Electron correlation effects at semiconductor interfaces: a comparison of the Si(111)-3 × 3 and the Sn/Ge(111)-3 × 3 reconstructions

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Abstract

Electron correlation effects for the Si(111)-3 × 3 and Sn/Ge(111)-3 × 3 reconstructions are analysed introducing 2-dimensional (2D) Hamiltonians whose parameters are deduced from DFT calculations. We find that these two surfaces present striking similarities, with two dangling bonds and one electron per unit cell defining the surface states properties around the Fermi level. Upon introduction of electron correlation effects, the Sn/Ge(111)-3 × 3 remains metallic, while the Si(111)-3 × 3 is found to be semiconducting, mainly due to a kind of charge transfer metal–insulator transition associated with the faulted-unfaulted asymmetry of the surface. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The reduced dimensionality and the presence of metallic narrow bands at semiconductor surfaces and interfaces determine that electron correlation effects play a crucial role in the determination of their structural and electronic properties [1]. A very recent example concerns the gradual and reversible change, as the temperature is lowered, from a $(\sqrt{3} \times \sqrt{3})$ to a (3×3) periodicity observed in Sn and Pb(1/3 ML) deposited on Ge(111) surfaces [2,3]. This structural transformation, characterized by LEED, is accompanied by a change in the electronic charge distribution as shown by the STM images: While at room temperature (RT), all the Sn adatoms on T_4 sites over the Ge(111) appear equivalent, at low temperatures (LT) the images display a 3×3 pattern with empty and filled states located on different adatoms.

These unusual properties, which seem to point to a metal–insulator transition, and the failure of the early density functional theory (DFT) calculations [2,3] to find a global minimum with the correct 3×3 symmetry prompted different authors [2–4] to suggest that the 3×3 phase is a 2D charge density wave (CDW) and that the transition to the CDW state was driven by correlation effects. Our theoretical analysis using a combination of local-orbital (LO) and plane-wave (PW) DFT methods shows, however, that a 3×3 structure with two different

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types of Sn adatoms (both on T_4 sites but whose vertical positions differ by ~ 0.35 Å) is the ground state [5].

In this communication, we also discuss how correlation effects modify the DFT solutions. For this purpose, we have also analysed the case of the Si(111)-3 × 3 reconstruction. The band structure which emerges from a DFT calculation is very similar to the one of the Sn/Ge(111), with a doubly occupied lower band, associated with the corner hole, and two bands, associated with the adatoms, around E_F and occupied by one electron. Correlation effects do not change the metallic character in the case of the Sn/Ge(111), in agreement with recent experimental evidence [5,6], but they modify completely the metallic character of the DFT solution, opening a gap in the DOS, in the Si(111)-3 × 3 surface.

2. Surface bands: DFT calculations

2.1. A. Sn / Ge(111)-(3 × 3)

The main feature of the 3 × 3 ground state we have found is a vertical distortion of the Sn-layer in which one Sn-atom (A_0) is displaced upwards and the other two Sn-atoms (B_0 and C_0) are displaced downwards, with $z(A_0) - z(B_0, C_0) \sim 0.35$ Å (see Fig. 1). This distortion in the Sn-layer is accompanied by a related distortion in the first 4 Ge-layers. Both the LO and PW methods show the same structural trends, with quantitative differences less than 0.04 Å in all the structural parameters, except for the average vertical distance of the Sn layer to the first Ge layer where the difference is 0.08 Å. The PW calculation confirms the prediction of the LO method that a 3 × 3 reconstruction with a large vertical distortion among the Sn atoms is the global energy minimum. Our results agree quantitatively with two recent experimental studies for the Sn/Ge(111) (combining the distinct sensitivities of LEED and SXRD) [7] and Pb/Ge(111) (SXRD) [8] (see Ref. [9] for a detailed comparison).

