Interfaces between crystalline Si and amorphous B: Interfacial interactions and charge barriers

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(Received 29 November 2020; accepted 21 January 2021; published 9 February 2021)

The recently found crystalline silicon-amorphous boron (c-Si/a-B) heterojunction has been successfully applied in the detection of short-wave UV photons. These detectors play a decisive role in the progress of nanoelectronics fabrication. The *c*-Si/*a*-B heterojunction could not be explained using the existing 'instrumentarium' in semiconductor physics. We investigated the *c*-Si/*a*-B interfaces using *ab initio* molecular dynamics simulations. The simulations reveal atomic ordering of the *a*-B atoms adjacent to both the Si{0 0 1} and Si{1 1 1} substrates. Charge transfer occurs from the interfacial Si to B, thereby forming Si⁺/B⁻ charge barriers, which induce an electric field in the nearby regions. The obtained information here is helpful in furthering our understanding of the physics behind the *c*-Si/*a*-B junctions, as well as driving the development of a new 'instrumentatrium' in solid state physics.

DOI: 10.1103/PhysRevB.103.075301

I. INTRODUCTION

Progress in nanoelectronics fabrication is at present highly dependent on advances in UV photolithography techniques. This in turn has lead to a demand for high-performance shortwave UV detectors (for wavelengths between 1–200 nm) [1–5]. These UV photons have very shallow penetration depths; junctions with ultrathin deposition layers are therefore a requirement. Si-based junctions (or photodiodes) are good candidates for this application due to both their low cost and the availability of well-established production techniques.

A promising candidate is the crystalline silicon-amorphous boron (c-Si/a-B) junction. The junction consists of a nanometer-thin (typically 1 to 5 nm) amorphous boron (a-B)layer on a crystalline silicon (c-Si) substrate. This junction is produced by deposition of amorphous B on Si wafers via decomposition of borane at an elevated temperature, through a technique referred to as the PureB process [1-4,6-9]. While this technology has already been successfully applied in the design and creation of new UV detectors [4], there is a lack of profound understanding concerning the exact mechanism behind this new type of junction. The classic theory for semiconductor devices is based on descriptions for either doped Si⁺ on Si⁻ (e.g., B-doped Si⁺ on P-doped Si⁻, p-n junctions) or Si-metal interfaces (Schottky diode) [10–12] and proves to be insufficient to describe this class of junction [13].

Currently, experiments have primarily been focused on studying the PureB processes as well as the optoelectrical properties of the produced c-Si/a-B junctions [5,14–16]. In more recent studies the local structure and composition of the interface were investigated using high resolution electron

microscopy (HR-EM) techniques [7,16,17]. The HR-EM images revealed the formation of mixed B-Si layers for samples prepared at high temperature (\sim 700 °C), whereas little B-Si mixing was observed for samples with a lower preparation temperature (\sim 400 °C) [1–3,7,18,19].

On the theoretical side, parameter-free first-principles approaches are very useful to get insight into the mechanism of heterojunctions. In particular, *ab initio* molecular dynamics (AIMD) simulation techniques have been successfully applied before investigating the interfaces between crystalline Si and amorphous silicon oxide (c-Si/a-SiO₂) [20] as well as crystalline Si and amorphous silicon nitrides (c-Si/a-Si₃N_{4-x}) [21–23]. First-principles methods were also used to study the bulk properties of silicon, its clean [24] and hydrogen passivated surfaces [25], borane radicals deposited on the surfaces [6,8,26,27], and some Si-metal (Schottky) barriers [12]. Recently, we also performed AIMD simulations on the Si{1 0 0}/a-B interface to aid experimental observations [7]. However, details on the local chemical bonding and electronic properties at the c-Si/a-B interfaces are sparse.

Within the semiconductor industry Si $\{0 \ 0 \ 1\}$ is used predominantly in the production of electronic devices. However, Si $\{1 \ 1 \ 1\}$ wafers are available commercially as well. The Si $\{1 \ 1 \ 1\}$ atoms exhibit different symmetry and chemical properties. The atoms at the pristine Si $\{0 \ 0 \ 1\}$ surface lose two Si neighbors when considering coordination numbers, whereas an interfacial Si atom at the pristine Si $\{1 \ 1 \ 1\}$ surface loses only one neighbor.

