Structural models for Si(553)–Au atomic chain reconstruction

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Abstract
Recent photoemission experiments on Si(553)–Au reconstruction show a one-dimensional band with a peculiar \( \sim \frac{1}{4} \) filling. This band could provide an opportunity for observing large spin–charge separation if electron–electron interactions could be increased. To this end, it is necessary to understand in detail the origin of this surface band. A first step is the determination of the structure of the reconstruction. We present here a study of several structural models using first-principles density functional calculations. Our models are based on a plausible analogy with the similar and better known Si(557)–Au surface, and compared against the sole structure proposed to date for the Si(553)–Au system (Crain et al 2004 Phys. Rev. B 69 125401). Results for the energetics and the band structures are given. Avenues for future investigation are also outlined.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
When restricted to move in one dimension, electrons have been predicted to behave in a fundamentally different way than in three dimensions. The nature of the low-energy electronic excitations changes dramatically. The single-particle excitations do not provide a good description and have to be replaced by separate spin and charge collective excitations [1]. This collective behaviour leads to several exotic phases at low temperatures. However, although these theoretical predictions are clear and well-founded, the observation of the spin–charge separation and other effects has proven quite elusive. The main difficulty is the fabrication of clean and well-ordered arrays of one-dimensional systems with electronic properties that can be tailored and are stable against structural distortions.

Monatomic chains of gold atoms are spontaneously formed on several vicinal Si(111) surfaces after the deposition of gold in the sub-monolayer regime. Each terrace contains a chain of gold atoms running parallel to the step-edge. Since the average terrace width can be controlled by the miscut angle, vicinal substrates provide an unique route to create regular arrays of monatomic metallic wires with tuneable inter-chain distances and interactions [2]. Therefore, these surfaces can be an ideal playground to prove the physics of one dimension and, consequently, have attracted much attention in recent years. Some examples are Si(557)–Au [3] and Si(111)-\((5 \times 2)\)–Au [4] reconstructions.

The angle resolved photoemission (ARPES) spectrum of the Si(557)–Au surface is dominated by an almost half-filled one-dimensional band that splits in two peaks near the Fermi energy (\(E_F\)). This was first assigned to the spin–charge separation in a one-dimensional metal [3]. However, later photoemission experiments [5] and calculations [6] seemed to discard this interpretation. In fact, according to a recent study combining ARPES and scanning tunnelling microscopy (STM), the surface suffers a metal–insulator transition at low temperatures [7]. We have proposed an explanation for these observations in a recent theoretical paper [8]. The opening of a gap at \(E_F\) is associated with several structural distortions. The metal–insulator transition, along with the temperature dependence of the STM images, relates to the dynamical
fluctuations of the silicon atoms in the step-edge. The observed band splitting is caused by the spin–orbit interaction [8]. This opens the possibility to create or transport spin-polarized currents in these systems, which might be useful for future spintronic devices.

The flat Si(111)-(5 × 2)–Au surface has also been shown to exhibit interesting phenomena. The STM images show very prominent chains formed by silicon adatoms with variable concentration [9–12]. Individual adatoms can be manipulated with the STM and could be used as bits of an atomic-scale memory [13]. The ARPES spectrum of this surface shows several bands with a strong one-dimensional character close to $E_F$ [14, 15]. However, the most recent photoemission data suggest that it is also non-metallic [16].

The existence of a metallic one-dimensional band with a peculiar $\frac{3}{4}$ filling has been recently reported for the Si(553)–Au surface [2, 17]. This quarter-filled band could create an opportunity for observing large spin–charge separation if electron–electron interactions ($U$) could be increased, for example, using a somewhat different substrate. This is in contrast with half-filled bands, which are unstable against a Mott–Hubbard transition for large values of $U$, preventing the observation of a Luttinger metal [2].

Unfortunately, the atomic structure of the Si(553)–Au reconstruction is not completely established. A reliable structure is necessary for a deep understanding of its electronic structure. We present here a study of several structural models using first-principles density functional calculations. We propose five models based on our earlier experience with the closely related Si(557)–Au surface [6, 8, 18]. At least within our computational scheme, the new models are energetically comparable or even more favourable than the sole structure proposed to date for the Si(553)–Au surface [2]. Band structures are analysed and the possible origin of the dispersive one-dimensional bands in this reconstruction is discussed. We also give ideas and guidelines for future research in finding the geometry of these stepped gold-induced silicon reconstructions.

