Two distinct metallic bands associated with monatomic Au wires on the Si(557)-Au surface

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The Si(557)-Au surface, containing monatomic Au wires parallel to the steps, has been proposed as an experimental realization of an ideal one-dimensional metal. In fact, recent photoemission experiments on this system (Nature \textit{402}, 504 (1999)) found two peaks that were interpreted in terms of the spin-charge separation in a Luttinger liquid. Our first-principles density functional calculations reveal two metallic bands associated with Au-Si bonds, instead of the single band expected from the Au 6\textit{s} states, providing an alternative explanation for the experimental observations.

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It has been recognized for several decades now that a one-dimensional metal should considerably deviate from the Fermi liquid behavior \cite{1,2}: quasiparticles would be replaced by two distinct collective excitations involving spin and charge, and some of the system’s properties would exhibit characteristic power-law dependences. Despite this theoretical understanding, the experimental observation of the so-called Luttinger liquid behavior has proven quite elusive, due in large part to the lack of well-characterized one-dimensional systems. Only very recently, signatures of Luttinger liquid behavior have been observed by means of transport measurements in carbon nanotubes \cite{4}, in edge states of the fractional quantum Hall effect \cite{5}, and in quantum wires with a single conducting channel \cite{6}, and by optical conductivity measurements in organic conductors \cite{7}, and in the quasi-one-dimensional CuO chains in PrBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8} \cite{8}.

More direct evidence of the Tomonaga-Luttinger behavior can be provided by angle-resolved photoemission experiments, in which the spin-charge splitting of the low-energy excitations can, in principle, be measured. This has been tried for several systems containing quasi-one-dimensional metallic chains \cite{9,10}. However, in most cases the results were inconclusive due to the lack of energy and angular resolution \cite{11}, the difficulties to correctly align the chains, and other uncertainties associated with the crossover of dimensionality in the bulk samples. To avoid some of these problems, Segovia \textit{et al.} \cite{12} studied the photoemission from a monophase sample of the stepped Si(557)-Au surface, in which the gold atoms are believed to form single rows running parallel to the edge of each step. For this system, the measured spectra were assigned to a single one-dimensional band derived from the gold 6\textit{s} states. The observed splitting of this band close to the Fermi level was interpreted in terms of the spin-charge separation in a one-dimensional electron liquid, providing the first direct measurement of two distinct peaks for spinons and holons. If such behavior is intrinsic to Au wires, it could also apply to monatomic gold wires fabricated using a scanning tunneling microscope (STM) and to mechanically controllable break junctions \cite{13,14}.

In spite of this extraordinary observation, very little is still known about the atomic and the electronic structure of the Si(557)-Au surface. In this context, theoretical studies can be useful to complement and guide experimental efforts. With this aim, we present in this Letter a first-principles density-functional study of the electronic structure of simple models of this stepped surface. We obtain the surprising result that two metallic bands, not just one, are associated with the monatomic gold chains in this system. This could explain the photoemission data of Segovia \textit{et al.} \cite{12} without the need to appeal to electron correlation effects in the monatomic gold chains, and seems to be in agreement with more recent experimental evidence \cite{15}.

Our calculations have been performed with the SIESTA code \cite{16}, which performs standard pseudopotential density-functional calculations using a linear combination of atomic orbitals (LCAO) as a basis set. We have used Troullier-Martins pseudopotentials \cite{17}, the local density approximation for the exchange-correlation functional, and a double-\textit{ζ} polarized (DZP) \cite{18,19} basis set for all the atomic species. A Brillouin zone sampling of 10 inequivalent k-points, and a real-space grid equivalent to a plane-wave cut-off of 100 Ry (up to 40 k-points and 200 Ry in the convergence tests) have been employed. These parameters guarantee the convergence of the total energy, for a given basis, within \textasciitilde0.02 eV/Au (due to the large supercells this becomes \textasciitilde0.5 meV per atom).

The Si(557)-Au surface presents a (5\times1) reconstruction formed after the deposition of \textasciitilde0.2 monolayers (ML) of gold on top of a vicinal Si(111) surface, as described in Ref \cite{13}. The misorientation is chosen along the [1 1 1]
direction and therefore the steps, with a width of five Si(111) 1x1 unit cells, are parallel to the [1\overline{1}0] direction. A single row of gold atoms is supposed to run parallel to each step, consistent with the gold coverage. However, the detailed structure of the Si(557)-Au surface is unknown. It is probably related to the better studied (5\times2) reconstruction [20], which is formed on flat substrates, and contains twice as much gold (∼0.4 ML). In the absence of precise structural information, we have adopted in this study the simplest possible models consistent with all the available experimental data.

