The role of quantum confinement in the formation of Schottky barriers in Pb-Si interfaces

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Schottky barriers form when semiconductors are in contact with metal overlayers establishing a common Fermi level. Few theoretical studies of these materials exist as electronic structure calculations are computationally intensive for mismatched interfaces. We explicitly model a Pb(111) film on a Si(111) substrate. For thick Pb overlayers, we find a bulk regime where the Fermi level is pinned. For thin film regimes (less than five overlayers), structural relaxations dominate the interfacial energy as charge transfer is suppressed by quantum confinement. In this case, the Schottky barrier height follows the trend of the metal work function.

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One of the first models to predict the formation of a Schottky barrier is from Schottky^{1,2} and Mott³ some 70 years ago. The Schottky-Mott theory assumes the metal and the semiconductor are not strongly interacting at the interface. Under such an assumption the vacuum levels are aligned, and the size of an n -type Schottky barrier $\Phi_{B,n} = \phi_M - \chi$, which is the difference between the work function of the metal, ϕ_M and the electron affinity of the semiconductor, χ . If the Schottky-Mott picture were to be correct, then one might consider altering the barrier by changing the work function of the metal, *e.g.*, by using different metals or by physically changing the thickness of the metal to alter the work function by quantum confinement. For some semiconductors, such as those with a wide band gap, $\Phi_{B,n}$ exhibits an increasing trend with larger ϕ_M ; however, the Fermi level E_{Fermi} is often pinned within a small range for a given semiconductor regardless of the work function of the metal, especially for small gap semiconductors or elemental semiconductors like Si or Ge⁴⁻⁶. The Schottky-Mott model was rapidly abandoned for some semiconductor systems because of experimental evidence for a pinned Fermi level⁷. E_{Fermi} when pinned is essentially independent of the metal contact. Bardeen⁸ considered the role of surface states, whose theory had been previously developed by Tamm⁹ and Shockley¹⁰, and argued that these states would control the formation of a dipole at the metal-semiconductor interface and pin E_{Fermi} .

Later, Heine¹¹ and Louie *et al.*^{12,13} refined the ideas of Bardeen by noting that intrinsic surface states could not

exist in the presence of an intimate contact with metallic states. They argued that the role played by the surface states pinning E_{Fermi} in the Bardeen model could be played by the tails of intrinsic metallic states, which were capable of penetrating several layers into the semiconductor side. These metal induced gap states (MIGS) have been widely studied theoretically since the mid 1970s. For example, Louie and coworkers¹²⁻¹⁵ used a jellium model for the metal films, replacing the nuclear charges by a uniform electronic charge density.

The jellium model removes structural details of a metal overlayer and avoids the complexity of any lattice mismatch between the metal and semiconductor crystal structures. Although these studies with jellium have led to important insights on the role of MIGS in the formation of Schottky barriers, the lack of an atomistic description makes the jellium model inappropriate for considering the details of the metal-semiconductor bond and any structural issues, which become increasingly important when the film thickness approaches monolayer or sub-monolayer coverages. In particular, assessing the role of quantum confinement as a function of metal coverage is outside the scope of a jellium model. These drawbacks have been well documented in the literature^{5,16-20}.

Here we examine the Schottky barrier changes at the early stages of metal overlayers. We chose the Pb(111) film on Si(111) substrate as a prototypical system for this study because Pb does not form a silicide with Si, so the interface is atomically sharp and interatomic diffusion of the Pb into Si is not a significant factor. We performed atomistic calculations instead of jellium such that the effects of lattice mismatch and structural relaxations are taken into account. We found that the Pb/Si

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interface energy can be minimized by charge transfer across the interface and by interfacial structural relaxation. When the Pb film is less than a nanometer thick, structural relaxations play a dominant role and $\Phi_{B,n}$ follows the Schottky-Mott theory qualitatively. For thicker Pb films, charge transfer contributes to minimizing the interface energy by reducing the potential jump across the Pb/Si interface and leads to E_{Fermi} pinning. However, the jellium model alone cannot describe E_{Fermi} pinning because the charge transfer has to be accompanied by structural relaxation.

