First principles study of Si(335)-Au surface

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Abstract

The structural and electronic properties of gold decorated Si(335) surface are studied by means of density-functional calculations. The resulting structural model indicates that the Au atoms substitute some of the Si atoms in the middle of the terrace in the surface layer. Calculated electronic band structure near the Fermi energy features two metallic bands, one coming from the step edge Si atoms and the other one having its origin in hybridization between the Au and neighboring Si atoms in the middle of the terrace. The obtained electronic bands remain in good agreement with photoemission data.

Keywords: density functional calculations; silicon; high index surfaces; surface structure; photoelectron spectroscopy

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1 Introduction

Physics of one-dimensional (1D) objects is predicted to be qualitatively different form that of higher dimensions \[1\]. The most spectacular examples include a breakdown of the Fermi liquid theory \[2, 3\] and Peierls metal-insulator transition \[4\]. Theorists found the one-dimensional physics to be very elegant, as many problems can be solved in 1D but not in higher dimensions. On the other hand, experimentalists face with great difficulties in fabricating truly one-dimensional structures. The most promising way is a creation of such structures on semiconducting or insulating substrates \[5, 6\]. In this case, the chain atomic structure is governed by the substrate lattice. More importantly, the electrons near the Fermi energy are completely decoupled from the substrate, as there is a band gap in the electronic spectrum of the substrate. Of course, there are low energy states responsible for holding chain atoms on the surface. Fortunately, only the states near the Fermi level determine electronic properties of the system.

Recently, the most extensively studied templates for fabrication of one-dimensional objects are vicinal Si(111) surfaces \[7, 8\]. Those include gold induced chains on Si(111) \[9, 10\], Si(335) \[11\]-\[14\], Si(553) \[12\], \[15\]-\[17\], Si(557) \[18\]-\[27\], Si(775) \[7, 15\] or Si(5512) \[28\]-\[31\].

The stepped Si(335)-Au reconstruction is observed at the gold coverage of 0.28 ML and consists of Si(111) terraces \(3\sqrt{2}/3 \times a_{[112]} \) (1.26 nm) wide. Each terrace contains a single row of gold atoms running parallel to the step edge, i.e. in the [110] direction. A number of techniques has been employed to investigate structural and electronic properties of Si(335)-Au surface. Those include high-energy electron diffraction (RHEED) \[11\], angle-resolved photoemission spectroscopy (ARPES) \[12, 14\] and scanning tunneling microscopy (STM) \[12, 13\]. In particular, STM topography data show a single monatomic chain on each terrace, which has been interpreted as the Si atoms with broken bonds at the step edge \[12\]. As the Au atoms are more electronegative than Si, they pair neighboring Si bond with their 6s, p electrons. As a result, a low-lying bound state, not visible to STM, is created. The STM
experiments show a single chain within each terrace, so one would naively expect a single metallic band in electronic structure. However, ARPES data show not one but two bands crossing the Fermi level [12]. It is the purpose of the present work to solve this puzzle and to identify the bands observed in the ARPES experiment.

While the surfaces like Si(553)-Au or Si(557)-Au were extensively studied theoretically [12, 16, 17, 21, 23, 24], there are no first principles investigations of the Si(335)-Au surface. Moreover, there is no structural model confirmed by first principles calculations. However, the model of this surface, based on an analogy with Si(557)-Au surface, has been proposed in Ref. [12]. It is simply a truncation of the Si(557)-Au structure. So the second purpose of the present work is to check whether the model of Ref. [12] is a good candidate for the atomic reconstruction of Si(335)-Au surface. In the following, I will focus on the presentation of the results regarding structural model and electronic properties of the system.

2 Details of calculations

The calculations have been performed using the SIESTA code [32]-[35], which performs standard pseudopotential density functional calculations using a linear combination of numerical atomic orbitals as a basis set. I have used here the generalized gradient approximation (GGA) to DFT [36, 37], Troullier-Martins norm-conserving pseudopotentials [38], and a double-$\zeta$ polarized (DZP) basis set for all the atomic species [33, 34, 39]. A Brillouin zone sampling of 24 inequivalent $k$ points, and a real-space grid equivalent to a plane-wave cutoff of 225 Ry (up to 82 $k$ points and 300 Ry in the convergence tests) have been employed. This guarantees the convergence of the total energy within $\sim 0.1 \text{ meV per atom in the supercell}$.

