



ELECTRON CORRELATION EFFECTS AT SEMICONDUCTOR SURFACES AND INTERFACES: Si(111)-5x5, Si(111)-7x7 AND Sn/Ge(111)

J. ORTEGA, F. FLORES, R. PÉREZ and A. LEVY YEYATI

Departamento de Física Teórica de la Materia Condensada, Facultad de Ciencias,
Universidad Autónoma de Madrid, Madrid 28049, Spain

Abstract

Electron correlation effects associated with the dangling bond surface states of Si(111)-5x5, Si(111)-7x7 and Sn/Ge(111)-3x3 are analyzed. In all the cases, extensive LDA-calculations are performed and effective two-dimensional Hamiltonians are deduced. Our analysis of these Hamiltonians shows that: (a) the Si(111)-5x5 surface states exhibits a metal-insulator transition; (b) the Si(111)-7x7 surface shows important similarities with the Si(111)-5x5 case, but it has a dangling bond surface band having a metallic character; (c) finally, the Sn/Ge(111)-3x3 dangling bond surface bands also shows important correlation effects that are found, however, not to affect the metallic character of the surface bands.

1. Introduction

Electron correlation effects in two-dimensional (2D) systems is a fashionable topic, usually associated with the high- T_c superconductors and the Quantum Hall effect. Other 2D-systems, where important correlation effects also appear, are metal [1] and/or semiconductor [2,3] surfaces and interfaces, where a 2D-electron gas can be created, depending on the face orientation and the adlayer deposited on the crystal.

In this paper, we shall be concerned with semiconductor surfaces or interfaces, a case for which recent experimental evidence [4-7] shows how electron surface bands at the middle of the semiconductor energy gap exhibit interesting many-body effects. Alkali atom (or any other metal atom) adsorption [4] on semiconductor surfaces at the early stages of coverage corresponds to a typical correlation problem related to the metallization of the overlayer and, eventually, to the Schottky barrier formation. Experimental and theoretical evidence [2,8] has abundantly shown that a *metal-insulator* (M-I) transition occurs when the alkali atom adlayer reaches the

coverage of a physical monolayer. At lower coverages, the adlayer is in an insulating phase while, for coverages larger than a monolayer, a metal band is developed and the Schottky barrier is formed. The reader interested in these effects can find a full theoretical discussion of the M-I transition for the alkali-semiconductor system in [2]. In these references, it has been shown that this system can be understood on the basis of a Hubbard Hamiltonian, where U , the intrasite Coulomb interaction, and W , the band width, determine the insulating or metallic character of the system: For $U/W \gg 1$ an insulating phase is formed, while the opposite limit, $U/W \ll 1$, corresponds to the metallic phase.

We shall analyze in this paper other surface and interface structures, for which many-body effects have also been found to be important [9–11]. These three cases are: (a) Si(111)–5×5, (b) Si(111)–7×7, and (c) Sn/Ge(111) $\sqrt{3} \times \sqrt{3}$ and 3×3 structures. We find it interesting to discuss these three cases together in order to emphasize their differences and similarities. In particular, we shall show how the 2D-electron gas associated with the dangling bond states of the Si(111)–5×5 reconstruction exhibits a M-I transition that can be only understood in terms of an *extended* Hubbard Hamiltonian. The case of Si(111)–7×7 shows important similarities with the Si(111)–5×5 case, but, as shown below, it has a dangling bond surface band having a metallic character with strong correlation effects very much in similarity with the properties of mixed-valence compounds. Finally, the 2D-electron gas of the Sn/Ge(111) $\sqrt{3} \times \sqrt{3}$ dangling bond surface bands shows also important correlation effects that, however, are found to affect neither the structure of the most stable geometry found for the interface, i.e., a 3×3 reconstruction, nor the metallic character of the surface bands.

Sections 2, 3 and 4 will be devoted to the different systems mentioned above, namely, Si(111)–5×5, Si(111)–7×7, and Sn/Ge(111) $\sqrt{3} \times \sqrt{3}$, respectively. Finally, in Sec. 5, we will present our discussion and conclusions.