2. Studied structural models

We have based our investigation of the Si(553)–Au reconstruction on a plausible analogy with the closely related and better known Si(557)–Au surface. Both surfaces contain steps along the [110] direction. In fact, the orientation of the chains along the [110] direction seems to be common to all the silicon reconstructions forming monatomic gold chains [2]. The Si(557)–Au reconstruction is characterized by the following elements (see, for example, figure 1 in [18]):

(i) Gold atoms occupy substitutional positions in the top Si layer in the middle of the terraces;
(ii) the atoms close to the step-edge are strongly rebonded, forming a structure reminiscent of the so-called honeycomb chain (HC) [19];
(iii) the structure doubles its periodicity along the direction of the steps due to a buckling of the atoms in the step-edge;
(iv) there is also a row of adatoms on each terrace.

This structure has been determined using x-ray diffraction [20] and confirmed with ab initio calculations [2, 6, 18]. The miscut direction is opposite for the Si(553)–Au and the Si(557)–Au surfaces. This would open the possibility of a different rearrangement of the step-edge in both cases. However, we do not consider this possibility here, and our models for the Si(553)–Au are fabricated using the building blocks listed above.

The importance of the HC structure for the gold induced reconstructions on vicinal Si(111) has been recently emphasized by Crain et al [2]. The HC is known to occur in the Si(557)–Au surface [6, 18, 20]. It is also the key ingredient of a recent proposal for the structure of the Si(111)-(5 × 2)–Au reconstruction [12]. The HC was initially proposed to explain the low coverage reconstructions induced by some alkali metals (Li, Na, K), Mg and Ag on Si(111) [19]. The HC structure is illustrated in figure 1. We see that the HC structure involves two unit cells of the unreconstructed Si(111) surface, with one atom removed from the top Si layer. This flattens the surface and removes surface stress. The inset of figure 1 shows a side view of the HC. The unsaturated bonds are illustrated, clarifying the mechanism behind this reconstruction: the bonds of atoms $a$ hybridize to create an extra $\pi$-bond. This bond is further hybridized with the dangling-bond of atom $b$ below. The electron count of these bonds is odd, so one additional electron is needed to yield an electronic closed-shell structure. If there is a neighbouring alkali-metal atom, it donates one electron to the HC, thus contributing to the stabilization of the structure [19]. In the case of gold, which has a stronger electron affinity, the situation is different. Gold is likely to take electrons away from the silicon structure. In principle, this does not prevent an electronic stabilization mechanism: one electron may be transferred to the 6s Au state, leading again to a closed-shell structure. However, in reality we are far from this ionic situation. The states of gold are strongly hybridized with those of the neighbouring silicon atoms creating several dispersive bands that are, in principle, metallic [6, 8].
The structural elements presented above can be used to build many models for the gold induced reconstructions on stepped silicon surfaces. The length of the terraces and the registry with the underlying silicon layers (assumed to be unreconstructed) impose some geometrical restrictions. The effect of the introduction of the HC in the Si(111) is schematically illustrated in figure 1. While flattening the surface, the HC creates a stacking fault towards the [1$ar{1}$2] direction (at the right of the HC in the figure) that can be avoided by introducing a surface dislocation (SD). In the upper part of figure 1 the SD is introduced immediately after the HC, thus recovering the perfect stacking of silicon. On the lower part of the figure the stacking fault remains until the SD is introduced.

To name our structural models of the Si(553)–Au surface we have developed a notation which we believe may be useful for other similar systems. The first double-layer in the unreconstructed Si(111) can be expressed using a 1×1 unit cell with a two atom basis. This entity is named ‘S’. If this block contains a stacking fault (i.e. its bonds coincide with those of the second double-layer) it is called ‘Sf’, f standing for faulted. HC has a 2×1 unit cell and is indicated by ‘H’. The SD is indicated by ‘D’. It is basically equal to ‘S’, but one of its atoms is over coordinated. Using this notation, the upper part of figure 1 can be abbreviated as (starting from the HC) HDS and the lower part as HSfD. The substitution of a silicon atom by gold is indicated using a + superscript.