In this work we investigate the formation of interfaces between *a*-B and *c*-Si in both the $\{0\ 0\ 1\}$ and the Si $\{1\ 1\ 1\}$ orientations using AIMD simulation techniques. The simulations produce atomically sharp Si-B interfaces and further analysis reveals charge transfer at the interfaces. We consider this mechanism to play a key role in the electronic properties

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Interface	Lattice	Unit params.		No. of atoms		Bonding of pristine interface
		<i>a</i> (Å)	<i>c</i> (Å)	N _{Si}	NB	
$Si\{0 \ 0 \ 1\}/a-B_I$	Tetragonal	16.45	19.18	144	300	Each Si _{surf} loses two neighbors
$Si\{0 \ 0 \ 1\}/a-B_{II}$	Tetragonal	16.45	27.44	144	600	
$Si\{1 \ 1 \ 1\}/a-B_I$	Hexagonal	15.51	26.65	192	300	Each Si _{surf} loses one neighbor
$Si\{1\ 1\ 1\}/a$ - B_{II}	Hexagonal	15.51	40.30	192	600	

TABLE I. Input parameters of the supercells used for AIMD simulations of the c-Si/a-B interfaces.

of the c-Si/a-B junction. The information obtained here sheds some light on the formation of the c-Si/a-B junctions, and we believe it will be useful for a better understanding of the formation of other heterojunctions as well.

II. METHODS

The AIMD approach employs periodic boundary conditions (PBC). For the Si{0 0 1}/*a*-B systems, we utilized a tetragonal supercell with $a = b = 3a_0$ (with a_0 the lattice parameter of Si at the simulation temperature [28,29]). For the Si{1 1 1}/*a*-B system, a hexagonal lattice was used with the in-plane lattice parameter $a = b = 2\sqrt{2}a_0$. The length of the *c* axis was determined by the volume of the *a*-B atoms and the thickness of the Si part [28,29]. Different amounts of amorphous boron atoms were also used to avoid accidental cases. The lattice parameters and numbers of atoms used as inputs are listed in Table I. These supercells are required to provide statistically meaningful results.

Amorphous B (*a*-B) samples were first heated at 4000 K (T_{melt} for B is 2348 K) for 2000 steps (1.5 fs per step), or 3.0 ps in total, before cooling to the simulation temperature. The obtained samples and the Si slabs were then used to build in the interface systems. We used a two-step approach to simulate the interface systems.

We first performed simulations for the built systems with the Si atoms pinned in the substrates at 1000 K for about 1.5 ps. Then, we equilibrated the interface system with full relaxation of all atoms at 1000 K and 700 K for another 3000 steps, respectively. The simulations show that this two-step approach avoids the risks of collective movements of atoms. We took samples at an internal time of about 0.1 ps after the system reached equilibrium (at about 2 ps simulation time). Finally, the obtained samples were relaxed to remove the internal forces [30,31]. We also relaxed structures of amorphous B samples with different densities, which were then used to calculate the electronic structure.

In the current AIMD simulations, we employed a pseudopotential plane-wave approach within the density-functional theory (DFT) [32,33] within the first-principles code of the Vienna *ab initio* simulation package (VASP). This code utilizes the projector augmented-wave (PAW) method [34,35]. Moreover, it allows variable fractional occupation numbers and therefore works well for the semiconducting/metallic interfaces [32]. The AIMD simulation employs the finite-temperature density functional theory of the one-electron states, the exact energy minimization and calculation of the exact Hellmann-Feynman forces after each MD step using preconditioned conjugate techniques, and the Nosé dynamics for generating a canonical NVT ensemble

[32,33]. The exchange and correlation terms are described using the generalized gradient approximation (GGA) [36].

