The properties of isolated dangling bonds on hydrogenated 2H-SiC surfaces

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Using state-of-the-art electronic structure methods, we calculate the properties of silicon and carbon dangling bonds at several hydrogenated SiC surfaces including polar and non-polar cases. Generally, carbon defect levels are in the lower portion of the SiC band gap whereas silicon defect levels are in the upper portion. Additionally, surface work functions and hydrogen desorption energies are calculated and compared with experimental data. Carbon dangling bonds with hetero-polar back-bonding appear consistent with constraints derived from experiments on device quality nano-porous SiC. Finally, we make superhyperfine predictions which may help identify back bonded atoms involved in defect complexes.

I. Introduction

Silicon carbide (SiC) is a compound semiconductor whose surfaces play a role in a variety of applications.^{1, 2} Adsorption of molecules on SiC surfaces is common³ and SiC is used in gas sensors⁴ in part due to its known biocompatibility.⁵ Also, low dimensional structures, such as graphene, have recently been grown from SiC surfaces with many promising applications.⁶ Oxidation of SiC surfaces and passivation of interfacial defects by nitrogen and hydrogen are critical to the performance of many SiC-based devices including capacitors and transistors.⁷⁻¹¹ Oxidation mechanisms are in fact distinct at different SiC surfaces.¹² For power transistors, it has recently been demonstrated that the orientation of the 4H-SiC surface greatly influences the electrons' channel mobility.¹³ In SiC transistors generally, carbon related defects are found to be performance limiting.^{14, 15} For highly scaled integrated circuits, SiC surfaces occur inside nano-porous amorphous SiC, which is a new candidate material for back-end-of-the-line dielectric applications.^{16, 17} In the latter electrical example, isolated dangling-bond defects are suspected to inhibit device performance.^{8, 14, 15, 17} Despite the varied SiC surface applications, the fundamental properties of SiC surfaces are still being investigated. Recent studies illuminate the atomic and electronic properties of various SiC surfaces,¹⁸⁻²⁰ including interactions with hydrogen.²¹⁻²⁴

Given the significance of dangling bonds to a variety applications, there is a need to develop a better understanding of their fundamental properties at SiC surfaces. Experimentally, the growth and structure of bare²⁵ and hydrogenated SiC with hydrogen.^{21-24,25-27} have been examined with a variety of characterization techniques. Early fundamental studies focused on the nature of surface reconstructions on the bare surface.²⁸ However, more recent work has focused on employing the hydrogenated unreconstructed surface as the basis of electronics applications.¹ The properties of dangling bonds have been examined theoretically in the context of photoemission experiments on polar unpassivated SiC faces of n-type SiC.^{1, 29} Despite previous work, gaps remain in our present understanding of the nature of isolated dangling bonds on SiC surfaces that are important for many applications.

Here we present new first-principles calculations on the properties of isolated dangling bonds at SiC surfaces. These calculations will be most relevant for device applications where dangling bonds only appear in isolation. We first examine dangling bonds on polar surfaces. Then, we examine non-polar surfaces with heteropolar and homopolar bonding. The latter case is important for understanding the behavior of dangling bonds in amorphous SiC systems where homopolar bonding is common. For the three surfaces studied, we determine the gap levels, the acceptor and donor levels as well as the hyperfine parameters. The present results help elucidate the nature of isolated dangling bonds in a variety of technologically relevant systems. The balance of this paper is as follows: in Sect. II, we discuss our methodology, in Sect. III, we present our results along with some discussion and, in Sect. IV, we conclude.

II. Methodology

To examine the properties of dangling bonds at SiC surfaces we use periodic supercell models of hexagonal SiC which differ only by the ordering of hexagonal atomic layers and the number of layers in the primitive cell. The 2H-SiC polymorph has only two layers in its primitive cell and is useful for examining the cell size dependence of various properties. Also, 2H-SiC has a band gap close to 4H-SiC, the lowest energy SiC polymorph. While bulk properties were calculated for 4H-SiC and 2H-SiC, all surface results are for 2H-SiC. Details are given in Sect. III below.

