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Covalency in the adsorption of Na on Si(111)

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The linear muffin-tin orbitals method in the atomic-sphere approximation is employed to investigate the electronic structure of a semiconductor-metal interface at monolayer coverage. We studied the interface formed by one monolayer of Na adsorbed on Si(111). The analysis of both valence and core electron states gives information on the nature of the bond between Na and the Si surface, which is mainly covalent, and allows one to interpret the available experimental data.

In recent years the linear muffin-tin orbitals (LMTO) method[1] has been largely used for the calculation of the structural and electronic properties of crystals,[2] metal-semiconductor interfaces,[3-5] and semiconductor-semiconductor heterostructures.[6]

A particularly suitable form of the LMTO method is obtained by the use of the atomic-sphere approximation (ASA).[1] In this approximation the muffin-tin interstitial region is "annihilated" through the expansion of the muffin-tin spheres and the neglect of the slight overlap between the spheres. As a consequence, this approximation, which greatly reduces the complexity of the computation, works well only in close-packed solids. For this reason the LMTO-ASA method cannot be directly applied to surface calculations, since the presence of the vacuum region contradicts the close-packing requirement. LMTO surface calculations have been made only through the use of planar muffin-tin orbitals[7] or by Green function method.[8]

Very recently[9] we have demonstrated the possibility of calculating densities of states and energy bands for clean surfaces through the same LMTO-ASA technique usually applied to close-packed bulk systems. This surface LMTO-ASA (SLMTO-ASA) has been successfully applied to the ideal Si(111) surface.[9] The basic idea of the SLMTO-ASA is to describe the vacuum region by a solid formed by *empty spheres*. Empty-sphere atoms (i.e., with atomic number equal to zero) can be used to study electronic states in loosely packed solids.[10-12]

The aim of this work is the extension of the SLMTO-ASA to the case of surfaces covered with an ultrathin chemisorbed layer. We also modified the LMTO code in order to calculate core electron energies and wave functions.[13,14]

We have focused our attention on the Na-Si(111) interface for two reasons: first for the growing interest on the adsorption of alkali metal on semiconductor surfaces;[15] second to have a comparison with a pseudopotential calculation which exists in the literature,[16] that describes the bond between the Na and Si surface in terms of an ionic interaction. Since this conclusion is questioned by a recent experimental paper,[17] we decided to study this system more deeply.

The possibility of treating the two-dimensional surface problem as a bulk one relies on the supercell technique. The solid-vacuum interface is simulated by an infinite sequence of solid and vacuum films, which recover the third dimension periodicity. The film thickness should be large enough to avoid surface-surface interaction.

In SLMTO-ASA (Ref. 9) the vacuum layer is filled by empty-sphere atoms. We simulate the Si-metal-vacuum interface by a 12-layer Si(111) slab covered with a monolayer of Na atoms on each side and a vacuum region, which is equivalent to 10 layers in thickness; the entire structure repeats periodically in the (111) direction. In Si crystal the close packing is reached by adding one empty sphere (ES) to every Si atom. The empty-sphere lattice is equal to the Si one, with a simple shift of $(a/2,0,0)$, where a is the lattice constant of bulk Si. This procedure yields a close-packed solid that, neglecting the atom type, is bcc with lattice constant $a/2$. We extended this bcc lattice even in the adsorption and vacuum regions: Na atoms and empty spheres at the remaining (111) layers.

Our supercell crystal is formed by a three-dimensional unit cell with one atom per (111) layer. The total number of atoms per unit cell is 36: 12 Si+12 empty spheres for the Si side+2 Na atoms for the adsorbed layers on both sides of Si(111)+10 empty spheres to simulate the vacuum.

Three possible adsorption geometries have been considered up to now for an adlayer of Na atoms on Si(111): The onefold top site (OTS), the threefold filled site (TFS), and the threefold hollow site (THS). In the OTS the Na atoms are on top of the surface Si atoms; in the threefold triangular sites (TFS and THS) the metal atoms sit at the center of a triangle formed by the Si surface atoms. In the TFS the Na atoms are on top of the first sublayer Si atoms, whereas in the THS they are on top of the third sublayer Si. In all the different geometries (OTS, TFS, THS) the number of Na atoms is equal to the number of surface Si atoms.