The atomic electronic configurations in pseudopotentials for B and Si are [He] $2s^22p^1$ and [Ne] $3s^23p^2$, respectively. For structural optimizations, we used cutoff energies of 400.0 eV for the wave functions and 550.0 eV for the augmentation functions. These energies are higher than the corresponding default values ($E_{cut}/E_{aug} = 318.6/535.3$ eV and 245.3/322.1 eV resp. for B and Si). The electronic wave functions were sampled on dense grids, e.g., a 24 × 24 × 24 (413 k points) and 30 × 30 × 30 k mesh (183 k points) in the irreducible Brillouin zone (BZ) of the conventional cell for Si and the hexagonal cell of α -B, respectively [37].

For the AIMD simulations of the large supercells we used $E_{cut} = 320$ eV and simulated only the Γ point in the BZs. The dynamics of amorphous-solid/crystal interfaces, molecular/surface reactions and low-dimensional structure are typically modeled using Γ -point sampling due to the lack of periodicity of the overall system [6,30,31,38]. This helps in tuning the demand of computations to obtain reliable results to the capabilities of the computer cluster. Our prior simulations that tested different cutoff energies, ranging from 200.0 eV to 400.0 eV, demonstrated that the settings are reasonable.

III. RESULTS

First-principles structure optimizations were then performed for the elemental solids using the settings mentioned above. The calculated lattice parameter for the cubic Si is 5.469 Å, which is slightly larger than the experimental value (5.4309 Å) [28]. Each Si atom is in tetragonal coordination with Si-Si bond length of 2.37 Å. The calculations also produced lattice parameters for α -B which has a rhombohedral lattice. The calculated lattice parameters are a = 5.057 Å, $\alpha = 58.04^{\circ}$. These values agree with the experimental values, a = 5.06 Å, $\alpha = 58.09^{\circ}$ [29]. The boron atoms have six to seven neighbors with interatomic distances ranging from 1.71 to 2.02 Å. Such overestimation of lattice parameters of crystals is not unusual for simulations using DFT-GGA [39]. The results for the elemental solids are therefore well in agreement with the experimental data found in literature with a deviation of <1%.

Furthermore, band structure calculations were performed for crystalline Si and α -B. The calculations predict that Si is an indirect semiconductor: The top of the valence bands for both crystals are at the Γ point and the bottom of the conduction band is at (0.4167, 0.4167, 0.0) in the Brillouin zones. The calculated indirect gap for Si is 0.61 eV using this approach. The calculated energy gap is noticeably smaller than the experimental value (1.17 eV) [39]. The calculations



FIG. 1. Total density of states of boron atoms of the crystalline α and amorphous phase (a) with different densities (b) and of crystalline Si. The Fermi level is given in green. In (a), the density of *a*-B is represented by *a*B-V1, *a*B-V2, and *a*B-V3 with values of 2.44 g/cm³, 2.35 g/cm³, 2.08 g/cm³, respectively.

revealed a semiconducting nature for the crystalline boron when analyzing the density of states as shown in Fig. 1. The calculated band gap is 1.50 eV which is also smaller than the experimental value (2.0 eV) from resistivity measurements [40]. An underestimation of band gaps for semiconducting crystals is not unusual for the standard density functional calculations including the GGA method [39,41].

Figure 1 also includes the total density of states (DOS) for the *a*-B samples with different densities. The frame of the DOS curves of *a*-B and the crystalline phase are similar with the exception of a band gap for the latter. The calculated Fermi level of amorphous B is about 0.4 eV higher than the Fermi level of c-B. Correspondingly, the Fermi level of the calculated DOS curves is set at zero eV. The Fermi level of *a*-B is located in the valleys of the DOS curve. Analysis shows that the states around the Fermi level are strongly localized. This is due to local structural distortions/defects, a lack of long-range ordering, and strong interatomic interaction in *a*-B.

A. Interface formation and local bonding at the interfaces

During the AIMD simulations the amorphous B atoms move towards the pinned Si substrates and correspondingly the total electron energies of the systems decreased rapidly within the first 1 ps, which was then followed by a steady decrease. There was also a change in energy due to relaxation of both the Si and the B atoms. The systems reached equilibrium after 1.0 ps with full relaxation.