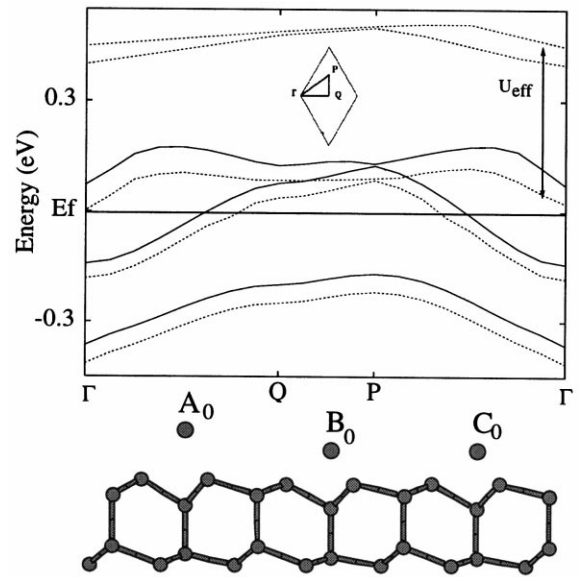Fig. 1 shows the Sn/Ge(111)-(3 × 3) DFT-LDA surface bands appearing close to E_F, as calculated

Fig. 1. Electronic structure (top) and atomic geometry (side view, bottom) of the Sn/Ge(111)-(3×3) surface. DFT (solid lines) and correlated (dashed lines) surface lines) surface bands along the Γ–Q and P–Γ directions (see inset).

with the LO method (FIREBALL96). These three bands are associated with the three Sn dangling-bonds. For the Sn atom displaced upwards, rehybridization makes its dangling bond to have a more s-like character and a corresponding lower energy. The lower surface band in Fig. 1 is associated with that atom and it is doubly occupied. The other two surface bands, located around E_F, are associated with the two dangling bonds of the Sn atoms displaced downwards, and are occupied by one electron.

2.2. B. Si(111)-(3 × 3)

Fig. 2 shows the geometry of the Si(111)-3 × 3 reconstruction, with two adatoms and a corner hole atom in the unit cell. Each of these atoms has a dangling bond filled only by one electron, and the surface band structure around E_F is determined by the behaviour of these unsaturated orbitals.

We have analysed the Si(111)-3 × 3 band structure taking advantage of previous calculations for the Si(111)-5 × 5 and 7 × 7 reconstructions [1]. From
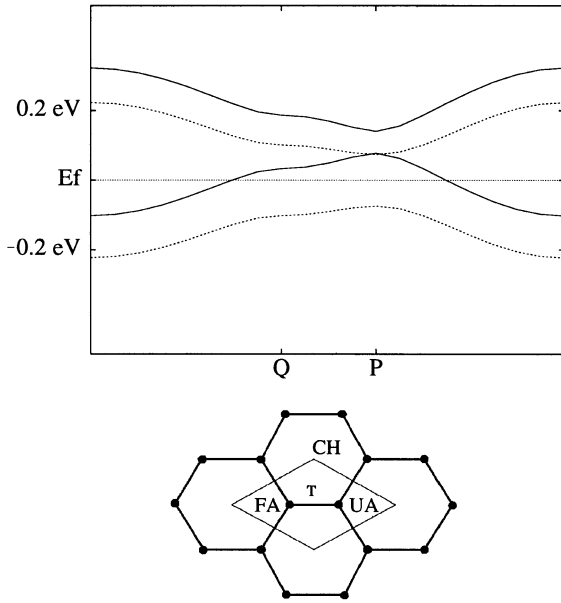
Fig. 2. Electronic structure (top) and atomic geometry (bottom) of the Si(111)-(3×3) surface. DFT (solid lines) and correlated (dashed lines) surface bands along the Γ–Q, Q–P and P–Γ directions. The labels correspond to the faulted adatom (FA), unfaulted adatom (UA) and the corner hole.

DFT calculations on these surfaces, we have found that the corner hole relaxes outwards in the direction perpendicular to the surface, changing accordingly the hybridization of its dangling bond. This relaxation makes this orbital a more s-like level, pushing its energy to more binding energies. This effect locates the band associated with this dangling bond around 0.7 eV below the surface bands associated with the dangling bond of the adatoms, and allows for its double occupancy. We can expect similar effects to appear in the Si(111)-3 × 3 reconstruction, suggesting that two electrons, out of the three electrons filling the dangling bonds, are transferred to the corner hole.