2. Si(111)–5×5 Reconstruction

A. LDA calculations

Figure 1 shows the geometry of the accepted structural *dimer-adatom-stacking* (DAS) fault model for this surface. Using a local orbital selfconsistent *local-density approximation* (LDA) method [12], we have calculated its relaxed geometry and its electronic ground state. Figure 2a shows the nine different surface bands located in the fundamental energy gap of Si.

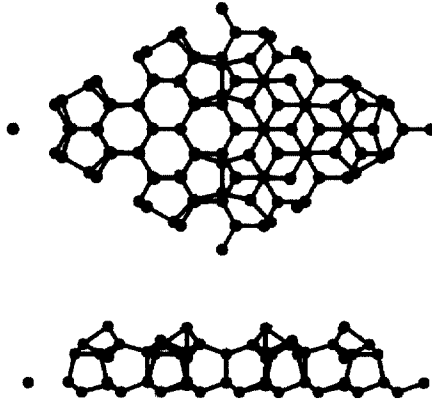


Fig. 1. Unit cell of the Si(111)-5×5 surface: top view and side view. The six adatoms are represented by black dots and the two rest atoms by the dark-grey dots. The corner-hole atom is the one on the corners of the unit cell.

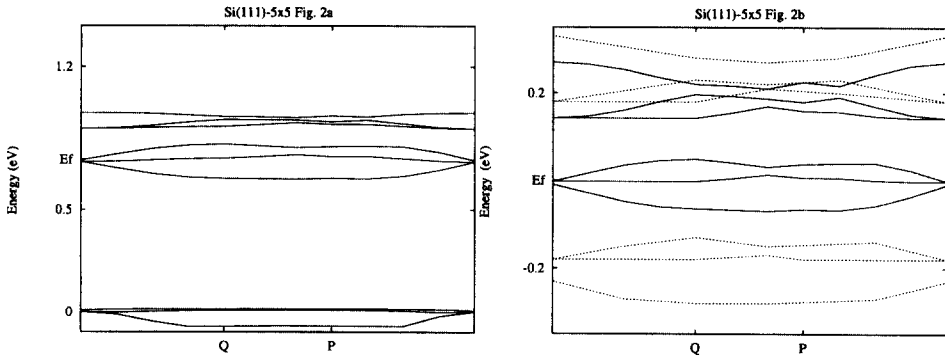


Fig. 2. (a) LDA surface bands corresponding to the Si(111)-5×5 reconstruction. The three surface bands ~ 0.8 eV below E_f are associated with the corner-hole and the two rest atoms dangling bonds, while the six bands close to E_f are related with the six adatom dangling bonds. The origin of energies corresponds to the Si valence band maximum. (b) Electron correlation effects in the six adatom surface bands. Solid lines: LDA bands; dashed lines: correlated surface bands (see text).

Notice that the three surface bands located around 0.8 eV below the Fermi level, E_f , are associated with the corner hole and the two rest atoms of the 5×5 unit cell (see Fig. 1). Around E_f , we find six bands that are essentially derived from the six adatom dangling bonds. A simple

electron counting rule indicates that these six bands are occupied by three electrons per unit cell [11]; this is easily found taking into account that the corner hole and the rest atoms dangling bond bands are doubly occupied. These arguments show that E_f is located in the middle of the second surface band associated with the adatom dangling bonds (see Fig. 2a), defining in this way a metallic *density of states* (DOS) at the Si(111)- 5×5 reconstruction.

