

MODELING ELECTRON BEHAVIOR IN THE B-SI PHOTODETECTOR

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Abstract. Photodiodes based on the Boron on Silicon junction (B-Si) show excellent responsivity to DUV and VUV photons, radiation hardness, and impressive electrical characteristics. However, the currently used models describing the working principles do not sufficiently predict the junction's properties. We review three models: the ultra-shallow δ -doping model, the charge transfer model, and the Schottky-Mott model. We recognize that the δ -doping model requires very high dopant concentrations, not attained at lower deposition temperatures (400°C). We note that in the charge transfer model that electron movement from the Si to the B layer creates a potential barrier, explaining the rectifying properties. Finally, we find that the B-Si heterojunction fits the Schottky-Mott model, which is unusual as a-B is not considered a metal.

Keywords: first-principles; heterojunction; p-n junction, charge-transfer junction model, Schottky-Mott theory, barrier height

1. INTRODUCTION

Within the field of UV photolithography, the ability to detect vacuum ultraviolet photons (<200 nm) plays an important role in further developments towards smaller node sizes. Within this frequency range, the photons are very easily absorbed by matter and, as such, typically have very low penetration depths, which makes UV photons difficult to detect for conventional pn-junction or metal-on-silicon heterojunctions. A good candidate to tackle this challenge is the Boron on Silicon photodiode (B-Si).

B-Si photodiodes have an extremely shallow depletion region and a nanometer-thin capping boron layer, making these devices highly responsive to photons in the Extreme and Deep Ultraviolet (EUV/DUV) wavelength range. This range includes the 193 and 13.5 nm wavelength lasers used in the photolithography industry today.

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Thus, the B-Si photodiodes show superior sensitivity and stability compared to commercially available Si-based VUV detectors [1] and have been found to be used in the chip-making industry.

These photodiodes are prepared through chemical vapor deposition (CVD) of pure boron from diborane gas (B_2H_6) on a Si substrate to create an amorphous Boron (a-B) layer [2]. The fabrication of B-Si devices was initially done at 700°C. At these temperatures, B atoms are known to penetrate the Si surface and diffuse into the bulk of the substrate near the interface, creating a p-doped region in the Si, which was initially thought to be the origin of the depletion region [2]. However, it was demonstrated later that a rectifying junction with similar properties could be created using the same process at temperatures as low as 400 °C. The expected marginal doping at 400°C seemingly creates an incompatibility with this model, as the low temperature leads to an insufficient doping level of the Si compared to the measured electrical properties of the realized devices. Furthermore, recent experimental and theoretical efforts have led to the creation of devices with sub-nm layers at temperatures down to at least 250°C [3]. It is thus clear from experimental evidence and modeling that the initial interpretation of the δ -doping of the interface is insufficient to explain the origin of the rectifying properties of the B-Si interface.

In this study, we will describe the current understanding of the B-Si junction formation using several models:

1. the δ -doping model, which relies on the diffusion of the deposited B into the substrate,
2. a charge transfer model obtained from theoretical simulations and
3. the Schottky-Mott model.

We will discuss the merits and pitfalls of each model as it applies to this interface and other related devices. Finally, we present the challenges impeding experimental and theoretical efforts to understand the junction.

2. JUNCTION MODELS

2.1 Ultrathin p^+ -doping layer

Boron is a known p-type dopant of silicon. The high-temperature deposition of a-B on Si has been postulated to dope the n-type Si near the interface, creating a layer of p-type Si and forming a pn-junction that induces a depletion zone [4, 5] as depicted in Fig. 1a. In this model, the role of the bulk boron itself is negligible, as only the B atoms that diffuse into the substrate play a role in the formation of the junction. What should be clear is that the silicon near the interface will require a very high doping concentration in a narrow width, as depicted in Fig. 1b, with qN_c given as the charge concentration over the device.

The formation of the diode appears independent of the amount of deposited B – that is, the thickness of the B layer – as was first shown in devices with deposition

times between 1 second and 30 minutes [6]. Later, it was revealed that a layer as thin as 1 nm is enough to create a rectifying junction [7] and therefore it is reasonable to assume that the bulk of a-B does not play a significant role in determining the electrical properties of the heterojunction.