Density functional calculations^{30, 31} were performed using the computer code VASP.^{32, 33} A plane-wave basis cutoff of 300 eV is used. Standard projected augmented wave (PAW) potentials were used to treat core electrons.^{34, 35} Calculations include relaxing all atoms to their T

= 0 K equilibrium positions using a force tolerance of 0.01 eV/Å. Lattice parameters are held fixed. Most calculations were performed with the generalized-gradient corrected functional (PBE)³⁶ to treat exchange and correlation. To determine work functions and to locate defect levels within the experimental gap, we need to accurately determine the position of the bulk valence band maximum (VBM). The PBE method underestimates band gaps and is not suited for determining relative band edges. Therefore, we use a hybrid functional to calculate the exchange interaction for the bulk electronic properties of 2H-SiC. The hybrid method uses PBE with a fractional amount of Fock exchange as determined by the mixing parameter. The hybrid method has been shown to reproduce accurate band offsets and defect levels for many semi-conducting systems, including SiC.^{37,38} Following Ref. [38], we apply a hybrid functional with a mixing parameter of 0.15 for our calculations. The method for calculating defect levels is formally valid only for localized defects. We have checked the charge localization of each of the defects examined in the present study to ensure that their charge is localized. Converged Monkhorst-Pack (MP)³⁹ k-point grids were used for all integrations over the supercell Brillouin zones. For the large supercell surface calculations, one special point at $\frac{1}{4}(1,1,1)$ was used.

The thermodynamic levels are the values of the Fermi level for which the defect has the same relaxed energy in two charge states. These levels are calculated by the difference of the total energies of the supercells with dangling bond atoms in two charge states, following standard practice. For more details on thermodynamic defect level calculations see Ref. [53]. The energetics of isolated dangling bonds have been calculated for both the Si- and C- faces. To estimate our uncertainty, we calculated the supercell size dependence of the charge level results. As previously shown, the formation energy of charged defects scales as approximately $1/L$, where L is the characteristic length of the supercell model.⁴⁰⁻⁴² We considered supercells with up to 300 SiC units and L up to 2 nm. Calculations reported below are for our largest supercell results. Based on our tests, we estimate that our reported energy level results entail uncertainties of ~ 0.1 eV.

III. Results and Discussion

The results below are organized as follows. First, we present some results for bulk 2H-SiC. Then, we present the new results for dangling bonds at 2H-SiC surfaces including the polar Si- and C-faces as well as the non-polar a-face.

III.a. 2H-SiC bulk properties

To determine reaction energies and defect levels, we need to know some bulk reference values. For this purpose, we examine the primitive 2H-SiC unit cell at the experimental lattice parameters with $a = 3.076 \text{ \AA}$ and $c/a = 1.641$.⁴³ With PBE, we determine the energetics and electronic structure of 2H-SiC. The energy per SiC of 2H-SiC is less than 0.01 eV higher than for 4H-SiC, close to previous calculations.⁴⁴ The valence band maximum occurs at the Γ point and the conduction band minimum occurs near the K point. The minimum PBE band gap is 2.29 eV for 2H-SiC and 2.21 eV for 4H-SiC, which is in agreement with prior work.³⁸ For 2H-SiC, the EXX minimum band gap is found to be 3.4 eV, close to the 3.3 eV value for 4H-SiC.³⁸