The initial and relaxed structures of one of these models, similar to the one proposed in Ref. [3], are shown in Fig. 1(a) and (b), respectively. In panel (a) the position of the Si dangling bonds present initially have been schematically indicated by arrows, while in panel (b) the rows of atoms are labelled according to their distances to the step edge. The typical slabs (see Fig. 1(b)) used in our calculations contain 4 silicon bilayers, with the Au atoms occupying some of the Si positions and forming a single row parallel to the step edge. Si atoms in the bottom layer are saturated with hydrogen, and remain at the ideal bulk positions during the relaxation process. The lattice parameter parallel to the surface is fixed at the calculated bulk value (5.41 Å) to avoid artificial stresses.

During the relaxation, the step edge moves considerably from its original position in order to saturate some of the surface dangling-bonds with the creation of additional Si-Si bonds. This also causes some rebonding of the neighboring Si atoms. The tendency of the Si atoms at the surface to adopt a sp² hybridization, which favors an expansion of the surface layer, also contributes to the movement of the step. These trends are common to the relaxed structures of all the structural models considered here.

Table 1 presents the total energy of several structures relative to that of the configuration shown in Fig. 1(b). The structures differ in the location of the Au chains, and are labelled according to Fig. 1(b). One can see that the vicinity of the step edge (position 1) is a highly unfavorable location for the gold row, whereas the energies associated to positions 2, 3 and, 4 are almost degenerate within the precision of our calculations. (In addition, the band-structure features described below are very similar for models 2, 3, and 4.) Consistent with these results, recent STM experiments [21] indicate that position 2 could be the preferred location for the Au chain in narrow terraces. Therefore, in the following we will concentrate on this structure (model 2).

It has been proposed [22] that a Peierls dimerization of the Au chains could lead to splittings of the bands. Our calculations show that in spite of the large Au-Au distance (3.83 Å), the dimerization is totally suppressed by the rigidity of Si structure.

The band structure near the Fermi level of the slab in model 2 is shown in Fig. 1(d) with the lines defined by the two-dimensional Brillouin zone in Fig. 1(c) (lines Γ-K-M are parallel and Γ-M almost parallel to the steps, while Γ-M′ is perpendicular to them). The use of a LCAO basis allows us to perform a Mulliken population analysis [23] to identify the main character of each band. Though not totally unambiguous, this identification is specially clear for surface states, which have a considerable weight only in the outermost atoms of the slab. In Fig. 1(d) each surface state has been marked with different symbols according to its origin: i) The rather flat band marked with stars comes from the unsaturated bonds of the Si atoms in the step edge. This band, strongly localized at the edge, is present, pinning the Fermi level, in all the models with Si dangling bonds at the edge. It could be eliminated by removing the extra Si atom at the edge and dimerizing the remaining atoms in analogy to the Si(100)-2\times1 reconstruction, with a doubling of the unit cell. However, our most stable relaxed ”edge-dimerized” model has a surface energy much higher (∼0.4 eV/Au) than model 2. ii) States marked with open symbols correspond to dangling bonds on the terraces. The partially occupied band marked with open triangles comes from the unsaturated bonds in row 3, while the unoccupied band marked with open circles is associated to those in row 4. iii) Two ”one-dimensional” bands, i.e. exhibiting an almost negligible dispersion in the direction perpendicular to the Au chain, have very similar amounts of gold character. The one marked with solid circles is more dispersive and crosses the Fermi energy, while the other, indicated with solid triangles, is quite flat and fully occupied. The presence of these two bands contradicts the intuitive picture that would assign a single band, coming from the 6s state, to the Au wire. In fact, our analysis reveals that a considerable weight of these ”gold bands” corresponds to the Si neighbors of the Au atoms. The most dispersive band in our calculations, with its bottom close to the edge of the Brillouin zone, can be identified with the experimentally observed one [3]. However, in this system there is no report to date of the flat bands that we have identified as due to unsaturated surface bonds (those marked with stars and open triangles in Fig. 1(d)). These bands are probably eliminated in the real surfaces by surface reconstruction and passivation. Even though we have no detailed information on the nature of the reconstruction, we can account for its main effect, i.e., the elimination of the dangling bonds, by saturating them with hydrogen. [22] This process is energetically very favorable (we gain ∼1 eV per bond relative to the unsaturated surface and the free H₂ molecule), and removes all the extra bands from the gap region. Fig. 1(a) shows the band structure of the hydrogen-saturated surface, clearly revealing two metallic bands associated to the Au wires, which correspond to those marked with solid symbols in Fig. 1(d) for the unsaturated surface. Interestingly enough, this band structure is in extremely good agreement with a very recent photoemission exper-
iment which seems to favor a two-band scenario over the spin-charge splitting [10].