B. Two-dimensional extended Hubbard Hamiltonian

The surface bands associated with the adatom dangling bonds are around 300 meV wide, narrower than the intrasite Coulomb interaction for these dangling bonds (see below). Then, we can expect correlation effects for these bands to be important. We have analyzed these properties by means of the following extended 2D Hubbard Hamiltonian:

$$\hat{H} = \sum_{i\sigma} E_{i\sigma} \hat{n}_{i\sigma} + \sum_{i\neq j,\sigma} T_{ij\sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}) + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum_{i\neq j,\sigma} J_{ij} \hat{n}_{i\sigma} \hat{n}_{j\bar{\sigma}}, \quad (1)$$

where $E_{i\sigma}$ is the energy level corresponding to each adatom dangling bond orbital, $T_{ij\sigma}$ defines the different hopping integrals, T and s , shown in Fig. 3a, and U_i and J_{ij} are the intrasite and intersite

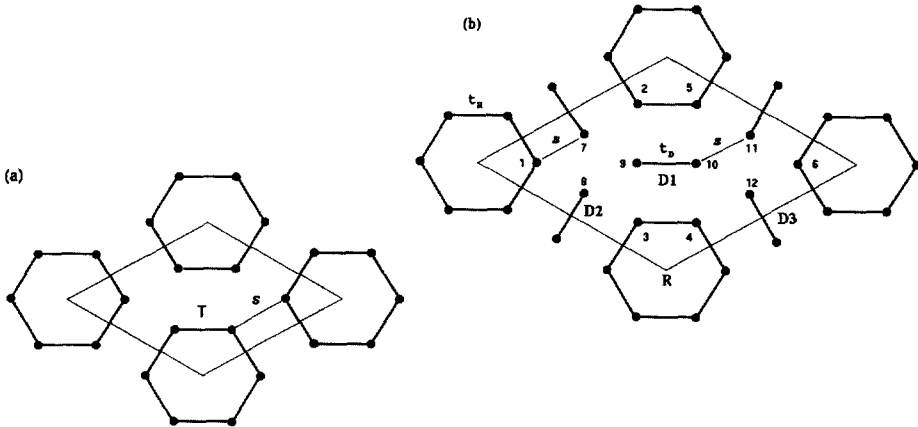


Fig. 3. Schematic representation of the adatom geometry and interactions: (a) Si(111)- 5×5 surface, (b) Si(111)- 7×7 surface. The adatoms are shown as black dots. The thick lines connecting adatoms represent the big hopping interactions, T , and the thin lines are the small hopping interactions s (for clarity, only a few s -interactions are represented). The unit cell border is also shown.

Coulomb interactions between dangling bonds. $\hat{n}_{i\sigma}$ defines the electron charge fluctuations with respect to the mean occupation number per spin, $n_0 = 1/4$ (three electrons in six orbitals).

In Hamiltonian (1), we have introduced not only U , but the intersite Coulomb interaction J_{ij} , too. This is crucial for analyzing our Si(111)- 5×5 reconstruction, as the mean number of electrons per site is $1/2$. For values different from 0, 1, or 2, the system would appear as metallic for a restricted Hubbard Hamiltonian, where $J_{ij} = 0$. In our case, the intersite Coulomb interaction appears as the main mechanism promoting an insulating behaviour of the system.

Parameters $E_{i\sigma}$ and $T_{ij\sigma}$ are calculated by a fitting to the bands shown in Fig. 2. U_i and J_{ij} are obtained from a restricted LDA calculation, and by introducing an electrostatic model in which J_{ij} corresponds to Coulomb interaction between point charges that replace the dangling bond states, in the presence of a semi-infinite Si crystal. This model is justified by the long distances (more than 6 Å) between different dangling bonds (see [11] for more details).

This model yields $E_f - E_u = -108$ meV (E_f and E_u are the two levels associated with the atoms of the faulted and unfaulted parts of the unit cell); $T = -70$ meV; $s = 21$ meV; $U \simeq 1.5$ eV, and J_{ij} ranging between 386 meV, for the nearest neighbour interaction, and zero.

C. Correlated surface bands

It is a formidable task to obtain the exact solution of Hamiltonian (1). We have found, however, that T is substantially larger than s ; this allows us to get an approximate solution by taking first $s = 0$, and introducing later, perturbatively, the effect of a finite s .