Northrup[16] performed a first-principles pseudopotential calculation for the Na-Si(111) system and, by minimizing the total energy, ruled out the OTS geometry, concluding that the THS was slightly favored with respect to the TFS. The equilibrium structure was predicted at a distance between the Na monolayer and the Si surface layer of 1.55 Å.

In our calculation we have considered the energetically favorite THS and TFS triangular adsorption sites. In both geometries our layer sequence is

$$\ldots \text{ES-Si-Si-ES-ES-Si-Si-ES}_1\text{-Na-ES}_2\text{-ES-ES-ES} \ldots .$$

In the bcc Si lattice the distance between layers of spheres is 0.78 Å. For the THS geometry we did not modify this distance also on the vacuum side; hence in this case the distance between the last Si layer and the Na layer is 1.56 Å, as in Ref. 16. In this geometry, the adsorbed Na atom has three surface Si nearest neighbors at 2.71 Å and it is located on top of the third sublayer Si atom at 5.48 Å. This value of 2.71 Å for the Na-Si first-neighbors distance may be compared with that of 2.90 Å found in bulk Na-Si compounds.[18]

In the TFS geometry the first sublayer Si atoms are located just below the Na atom. In order to maintain the 2.71-Å distance between Si and Na we locate the Na layer at a distance of 1.93 Å from the Si surface; as a consequence the Na atom has the first sublayer Si as a nearest neighbor at 2.71 Å and the three surface Si atoms at 2.94 Å.

The sphere sizes are fixed by the standard ASA packing requirement, starting from nonoverlapping spheres around each atom and then scaling them to fill all the space. In the THS geometry the radii are 1.347 Å for Si and for the empty spheres in the Si and vacuum region, 1.764 Å for the Na atom, and 0.829 Å (ES_1) and 1.097 Å (ES_2) for the interface empty spheres. The corresponding values in the TFS geometry are 1.344, 1.761, 1.255, and 1.094 Å.

The self-consistent local densities of states (LDOS), projected on the silicon, metal, and vacuum sites are shown in Fig. 1 for the TFS and THS geometries. In the THS case we show only the LDOS of the interface region, where differences are relevant. The LDOS of the central Si atom (curve *h*) is very similar to that of bulk Si.[9] The effect of the presence of Na atoms at the interface extends two or three layers into the Si region. Different features, due to the interface, are clearly present on the LDOS of the interface Si atoms (curves *c* and *m*). The most interesting ones are the peaks located near the gap zone; one fully occupied lying near the top of the valence band at energies similar in both geometries: 0.8–1.0 eV below the highest occupied state. A different behavior is found for the empty structure located at the bottom of the conduction band: in the TFS site it is located 1.4–1.6 eV above the highest occupied state, while in the THS case it moves to 1.7–1.9 eV. These features are present also in the LDOS relative to the Na adsorbed layer (curves *b* and *l*). They are originated from the combination of Na 3*s* orbitals and Si 3*p* dangling-bond orbitals. The nature of the bond between these states may be investigated by looking at the center of the LMTO-ASA band of the Na 3*s* orbital. For both geometries it is found around the bottom of the Si gap, where the Si 3*p* dangling-bond orbital is located. Therefore the bond between Na and the Si surface is mainly covalent in character, with bonding-antibonding structures forming a couple of states around the Si gap.

Additional information on the character of the bond in this system may be obtained by looking at the charge inside Si ASA spheres. On going from the clean Si(111) surface to the THS (TFS) chemisorption geometry we found a charge transfer of 0.29 (0.14) electrons per atom. The result in the two geometries is actually similar: in TFS the first sublayer Si atom, which is the first neighbor of Na, receives 0.13 electrons per atom. These data confirm the predominant character of covalent interaction, because in the ionic picture one would expect a charge transfer of ~ 1 electron per atom.[16,19] Note that the clean Si(111) calculation has been performed with exactly the same input of the Na-Si(111) case, in particular with the same sphere sizes, simply substituting $Z=0$ into the Na sphere.

