params(axis='both', which='minor', labelsize=8, width=1, length=4)
    ax.minorticks_on()
    ax.grid(False)
    ax.legend(plot_handles, [l[1] for l in legend_labels],
              title=legend_title, fontsize=10, title_fontsize=12,
              loc='upper left')

fig, ax = plt.subplots(figsize=(6, 4))
plot_csv_data(ax, 'hj_diode_z_acc_frwd_comp.csv', 'Turn-On Voltages')
plt.tight_layout()
plt.title('Sensitivity - Acceptor Trap Concentrations')
plt.savefig('anode_current_vs_voltage_frwd_sweep.png', dpi=300,
            bbox_inches='tight')
plt.show()

```