It is interesting to realize the similarity of this electronic structure and the one discussed above for the Sn/Ge(111)-3 × 3 reconstruction. In both cases, the atom relaxing outwards changes its dangling bond hybridization, becomes doubly occupied, and creates a very narrow surface band located a few tenths of eV below E_F.

Then we analyze the surface bands associated with the two adatom dangling bonds of the Si(111)-

3 × 3 reconstruction, by considering the following Hamiltonian:

$$\hat{H} = \sum_{i,\sigma} \varepsilon_i \hat{n}_{i\sigma} + \sum_{i \neq j,\sigma} t_{ij} \hat{c}^\dagger_{i\sigma} \hat{c}_{j\sigma} + \sum_i U_i \hat{\tilde{n}}_{i\uparrow} \hat{\tilde{n}}_{i\downarrow}$$

$$+ \frac{1}{2} \sum_{i \neq j,\sigma\sigma'} J_{ij} \hat{\tilde{n}}_{i\sigma} \hat{\tilde{n}}_{j\sigma'} \tag{1}$$

where ε_i is the energy level corresponding to each adatom dangling bond, $t_{ij} = T$ defines the hopping (only nearest neighbour hoppings are necessary in this case), U is the Coulomb interaction between electrons in the same site, and J_{ij} the interaction between electrons in sites i and j. In Eq. (1), $\hat{\tilde{n}}_{i\sigma}$ is the electron occupation number for the $i\sigma$ orbital measured with respect to the mean value, which in our case is $1/4$: $\hat{\tilde{n}}_{i\sigma} = \hat{n}_{i\sigma} - 1/4$. Notice that we only have one electron filling the two adatom orbitals of the unit cell.

The different parameters of Eq. (1) have been obtained by a generalization of similar quantities appearing in the Si(111)-5 × 5 and Si(111)-7 × 7 reconstructions. This suggests to use the following values: $\varepsilon_f - \varepsilon_u = -75$ meV, $T = -70$ meV, $U = 1.2$ eV, and J ranging from 350 meV for the nearest neighbours to zero at long distances. ε_f and ε_u define the levels of the adatoms located in the faulted and unfaulted half of the unit cell. We stress that at variance with the Sn/Ge(111)-3 × 3 case, in the case of Si(111)-3 × 3, the two dangling bonds contributing to the partially occupied bands do not have the same level due to the stacking fault present in this reconstruction. We shall see below that these inequivalent energy levels are responsible for the semiconducting character of the Si(111)-3 × 3 once correlation effects are included.

In this section, we analyse Hamiltonian 1 using a DFT approximation [1]. In this approximation, we introduce a mean field solution for the many-body terms of the Hamiltonian and an exchange potential associated with the Coulomb interaction between electrons in sites i and j. We have shown in Ref. [1] that the exchange energy of Hamiltonian 1 is well approximated by:

$$E^x(\{n_{i\sigma}\}) = -\frac{1}{2} \sum_{i,\sigma} J_i n_{i\sigma}(1 - n_{i\sigma}), \tag{2}$$

where J_i is the Coulomb interaction between n.n. electrons. This suggest to introduce the following exchange potential:

$$V_{i\sigma}^x = \frac{\partial E^x}{\partial n_{i\sigma}} = -J_i(1/2 - n_{i\sigma}), \qquad (3)$$

in such a way that the total many-body potential, $V_{i\sigma}$, associated with the orbital $i\sigma$ in Hamiltonian 1 is given by:

$$V_{i\sigma} = U_i\left(n_{i\bar{\sigma}} - \frac{1}{4}\right) + \sum_{j\sigma} J_{ij}\left(n_{j\sigma} - \frac{1}{4}\right) + V_{i\sigma}^x. \qquad (4)$$

Our effective one-electron Hamiltonian is, thus, defined by the following equation:

$$\hat{H}^{\text{eff}} = \sum_{i,\sigma}(\varepsilon_i + V_{i\sigma})\hat{n}_{i\sigma} + \sum_{i\neq j,\sigma}^{\text{n.n.}} T\hat{c}_{i\sigma}^{\dagger}\hat{c}_{j\sigma}, \qquad (5)$$

where $V_{i\sigma}$ and $n_{i\sigma}$ have to be determined selfconsistenly.