The difference in energy between filled and empty peaks is ~0.3–0.5 eV larger in the THS geometry than in the TFS one. This result is due to the different Na-Si interaction. On both triangular sites Na atom has the nearest Si neighbor at 2.71 Å; however, in the TFS site there is only one nearest-neighbor Si atom, while in the THS geometry there are three. Hence, in THS the Si-Na interaction is stronger and the energy difference between filled and

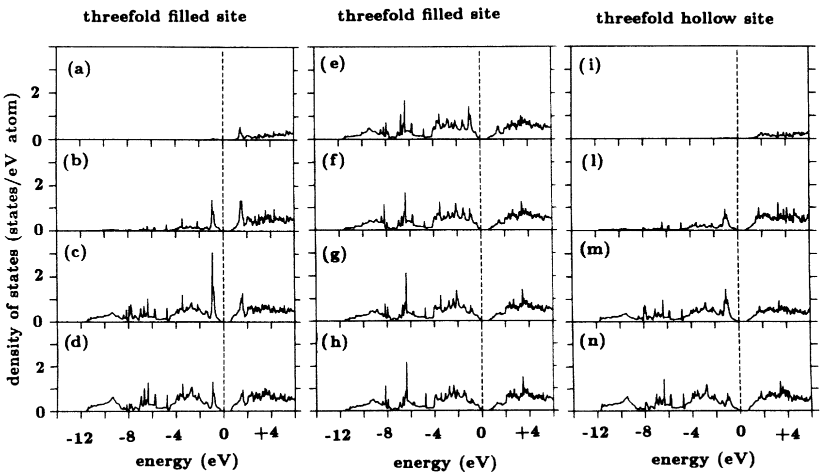

FIG. 1. Site-projected density of states for the Na-Si(111) interface with Na atoms adsorbed at the TFS geometry (left-hand-side and central panel) and at the THS geometry (right-hand-side panel). The different curves show LDOS for: (a) and (i), first empty sphere layer on the vacuum site; (b) and (l), adsorbed Na; (c) and (m), interface Si; (d) and (n), second layer Si; (e)–(h), third, fourth, fifth, and sixth layer Si respectively, for only the TFS geometry. Each Si (Na) PDOS contains contribution of the Si(Na) atom and of its neighbor empty sphere. Energies (in eV) are referred to the highest occupied state.

empty interface states is larger. It is interesting to note that the system formed by a monolayer of Na on Si(111) has a nonmetallic character; the same conclusion was reached by Northrup[16] and suggested by Batra and Ciraci on the basis of a study on K-Si(111).[19]

Accurate information on interface states and resonances can be obtained by looking at the two-dimensional band structure of the interface system superimposed upon the projected bulk band structure of Si.[9] Figure 2 shows the interface states, in the Si gap region, for both adsorption geometries. The presence of Na is responsible for the occurrence of two interface states that extend over a wide region of the Brillouin zone. The first is a filled band located at the bottom of the Si bulk gap, except near $\bar{\Gamma}$ where it becomes a resonance. The second band lies above the conduction-band minimum and becomes a well-localized interface state around $\bar{\Gamma}$ and in the $\bar{\Gamma}$-$\bar{K}$ direction. Both bands are related, as already pointed out, to the interaction between the Si $3p$ dangling bond states and the Na $3s$ orbitals; note that the dangling-bond band near the middle of the gap of the ideal Si(111) surface[9] has disappeared.

The last occupied state of the system is found near the top of the projected valence band; therefore the entire system is still a semiconductor. The upper antibonding band, in the TFS geometry, is located around +1.40 eV at $\bar{\Gamma}$, remains a well-localized state in the $\bar{\Gamma}$-$\bar{M}$ direction, and in the $\bar{\Gamma}$-$\bar{K}$ direction disappearing near $\bar{M}$ in the continuum of bulk states; the lower bonding band has its minimum at $\bar{K}$, extends in the gap zone over the entire $\bar{M}$-$\bar{K}$ direction and over large parts of the other directions, becoming a resonance near $\bar{\Gamma}$.

Concerning the THS geometry the filled state shows almost the same characteristics of the TFS case; the upper antibonding state is located higher in energy and only in small regions of the Brillouin zone it is found in the Si(111) projected bulk gap; at $\bar{\Gamma}$ it becomes a resonance and is located at around 2.00 eV above the top of the valence band.