We can also use the addition of hydrogen to make further predictions. By further increasing the hydrogen partial pressure we can decorate the Au wires with H, which is much less favorable than Si bond saturation (the energy gain is reduced to ∼0.1 eV in this case). The additional hydrogen atoms adopt a bridge position on top of the Si-Au bonds, and the band structure (Fig. 3(b)) exhibits a single metallic band. Thus, by increasing the H content we have been able to switch from a monatomic Au wire displaying two bands, to a single band situation. This points to the conclusion that it is in this hydrogen rich environment that signatures of Luttinger-liquid behavior should be looked for.

A simple model serves to explain the appearance of the two partially filled bands while ignoring all the details of the surface reconstruction. In this model (Fig. 3(a)), we have only considered the gold atoms and those Si atoms bound to them. The bonds connecting with the rest of the surface have been saturated with hydrogens \( H_{sat} \) (only a few of them visible in the figure). We show the band structure of this simplified model wire in Fig. 3(b). Open circles mark those states with main character on the 6s and 6p orbitals of gold. Clearly, the 6s states of Au form a fully occupied band located 3.6 eV below the Fermi level. Closer to the Fermi energy we find two bands which, although considerably hybridized with the gold orbitals, are basically derived from the 3sp "bonds" of the Si atoms. Therefore, while induced by the presence of the Au wire, those are silicon bands. The flat band pinning the Fermi energy (solid diamonds) comes from the Si chain schematically indicated in Fig. 3(a) by the hopping \( t_2 \). A more dispersive band (solid circles) originates from the other Si chain, where the interaction \( t_1 \) is stronger due to the more favorable orientation of the "bonds" facing each other. The appearance of two metallic bands can be expected by a simple local counting of electrons argument: There are four electrons in the chain per Au atom, one electron is provided by the 6s state of gold and three come from the Si neighbors. Consequently, a metallic wire, as observed in the experiments, in absence of considerable charge transfer from other atoms in the surface, must display two partially occupied bands.

The addition of hydrogen atoms decorating the chain (Fig. 3(c)), produces the band structure presented in Fig. 3(d), where the bands with high hydrogen character are marked by thick solid lines. In this case one electron is transferred to the hydrogen, leaving unoccupied the flat Si band, and only the most dispersive silicon band crosses now the Fermi level, in agreement with our calculations for the H-saturated surfaces.

In conclusion, we have presented an \textit{ab initio} study of total energies and surface state bands of the Si(557)-Au surface. Our results show that the Au chains lead to \textit{two half-filled metallic bands} associated with the Au-Si bonds that can be interpreted in a simple model. This is in accordance with very recent experimental photoemission results [16] and provide an alternative to the spin-charge separation interpretation proposed [13] to explain the two-peak photoemission spectra found for this system.

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TABLE I. Total energies (calculated with a double-\(\zeta\) (DZ) and a double-\(\zeta\) polarized (DZP) basis set) of structures of the Si(557)-Au surface differing in the positions of the Au rows. Structure numbers refer to the labelling defined in Fig.1-(b), and the energies, in eV per Au atom, are relative to model 2.

| Edge  | 1  | 2  | 3  | 4  |
|-------|----|----|----|----|
| DZP   | 0.55 | 0.30 | 0.00 | -0.07 | -0.03 |
| DZ    | 0.53 | 0.30 | 0.00 | 0.01 | -0.07 |

of H. The DZP basis has an additional \(d\) shell for Si, and \(p\) shells for Au and H.

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[24] We have also explored the effects of adding a chain of adatoms in model 2, partially saturating the dangling bonds in rows 3 and 4, as suggested by some STM images [21]. This inclusion is slightly favorable, with an energy gain of \(\sim 0.1\) eV/Au, but besides the doubling of the cell it does not produce any significant change in band structure, the Fermi level still pinned by the edge state band. In this case there is a very small (\(\sim 0.1\) \(\AA\)) dimerization of the Au chain.

FIG. 1. (a) Unrelaxed atomic positions in a model for the Si(557)-Au surface (hereafter model 2). (b) Same structure after relaxation. (c) Top view of the stepped surface, with the unit cell vectors indicated, and the corresponding surface Brillouin zone. (d) Electronic band structure of the slab presented in panel (b). Energies are referred to the Fermi level, and surface states have been marked with different symbols according to their character (see text).
FIG. 2. Band structure of the relaxed slab: (a) After the saturation of all Si dangling bonds with hydrogen. (b) After one additional hydrogen has been deposited on top of each gold atom.

FIG. 3. Simple models of (a) clean and, (c) hydrogen-decorated, Au monatomic wires in the Si(557)-Au surface. Panels (b) and (d) present the energy bands of the structures shown in (a) and (c), respectively. Energies are referred to the Fermi level, and states are marked according to their atomic character (see text).