Figure 2 shows the snapshots of the relaxed c-Si/a-B interfaces and related typical local chemical bonding and Si coordination at the interfaces. The snapshots provide us with direct impressions of the local structure of the interfaces. Figures 2(a) and 2(d) shows that for both interfaces the boron atoms away from the substrates remain disordered. The interfacing amorphous B atoms also remain well separated from the Si substrates. There are a number of subtle differences between the two interfaces:

(1) The spacing between the Si substrate to the amorphous B at the Si $\{1 \ 1 \ 1\}/a$ -B interface is larger than for Si $\{0 \ 0 \ 1\}/a$ -B;

(2) The B atoms adjacent to Si{1 1 1} are positioned mainly on top of Si atoms;

(3) The interfacial Si atoms at Si $\{0 \ 0 \ 1\}/a$ -B have dominantly two B neighbors [Figs. 2(b), 2(c)], whereas those at Si $\{1 \ 1 \ 1\}/a$ -B have one B neighbors [Figs. 2(e) and 2(f)];

(4) The density of boron atoms near the Si $\{0 \ 0 \ 1\}$ substrate [Fig. 2(a)] appears higher than in the case of the Si $\{1 \ 1 \ 1\}$ substrate [Fig. 2(d)].

These Si-B bonds were analyzed for ~ 20 samples per interface. The Si-B bond lengths are at most 2.28 Å, which is 10% longer than the average B-B (1.79 Å) and Si-Si bond length (2.35 Å) in the elemental solids, respectively, when taking into account the exponential decay of bond strength on interatomic distance [42]. The results of this analysis are shown in Fig. 3.

From this analysis it was found that 88% of Si atoms at the Si{1 1 1}/*a*-B interface are coordinated by one B which together with the three Si-Si bonds satisfies the tetragonal coordination (sp³ hybridization) [43]. Roughly 10% of the interfacial Si atoms coordinated with two B atoms. The analysis also revealed a few cases where a B atom is bonded to a Si at the subsurface Si layer. This is likely due to the kinetic factor present during the molecular dynamics simulations.



FIG. 2. Snapshots of simulated a-B/Si{0 0 1} (a) and a-B/Si{1 1 1} (d) interfaces. Also given are examples of Si coordination of an interfacial Si and local chemical bonding at the a-B/Si{0 0 1} [(b),(c)] and the a-B/Si{1 1 1} [(e),(f)] interface, respectively. The small green spheres and the larger blue spheres represent B and Si, respectively.



FIG. 3. Distribution of the number of closest nearest neighboring (CNN) B atoms for interfacial Si atoms at the Si $\{0 \ 0 \ 1\}/a$ -B (red circles) and Si $\{1 \ 1 \ 1\}/a$ -B (black squares) interfaces.

The Si coordination of Si at the Si $\{0 \ 0 \ 1\}/a$ -B interfaces is more complex (Figs. 2 and 3). The majority of the Si atoms at the Si $\{0 \ 0 \ 1\}/a$ -B interface have two B neighbors (57%). A certain 29% of the interfacial Si atoms have three B neighbors, a further 9% of the interfacial Si have only one B neighbor, and finally 4% of the surface Si at atoms have four B neighbors. The larger variety of Si coordination at the Si $\{0 \ 0 \ 1\}/a$ -B interfaces originates from the reduced constraint from the Si substrates as each surficial Si is bonded to only two Si atoms at the subsurface. The different local Si-B bonding indicates variation in B arrangements at the interfaces, as shown in Figs. 2(b), 2(c), 2(e), and 2(f). This corresponds to a variation in the B density along the direction perpendicular to the substrates The unusual steric hindrance and local Si-B (layering). bonding at Si $\{1 \ 1 \ 1\}/a$ -B indicate higher energy barriers for B diffusion into Si as compared with that at the Si{0 0 1 $\frac{}{a-B}$. This is in line with the previous experimental results that at high temperature (~ 1073 K) the B diffusion rate at the $Si\{0 \ 0 \ 1\}$ wafers is notably higher than that at $Si\{1 \ 1 \ 1\}$ during the molecular layer doping process [44]. To assess the layering phenomenon at the interfaces, we introduce the atomic density profile. It is defined as follows [31,45]:

