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Self-Consistent Pseudopotential Calculation for a Metal-Semiconductor Interface*

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The electronic structure of a jellium-Si interface is calculated with use of a jellium density corresponding to Al and self-consistent Si pseudopotentials. Local densities of states and charge densities are used to study states near the interface. The states which exist in the Si fundamental gap are bulklike in jellium and decay into Si with high concentration in the dangling-bond free-surface-like Si state. The calculated barrier height is in excellent agreement with experiment.

In this Letter we present the first self-consistent pseudopotential calculation for the electronic structure of a metal-semiconductor interface. The calculation models an Al-Si interface with a jellium potential representing the aluminum-ion potential in contact with the Si (111) surface. The calculated barrier height is in excellent agreement with recent experimental results.[1] Various states which exist near the interface are identified and discussed. In addition to displaying the total valence charge density and the charge density of a localized interface state, we present a local-density-of-states (LDOS) calculation. The LDOS, which displays the density of states in real space, facilitates the identification and illustrates the characteristics of the various kinds of states at the interface.

Metal-semiconductor interfaces have been subjected to many discussions and speculations[2-9] as a result of their great importance in device application. However, regrettably, past theoretical investigations into their electronic structure have been mostly qualitative or semiquantitative. Experimentally, for covalent semiconductors such as Si, the interface barrier height is found to be essentially independent of the metal contact and of the doping in the semiconductor.[1,10,11] Bardeen[2] attributed this behavior to a high density of surface states in the semiconductor gap; that is, the Fermi level is pinned by the surface states. Heine,[3] on the other hand, pointed out that semiconductor surface states cannot exist in the semiconductor gap if this energy range is inside the metallic band. He suggested that the pinning of the Fermi level is due to states of a different type in the semiconductor gap. These states are composed of the states from the tails of the metallic wave functions decaying into the semiconductor side. Recently Inkson,[4,6] using a model-dielectric-function formulation, proposed that the pinning of the Fermi level arises from the narrowing of the semiconductor gap at the interface. According to Inkson, the screenings for the valence band and for the conduction band are different near the interface. This causes the valence band to bend up and the conduction band to bend down and eventually the bands merge together at the interface for a covalent semiconductor.

Our calculations give results which are closer to Heine's picture of the electronic structure of a metal-semiconductor interface. Within our model, we find that four different types of states can exist near the Al-Si interface. Aside from the usual states which are bulklike in both materials, there are states with energy below the Al conduction band which are bulklike in the Si side but decay rapidly in the Al side. Also, in the two-dimensional Brillouin zone, we find extra "gap" states in the semiconductor energy gaps whenever the range of the gap is inside the metallic band. They are somewhat similar to the states suggested by Heine; i.e., they are bulklike in Al and decay rapidly in Si. However, at the Si surface, these "gap" states retain the characteristics of the "free-surface" Si *surface states* which existed in the absence of the metal. It is these states which pin the Fermi level and dominate the properties of the Si-Al junction. In addition, we find truly localized interface states which decay in both directions away from the interface. These appear in the Si energy gaps in the energy range below the Al conduction band.

The method we have employed to calculate the interface electronic structure is similar to the method which we have used previously in surface and molecular calculations.[12-15] We consider a unit cell consisting of a slab of Si with the (111) surfaces exposed to a jellium of Al density on both sides. The unit cell used consists of twelve layers of Si plus an equivalent distance of jellium. This cell is then repeated and the electronic structure of the system is calculated self-consistently. The basic idea is that, if the interfaces are separated by a large distance (36 Bohr radii in the present case), one can then obtain the essential features of a single interface by calculating the electronic structure of this periodic system.

With the above geometry, the jellium edge is one-half of a Si-Si bond length away from the atoms on the Si (111) surface. This is a physically reasonable choice since the length of an Al-Si bond is approximately the same as a Si-Si bond. The slab sizes were chosen on the basis of information from surface calculations,[12,13,15,16] which illustrate that such a thickness allows the bulk properties of the materials to be adequately reproduced, and also prohibits surfaces from opposite sides of the same slab from interacting appreciably.

To insure an accurate determination of the screening potential, the electronic wave functions were expanded in a basis set consisting of approximately 270 plane waves; an additional 300 plane waves were treated by use of second-order perturbation technique. The final total charge density was evaluated at 21 $\vec{k}$ points in the irreducible part ($\frac{1}{12}$) of the two-dimensional hexagonal Brillouin zone with the Fermi level determined by demanding charge neutrality in the unit cell. Our final screening potential is stable to within 0.01 Ry.