For $s = 0$, Hamiltonian (1) is decoupled into finite Hamiltonians associated with the hexagonal rings of Fig. 3a. This Hamiltonian can be solved exactly, and using conventional Green-function techniques we can calculate the DOS associated with electrons and holes. This DOS shows 3 electrons and 3 holes around E_f , other 6 more empty states are located above the Fermi energy by an energy of U .

In a further step, we introduce perturbatively the effect of taking $s \neq 0$. Figure 2b shows, in dashed lines, the surface bands as calculated in this way. Although these bands show an interesting resemblance with the LDA bands, the main difference with this case comes from the DOS associated with the new bands: due to the high U value appearing in Hamiltonian (1), the new bands of Fig. 2 are singly degenerate; this is the reason why the Fermi level is now located in an energy gap, above the first three singly degenerate bands associated with the adatom dangling bonds.

It is also worth commenting other differences between the LDA and the correlated bands. In addition to single degeneracy of these correlated bands, notice how the energy gap between the two bunches of 3 bands around E_f has increased in the correlated solution by about 150 meV: this is the effect of the intersite Coulomb interactions, J_{ij} , tending to create an insulating state by increasing the splitting between the occupied and empty bands.

3. Si(111)- 7×7 Reconstruction

A. LDA calculations

Figure 4 shows the surface bands located in the fundamental energy gap of Si, as calculated for the DAS model of the Si(111)- 7×7 reconstruction, using a local orbital selfconsistent LDA method [12]. Notice that the bands located around 0.55 eV and 0.9 eV below E_f are associated with the corner-hole atom and the rest-atom dangling bonds of this surface. As these 7 bands (there are 1 corner-hole and 6 rest-atom dangling bonds per unit cell in this 7×7 reconstruction) are doubly occupied, the surface bands associated with the adatom dangling bonds have to accommodate only 5 electrons per unit cell.

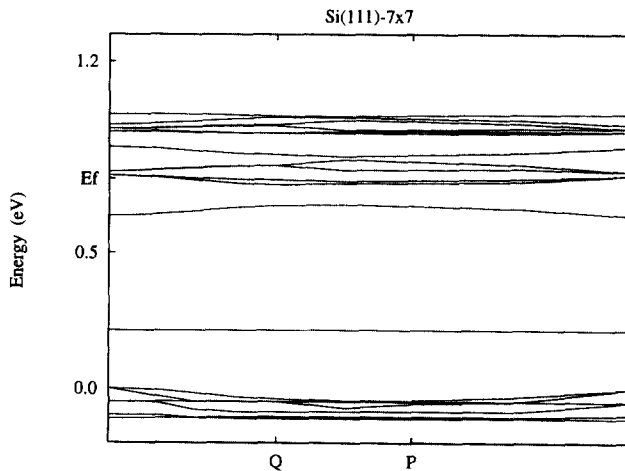


Fig. 4. LDA surface bands corresponding to the Si(111)- 7×7 reconstruction. The six surface bands ~ 0.8 eV below E_f are associated with the six rest atoms dangling bonds, the band ~ 0.55 eV below E_f is related with the corner-hole atom dangling bond, and the 12 bands around E_f are essentially derived from the 12 adatom dangling bonds. The origin of energies corresponds to the Si valence band maximum.

These LDA results yield a Fermi level (see Fig. 4) crossing two of the adatom surface bands, suggesting that the Si(111)-7×7 has a metallic character. In view of the previous discussion for the Si(111)-5×5 reconstruction, one could anticipate that the LDA results should be dramatically modified by electron correlation effects.

B. Two-dimensional extended Hubbard Hamiltonian

As for the 5×5 reconstructed surface, we also analyze the 7×7 reconstruction by introducing the same 2D Hamiltonian given by (1). In this particular case, T_{ij} is defined by the hopping integrals t_R , t_D and s , shown in Fig. 3b. In the Si(111)-7×7 surface, $\hat{n}_{i\sigma} = \hat{n}_{i\sigma} - n_0$ defines the electron charge fluctuation with respect to the mean occupation number per spin, $n_0 = 5/24$.