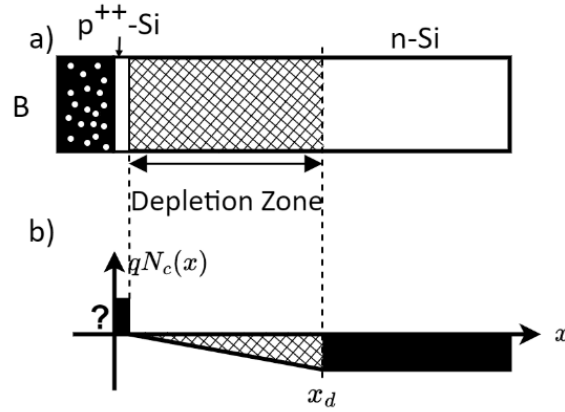


Fig. 1. (a) Cross-section of a B-Si δ-doped heterojunction.
(b) Dopant concentration distribution near the associated B-Si interface.

The required doping concentration levels can be obtained from experimental data and Poisson's equation to find the space charge region. The depletion width for a diode using the depletion approximation, e.g., with an abrupt change in doping concentration, is given as follows:

$$x_d = \sqrt{\frac{2\epsilon(N_D + N_A)V_{bi}}{eN_DN_A}} \quad (1)$$

where $\epsilon = \epsilon_{Si}\epsilon_0$ is the permittivity of Si, N_D and N_A are the dopant concentrations of the donor and acceptor states, V_{bi} is the built-in potential and e is the elementary charge constant. For an n-doped wafer with a resistivity of 1-5 Ωcm, the donor concentration is approximately $N_D = 10^{16}$ cm⁻³, while for the B-doping concentration of the Si at the interface, a figure of $N_A = 10^{19}$ cm⁻³ is known to be the doping limit of B in Si [2]. However, N_A quickly decreases in the p-region and averages out to approximately $N_A = 10^{17.5} = 3.2 \times 10^{17}$ cm⁻³.

The built-in potential for a pn-junction can be found using the following equation:

$$V_{bi} = \frac{k_B T}{e} \ln \frac{N_A N_D}{n_i^2} \quad (2)$$

where the thermal energy at room temperature is $k_B T \approx 0.025$ eV and $n_i = 8 \times 10^9$

cm^{-3} is the intrinsic carrier concentration of Si. Using the previously mentioned dopant concentrations, a built-in potential of 0.78 V can be found using Equation 2. Taking into account that $N_D \gg N_A$ and by applying the results from Equation 2 to Equation 1, a value of 0.32 μm is found for the depletion width.

Finding how far the depletion zone extends into the “p”-layer and n-type substrate can be done by taking the fraction of the depletion width:

$$x_d^n = \frac{x_d \times N_A}{N_D + N_A}; x_d^p = \frac{x_d \times N_D}{N_D + N_A} \quad (3)$$

By using a ratio between N_D and N_A of $3 \times 10^{17} : 10^{16}$, we find that this depletion zone extends approximately 0.31 μm into the n-type Si substrate and 9 nm into the p-type δ -doped layer. In other words, there is a very thin layer of p-doped Si and most of the depletion layer extends less than 1% into the width of a typical n-doped wafer.

A significant problem with this principle is in the diffusion of B into Si, as this process is strongly hindered when the deposition process of B is performed at a lower temperature ($\sim 400^\circ\text{C}$); the diffusion rate is reduced by a factor of 3.1×10^8 compared to the previously used 700°C [8], due to high diffusion barriers ($3.25 \div 3.85$ eV).

Therefore, this junction formation model is incomplete, as the doping concentration necessary to reach the measured barrier height is too high to be attained by the determined diffusion. As it has already been demonstrated that the amorphous boron layer thickness does not play a role in the junction formation, the formation mechanism is concluded to be determined by the reactions between Si and B atoms at the interface.

2.2 Charge transfer model

An alternative junction formation method based on ab initio first-principles simulation results was explored. The Vienna *ab initio* Simulation Package is based on the well-established Density Function Theory and has been used to simulate amorphous materials [9] as well as the growth of such materials on a crystalline solid from a liquid phase [10]. Strictly speaking, this ideal junction formation differs from the CVD process used to create B-Si devices. However, we use this approach to obtain an idealized interface to optimize the computational resource requirements.