$$\rho(z) = \frac{\langle N_z(t) \rangle}{L_x L_y \delta z},\tag{1}$$

where L_x and L_y are the in-plane x and y dimensions of the cell, respectively, with z the dimension perpendicular to the interface, δz the bin width, and $N_z(t)$ the number of atoms between $z - (\delta z/2)$ and $z + (\delta z/2)$ at time $t. < N_z(t) >$ is the time-averaged number of atoms in the duration. The atomic density profiles for the *c*-Si/*a*-B interfaces were analyzed for the relaxed configurations. The results are plotted in Fig. 4.

Our calculations for the interfaces of different *a*-B thicknesses also showed that there is no notable difference between the two density profiles. The atomic density profiles confirm our impression from the snapshots (Fig. 2). The Si substrates



FIG. 4. Atomic density profiles of the (above) Si $\{0\ 0\ 1\}/a$ -B and (below) Si $\{1\ 1\ 1\}/a$ -B interface equilibrated and annealed interface at 0 K, where the black lines represent $\rho(z)$ for Si atoms and the green for B atoms. The broken blue lines show the first boron peaks and the dotted blue line represents the outermost Si layer.

are well separated from the amorphous B. The single Si peaks in the Si $\{0 \ 0 \ 1\}$ substrate and the double Si-Si peaks in the Si $\{1 \ 1 \ 1\}$ substrates can easily be recognized. The statistics show a clear gap between the substrates and the amorphous boron. The *a*-B atoms near the substrates exhibit density variations.

The analysis also shows a larger spacing (1.9 Å) at the Si $\{1 1 1\}/a$ -B interfaces compared to Si $\{0 0 1\}/a$ -B (1.1 Å). Moreover, the amorphous B adjacent to the Si substrates form peaks. The amorphous B forms a broad peak centered at about 1.7 Å (peak 2) and a valley at about 2.3 Å. A second B peak is centered at 2.3 Å (peak 2), and a third peak is seen at 2.8 Å with a valley at 3.6 Å. Such unevenness and fluctuation in the B densities comes from the chemical interaction at the Si-B interfaces.

B. Electronic properties of the *c*-Si/*a*-B interfaces

Band structure calculations were also performed to study the interfacial interaction and related electronic properties. The partial density of states (pDOS) and total DOS (tDOS) of selected Si and B atoms both at the substrate/amorphous B as well as at the interfaces with typical Si-B bonds are shown in Figs. 5 and 6, respectively. The dispersion curves around the Fermi level in the *ab* planes for the two interfaces were also plotted in Fig. 7.

At both interfaces, all the Si and B atoms have similar electronic structure with a valence band and a conduction band as shown in Fig. 5. Both Si/B s and p states are all over the entire valence and conduction bands. The states of s character dominate the lower part of the valence band and extend to the conduction band, whereas the p states dominate the upper part of the valence band and the conduction band. This corresponds to the sp hybridization in crystalline Si and amorphous B parts. Figure 5 also shows that the Si in both substrates have an energy gap of about 0.7 eV. This band gap is



FIG. 5. Partial density of states (pDOS) of the Si 3s and 3p states as well as the B 2s and 2p states at the Si $\{0 \ 0 \ 1\}/a$ -B (a) and Si $\{1 \ 1 \ 1\}/a$ -B (b) interfaces around the Fermi level (0 eV). The black and red curves represent Si/B 3s/2s characters and 3p/2p states, respectively. The dotted line at zero eV represents the Fermi level.

close to the calculated band gap of bulk Si. The Fermi level is also at the top of the valence band for the interfacial Si atoms. There are unoccupied defect states at the forbidden gap of the interfacial Si atoms, as shown in Fig. 7, corresponding to electron loss from Si to its neighboring B atoms. These results indicate a valence-band offset for Si atoms near the interfaces.