All the parameters appearing in Hamiltonian (1) can be obtained from the selfconsistent LDA bands, and from a restricted LDA calculation that allows for some charge transfer between the adatom surface bands. We also introduce the same electrostatic model discussed for the Si(111)-5×5 reconstruction, for calculating J_{ij} .

From these calculations we obtain the following parameters for the 2D Hamiltonian (groups of atoms (1,2,3), (4,5,6), (7,8,9) and (10,11,12) in Fig. 3b are called r_1 , r_2 , d_1 and d_2 , respectively): $E_{d1} - E_{d2} = -42$ meV; $E_{r1} - E_{r2} = -33$ meV; $E_d - E_r = 260$ meV; $t_R = -85$ meV; $t_D = -68$ meV; $s = -25$ meV; $U = -1.1$ eV and J ranges from 386 meV (nearest) to zero.

C. Correlated surface bands

An approximate solution of Hamiltonian (1) with the parameters calculated for the Si(111)-7×7 reconstruction can be obtained proceeding in the same way as above. We first take $s = 0$, solve Hamiltonian (1) for this particular case, and then introduce perturbatively $s \neq 0$.

The solution for $s = 0$ is similar to the 5×5 reconstruction, but for some important details that we discuss below. In the 7×7 reconstruction, the case $s = 0$, leaves the hopping parameters t_R and t_D , that only link six atoms around the corner hole, or two atoms like 9 and 10 in Fig. 3b. Due to this fact, structures having a hexagonal-ring or a *dimer* geometry are decoupled from each other. The hexagonal-ring structure is similar to the one found in the 5×5 reconstruction, while the *dimers* ($D1$, $D2$ and $D3$ in Fig. 3b) are specific to the 7×7 reconstruction. A detailed analysis of the ground state for this case [10] (Hamiltonian (1) and $s = 0$) shows that in the 7×7 reconstruction, 3 electrons per unit cell are localized in the rings and two electrons in the

two dimers. It is important to realize that having 2 electrons filling the dimers corresponds, for $s = 0$, to a three-fold degeneracy of the Si(111)- 7×7 ground state: this degeneracy is responsible for the metallic character of this surface. Summarizing these results, we conclude that, for $s = 0$, the 7×7 reconstruction shows a LDOS with two independent components associated with (a) the hexagonal ring structure, similar to the one found in the 5×5 reconstruction, and (b) the dimers; this one presents a three-fold degeneracy and can be described as two electrons filling three states located at the Fermi level.

The effect of introducing $s \neq 0$ is the following: First, the hexagonal ring structure is going to be broadened, yielding a DOS similar to the one found above for the 5×5 reconstruction. In addition to this one, a metallic band is going to appear due to the broadening of the three states associated with the dimers. These states are occupied with two electrons per unit cell, and the metallicity of the Si(111)- 7×7 reconstruction can be associated with the motion of those two electrons along the dimers $D1$, $D2$ and $D3$ of Fig. 3b.

In conclusion, the Si(111)- 7×7 reconstruction exhibits an electronic structure associated with rings and dimers (Fig. 3b). Rings are basically decoupled from the dimers and behave, in a first approximation, like the rings of the 5×5 reconstruction. Dimers contribute basically to the formation of a metallic band, which we can describe as appearing in the middle of the energy gap shown in Fig. 2b (dashed lines) for the 5×5 reconstruction, and presenting a broadening of around 100 meV (see [10]).

Moreover, it is interesting to realize that the coupling between the rings and dimers introduce charge fluctuations in the rings that—like in mixed-valence compounds—lead to a Kondo-like resonance in the DOS associated with our sort of *impurity* (the rings in our case). This effect is discussed in more detail in [11].