The Si(335)-Au system has been modeled by slabs containing up to four silicon double layers plus reconstructed surface layer. All the atomic positions were relaxed except the bottom layer. The Si atoms in the bottom layer were saturated with hydrogen and remained at the bulk ideal positions during the relaxation process. To avoid artificial stresses, the
lattice constant of Si was fixed at the calculated bulk value, 5.42 Å, which is very close to the experimental value of 5.43 Å.

3 Structural model

The total energy calculations show that it is energetically very favorable for the Au atoms to substitute into the top Si layer. The surface energy gain per unit cell is more than 1 eV as compared to adsorption above the surface. Furthermore, the Au substitution in the terraces is more stable than adsorption of the Au atoms at the step edge (by about 0.5 eV per unit cell). Similar conclusions have been obtained for the case of Si(557)-Au surface, where the Au atoms prefer to substitute in the topmost Si layer, too [12, 21, 23, 24]. Therefore, in the following, I will focus on the structural models featuring the Si top layer atoms substituted by the gold.

The most stable model is shown in Fig. 1. However, the other models, in which the Au atoms occupy various top layer silicon positions, from Si$_1$ to Si$_5$ (see Fig. 1 for labeling), have comparable energies. The differences are usually less than $\sim 0.7$ eV per unit cell, and the next 'best' structural model, in which the gold occupies the Si$_3$ position, differs in energy by 182 meV only. The total energies of the above models with respect to the most stable model are summarized in Table 1.

The present model is simply the model proposed by Crain et al. [12], which has not been deduced from any total energy calculations but was based on an analogy with Si(557)-Au model—a simple truncation of Si(557)-Au surface. Here, the DFT calculations confirm that this model is a good candidate for Si(335)-Au surface reconstruction. As one can read off from Fig. 1 the Au atoms sit in the middle of the terrace and the rigidity of the Si structure keeps the Au wire stable against dimerization. The calculated Au-Si$_4$ bond length 2.43 Å and 2.38 Å for Au-Si$_5$ (see Fig. 1) is quite close to calculated bulk Si-Si distance of 2.35 Å, indicating that Au atoms affect the Si structure very little. Another important feature is a
strong rebonding of the Si atoms near the step edge. The step edge atoms tend to saturate the dangling bonds in the neighboring terrace. As a result, a sort of 'honeycomb' building block is created at the step edge, originally proposed for the alkali-induced $3 \times 1$ reconstruction of Si(111) surface [40]. It turns out that this sub-structure is a common feature of other Au-decorated Si vicinal surfaces [12].

4 Band structure

The calculated band structure for this structural model, along the high symmetry line of two-dimensional Brillouin zone (Fig. 2), is shown in Fig. 3. The line defined by points $\Gamma$, $K$ and $M'$ is parallel to the steps, i.e. it goes along the Au chains. The Mulliken population analysis [41] has been performed in order to identify the main character of the bands. Although this analysis is not completely unambiguous, it is particularly useful for surface states. The band marked with open circles in Fig. 3, pinning the Fermi energy, comes from unsaturated bonds of the Si atoms at the step edge. A rather flat band around 0.5 eV below the Fermi energy (open squares), as well as a more dispersive band crossing the Fermi energy (filled squares) have the Au character. This picture looks a little bit counterintuitive, as one would expect a single band associated with 6s electrons of gold. In fact, these bands come from the Si atoms neighboring to the Au chain (Si$_4$ and Si$_5$ in Fig. 1), and have gold character due to the hybridization. The 6s state of gold is well below the Fermi energy, thus completely occupied. The flat band marked with open squares comes from the Si$_4$ atoms, while the other, more dispersive one (filled squares), comes form the Si$_5$ atoms. There is one more band worth mentioning, not shown in Fig. 3, having its origin in unsaturated bonds of the Si$_3$ atoms. This band is also very flat, indicating its surface nature, and is located around 1 eV above the Fermi level. All the bands discussed above have also been identified in the case of Si(557)-Au surface [21, 23]. This similarity can be easily understood if one recalls that the Si(335)-Au surface is a truncation of the Si(557)-Au surface, as discussed previously. Thus,
similar bands, although having different $k_\parallel$ dependence, should also be observed here.