The results of this simulation do not directly yield the charge transfer. We use the Bader approach to assign charge densities to atoms [11]. In doing so, we find the transfer of electrons between atoms. From the charge density distribution and subsequent charge analysis, the results from the simulations show charge transfer at the interface occurring from the interfacial Si atoms to the neighboring B atoms [8, 12]. The average number of electrons lost per Si atom, which we name ρ_{Si} , is approximately 0.76 e/Si for a-B on Si{0 0 1}.

A sharp interface has been found between Si and B, and the charge transfer appears to be strongly localized at the surfaces of the two materials. In prior work, we applied the parallel plate capacitor theory to find the potential difference and barrier height between the two layers, as shown in Fig. 2, and approximated a charge barrier as follows [13]:

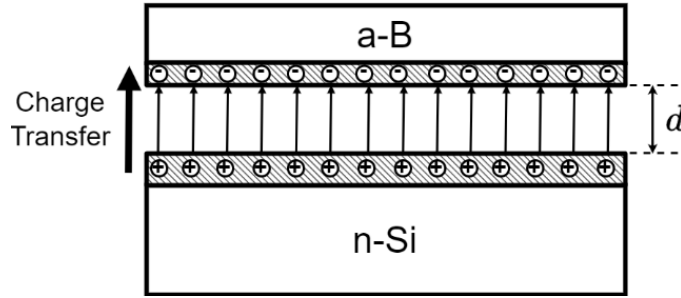


Fig. 2. Schematic representation of the charge transfer at the B-Si interface.

$$\Delta V = \frac{\sigma_e d}{\epsilon_0 \epsilon_r} \quad (4)$$

where the charge barrier is given as ΔV , σ_e is the charge density of the plates ($\sigma = Q/A$), d is the distance between the two plates, and ϵ_0 and ϵ_r are the vacuum permittivity and the relative permittivity of the dielectric (we use 11.7 for Si here). Note that the energy required for one electron to cross a barrier of 1 V is $E_{kin} = q \times V = 1$ eV. The values used for the calculation of the energy barrier of the simulated system are shown in Table 1, giving us a value of 0.95 eV. Here, n_{Si} is the density of Si at the surface of the crystal in the $\{0\ 0\ 1\}$ plane, and ρ_{Si} is the number of electrons lost per Si atom at the interface to find the surface charge density $\sigma_e = n_{Si} \times \rho_{Si}$.

Table 1. Values for calculating the potential difference and energy barrier of the B-Si interface using the parallel plate capacitor model.

Si surface density n_{Si} (Si/m ²)	Charge transfer ρ_{Si} (e/Si)	Surface charge density σ_e (e/m ²)	Interatomic distance d (Å)	Potential ΔV (V)
6.78×10^{18}	0.76	5.2×10^{18}	1.2	0.95

However, what if we instead consider the charge transfer as a way to dope the interfacial Si atoms? Supposing that the charge transfer at the interface acts to dope the Si at the interface effectively, a pn-junction is created as electrons diffuse from the bulk of the n-type Si toward the interface, as depicted in Fig. 3. As a result, a

depletion zone is created, which is responsible for the rectifying properties of the junction.

Table 2. Values for the depletion zone calculation for a B-Si interface using surface doping from charge transfer.

Surface charge density σ_e (e/m ²)	Acceptor concentration N_A (m ⁻³)	Built-in pot. V_{bi} (V)	Depletion width x_d (m)
5.2×10^{18}	$\sim 10^{28}$	1.05	0.37×10^{-6}