Fig. 2 shows in full lines the surface bands that have been calculated using this approach. Notice that there is an energy gap between the two bands — not present in the Sn/Ge case — that is mainly determined by the difference of the bare levels, $\varepsilon_f - \varepsilon_u$. Due to the large intraatomic interaction, U, the charge transfer between adatoms is negligible in the selfconsistent solution of Hamiltonian 5.

It is important to realize that in this solution, we have an electron per unit cell filling two bands. We conclude that E_F is in the middle of the lower band, the system showing a metallic character. In the next section, we will show how correlation effects modify dramatically this picture, giving a semiconducting behaviour for the Si(111)-3 × 3 reconstruction.

3. Many-body effects

3.1. Sn / Ge(111)-(3 × 3)

We analyze many-body effects in this surface by introducing a 2D Hamiltonian associated with the equivalent Sn dangling bonds forming the two bands shown in Fig. 1 around E_F. We have considered a Hamiltonian analogous to Hamiltonian 1 where $\varepsilon_i = \varepsilon_o$ defines the same (arbitrary) level for each dangling bond, t_{ij} includes in this case terms up to

second nearest neighbour orbitals in order to get an appropriate description of the surface bands, and U and J define the intrasite and intersite electron–electron interaction terms. U has been determined using a restricted DFT calculation for the reconstructed surface: In this calculation, the filling factors of the bands are changed and some electronic charge is transferred between the Sn adatoms. The surface bands are then determined selfconsistently, keeping the filling factors fixed. This provides us with an effective intrasite Coulomb interaction, $U–J_o$, which is found to be 0.55 eV (J_o is the Coulomb interaction between electrons in n.n. sites). As J_{ij} ranges from 0.35 eV (for n.n. charges) to zero, we deduce that $U \approx 0.9$ eV.

In a first step, this Hamiltonian is solved like Hamiltonian 1 via an effective Hamiltonian:

$$\hat{H}^{\text{eff}} = \sum_{i,\sigma}(\varepsilon_o + V_{i\sigma})\hat{n}_{i\sigma} + \sum_{i\neq j,\sigma} t_{ij}\hat{c}_{i\sigma}^{\dagger}\hat{c}_{j\sigma}, \qquad (6)$$

which yields essentially the DFT bands shown as continuous lines in Fig. 1.

Electron correlation effects can be introduced by means of a local self-energy, $\Sigma(\omega)$. In our particular case, we can use the atomic limit to calculate $\Sigma(\omega)$ as the effective intrasite Coulomb interaction $U–J_o = 0.55$ eV (the role of J_o is to screen the intrasite Coulomb interaction), which has a value substantially larger than the bandwidth (≈ 0.25 eV). In this limit, we have the following self-energy:

$$\Sigma_{i\sigma}(\omega) = U^2\left\{\frac{(1 - n_{i\bar{\sigma}})}{\omega - \varepsilon_o} + \frac{n_{i\bar{\sigma}}}{\omega - \varepsilon_o - U}\right\}. \qquad (7)$$

We have calculated correlation effects in the Sn/Ge(111) surface replacing $(\varepsilon_o + V_{i\sigma})\hat{n}_{i\sigma}$ by the following "effective" level $(\varepsilon_o + V_{i\sigma} + \Sigma_{i\sigma}(\omega))\hat{n}_{i\sigma}$. The corresponding Greens function, $G_{ii\sigma}(\omega)$, yields the new correlated bands that we show in Fig. 1 by the dashed lines. Important points to notice about these results are the following: (i) Due to the many-body interactions, there appears a new structure located around 0.55 eV above the initial band. The total weight of this new structure is of one electron per unit cell. (ii) The initial band is slightly narrowed and its total weight is reduced from four to three electrons. As we only have one electron per unit cell, we find that E_F is still in the middle of the lower

band, giving a metallic character to the Sn/Ge(111) interface. (iii) Moreover, the correlated surface bands show, around E_F, practically the same dispersion relation yielded by the DFT calculation.