4. Sn/Ge(111)- 3×3 Reconstruction

Recently, Carpinelli *et al.* [5,13] have reported STM and LEED results conclusively showing a phase transition from the room temperature $\sqrt{3} \times \sqrt{3}$ Sn/Ge(111) (or Pb/Ge(111)) to a 3×3 structure at low temperature. The origin of this transition is still under debate, with different proposals going from a charge density wave mechanism to the consideration of many-body effects [9,13].

In this section, we analyze the Sn/Ge(111)- 3×3 reconstruction and discuss its surface band structure and how electron correlation affects its DOS.

In the first place, we have considered the ground state geometry of a 3×3 reconstruction. This has been analyzed by means of a first-principles Molecular Dynamics technique. In this method, a local orbital selfconsistent LDA approach is used to obtain first-principles atomic forces efficiently [12]. Our calculations show a 3×3 reconstruction with one Sn-atom displaced upwards 0.24 \AA and the other two Sn-atoms displaced downwards by 0.12 \AA w.r.t. the Sn-layer of the $\sqrt{3}\times\sqrt{3}$ symmetry. Thus, we conclude that the 3×3 reconstruction is lower in energy than the $\sqrt{3}\times\sqrt{3}$ by $\sim 40 \text{ meV}$ per Sn-atom [7].

In Fig. 5 (solid lines), we show our LDA-surface bands for the 3×3 reconstruction. In this calculation we find three surface bands associated with the three dangling-bonds of Sn; notice that the lowest energy band is associated with the Sn-atom displaced upwards, while the two other bands are associated with the Sn-atoms moving towards the surface. The lowest band is fully occupied (with two electrons per unit cell), leaving only one electron per unit cell filling the bands associated with the downwards Sn-atoms.

Many-body effects in these bands can be important. Notice that the bandwidth ($\sim 0.5 \text{ eV}$) is smaller than the order of magnitude of U ($\sim 0.9 \text{ eV}$, see below) calculated for this interface. We have also calculated U and J_{ij} (the intrasite and the intersite coulomb interactions associated with the Sn dangling bonds) using a restricted LDA calculation. From this calculation, we deduce

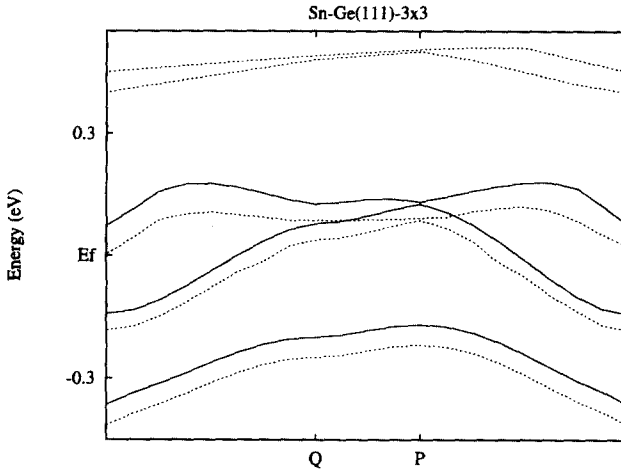


Fig. 5. LDA (solid lines) and correlated (dashed lines) surface bands for the Sn/Ge(111)- 3×3 surface.

that the effective Hubbard interaction, U_{eff} (this represents the initial U screened out by the positive charge induced around two electrons of opposite spins located at the same site), is 0.55 eV.

Using U_{eff} and introducing an appropriate selfenergy [14], we calculate for the Sn dangling bonds the new surface bands shown as dashed lines in Fig. 5. The main conclusions we draw from these results are the following: (a) the lowest band, filled by 2 electrons, is practically unaffected by correlation effects; (b) the surface bands associated with the two Sn-atoms moving downwards are strongly modified by many-body effects. In particular, the highest energy structure has a total weight of 1 electron (spin included), while the remaining structure around the Fermi energy—with a total weight of 3 electrons—is similar, although a little narrower than the LDA bands shown by the filled line.

In conclusion, correlation effects do not change too much the surface states band structure associated with the bands located below the Fermi energy, but introduce a new structure at energies located 0.4 eV above E_f . It is worth commenting that the two bands located below E_f have been observed with photoemission [7] and yield a strong support to the results presented in this section for the system Sn/Ge(111)-3×3.