III.b. Surface Results for the (0001) and (000-1) faces

First, we consider a surface model which includes 8 SiC layers perpendicular to the surface and has a lateral size 6 times the primitive cell, for a total of 288 SiC units. The surface is passivated with 72 H atoms. We remove one hydrogen to create the isolated dangling bond. A vacuum region of 20 $\text{\AA}$ is added to isolate the Si-face from the C-face. A slice of this supercell model is shown in Fig. 1a, where we show both the Si- and the C-faces. To determine the variation in the electrostatic potential as a function of distance from the interface, we calculate the Hartree potential and average the values over the planes parallel to the interface. The planar averaged Hartree potential (V_H) is reported in Figure 1b. As illustrated in the discontinuity of V_H in the vacuum region, we employ a dipole correction because of the polar nature of the two surfaces. Without the correction, there would be a distinct slope to the potential across the entire SiC model and across the vacuum. Interestingly, the convergence to the vacuum level occurs within 5 $\text{\AA}$ of the physical surface, which is similar to results found at Si and SiO₂ surfaces.⁴⁵ In Figure 1b, two horizontal lines are included to indicate the calculated values for (1) the average Hartree potential in the bulk region of the surface supercell and (2) the bulk valence band maximum (VBM). The latter value is established by aligning the Hartree potential between the surface and bulk calculations using the now standard alignment method.^{38, 46, 47}

For the hydrogenated 2H-SiC, the work function is found to be 6.6 eV, for the Si-face, and 4.1 eV, for the C-face. The large difference in work functions represents the differing dipoles of the two surface faces. Theoretical or experimental work function results have not been previously reported for the hydrogenated 2H-SiC surfaces. However, the work function for the polar Si-face 6H-SiC is found experimentally to be 4.75 eV for n-type and 4.85 eV for p-type SiC.⁴⁸ The variation in work functions with doping is much less than the variation of the bulk Fermi level in the gap indicating that the surface Fermi level is pinned by surface defect states. Setting the surface Fermi level at mid-gap for our Si-face 2H-SiC calculations results in a work function of 4.9 eV, in close agreement with the experimental results. The close agreement is fortuitous given the differences between the 2H- and 6H-SiC electronic properties and other factors.

We calculate the hydrogen bond strengths at the Si-face and C-face polar surfaces. We consider neutral hydrogen release from the surface. To remove hydrogen to vacuum costs 3.8 eV and 4.5 eV from the hydrogenated Si- and C-faces, respectively. The final state for hydrogen in the calculation is the neutral atomic state. While molecular hydrogen is the favored state in the gas phase, hydrogen may release from bonds as a mono-atomic species in cases where other hydrogen atoms are not present nearby. Since thermal desorption experiments determine the energy barrier to remove hydrogen, the neutral atomic gas state is usually the pertinent state. Indeed, the 4.5 eV value calculated for the C-H bond strength is close to the 4.3 eV desorption energy observed for paramagnetic defect annealing in porous SiC.⁴⁹ The corroboration of these results suggests hydrogen desorbs as a mono-atomic species and that C-H bonds dominate in porous SiC. The hydrogen desorption energy at the SiC/SiO₂ interface is significantly larger than at the Si/SiO₂ interface.^{49, 50} The difference is due in part to the increased bond strength of C-H over Si-H bonds as found in the present calculations. However, the final hydrogen state also differs between Si and SiC. A study of hydrogen desorption at the Si/SiO₂ interface found that the low-energy (~ 2.5 eV) desorption path involves atomic hydrogen diffusing along the surface which is less favorable in the case of SiC.⁵¹

III.b.i Defect levels

In Figure 1c, we show the defect levels of the neutral isolated dangling bonds. Note that in the panel dashed horizontal reference lines are included at $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$ of the band gap. The defect levels have been clearly identified due to the associated eigenstates having charge local-

ized on the respective dangling-bond atom. The dangling-bond state has two levels in a spin polarized calculation with the lower level being occupied by one electron. For each dangling bond panel, on the right side we show our calculated values for the thermodynamic donor (+1/0) and acceptor (0/-1) levels.