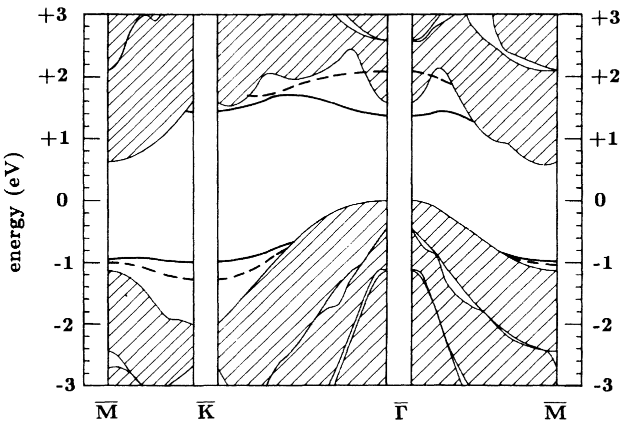

FIG. 2. The (111) projected band structure of bulk Si (hatched areas) and the dispersion of the localized states for the Na monolayer in the TFS geometry (solid lines) and in the THS geometry (dashed lines). Energies (in eV) are referred to the highest occupied state.

Unlike the bonding states, the antibonding ones are quite sensitive to the Na-Si distance: a contraction of this distance by 20% increases their energy of ∼1 eV. They are quite sensible even to the number of empty spheres describing the vacuum region: a reduction of their number from 10 to 4 decreases their energy of ∼1 eV. To our knowledge, the only existing calculation for the ideal Na-Si(111) interface is the pseudopotential calculation of Northrup.[16] The agreement with the Northrup result is good for both energy location and dispersion of the metal-induced interface bands but the picture of the chemical bond is different. Regarding the available experimental data there is an interesting energy-loss spectroscopy study of Avci[20] for Na adsorbed on the reconstructed Si(111) 7×7 surface. At the monolayer stage a coverage dependent loss feature at about 2.8 eV is observed, partly due to single-particle excitations. Our results of Fig. 1 show that the energy difference between the bonding and antibonding interface peaks is ∼2.4 eV (TFS) and ∼2.7 (THS). The usual local-density-approximation underestimate of the Si energy gap[9] can be roughly taken into account by adding ∼0.5 eV to these energy differences. We obtain ∼2.9 eV (TFS) and ∼3.2 eV (THS). These results refer to the ideal 1×1 surface; they compare favorably with the transition of 2.8 eV detected on the Si(111) 7×7, considering that we did not make any attempt to optimize the Na-Si distance. The approximations involved in this evaluation are such that it is not possible to discriminate between the different TFS and THS geometries on this basis. The important result relies on the interpretation of the 2.8-eV energy-loss feature in terms of transitions from the bonding to the antibonding interface states.

Our analysis of the interaction between the Na and Si(111) surface on the basis of the valence electron states is confirmed by the results for core levels. We found that the Si $2p_{3/2}$ (local density) eigenvalue is essentially unchanged on going from the bulk environment to the interaction with the Na atom at the surface.[14] In the THS (TFS) geometry this level moves +0.08 eV (−0.03 eV), where a positive shift means towards the vacuum level. These results refer to the local-density core-eigenvalue term. The observed shift of the core-level binding energy is equal to this term plus the variation in the relaxation energy, plus the second difference in the correlation energy not incorporated in the core eigenvalue term.[21] In spite of the fact that we do not include these two last terms, the agreement with the experimental findings is significant: no detectable shift has been measured experimentally on going from bulk Si to the Na-Si(111) interface.[17,22] We observe that such a result does not imply that the ionic interaction is completely absent: the charge transfer from Na to Si shifts the Si $2p_{3/2}$ core level towards the vacuum level, but an extra atomic Madelung contribution, of opposite sign, cancels this effect.[14]

In conclusion we have shown that the SLMTO-ASA technique can be used to investigate the electronic properties of semiconductor metal interfaces at low coverage. The energy bands and densities of states can be favorably compared with the outcomes of other first-principle approaches. The energy location of the interface states are consistent with the energy-loss data. The experimental data on core-level binding-energy shifts are successfully interpreted in terms of both core-level and valence-charge properties. We have proved that the interaction between Na and the Si surface presents both covalent and ionic characters, but that the covalent one is dominant.

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