The tDOS curves provide information on the Si substrates, the amorphous B, and interfaces Si and B atoms (Fig. 6). The shapes of the two curves are similar to each other: The valence bands start at around -16.3 eV and the density increases with energy up until roughly 2 eV below the Fermi level. Then the density of states decreases as energy increases. There is a pseudogap around the Fermi level at both interface systems. This gap is largely due to Si (see Fig. 5). The tDOS above the gap increases with energy. The states at the energy gap originate from the interfacial Si/B and the amorphous B, as detailed in Fig. 5. The dispersion curves show localized bands ranging from the Fermi level to about 0.7 eV (Fig. 7), originating from the *a*-B and the surficial Si/B atoms.

The valence band of a-B starts at about -16.3 eV for both interfaces. The DOS of the Si in the substrates starts at about -12.0 eV in Fig. 6. There are also some states between -16.3 eV to -12.0 eV for the interfacial Si atoms. This comes from the Si-B hybridization at the interfaces. The p states are suppressed and evenly distributed between -4.0 to -1.0 eV for the Si in the substrate, whereas they are dominant at approximately -3.0 to 0.0 eV for the interfacial Si, especially at the Si $\{001\}/a$ -B interface. At the Si $\{001\}/a$ -B interface, the interfacial B atom has a unique DOS of the 2p states with high density near the Fermi level, whereas the 2p states of an a-B atom are distributed from -5.0 to 0.0 eV. There is an energy gap for the Si atoms in the substrates at both systems. The DOS above the Fermi level for the interfacial B atoms is weak while there are 2p states up to 3.5 V for a-B. This unusually high density of 2p states for the interfacial B indicates extra band filling with charge from the nearby Si atoms. It is also notable that the interfacial effect on the electronic properties at the Si $\{0 \ 0 \ 1\}/a$ -B is more pronounced that that at the Si $\{1 \ 1 \ 1\}/a$ -B interface.



FIG. 6. Total DOS of the Si $\{0 \ 0 \ 1\}/a$ -B and Si $\{1 \ 1 \ 1\}/a$ -B interfaces. The dotted line at zero eV represents the Fermi level.



FIG. 7. Dispersion curves around the Fermi levels (green lines at zero eV) for the (a) Si $\{0 \ 0 \ 1\}/a$ -B and (b) Si $\{1 \ 1 \ 1\}/a$ -B interfaces in the *ab* planes.



FIG. 8. Charges at the c-Si/a-B interfaces. The red dots, black squares, and green circles represent the average charge values of each layer, the Si sites, and the B sites, respectively. The black dotted vertical lines indicate the peak of the outermost Si, while the dotted green one represents the first peak of B atoms.

C. Charge transfer and charge barrier at the c-Si/a-B interfaces

The charge density between atoms/ions as well as the charge transfer at this interface provide a more direct message to understand the interfacial interaction. Bader employed a unique way to define the shape and volume and electrons of an atom in solid using the electron density distributions from first-principles calculations [46]. This approach has been successfully applied to various systems [47,48]. Figure 8 shows the charges at the atomic sites at the two studied interface systems using the Bader charge analysis approach. The Si and *a*-B atoms away from the interfacial layers are electronically neutral. Charge transfer only occurs from interfacial Si atoms to interfacial B atoms. The average amount of charge transfer is calculated to be 0.75 e/Si for Si $\{0 \ 0 \ 1\}/a$ -B. In the case of Si $\{1 \ 1 \ 1\}/a$ -B this is 0.40 e/Si. From these values we estimate the charge densities at the interfaces. The atomic density of Si $\{0, 0, 1\}$ is $6.78 \times 10^{18} \text{ m}^{-2}$, which is the same at the Si{1 1 1} surface when only the top Si atoms are counted as shown in Fig. 8. The charge density then is 4.7×10^{18} em⁻² or 0.815 Cm⁻² ($e = -1.602 \times 10^{-19}$ C) for Si{0 0 1}/a-B and 2.7 × 10¹⁸ em⁻² or 0.435 Cm⁻² for {1 1 1}/a-B.