Our models for the Si(553)–Au surface can be seen in figure 2. Models I to V are generated by placing the HC structure with the accompanying dislocation and the chain of gold atoms in different positions on the terrace. Model VI has been previously proposed by Crain et al [2]. The unit cell of the structure VI is three times larger along the step direction than that of the other models. This is due to the extra Si atoms attached to the step-edge: there are two atoms every three possible sites. This was proposed as an explanation for the 1×3 superlattices frequently observed in the STM images [2, 17]. We have decided not to impose the appearance of superlattices in our models. Instead we studied the stability of the step-edge against structural distortions that might also be responsible for the STM images as in the case of the Si(557)–Au surface [8].

The main results of our work can be found in figure 2 and table 1, where the relaxed structures and the relative surface energies of the different models of the Si(553)–Au reconstruction are presented. Model I is the most stable structure. It presents a strong similarity with the Si(557)–Au reconstruction [18, 20]. The HC is placed at the step-edge and the gold atoms reside in the middle of the terrace. The main differences in the present case are the presence of a SD, associated with the HC and the different orientation of the steps, and the absence of adatoms due to the smaller terrace. Models I and II only differ in the position of the SD and have almost degenerate energies. Changes in the location of the
Table 1. Relative surface energies (in meV Å⁻²) of different structures of the Si(553)–Au surface. The numbers in the first column refer to figure 2, while the names of the models are assigned according to the nomenclature explained in the text. Column labelled × 1 presents the results for the smaller unit cell (with a single Au atom). The systems in columns × 2 and × 3 included, respectively, two and three unit cells along the step direction. This was done in order to study the stability of the step-edge with respect to several structural distortions. However, the relaxed structures always returned to an almost perfect undistorted × 1 periodicity. The × 1 and × 2 slabs contained four silicon double-layers, while the × 3 slabs only had three silicon double-layers. The number in parenthesis was obtained using a DZP basis.

| Model | ×1 | ×2 | ×3 |
|-------|----|----|----|
| I     | 0  | 0  | 0  |
| II    | 1.4| —  | —  |
| III   | 7.0| 7.3| —  |
| IV    | 11.3| —  | —  |
| V     | 5.3 (5.6)| 6.0| 5.8|
| VI    | Crain et al | —  | 5.7|

gold chain have stronger impact on the energy. This becomes clear by comparing models I and III, which solely differ in the site occupied by the gold atoms. This suggests that the ideal location of the gold chain is in the middle of the terrace, as was previously found for the Si(557)–Au reconstruction [6, 18].

We also tried structures where the HC has been moved away from the step-edge. In both cases, model IV and V, this yields to an increase of the surface energy. This seems to indicate that the HC is an especially stable rearrangement of the step-edge in vicinal Si(111) surfaces. In fact, in the case of Si(557)–Au surface, the HC structure formed spontaneously at the step-edge during the geometrical optimizations using a density-functional calculation [6]. The model IV, with the gold chain in a position neighbouring the step-edge, is the most unstable configuration. This points again to the larger stability of the gold substitution in the middle of the terraces.

The model by Crain et al [2] (model VI) is indeed a simple variant of model V. A silicon dimer is attached to two of the step-edge atoms and another two silicon atoms in the terrace. This creates a × 3 modulation along the step-edge direction similar to that observed in some STM images [2, 17]. Interestingly, the addition of these silicon dimers leaves the surface energy almost unchanged (see table 1). This is consistent with the observation of large variations in the concentration of the extra silicon atoms attached to the step edge and, probably, a high mobility of these atoms. Again this seems to be consistent with the STM observations.

In the case of the Si(557)–Au surface the doubling of the periodicity observed with the STM [5, 7] can be explained as a result of a buckling of the step edge [8, 18]. Since this could also provide an explanation for the modulations observed in the Si(553)–Au surface, we have explored the stability of two of our models (I and V) with respect to similar distortions. We have used supercells containing two or three unit cells along the step. Our relaxations started from structures where one of the atoms of the step edge was moved either upwards or downwards by ~0.3 Å. In some cases, the atoms with unsaturated dangling-bonds in the terrace (see figure 2) were also moved upwards in an attempt to force their charging with electrons transferred from the step edge. In the case of model I this would leave a metallic step-edge band, susceptible to favour structural distortions. In other cases, the whole structure was relaxed under the constriction of a particular step-edge configuration. However, in all cases we were unable to stabilize the step-edge buckling. Once all the degrees of freedom were optimized the structures always returned to an almost perfect × 1 periodicity.

