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Influence of substrate temperature on submonolayer Au adsorption on an Si(111)-(7 × 7) surface studied by scanning tunneling microscopy

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Abstract

The influence of substrate temperature on the adsorption of submonolayer Au on an Si(111)-(7 × 7) surface was investigated using a scanning tunneling microscope. With a small amount of Au deposited at room temperature, Au atoms form small clusters located inside the half unit cells (HUCs) of the Si(111)-(7 × 7) surface while most parts of the surface are undisturbed. When the substrate temperature during deposition of the same Au amounts increases from room temperature up to 565 °C, the small Au clusters grow, coalesce into larger clusters, incorporate Si atoms, and finally form a (5 × 2) reconstruction. The Si(111)-(5 × 2)–Au reconstruction takes place in the form of island–hole pairs on a terrace, whereas only holes are formed in the upper terrace at a step. Both the islands and the holes display the (5 × 2) reconstruction. The occurrence of the island–hole pairs of the (5 × 2) reconstruction results from the fact that the Si atom density in the (5 × 2) reconstruction is lower than in the (7 × 7) reconstruction.

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

1. Introduction

The Au/Si(111)-(7 × 7) interface has been extensively investigated with respect to chemical and electronic properties, surface reconstruction, and film morphology [1–5]. The Au/Si(111) interface is also important with interest in Schottky barrier heights or ballistic electron emission microscopy [6]. Although Au is a very stable noble metal, photoemission spectroscopy results show that the Au/Si(111)-(7 × 7) interface is reactive even at room temperature at an Au coverage higher than 1 monolayer (ML) (1 ML is equal to 7.84×10^{14} atoms cm^{-2}, corresponding to the atom density on an unreconstructed Si(111) surface). A layer of stable Au_3Si-like film was found to form at 3–4 ML Au film thickness [1]. At elevated temperatures, Au adsorption can lead to different types of reconstructions depending on the coverage,

i.e. 5×2, α-$\sqrt{3}\times\sqrt{3}$, β-$\sqrt{3}\times\sqrt{3}$, and 6×6, which correspond to 0.4, 0.8, 1.0, and 1.0 ML Au coverage, respectively [2–4]. In addition, substrate temperature also plays an important role in determining the type of reconstruction, since different types of reconstruction require different thermal activation energies. For example, the thermal activation energy of the 5×2 phase is higher than that of the $\sqrt{3} \times \sqrt{3}$ phase. Consequently, the $\sqrt{3} \times \sqrt{3}$ phase occurs instead of the 5×2 phase at lower substrate temperatures ($\leqslant$280 °C) even at an Au coverage of less than 0.4 ML [5]. Therefore, the appearance of the type of surface reconstruction depends on both Au coverage and substrate temperature.

In the case of a very low Au coverage (less than 0.1 ML), the unoccupied parts of the Si(111)-(7×7) surface remain intact due to its high stability and can serve as a reference to those of Au adatom-occupied areas. We can monitor the initial process of Au atoms adsorption, nucleation, coalescence, and reconstruction formation by means of scanning tunneling microscopy (STM).

In this work, we deposited identical amounts of Au film ($\sim$0.07 ML) on a Si(111)-(7×7) surface at different substrate temperatures from room temperature (RT) to 565 °C and studied the evolution of the Si(111)-(7×7) surface with substrate temperature using STM. We found that with increasing substrate temperature during deposition, clusters occupying half unit cells (HUCs) of the Si(111)-(7×7) surface form, and subsequently start to coalesce, incorporating nearby Si atoms. In the end, a Si(111)-(5×2)–Au reconstruction takes place. The Si(111)-(5×2)–Au reconstruction occurs either on terraces in the form of island–hole pairs or as holes only at steps. The profile measurement reveals the height relations between the islands and holes at the same or different terraces.

2. Experimental details

The experiments were performed with a commercial STM (SPECS STM-150) in ultrahigh vacuum (base pressure $\sim2 \times 10^{-10}$ Torr). The substrate was a p-type Si(111) wafer with a resistivity of 1–10 Ω cm. The Si(111) sample was first outgassed at 600 °C for 10 h, then flashed several times at 1200 °C until a clean (7×7) surface was obtained. Au was evaporated from a heated tungsten filament onto the Si substrate which was heated by passing a direct current during the deposition. The same amount of Au was deposited on the Si(111)-(7×7) surface at different substrate temperatures, as monitored by a quadruple mass spectrometer. The temperature of the Si substrate was calibrated with a thermocouple in a separate experiment. After the samples were cooled to RT, they were first checked by low-energy electron diffraction (LEED) and then STM measurements were performed. The Au coverage was estimated using the sample with Au deposition at 565 °C which results in the island–hole pairs. The Si(111)-(5×2)–Au reconstruction happens on the islands and holes. Using the known Au coverage of 0.4 ML in the Si(111)-(5×2)–Au reconstruction, the amount of deposited Au was estimated from the percentage of the areas of the islands and holes on the Si(111)-(7×7) surface. All the STM images presented in this paper were obtained at room temperature using a Pt–Ir tip.