Figure 1 displays the the total valence charge density in a (110) plane along with the function $\bar{\rho}_{\text{tot}}(z)$ which is the total charge density averaged parallel to the interface with z being the direction perpendicular to the interface. For the purpose of discussing the charge densities and the local density of states, we have also divided the unit cell into twelve equal regions (slices) as shown partially in Fig. 1(b). The jellium edge is indicated by the double dashed line. Only the charge within a few angstroms from the interface is significantly perturbed from the bulk values. The charge densities in regions I and II and regions V and VI are in good accord with bulk densities.[17] From Fig. 1(b) one sees the well-known Friedel oscillations in the Al charge density and there is a net transfer of charge from aluminum to silicon. Approximately 0.3% of the total charge in the unit cell has been transferred from region III to region IV. Hence a dipole potential with an electric field pointing toward the Si side is set up at the interface. This is a consequence of equalizing the Fermi levels in the two materials. As seen from Fig. 1(a), the Al charge is spilling

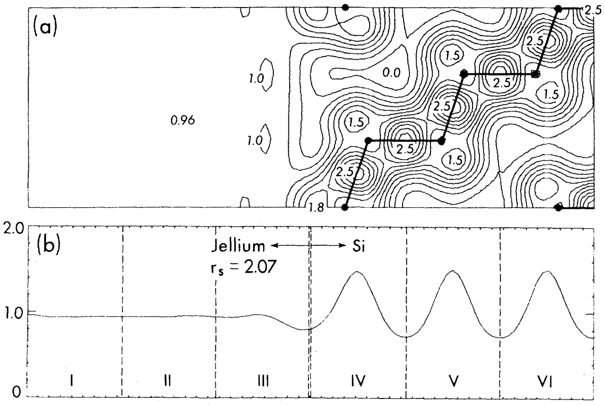

FIG. 1. (a) Total valence-charge-density contours in a (110) plane. The Si atoms are indicated by dots. (b) Total valence charge density averaged parallel to the interface and plotted along the direction perpendicular to the interface. The charge densities are normalized to one electron per unit cell.

into the empty "channels" in the Si charge density and into the dangling-bond sites. The charge at the dangling-bond sites in the present case is significantly higher than that in the free-surface case.[12,13] This indicates the formation of a metallic-covalent-like bond between Si and a jellium of Al density.

We have computed the LDOS for the Si-Al system. We define the LDOS by

$$N_i(E)=\sum_{\vec{k}_{\|},n}\int_{\Omega_i}|\psi_{\vec{k}_{\|},n}(\vec{r})|^2\,d^3r\,\delta(E-E_n(\vec{k}_{\|})),\qquad(1)$$

where $\vec{k}_{\|}$ is the wave vector parallel to the interface, n is the band index, $\psi_{\vec{k}_{\|},n}$ is the electronic wave function, and Ω_i is the volume of region i as defined in Fig. 1(b). Physically $N_i(E)$ can be interpreted as the probability that an electron with energy E is in the region i. We have calculated the six $N_i(E)$'s by using 21 points in the irreducible part of the two-dimensional zone. The histograms of the LDOS for regions I, III, IV, and VI are displayed in Fig. 2. The density of states of bulk Si from Ref. 17 is superimposed onto the LDOS of regions IV and VI and a free-electron density of states [i.e., $N(E)\sim\sqrt{E}$] is superimposed onto the LDOS of regions I and III. The Fermi level is indicated by the dashed line. From the Fermi level we obtained a barrier height of 0.6 ± 0.1 eV which is in excellent agreement with the recent experimental result of 0.61 eV.[1,18]