A comparison of the calculated band structure with the photoemission spectra of Ref. [12] is shown in Fig. 4. As one can see, the present DFT calculations agree very well with the experimental data. In particular, there are two bands crossing the Fermi energy, one associated with the step edge Si atoms, and the other one coming mainly from the Si atoms neighboring to the Au chain. Moreover, the shape of those bands and the values of $k_\parallel$, for which the bands cross the Fermi level, remain in good agreement with experiment. Unfortunately, a more detailed comparison between present calculations and experiment of Ref. [12] is not possible, as the photoemission spectra were measured in the energy window between $E_F$ and -0.5 eV. However, I expect the agreement not be worse for lower energies.

At this point I would like to comment on the band structure of the other models studied here. Since the energy differences between all these models are rather small, it is natural to compare the band structure with the ARPES data. This would be the convincing criterion that the structural model is the correct one or at least is very close to the true Si(335)-Au surface reconstruction. Figure 5 shows a comparison of the ARPES data (Ref. [12]) and the band structure calculated for the next ‘best’ structural model, in which the Au atoms occupy the Si$_3$ positions (see Fig. 1). This model does not give as good agreement with the experimental data as the original one. In particular, there are three electronic bands crossing the Fermi energy, and none of them crosses the $E_F$ at the correct $k_\parallel$. The other models studied here also give wrong values of $k_\parallel$ at which the electronic bands cross the Fermi energy. Thus, this is an additional argument supporting the validity of the model shown in Fig. 1.

5 Conclusions

In conclusion, the structural and electronic properties of Si(335)-Au surface have been discussed within the density functional theory. The DFT calculations revealed that the most
stable structural model contains one Au atom per unit cell, which substitutes the Si atom in the middle of terrace in the surface layer. The calculated electronic structure agrees well with photoemission experimental data, showing two metallic bands. The less dispersive band comes from the Si atoms at the step edge, while the other one originates from hybridization between the Au and the neighboring Si atoms in the middle of the terrace in the surface layer.

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Basis orbitals were generated with an energy shift of 500 meV. Double-ζ basis has two radial functions for the 3s and 3p orbitals of Si, 6s and 5d of Au, and 1s of H. Additionally, it has d shell for Si, and p shells for Au and H.

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Tables

Table 1: Total energies of the structures of the Si(335)-Au surface for various positions of the Au atoms, as labeled in Fig. 1. The energies (in eV per unit cell) are relative to the most stable model, shown in Fig. 1.

| Au substitution: Si | Si₁ | Si₂ | Si₃ | Si₄ | Si₅ |
|--------------------|-----|-----|-----|-----|-----|
| total energy:       | 0.337 | 0.608 | 0.182 | 0.384 | 0.668 |
Figure 1: The most stable model of the Si(335)-Au surface. See the text for details.
Figure 2: Surface unit cell (left panel) and the corresponding Brillouin zone (right panel) of the Si(335)-Au surface.

Figure 3: Calculated band structure along high symmetry lines in the two-dimensional Brillouin zone (Γ–K–M'). The band marked with open circles comes from the step edge Si atoms, while those marked with squares — from the Au and the neighboring Si atoms in the middle of the terrace.
Figure 4: A comparison of the measured photoemission intensity along the Γ–K–M’ line (Ref. [12]) and the calculated band structure within the present model. Note that Γ point corresponds to $k_{\parallel} = 0$, K to $k_{\parallel} = 0.82$ Å$^{-1}$, and M’ to $k_{\parallel} = 1.64$ Å$^{-1}$. The photoemission intensity is plotted in a gray scale with high intensity shown dark.

Figure 5: A comparison of the measured photoemission intensity along the Γ–K–M’ line (Ref. [12]) and the calculated band structure within the model in which the top layer Si$_3$ atoms are substituted by the gold atoms.