These values correspond to the number of Si-B bonds at the interfaces: Most of the interfacial Si atoms at Si $\{1 \ 1 \ 1\}/a$ -B have one B neighbor, whereas most interfacial Si atoms at Si $\{0 \ 0 \ 1\}/a$ -B have on average more than two B neighbors, referring back to Fig. 3. The amount of charge at the interface (0.75 e/Si for Si $\{0 \ 0 \ 1\}/a$ -B and 0.40 e/Si for Si $\{1 \ 1 \ 1\}/a$ -B) is smaller compared to the values obtained using an ionic model [1.0 e/Si and 2.0 e/Si, respectively, according to the averaged coordination numbers of Si by B (Fig.3)]. This is an indication of the ionic and covalent dual nature of the interfacial Si-B bonding. Such strong interfacial bonding also indicates strong mechanical properties of the interfaces.

The AIMD simulations revealed the formation of sharp *c*-Si/*a*-B interfaces. Charge transfer from the interfacial Si to B takes place at the atomic level, forming Si^{+q}/B^{-q} dipole layers at the *c*-Si/*a*-B interfaces. This charge transfer originates from a difference between the electronegativity of Si (1.90 in Pauling scale) and B (2.04). In the Si-B bonds electrons move from Si⁺ to B⁻ freely. Outside of the dipole plane, the Si-B dipoles induce a positive/negative electric field in the nearby *c*-Si/*a*-B region. The potential energy of linear dipoles decreases with r^{-3} or even faster) [49,50]. The formed electric fields at the *c*-Si/*a*-B interfaces bans/permits hole/electron carriers from passing through entering from the Si/B side. This is what is responsible for the rectifying and the electronic properties of the diodes.

IV. DISCUSSION

A. Intrinsic electronic properties of *a*-B

Elemental boron exhibits a large number of allotropes, most of them containing over a hundred atoms in the unit cell [51–53]. Theoretical studies based on quantum-mechanical approaches showed that several boron phases, including the α -rhombohedral phase (B₁₂), are stable at ambient conditions [53]. Structurally, the B phases of high stability at ambient conditions are composed of B₁₂ octahedral building blocks. We have calculated the electronic structure of the crystalline α -rhombohedral phase as shown in Fig. 1. The calculated energy gap is 1.5 eV which is smaller than the experimental value (2.0 eV) from resistivity measurements [40].

Amorphous boron (*a*-B) has also been investigated intensively before. The studies showed that there is no long range ordering in *a*-B. However, a short-range ordering is present in *a*-B. The overall structure of *a*-B also contains B_{12} octahedra albeit in a distorted form [54,55]. When compared to amorphous Si [56], the electronic structure of *a*-B contains higher concentrations of tailed states and defects in the forbidden gap due to the higher concentration of structural distortions and defects.

This is confirmed by our band structure calculations as shown in Fig. 1. The Fermi level clearly falls in the valley in the tDOS curve. There still is a considerable density around the Fermi level, indicating a metallic nature. The calculations also showed that the variation of a-B density from 2.43 g/cm³ (similar to that of solid B [29]) to 2.08 g/cm³ (close to that of liquid B [29]) has little influence on the electronic properties as shown in Fig. 1. However, the lack of long-range ordering (LRO) indicates that these states are localized. Experiments provided a large variance of energy gaps for a-B depending on preparation conditions and impurities as reviewed in a recent paper [57]. For deposited a-B samples, the experimental value of the energy gap is 0.5 to 0.75 eV [58-60]. The electrical transport properties measurements showed that the dominant charge carriers in a-B are holes [61,62]. Experiments also showed that impurities, including hydrogen and oxygen, may play a role on the band gap opening and electrical properties [57,63–65].

Overall, based on our AIMD simulations and band structure calculations, we conclude that a-B is intrinsically a 'bad' metal which consists of localized states. This indicates



FIG. 9. A schematic drawing of (a) band bending and (b) charge transfer at an ideal Si/a-B interface.

hopping mechanism for electrical transport, which corresponds to the high resistance of a-B [57,59–62]. This influences the electrical properties and the band offset at the c-Si/a-B interfaces. This is somewhat different from the experiments. Such discrepancy comes from the widely existing impurities, such as H and O and partial crystallization in prepared samples. The widely existing impurities, such as H, may cure the defects and related defect states and open an band gap in amorphous materials [56,66]. The charge carriers in pure a-B originating from the localized defect states have large effective masses and hop under electrical fields. Another point is partial crystallization of amorphous B samples during annealing at high temperature. Due to this, further investigation is necessary to reconcile our theoretical results with experimental values.