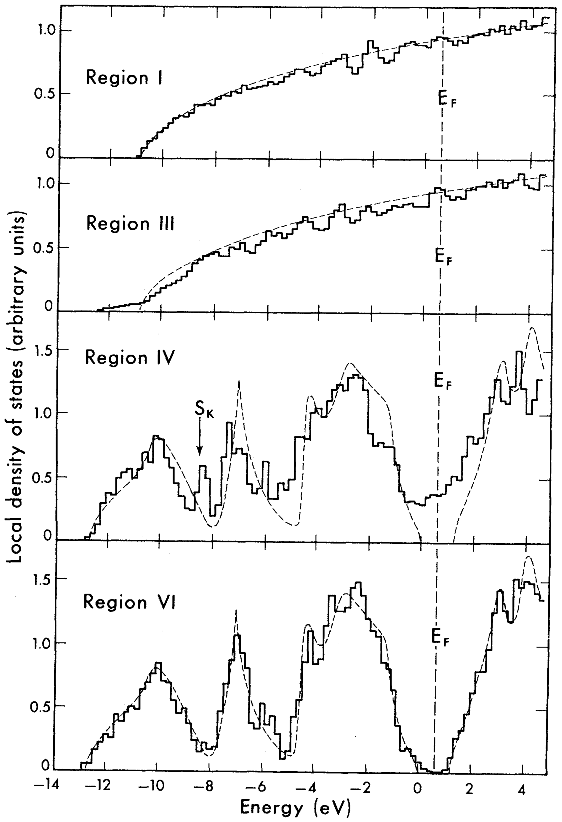

FIG. 2. Local density of states in arbitrary units as defined by Eq. (1).

The various types of states which appear near the interface can be seen from the LDOS. States with energy below −11.1 eV (i.e., below the onset of the Al conduction band) are bulklike in Si and do not penetrate into the bulk of Al. Of course there are states with higher energy that behave similarly. From the LDOS of region IV, we see that the dips in the bulk Si density of states which are due to gaps in the Si band structure are being filled up by either interface states or "gap" states at the interface. The extra states centered at ∼ −8.2 eV are partially interface states and partially gap states whereas the states centered at ∼ −5.0 eV and states in the optical gap are gap states. The gap states in the optical gap are of particular importance because they sensitively influence the Fermi level. These states have a charge density which is metallic in the Al slab, becomes dangling-bond-like at the Si surface, and decays rapidly to zero in the Si slab.

The interface states centered at −8.5 eV, labeled S_K in Fig. 2, appear near the point K in the two-dimensional zone. At first sight, localized states should not appear because there are aluminum states in this energy range. This appearance of interface states is a band-structure effect. Near the point K in $\vec{k}$ space, the two-dimensional Si band structure has a gap between −7.2 and −9.5 eV which is below the Al conduction band. In Fig. 3 we show a contour map of the charge of the states at K at −8.5 eV. The charge density is s-like and localized on the outermost Si atoms. Note that the charge is highly localized; it is almost completely confined to region IV.

Our calculated LDOS for region V more closely resembles the LDOS of region VI than that of region IV. Hence, contrary to Inkson's model,[4] there does not seem to be a merging of the valence band with the conduction band near the interface. Furthermore, it is not very meaningful to talk about a band picture on such a microscopic scale.

The present calculation is for a high-density metal, $r_s=2.07$, in contact with Si. For metals

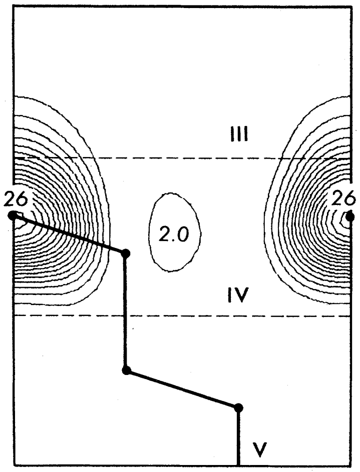

FIG. 3. Charge density for the interface states at K at -8.5 eV in the same plane and normalization as in Fig. 1(a).

with a low density of s-p electrons, interface states can coexist with gap states in the energy range of the Si optical gap such as in the gap -7.2 to -9.5 eV in the present calculation. Under such conditions, one expects that an even higher density of extra states will appear near midgap[12,13] and the Fermi level is again pinned in the thermal gap.

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Electronic Properties of Polymeric Sulfur Nitride*

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We present a three-dimensional band-structure calculation of $(\mathrm{SN})_x$ using the empirical pseudopotential scheme. The density of states, Fermi surface, and optical spectrum are calculated. Estimates for the electron-phonon coupling constant λ are given and the increase of T_c with pressure is discussed. The assumption of an electron-phonon mechanism for superconductivity in $(\mathrm{SN})_x$ is consistent with our results.

The discovery of superconductivity in polysulfur nitride[1a] has stimulated great interest in this material.[1b] The high normal-state conductivity, the high anisotropy (possible one-dimensionality), and the fact that this is the first observance of superconductivity in this region of the periodic