For the carbon dangling bond (C_{DB}), the occupied level is resonant with the valence band at $\sim .7$ eV below the valence band maximum so there is no donor level in this case; the unoccupied gap level ($E_{VBM} + 0.8$ eV) is close to the acceptor level [$E(0/-1) = E_{VBM} + 0.9$ eV]. For a Si dangling bond (Si_{DB}), the defect levels are higher in the SiC band gap. The occupied gap level is near mid-gap ($E_{VBM} + 1.5$ eV) and the unoccupied level is in the upper part of the band gap ($E_{VBM} + 2.9$ eV). The donor level is close to mid-gap [$E(+1/0) = E_{VBM} + 1.6$ eV] and the acceptor level is well above mid-gap [$E(0/-1) = E_{VBM} + 2.6$ eV]. While previous calculations have not been performed for dangling bonds at SiC surfaces, in a hybrid DFT study of vacancies in bulk SiC, donor and acceptor levels were determined.⁵² Consistent with our findings here, Ref. [52] reported that the carbon dangling bond in the silicon vacancy had no donor (+/0) level in the SiC gap and an acceptor level at $\sim E_{VBM} + 1.3$ eV above the valence band edge; moreover, the silicon dangling bond in the carbon vacancy had an acceptor level at $\sim E_{VBM} + 1.8$ eV and a donor level at $E_{VBM} \sim 2.8$ eV. The two results differ by just a few tenths of an eV which is reasonable given the difference between isolated surface dangling bonds and vacancies, which involve four nearby dangling bonds.

III.b.ii Hyperfine parameters

An important method for identifying the point defects in semiconductors and insulators is to determine the hyperfine parameters which are determined from a defect's nuclear interaction with its spin density.^{53, 54} See References [34, 53] for details regarding the method for calculating hyperfine parameters. Figure 2 shows the spin density for the surface dangling bond defects of (a) silicon (Si_{DB}) and (b) carbon (C_{DB}). The spin density is highly localized. Both dangling bonds undergo very small relaxations as illustrated in Figure 2. The Si_{DB} spin density displays the expected sp^3 hybridization whereas the C_{DB} spin density resembles mainly the lone p-state of an sp^2 hybridized carbon atom. Dipole corrections have been included but are found to have only modest effects on the hyperfine parameters of the Si and C dangling bonds. For the Si (C) dangling bond, the parallel and perpendicular hyperfine parameters are 620 MHz. (270 MHz.) and 410 MHz. (110 MHz.), respectively. The Si and C hyperfine param-

ters at vacancies in bulk SiC⁵⁵ are about 30 % lower than the present results indicating that electronic spin densities are more localized at surfaces. The present hyperfine results for surface carbon dangling bonds are close to experimental hyperfine measurements of Cantin et al.¹⁴ They examined the defects in oxidized porous SiC. Our calculations corroborate their conclusion that carbon dangling bonds are the dominant defects. It should be noted that for the technologically more relevant 4H-SiC/SiO₂ interface, the observed carbon hyperfine signal is more closely aligned with those of bulk silicon vacancies than of isolated carbon dangling bonds.⁵⁶

III.c. Surface results for the non-polar (11-20) a-face

For the non-polar (11-20) *a*-face, we consider two surface termination cases. In both cases, we consider surface models with 6 SiC layers and a lateral size 6 times the primitive cell. There are 216 SiC units and the surface is passivated with 72 H atoms. There is 16 Å of vacuum to isolate the two surfaces. In the ideal case (Figure 3a), all Si (C) surface atoms are bonded to three C (Si) atoms and one H atom which protrudes from the surface. In Figure 3b, the Hartree potential is plotted for the ideal SiC *a*-face. In the puckered case (Figure 4a), there are C-C and Si-Si bonds parallel to the surfaces. These bonds are due to Jahn-Teller reconstructions similar to those on the Si(100):2x1 surface. The bonds are relatively strong with C-C bond lengths of 1.61 Å and Si-Si bond lengths of 2.49 Å. The puckered SiC *a*-face is (1.0 eV / per surface SiC unit) higher in energy than the ideal case. Nevertheless, this surface provides an estimate for the properties of isolated dangling bonds in disordered SiC systems where homopolar bonds are common. In Figure 4b, the Hartree potential is plotted for the puckered SiC *a*-face. The work functions are calculated to be 5.4 eV for both the ideal and puckered surfaces. These work function results are very close to the average of the Si-face and C-face non-polar surface results (5.2 eV), which is reasonable.