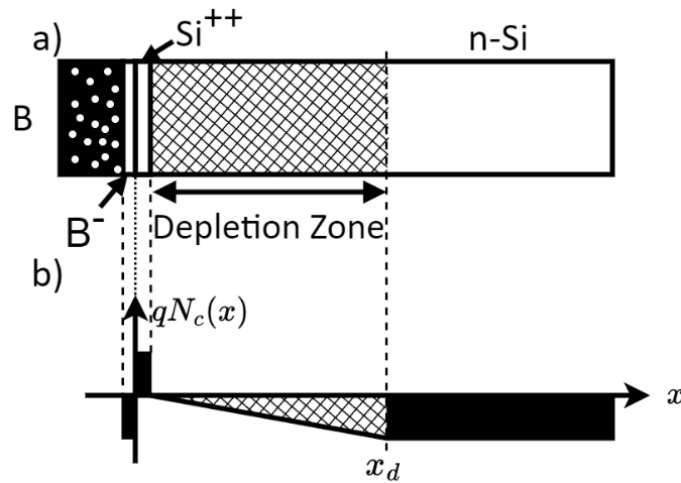


Fig. 3. (a) Cross-sectional representation of the B-Si interface according to the charge transfer model. (b) Distribution of dopant levels throughout the interface.

The charge concentration in the B layer at the interface is known from the calculated charge transfer in Fig. 3b, unlike the δ -doping model in Fig. 1b. If we consider the p-layer as our p-type doped Si, we can find similar values to those used in Eqs. 1-2. We approximate N_A from the total amount of charge from the surface charge density in the affected Si layer found in Table 1.

The depletion width is similar to what has been found for the δ -doping model. This is because the lower dopant concentration of the substrate determines the total depletion width. However, the built-in potential here is much higher due to the charge transfer and the density of Si at this interface, which results in a value closer to what was measured experimentally.

2.3 Schottky-Mott model

The formation of a clean B-Si interface forms the basis of the next model we consider. Traditionally, the Schottky junction has been used for metal-semiconductor junctions. For an n-type semiconductor, the Schottky Barrier Height (SBH) is found using the Schottky-Mott relation:

$$\Phi_B = \phi_m - \chi_s \quad (5)$$

where Φ_B is the Schottky BH, ϕ_m is the Work Function (WF) of the metal, and χ_s is the Electron Affinity (EA) of the semiconductor. This junction is represented in Fig. 4.

In this model, electrons pass through the semiconductor-metal interface into the metal; this is the origin of the band bending associated with the Schottky-Mott barrier, which then leads to the formation of an area devoid of free carriers, the depletion zone [14].

Bulk a-B has long been known to be a semiconductor [15], though we have found in our simulations localized states within the band gap, which we attribute to the amorphous structure of the layers [12]. Thus, we can consider the a-B layers to be a reservoir into which the electrons from the Si can drain, similar to the metal in a Schottky diode.

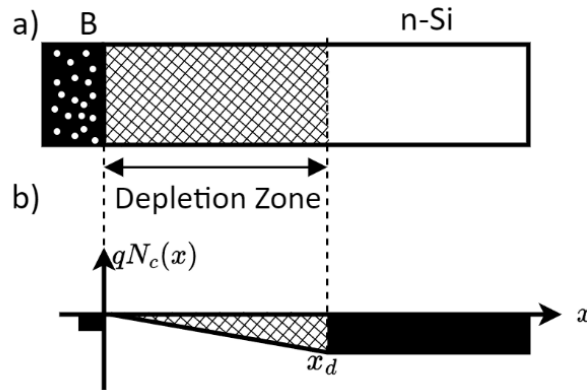


Fig. 4. (a) Schematic representation of the B-Si interface according to the Schottky-Mott model. (b) Dopant level distribution near the B-Si interface.

To verify this, we have applied the model for Schottky diodes to the B-Si interface. For Si, the EA is known to be 4.05 eV, and we have calculated the WF of a-B using AIMD to be 5.0 eV, as shown in Fig. 5. This results in an SBH of 0.95 eV according to Equation 2. This value is in the same range as that of experimental values for the B-Si interface.