Our calculations are based on density functional theory^{21,22} under the local density approximation^{23,24}. Our code PARSEC^{25,26} uses the Troullier-Martins pseudopotential²⁷, and calculates on a real space grid with a grid spacing of 0.66 a.u., which is sufficient to converge the surface energy of the structures. For our atomic model, we took the Si substrate to be a slab of four layers with the surface structure a (1×1) relaxation. The bottom of the Si slab was passivated by H atoms. Since the lateral dimension of the Pb overlayer corresponds to islands that are at least a few tens nm²⁸, the islands were modeled by periodically repeating films with thickness up to 11 atomic layers on top of the Si substrate. The $(1\bar{1}0)$ direction of the Pb film was aligned to the $(1\bar{1}0)$ direction of the underlying substrate. From LEED experiments^{29–31}, the Moiré pattern owing to the lattice mismatch between Pb and Si has an average periodicity of 35 Å. This corresponds to fitting 10 Pb atoms onto 9 Si atoms and reflects the $\sim 10\%$ lattice mismatch of Pb versus Si. We modeled the Pb/Si interface using a (9×9) unit cell for the Si substrate, and the overlaying Pb film containing 10×10 atoms per layer. An atomic model of Pb/Si interface is illustrated in Fig. 1. We imposed a confined boundary condition along the z direction.²⁵ These boundary conditions removed any inter-slab interactions. The wave function was constrained to vanish 8 Å above the top of the Pb film, and 4 Å below the H passivation at the bottom. All structures were fully relaxed; the residual force on each atom was less than 0.005 Ryd/a.u.

With the structural model established, we can calculate the Schottky barrier and examine the change of the barrier with the thickness of the metal overlayer. First,

FIG. 1. An atomic model of the unit cell for a Pb/Si junction: a three layer Pb(111) film on a four-layer Si(111) substrate passivated by H atoms at the bottom.

FIG. 2. (a) Variation of the n -type Schottky barrier $\Phi_{B,n}$ and the work function of free-standing Pb film ϕ_M with film thickness. $\Phi_{B,n}$ is calculated using either an atomistic Pb film or by a jellium model to replace the film. (b) $\Phi_{B,n}$ and the potential jump across the Pb/Si interface ΔV^0_{Pb-Si} as a function of Pb film thickness.

we determine the p-type Schottky barrier $\Phi_{B,p}$ by computing the difference between E_{Fermi} of the interface and E_V , the valence band maximum of Si. Both quantities are calculated with respect to the average self-consistent potential inside the Si slab. The p-type and n-type Schottky barriers are related via E_G , the gap of the semiconductor: $E_G = \Phi_{B,n} + \Phi_{B,p}$. The density functional energy gap of bulk Si, $E_G = 0.6$ eV, is then used to extract the n-type Schottky barrier $\Phi_{B,n}$. We find that $\Phi_{B,n}$ converges to a bulk limit once the Pb thickness exceeds five atomic layers. $\Phi_{B,n}$ varies less than 0.03 eV as additional Pb layers are added (Fig. 2(a)). In this thickness regime, $\Phi_{B,n}$ follow a Bardeen type model, *i.e.*, the Fermi level is pinned. We find E_{Fermi} to be located slightly below the mid-gap of Si in this limit, which agrees with experiment^{32–34}. For less than five Pb layers, we find a transition region wherein the barrier follows a Schottky-Mott type behavior. Within this sub-nanometer regime, $\Phi_{B,n}$ exhibits quantum oscillations as a function of the Pb film thickness following the changes in the *free-standing* Pb film work function ϕ_M (Fig. 2(a)). The bilayer oscillations of ϕ_M is owing to the nearly half-integer phase matching between the Fermi wavelength and the lattice spacing along the (111) direction, which have been examined both theoretically^{35,36} and experimentally^{37,38}.

FIG. 3. (a) The self-consistent potentials of a free-standing H-passivated Si(111) substrate and a free-standing 6-layer Pb(111) film. The two potentials are obtained by two separate calculations but plotted in the same figure. The potentials are averaged in the $x-y$ plane and plotted along the z direction only. The dashed lines indicate the average of the self-consistent potentials in the interior of the Si substrate and the Pb film. (b) The self-consistent potential after the 6-layer Pb film is put on top of the Si substrate. (c) The difference in self-consistent potentials between Pb and Si as indicated in (a) and (b) plotted as a function of Pb film thickness. (d) The self-consistent charge density of the 6-layer Pb film on Si(111) substrate. The charge density is also averaged on the $x-y$ plane. The numbers at the top of the plot indicate the average number of electrons per atom for the atomic layer. The dots and squares indicate the positions of Si and Pb atomic planes.

Although our Si substrate has only 4 atomic layers, we checked that a thicker Si substrate does not modify the trend qualitatively.

It has been found that the unpinning of the Fermi level can be controlled by adjusting the density and charges of the interface electronic states³⁹ or by inserting ultrathin insulator layer at the interface^{40,41}. Unpinning has also been observed for nanocrystalline contacts^{42,43} and at metal-semiconductor nanowire interfaces⁴⁴. In the nano regime, the unpinning was attributed to a reduced density of pinning states⁴⁴ and the effect of quantum confinement on band bending⁶. In this paper, the pinning and quantum oscillations of the Schottky barrier are only controlled by varying the metallic film thickness without modifying the chemistry of the interface. We can understand the trend in Fig. 2(a) by examining the details of the potential and charge density near the interface. In Fig. 3(a) and (b), we illustrate the difference in the average self-consistent potential between Si and Pb before and after contact. The self-consistent potential is an effective mean-field potential that an electron experiences within the system. The average self-consistent po-