We consider hydrogen release from the surface as a mono-atomic species. To remove a mono-atomic hydrogen from the hydrogenated surface to vacuum costs 3.8 eV and 4.3 eV from the Si-H and C-H bonds, respectively, for the ideal surface. The puckered surface results are 0.3 eV and 0.1 eV lower for Si-H and C-H bonds, respectively. Both results are close to the H desorption energies reported for the polar faces. Therefore, the polarization of the surface and the secondary back bonds have only modest effects on the hydrogen bond strengths.

III.c.i Defect levels

The properties of carbon and silicon dangling bonds have been examined for both ideal and puckered non-polar surfaces. The defect levels are reported for the ideal non-polar surface in Figure 3c. For the carbon dangling bond (C_{DB}), the occupied gap level is just below the valence band maximum ($E_{VBM} - 0.3$ eV) and the unoccupied level is close to mid-gap ($E_{VBM} + 1.3$ eV). The donor level is $E(+1/0) = E_{VBM} + 0.8$ eV and the acceptor level is $E(0/-1) = E_{VBM} + 2.1$ eV. For the silicon dangling bond (Si_{DB}), the occupied gap level is just below mid-gap ($E_{VBM} + 1.1$ eV) and the unoccupied level is above mid-gap ($E_{VBM} + 2.4$ eV). The donor level is below mid-gap [$E(+1/0) = E_{VBM} + 1.1$ eV] and the acceptor level is in the upper portion of the band gap [$E(0/-1) = E_{VBM} + 2.1$ eV]. These results show similar trends with slightly higher values than our results for dangling bonds at the polar surfaces.

The puckered surface dangling bond results reported in Figure 4c show some interesting variation. For the carbon dangling bond, the occupied gap level is $E_{VBM} + 0.6$ eV and the unoccupied level is close to mid-gap ($E_{VBM} + 2.0$ eV). The donor (+/0) level at $E_{VBM} + 0.4$ eV is lower than the ideal surface case whereas the carbon acceptor (0/-) level (at $E_{VBM} + 2.0$ eV) is very close to the ideal result. For the silicon dangling bond, the occupied gap level is just below mid-gap ($E_{VBM} + 1.2$ eV) and the unoccupied state is above mid-gap ($E_{VBM} + 2.2$ eV), both close to the respective ideal results. The donor level is below mid-gap [$E(+/0) = E_{VBM} + 1.1$ eV] and the acceptor level is in the above mid-gap [$E(0/-) = E_{VBM} + 2.2$ eV]. These levels are both lower than the respective ideal non-polar surface results. Below we examine the spin density of these dangling bonds to elucidate their chemical natures.

III.c.ii Hyperfine parameters

The calculated spin densities for the C and Si dangling bonds at the non-polar surfaces closely resemble the spin densities reported in Figure 2. For the ideal non-polar surface, the Si (C) dangling-bond parallel and perpendicular hyperfine parameters are 610 MHz. (270 MHz.) and 410 MHz. (100 MHz.), respectively. These results are almost identical to the polar surface results. For the puckered surface, the Si_{DB} hyperfine parameters are significantly lower than in the previously considered cases above. The Si (C) dangling bond parallel and perpendicular hyperfine parameters are 470 MHz. (310 MHz.) and 270 MHz. (130 MHz.), respectively. It is noteworthy that, for the puckered surface, the hyperfine parameters for the C_{DB} are close to the ideal surface results indicating the carbon's spin density is insensitive to switching one C-Si bond for a C-C bond.