We now turn our attention to the electronic band structures of our most stable models. From our studies of the Si(557)–Au surface we expect to find two surface bands with different dispersions near the Fermi level associated with the Si–Au...
bonds [6, 18]. A flat band originating from the Si$_2$–Au bonds, and a dispersive band coming from the more overlapping Si$_1$–Au bonds (see figure 2 for the labelling of the atoms). In the present calculations we have only included scalar-relativistic effects for gold. In fact, the effect of the spin–orbit interaction is expected to be negligible for the total energy of these surfaces (we have zero spin polarization). However, we have recently discovered that the dispersive Si$_1$–Au band shows a considerable spin–orbit splitting (up to $\sim$200 meV near the Fermi level) [8]. This is instrumental to reconcile the theoretical band structure with the photoemission spectra for the Si(557)–Au surface [8]. The photoemission of the Si(553)–Au surface shows a half-occupied band featuring a clear splitting, almost identical to that observed for the Si(557)–Au, and a dispersive quarter-filled band at lower binding energies [17]. We think that the surface bands showing splitting in the experiment have to be identified with those coming from the Si$_1$–Au bonds.

Figures 3(b) and (c) show the band structures of the models I and V, respectively. The different symbols reflect the main atomic character of the surface bands, as obtained from a Mulliken population analysis [26]. In figure 3(b) we can find an almost fully occupied band pertaining to the Si$_1$–Au bonds very close to the Fermi level. A dispersive band, coming from the dangling bonds in the terraces, appears practically empty. The agreement with the experimental spectra could be improved if the population of this band were to increase [17]. Such electron doping can occur associated with the presence of extra silicon atoms attached to the step-edge [2], or to the terraces [12]. A surface band associated with the step-edge crosses the Si$_1$–Au band and almost reaches the Fermi level. There is no evidence of this band in the experiment. The band structure of model II is almost identical to the band structure of model I.

The band structure of model V (figure 3(c)) features both a dispersive and a flat band associated with the Si–Au bonds. The step-edge gives rise to a metallic band with a small filling. The presence of this band implies that structural distortion of the step-edge with an electronic driving force are possible. However, as described above, we have failed to stabilize such distortion in our calculations up to now.

The band structure of the model VI is presented in figure 4. The larger unit cell makes the comparison with the band structures in figure 3 somewhat complicated due to the backfolding of the bands. There is a clear gap in the Si$_1$–Au band associated with the symmetry breaking induced by the silicon dimers attached to the step-edges and to some of the atoms in the terraces. The changes in the three Au–Au distances in the unit cell are $-0.12$, $-0.16$ and $+0.28$ Å, while the corresponding Si$_1$–Au–Si$_1$ bond angles are 103°, 100° and 115°. Notice that the possible mirror symmetry of the structure is also broken in our final relaxed configuration. This can also be noticed in the slight buckling of the silicon dimers, visible in figure 1.

None of the band structures of our models provides a convincing description of all the available photoemission data for the Si(553)–Au surface [17]. However, some of the main qualitative features are reasonably described by the band structure of model V, shown in figure 3(c). There are two metallic bands with quite similar dispersions. One of them is close to half-filled and comes from Si$_1$–Au bonds (and, therefore, likely to exhibit an observable spin–orbit splitting). The other one comes from the step-edge and presents a small fractional filling. However, the band originating from the Si$_2$–Au bonds is not seen in the experiment and the details of the band structure are far from those observed experimentally.

5. Conclusions

We have presented five possible models for the Si(553)–Au surface constructed using the silicon honeycomb structure [19] and the substitution of the gold atoms in the surface layer. These models were compared to an earlier proposal [2], which corresponds to one of our models (model V) with the addition of silicon dimers at the step edge. Although the energy differences between different structures are relatively small, one of our models (model I) is clearly the most favourable. This result is stable against changes in the thickness of the slab and the basis set used (variations smaller than $\sim$0.5 meV Å$^{-2}$). Unexpectedly, the attachment of extra silicon atoms to the step edge in model V has little effect on the surface energy. This opens a route for the modification of the structures that we plan to investigate in the future for several models. We have also investigated the possibility of inducing periodic modulations in the structures that might lower the energy and reproduce some of the patterns seen in the STM images [17]. However, although further investigation is also necessary, our structures have proven to be quite stable against distortions that would have doubled or tripled the unit cell.

Neither the band structures of our models nor that of the model proposed by Crain et al seem to provide a complete description of the photoemission spectra. However, the band structure of model V presents some of the main features of the experimental data.

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