tentials are obtained by considering the interior of the Si substrate and the Pb film. As expected from the work functions of the bulk, the potential is lower on the Si side. Before the Si substrate and the Pb film are brought together, the difference ΔV_{Pb-Si}^0 is ~ 2.8 eV as shown in Fig. 3(c). There are oscillations in ΔV_{Pb-Si}^0 owing to quantum confinement in the Pb film. After the Pb/Si interface is formed, the self-consistent potential jump across the interface $\Delta V'_{Pb-Si}$ is reduced by ~ 0.5 eV for Pb films thicker than five layers. The reduction is obtained by establishing an interface dipole with the Si surface negatively charged and the Pb positively charged as depicted in Fig. 3(d), raising the potential for the Si side of the interface, but lowering it for Pb. Our result suggests that the interface energy can be minimized by reducing the potential jump as a result of charge transfer across the interface⁵. The Pb/Si interface dipole extends for two atomic layers into the Pb film. The dipole width is related to the Thomas-Fermi screening length in the metal. When the Pb film thickness is reduced to four atomic layers where the interface and surface dipoles can interact, we find that the screening of ΔV across the

Pb/Si interface becomes very ineffective: ΔV is only reduced by ~ 0.1 eV after Pb and Si are brought together, compared to ~ 0.5 eV for thicker Pb films.

The correlation of $\Phi_{B,n}$ with ΔV_{Pb-Si}^0 is depicted in Fig. 2(b). When E_{Fermi} is aligned close to the middle of the energy gap (*i.e.* the charge neutrality level of Si), the Si is locally charge neutral at the surface, and no interface dipole will be formed at the interface. If E_{Fermi} is above mid-gap, then the Si surface becomes slightly negatively charged, thus raising the potential of Si and reducing ΔV across the Pb/Si interface. We expect a larger ΔV_{Pb-Si}^0 will require E_{Fermi} to reside above the charge neutrality level to establish a larger interface dipole and reduce the potential jump leading to a smaller $\Phi_{B,n}$ (as $\Phi_{B,n} = E_{CBM} - E_{Fermi}$), *i.e.*, the variation in $\Phi_{B,n}$ should be inversely correlated with that of ΔV_{Pb-Si}^0 . Our prediction is verified by Fig. 2(b). This correlation between $\Phi_{B,n}$ and ΔV_{Pb-Si}^0 holds till the Pb film approaches a sub-nanometer thickness, where $\Phi_{B,n}$ becomes correlated with ϕ_M instead. The correlation between $\Phi_{B,n}$ and ϕ_M suggests that the charge transfer is small across the interface because the Schottky-Mott theory neglects the chemistry and charge transfer at the junction. Hence for the sub-nanometer thickness, the Pb/Si interface energy must be minimized by interfacial atomic relaxation predominantly. The reduction of potential jump across the interface by charge transfer is energetically less effective as discussed above.

To assess the role of the atomic relaxation, we replaced the Pb film by jellium. The density and extent of the jellium are assumed to match the ones used in the previous calculations.^{12,13} The Si layers are represented as in the atomistic simulation, but no relaxation from the bulk geometry was considered. The two regimes, “unpinned and pinned,” are no longer distinct as shown in Fig. 2(a). $\Phi_{B,n}$ from the jellium calculation qualitatively mimics the trend of ϕ_M , but slowly becomes pinned as the jellium thickness increases. Such a Schottky-Mott behavior is already discussed above for Pb films with sub-nanometer thickness. For a Pb film beyond 5 atomic layer thick, the jellium calculation implies that the charge transfer is reduced across the interface because the Schottky-Mott behavior presumes small interaction between the Pb and Si. Therefore, the jellium model alone without atomic and lattice descriptions cannot explain E_{Fermi} pinning⁴⁵.

In summary, we calculated the Schottky barrier across the Pb/Si interface using an atomistic model including lattice mismatch and structural relaxation. The interfacial dipole screens the potential jump across the Pb/Si interface, which is found to be the driving force for the interface charge transfer. The charge transfer has to be facilitated by structural relaxation, and Fermi level pinning is observed. When the Pb film thickness is less than ~ 5 layers, screening by the interface dipole becomes ineffective resulting in a Schottky-Mott behavior owing to quantum confinement. In this sub-nanometer regime, the interface energy is minimized by structural relaxation. Since the unpinning of the Fermi level is obtained by

varying the metal film thickness, the phenomenon is expected to be general for nano-contacts. Experimentally, the observation of the Schottky barrier oscillations requires an atomically flat metal film.

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(111)

Pb

Si

H

$(\bar{1}\bar{1}0)$

figure 1

figure 2

figure 3