We have also analyzed the possibility of having a CDW instability, associated with the charge transfer between the two Sn atoms having the same height, and promoted by the intersite Coulomb interaction J. We have found that this transition should appear only if J were a factor of 2 larger than the value determined for this system. We conclude that regarding the electronic structure around E_F, correlation effects introduce minor modifications in the DFT results.

3.2. Si(111)-(3 × 3)

For this surface, contrary to the Sn/Ge case, the inclusion of correlation effects shows that the system has a CDW instability related to the charge transfer between the two adatom dangling bonds. Thus, intersite correlations associated to J (as intrasite correlations are associated to U), described by an off-diagonal self-energy $\Sigma_{12} \omega$, cannot be neglected as done for the Sn/Ge(111) interface.

This is the reason why we have chosen to analyse the Si(111)-3 × 3 case using a different approach. The critical point to realize is that U, or $U–J$, the intrasite effective repulsion between electrons, is much larger than the surface bandwidth. This implies that electrons tend to avoid each other at any site, and we can describe this effect conveniently using a spinless Hamiltonian that incorporates the exchange interaction preventing two electrons to occupy the same site simultaneously.

Accordingly, we introduce a spinless Hamiltonian and write the following equation:

$$\hat{H}^{\text{spinless}} = \sum_i \varepsilon_i \hat{n}_i + \sum_{i \neq j}^{\text{n.n.}} T \hat{c}_i^\dagger \hat{c}_j + \frac{1}{2} \sum_{i \neq j} J_{ij} \hat{n}_i \hat{n}_j. \quad (8)$$

A word of caution has to be put here: once we solve the Hamiltonian, we expect its occupied states to represent a fair approximation to the exact solution of the problem (with its spin fluctuating between up and down values); for the empty states, we expect, however, the exact solution to be better represented by the solution of Hamiltonian 8, including

now a factor of 2, due to the fact that those states are empty and do not repel those electrons having opposite spins.

Hamiltonian 8 has been solved replacing the electron–electron interaction term by $\sum_j J_{ij} n_j V_i^x$, where V_i^x is the exchange potential introduced in Eq. (3). This effective Hamiltonian can be solved selfconsistently in the charge, giving the band structure shown by dashed lines in Fig. 2. We find an important charge transfer between the inequivalent adatoms of the Si(111)-3 × 3 unit cell; in particular, we find 0.75 and 0.25 electrons in the two adatoms. This charge transfer increases the difference between the effective levels of the faulted and unfaulted adatoms, which leads to an enlargement of the gap between the two bands shown in Fig. 2: this gap is around 150 meV, 75 meV larger than in the DFT solution. We stress that this charge transfer has not been found in the Sn/Ge case because the intersite Coulomb interaction, J, is not large enough. For Si(111)-3 × 3, although J is also not sufficient to drive the CDW transition by itself, we find that the difference between the levels of the faulted and unfaulted sites operates as a driving force for the stabilization of the CDW phase.

This solution also shows that the lower band in Fig. 2 is fully occupied by one electron (due to the spinless solution), while the higher band is empty with a total weight of two electrons. Comparing with the solution presented for the Sn/Ge(111)-3 × 3 interface, we also find that the total density of states associated with the surface bands located around E_F has a total weight of three electrons. This suggests that in the solution shown in Fig. 2, we have neglected another structure (similar to the one shown in Fig. 1, around 0.55 eV above E_F) that should appear around $U \sim 1$ eV above E_F with a weight of one electron. Notice that including this structure, the center of gravity of the total DOS remains practically unchanged.

4. Conclusions

DFT calculations show that the Si(111)-3 × 3 and Sn/Ge(111)-3 × 3 reconstructions present striking similarities, with two dangling bonds and one elec-

tron per unit cell defining the surface states properties around the Fermi level. Electron correlation effects do not modify the metallic character of the Sn/Ge(111)-3 × 3, while a metal–insulator transition takes place in the Si(111)-3 × 3. This behaviour is related to the difference in energy levels of the two adatoms, not present in the Sn/Ge case, which operates as the driving force to stabilize the charge transfer between these atoms in the correlated solution.

Acknowledgements

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