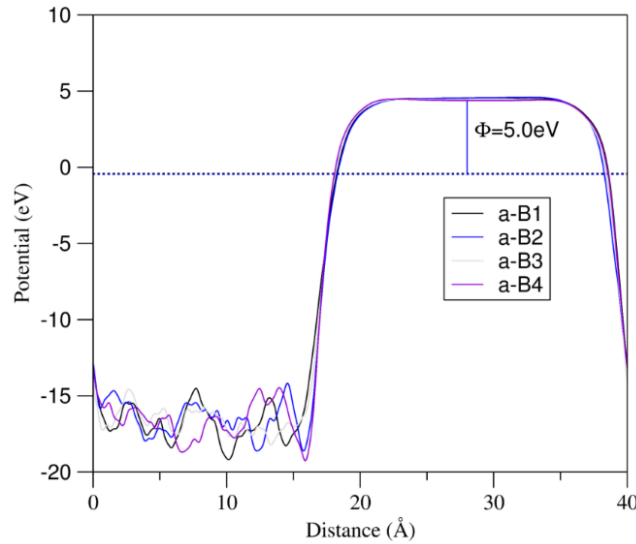


Fig. 5. The potential energy of an electron over the B-Si interface.

2.4 Model comparisons

A quick comparison of the energy barriers from the previously discussed models can be found in Table 3. The δ -doping model underestimates the measured barrier height the most of the three models. The charge transfer and Schottky-Mott models are both closer to the experimental values.

Table 3. Summary of the calculated and known barrier heights according to the three models discussed.

Model	Barrier Height (eV)	Built-in Potential (V)
δ -doping	—	0.78
Charge transfer	0.95	1.05
Schottky-Mott	0.95	—
Measured	~ 1.05 -1.15 [16]	—

The δ -doping and charge transfer models are similar in that both models predict a thin charged p^{++} -doped Si layer near the interface, which induces the formation of a pn-junction and its subsequent depletion zone. However, the two models differ in the concentration levels at the interface. The charge transfer model is not limited to the diffusion and doping limit of B in Si. Therefore, this creates the possibility of a much

higher acceptor state concentration at the interface, resulting in an increased built-in potential.

The Schottky-Mott and charge transfer models share a common point: A sharp interface between the two layers and movement of electrons across, albeit in different directions. In either configuration, the models do not reach the amount of diffusion necessary for the δ -doping model to apply. The two models only use the interface effects deduced from experiments. Would it be possible then for the charge transfer and Schottky-Mott models to be compatible, and what would be the physical meaning if it were possible to link Schottky diodes to B-Si heterojunctions? However, there is currently no strong evidence to support this hypothesis.

3. CHALLENGES

3.1 Measurability

When characterizing and measuring the B-Si devices, several difficulties arise due to the unique characteristics of the interface. As mentioned previously, the simulated systems are on a sub-nm scale. This level of detail can be reached using High-Resolution Tunneling Electron Microscopy, to find the positions of the atoms depending on the phase strength of the atoms. However, it may be challenging to create samples with the necessary level of cleanliness and precision for these measurements. The samples may not necessarily be quantifiable using these techniques, either.

The thickness of the B layer itself has a minimal impact on the electrical characteristics of the device [6]. However, the robustness of the layer is necessary as otherwise, deposition of the metal contacts leads to the formation of Al-Si Schottky junctions at the pinholes [16]. One method to maintain proper coverage of the layer on top of the substrate is the deposition of a thicker B layer. This adds to the difficulty of measuring the interface, as the signal from the bulk species is likely dominant in spectroscopic measurements such as X-ray Photoelectron Spectroscopy and Resonant Photoemission Spectroscopy, and, as a result, very little information about the interface proper is recorded.

Further problems arise when considering how to make a meaningful distinction between the Si layers δ -doped through the diffusion of B and the interface layer doped through charge transfer. A possible solution could be provided by considering the role of the a-B layer: Do the electrons in the a-B layer stay at the B-Si interface, dissipate into the a-B bulk, or form a depletion region? This should have a measurable effect in the latter situation, and should be a more straightforward experiment.

The deposition process of the amorphous B layer is performed under vacuum. In addition, the native oxide layer on the Si wafer is removed with a HF dip, and the surface is then passivated with hydrogen. This may pose an issue for our model, as our understanding is based on a clean Si and B interface. The role of H, oxides, and

other possible contaminants has not been explored yet and remains a consideration for further efforts.