5. Conclusions

We have presented a systematic analysis of the correlation effects associated with the dangling bond surface bands of Si(111)-5×5, Si(111)-7×7 and Sn/Ge(111)-3×3. In our approach, LDA calculations for the ground state and for restricted surface band occupancies allow us to calculate the effective 2D Hamiltonian describing the many-body effects associated with these surfaces.

Our analysis shows that in the Si(111)-5×5 reconstructions, three electrons tend to be localized in the hexagonal ring structures shown in Fig. 3a, exhibiting a semiconducting character. In the Si(111)-7×7 reconstruction, we also find the same hexagonal structure and three electrons localized in these rings; but, in addition to it, we find two other electrons per unit cell filling the *dimers* shown in Fig. 3b. These two electrons are responsible of the metallic character found in this Si(111)-7×7 reconstruction.

Finally, we have analyzed the Sn/Ge(111)- $\sqrt{3}\times\sqrt{3}$ reconstruction and found that the 3×3 reconstruction is more stable, showing one Sn-atom displaced upwards 0.24 Å and two Sn-atoms displaced downwards by 0.12 Å with respect to the Sn-layer of the $\sqrt{3}\times\sqrt{3}$ symmetry. Then, we

have analyzed correlation effects associated with the three dangling bond surface bands and have found that the DOS below E_f is practically unaffected by these many-body effects, although a new structure above E_f appears.

Acknowledgements

This work was funded by the Spanish CICYT under contracts No. PB92-0168C and PB93-0260.

References

1. E. Tosatti, in *Electron surface and interface states in metallic systems*, E. Bertel and M. Donath (Eds.), World Scientific, Singapore (1995).
2. F. Bechstedt and M. Scheffler, Surf. Sci. Rep. **18**, 145 (1993); F. Flores, Surf. Rev. Lett. **2**, 513 (1995).
3. B.N.J. Persson and J.E. Demuth, Phys. Rev. B **30**, 5968 (1984).
4. E.W. Plummer and P.A. Dowben, Prog. Surf. Sci. **42**, 201 (1993); N.J. DiNardo, T. Maeda Wong and E.W. Plummer, Phys. Rev. Lett. **65**, 2177 (1990).
5. J.M. Carpinelli, H.H. Weitering and R. Stumpf, Nature **381**, 398 (1996).
6. R.I.G. Uhberg, T. Kaurila and Y.C. Chao, Phys. Rev. B **58**, 1730 (1998).
7. J. Avila, A. Mascaraque, E.G. Michel, M.C. Asensio, G. Le Lay, J. Ortega, R. Perez and F. Flores, to be published (1998).
8. K. Stiles and A. Kahn, Phys. Rev. Lett. **60**, 440 (1988); W.E. Spicer, Appl. Surf. Sci. **44/42**, 1 (1989); M. Prietsch, M. Domke, C. Laubschat and G. Kaindl, Phys. Rev. Lett. **60**, 436 (1988).
9. A. Goldoni and I. Modesti, Phys. Rev. Lett. **79**, 3266 (1997).
10. J. Ortega, F. Flores and A. Levy Yeyati, Phys. Rev. B **58**, 4584 (1998).
11. J. Ortega, A. Levy Yeyati and F. Flores, Appl. Surf. Sci. **123/124**, 131 (1998).
12. O.F. Sankey and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989); A.A. Demkov, J. Ortega, O.F. Sankey and M.P. Grumbach, Phys. Rev. B **52**, 1618 (1995).
13. J.M. Carpinelli, H.H. Weitering, M. Bartkowiak, R. Stumpf and E.W. Plummer, Phys. Rev. Lett. **79**, 2859 (1997).
14. A. Levy Yeyati, A. Martin-Rodero, F. Flores, J. Ortega and R. Rincon, Appl. Surf. Sci. **104/105**, 248 (1996).