Isolated dangling bonds rarely occur at SiC surfaces. For instance, on the bare SiC surface, dangling bonds interact to form various reconstructions. To create isolated dangling bonds one would have to partially passivate the surface, which is technically challenging. While an STM can selectively remove isolated hydrogen atoms from a hydrogen passivated surface, hydrogen strongly tends to desorb in its molecular form leaving behind two interacting dangling bonds.²⁴ Isolated dangling bonds are known to form unintentionally during the oxidation of silicon surfaces.^{57, 58} However, oxidation of SiC is more complicated and there is no clear evidence for isolated dangling bonds.^{38, 59}

The present results for SiC surfaces may have applicability to porous SiC materials which include hydrogenated surfaces throughout the material. Nano-porous SiC alloys are leading candidates for back-end-of-the-line low-k dielectrics for next generation integrated silicon circuits.⁶⁰ Electron Spin Resonance (ESR) experiments have identified the primary point defects to be carbon related.^{17, 61} These defects are correlated with leakage currents through a defect level in the upper portion of the SiC band gap.¹⁷ ESR experiments which analyze hyperfine signatures could determine if these carbon defects are bulk or surface carbon atoms based on our present calculations. The carbon defects are likely to occur at the surface of a nanopore within a-SiC. Comparing Figures 1, 3, and 4, we find only the puckered non-polar surface has carbon related defect levels above mid gap. These carbon defects have one C-C bond and two C-Si bonds. Experiments on nanoporous SiC show that homopolar bonds are common in these materials.¹⁷ Careful hyperfine experiments could more clearly distinguish between competing models. To help in this process, we have calculated the hyperfine signatures on the carbon defect's nearest neighbors. In the case of the ideal surface, the three silicon neighbors each have an isotropic hyperfine value of ~ 22 MHz. In the case of the puckered surfaces, the carbon neighbor $1.55 \text{ \AA}$ away has a hyperfine value of ~ 15 MHz, whereas the silicon neighbors both have an isotropic hyperfine value of ~ 22 MHz, similar to the ideal case. The additional carbon super-hyperfine signature could help distinguish candidate carbon defects.

IV. Conclusions

The present results allow one to draw several conclusions regarding isolated dangling bonds in a variety of SiC surface systems. First, consider the influence of doping on the

charge state of the isolated dangling bonds. Silicon dangling bonds have defect levels in the upper part of the SiC band gap and carbon dangling bonds have levels in the lower portion of the band gap. Comparing their respective donor and acceptor levels, both neutral Si_{DB} and C_{DB} co-exist only for non-polar, intrinsically doped surfaces. Both carbon and silicon dangling bonds would tend to pin the surface Fermi energy by countering shallow dopants. The defect levels and hyperfine parameters calculated here are useful for identifying defects in systems with SiC surfaces. Comparing our calculations to recent experiments, we tentatively identify leakage-causing defects in porous SiC dielectrics as carbon atoms with a mixture of hetero- and homo-polar back bonding.

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Figure Captions

1. Polar SiC Surface: In (a) we show a slice of the supercell ball-and-stick model used. The blue, brown and white balls are silicon, carbon and hydrogen, respectively. In (b) we show the planar averaged Hartree potential curve along with horizontal lines for the average bulk potential and the aligned bulk valence band maximum (VBM). In (c) we present our isolated dangling bond results for carbon (C_{DB}) and silicon (Si_{DB}). The left side for each DB shows the eigenlevels for the neutral DB with the occupied and unoccupied levels connected by a dotted line. The right side shows the acceptor and donor levels.
2. Polar SiC Surface Dangling Bonds: We show the ball-and-stick model and the spin density (ρ) for the neutral isolated carbon (left) and silicon (right) dangling bonds. The blue, brown and white balls are silicon, carbon and hydrogen, respectively. The yellow feature represents an iso-surface of the spin density with value of $\rho = 0.02$ electrons per supercell volume.
3. Non-Polar ideal SiC Surface with only heteropolar surface bonds: Same caption as Figure 1.
4. Non-Polar puckered SiC Surface with homopolar surface bonds : Same caption as Figure 1.

Fig 1a

Fig 1b

Fig 1c

Fig 2

Fig 3a

Fig 3b

Fig 3c

Fig 4a

Fig 4b

Fig 4c

Graphical abstract