B. Band offset at *c*-Si/*a*-B interfaces

The present study revealed formation of strong interfacial interaction at the c-Si/a-B interfaces. There is charge transfer from the interfacial Si to B, forming Si⁺/B⁻ charge barriers, which induce positive/negative electric fields at the nearby Si/B regions. This is also an indicator for the strong mechanical properties of this heterojunction. The charge model is schematically shown in Fig. 9(b). Moreover, we also built band bending [Fig. 9(a)] for an ideal c-Si/a-B junction/diode based on the assumptions:

(1) The charged interface is described by $(c-)Si^{+q}/(a-)B^{-q}$ with the values for q given in the previous section.

(2) The Fermi level of a-B is higher than that of c-Si as discussed at the beginning of Sec. III.

(3) The Fermi level for Si atoms away from the interface is near the top of the valence band which bends upwards and part of this band becomes unoccupied.

(4) Amorphous B away from the interfaces is a 'bad' metal with localized defect states. Therefore, its Fermi level will be changed nearby the interface due to filling of the defect states by extra electrons from Si.

The simulated c-Si/a-B interfaces contain no B doping. Thus, the junction is not a p-n type as believed before [3]. Figures 2 and 4 showed that the a-B atoms near the Si substrates are of certain content of ordering with layering along the direction perpendicular to the substrates. The densities of states of the *a*-B atoms near the substrates are rather low (Figs. 5 and 6) and the states at the Si band gap are localized as shown in Figs. 5 and 7. This indicates that though the *a*-B adjacent to the Si substrates are not semiconducting, the related electron states are localized. The *a*-B atoms adjacent to the substrate are 'bad' metals. This *c*-Si/*a*-B junction fits not in the category of Schottky-type as well. It could not be assigned to any existing type of heterojunctions. The rectification originates from the electric field induced in the regions nearby the interface by the Si⁺/B⁻ dipoles.

This model can be applied to the present c-Si/a-B devices with a-B deposited on a n-type silicon wafer [1–5,13]. The strong electric fields across the c-(n-Si)/a-B interface caused by the interfacial charge transfer is responsible for the creation of a depletion zone in the n-silicon. As shown in Ref. [7], the formation of a depleted region reduces the charge at the interfacial Si atoms/ions just slightly. The electric field at the nearby a-B region together define the rectifying properties of the diode.

V. CONCLUSION

Ab initio molecular dynamics simulations were performed for the Si $\{0\ 0\ 1\}/a$ -B and Si $\{1\ 1\ 1\}/a$ -B interfaces. The simulations revealed the formation of sharp *c*-Si/*a*-B interfaces which are chemically bonded. Each interfacial Si atom has predominantly two Si-B bonds for Si $\{0\ 0\ 1\}/a$ -B and one Si-B bond for Si $\{1\ 1\ 1\}/a$ -B.

Band structure calculations and charge analysis reveal charge transfer occurring from the interfacial Si to nearby B atoms with $\Delta q = 0.75 \text{ e/Si} (5.1 \times 10^{18} \text{ e/m}^2)$ for Si $\{0 \ 0 \ 1\}/a$ -B and 0.40 e/Si $(2.7 \times 10^{18} \text{ e/m}^2)$ for Si $\{1 \ 1 \ 1\}/a$ -B, forming a pair of oppositely charged plates. This originates from the electronegativity differences between Si and B. The induced electric fields in the nearby regions by the Si⁺/B⁻ dipoles rectify the charge-carrier flow. We also built band diagrams for a pure *c*-Si/*a*-B diode accordingly. The obtained information here is not only useful to get insight into the mechanism of the *c*-Si/*a*-B junctions/diodes, but also for further developments of new heterojunctions/diodes.

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