Finally, let us consider the possibility of measuring the work function difference between the Si substrate and the a-B layer. A method commonly used to measure this quantity is the Kelvin Probe Method [17]. However, this will likely be difficult to achieve with the B-Si interface due to problems creating a cross-section to scan over. The thickness of the B layer causes complications during the cleaving of the samples. Further difficulties arise from the resolution required to prove or disprove the charge transfer. Since the simulation results occur on a sub-nm scale, this does not necessarily transfer well to the microscopic world.

A second method we have considered is the creation of a thermocouple, traditionally applied to measure temperature using the work function difference between two metals. A measurable potential difference is created by introducing a temperature difference between two interfaces due to the Seebeck effect. However, it is unclear if any signal from this measurement would only result from the Seebeck effect or whether the depletion zone and the built-in voltage would overpower this signal. Additionally, a distinction must be made between the work function difference and the Volta potential, which applies doubly to a semiconductor-semiconductor or semiconductor-metal interface.

3.2 Al-Si Schottky junction

The charge transfer model has provided an excellent initial estimation of the barrier height for B-Si devices. However, a problem arises when the model is applied to the aluminum-on-silicon (Al-Si) interface. Al is in the same group on the periodic table as B, and the two elements share the same number of valence electrons. It follows that the model we use on the B-Si devices should then work on devices that are created using Al instead of B.

The magnitude of the charge transfer found for Al-Si is smaller, while the transfer points in the opposite direction; Al loses electrons to Si in first-principles simulations of the interface [18]. This leads to a fundamental incongruity between this model and the existing theory, particularly the Schottky-Mott model. The direction of the dipole found from charge transfer is opposite to what is posited by the Schottky-Mott model for n-type Si. For a Schottky-Mott diode, electrons tunnel across the interface into the metal [14]. Charge transfer thus appears to work against establishing a Schottky diode, resulting in a lowered barrier height.

However, applying the Schottky-Mott approach without the Bardeen correction term also results in an ohmic contact, contrary to experimental results. Is the charge transfer then part of what weakens the Schottky barrier? The dipole layer that forms likely impacts the movement of diffused electrons. This could explain the low barrier height for the Al on the n-Si diode if we consider the Schottky-Mott model without the Bardeen correction term.

Finally, how does an increase in electronegativity difference (2.04 for B, 1.90 for Si, and 1.61 for Al) lead to less charge transfer? It is clear that these models do not quite explain the properties of the B-Si interface and that further investigation is required to fully understand the interactions responsible for this discrepancy.

3.3 Dynamic model

An important distinction has to be made with the charge transfer model proposed in this paper: The charge transfer that has been found is at a pseudo-equilibrium state. In reality, the conduction barrier responsible for the diode's rectifying properties is a direct consequence of the formation of the depletion zone.

The potential barrier found using the charge transfer model does not determine the device's electrical properties. This is because our interface barrier is much smaller (<1 nm) than the mean free path of an electron, so any electrons from the current induced by an external voltage could tunnel through this barrier, albeit with attenuation of the electron current.

Any measurable electrical properties must come from the transport mechanism by which the electrons reach the interface through the bulk Si and B. In particular, the depletion zone determines the transport properties. The assumption is that our barrier height directly correlates with the energy barrier that the induced transport electrons encounter while moving across the device.

Our assumptions may not necessarily hold, so extra scrutiny is necessary when determining the depletion zone according to our models.

4. CONCLUSION

We present our current understanding of the junction formation mechanism at the Boron on Silicon heterojunction. Using data from experimental and theoretical studies, we show that doping from the deposition process is insufficient to explain the formation of the junction. Instead, we propose an alternative model, using results from first-principle calculations to postulate the existence of charge transfer at the interface, which in turn induces a depletion region. This model does not rely on δ -doping and has implications for the exact formation mechanism of semiconductor heterojunctions. We additionally apply the Schottky-Mott model to the interface and show a similar barrier height.

Finally, we have identified the currently outstanding issues that need to be addressed before a clear picture of the B-Si interface can emerge as follows: Experimental difficulties in measuring the devices using optical and electrical characterization methods, and theoretical problems in applying the charge transfer model to the Al on Si junction, which should show similar properties, as well as problems with using a static picture to model a dynamic process.

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