3. Results and discussion

LEED patterns of the Si(111) surface with Au adsorption at temperatures up to 460 °C, measured after the sample was cooled to room temperature, are nearly the same as that of the bare substrate, except with a higher background. This implies that the Si(111)-(7×7) reconstruction was retained on a large scale after Au deposition at these substrate temperatures. However, in addition to the bright (7×7) superspots, weak (5×1) superspots were observed

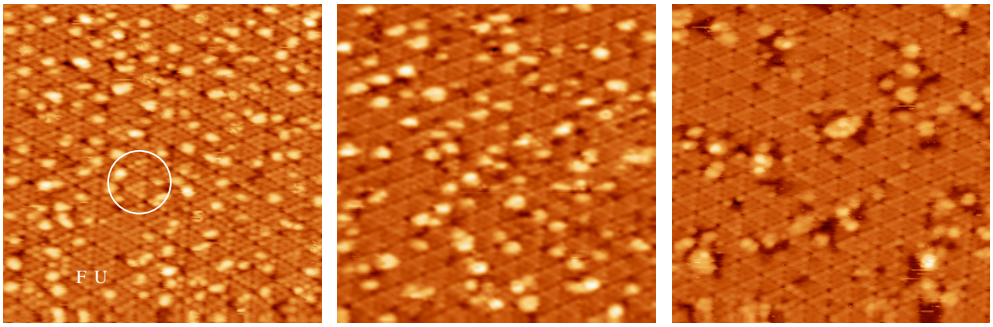

Figure 1. Filled-state STM images (30×30 nm^2) of Au adatoms on the Si (111)-(7×7) surface deposited at (a) RT; (b) 320 °C and (c) 390 °C. The images were taken at the same sample bias of −1.4 V, but with different tunneling currents of 0.2 nA for (a) and (b), and 0.3 nA for (c).

after the 565 °C deposition, indicating that small areas of the Si(111)-(7×7) reconstruction had changed into the Si(111)-(5×2)–Au reconstruction.

The STM images of the Si(111)-(7×7) surface with Au deposition at three different substrate temperatures (RT, 320, and 390 °C) are shown in figure 1. At RT deposition (figure 1(a)), small clusters were formed on the undisturbed Si(111)-(7×7) surface. All of these clusters were located inside the HUCs of the Si(111)-(7×7). Many of the clusters were in the center of the HUCs, some close to the corners. The constraint of the clusters being inside HUCs is due to the fact that (1) the stable adsorption sites for Au adatoms are located at the high-coordination sites inside a HUC [7, 8]; (2) a HUC is like a potential well with a barrier created by the dimer rows which helps to retain Au adatoms inside the well. This also explains why corner holes are avoided by the clusters. In addition, the Si adatom sites in some HUCs without clusters (e.g. inside the white circle in figure 1(a)) appear brighter than those in the normal bare HUCs. This highlighted triangle feature was observed in previous studies [8, 9]. This was interpreted to be due to a single Au adatom moving fast between stable adsorption sites inside a HUC [8] or Au adatoms on the Si rest atom sites [9]. We have recently observed that this highlighted triangle was able to hop to a nearest-neighbor HUC at RT [10]. This observation supported the interpretation of a single atom in fast motion within a HUC.

In figure 1(a), we see that about 45% of the HUCs are occupied by clusters with a slight preference in the faulted HUCs. When the substrate was moderately heated during deposition so as not to destroy the (7×7) reconstruction, Au adatoms gained energy to overcome the potential well barrier and join neighboring clusters. This leads to bigger clusters and a coalescence of clusters. At 320 °C deposition (figure 1(b)) of the same Au amount, the clusters remained inside the HUCs, but apparently were bigger than those at the RT deposition. The occupation rate of the HUCs dropped to 30%. Increasing the substrate temperature up to 390 °C resulted in a cluster growing beyond the HUCs (figure 1(c)), as well as a gathering of small clusters. The occupation rate of the HUCs reduced to 20% in this case. In addition, dark areas appeared around the clusters, suggesting an incorporation of substrate Si atoms into the nearby clusters (i.e. Au–Si intermixing or chemical reaction), in agreement with the photoemission results [1]. Alternatively, the dark areas around the clusters may result from a downward band bending (thus a smaller tunneling current in the filled-state image) at these interface areas, since band bending at a metal/semiconductor interface is a well-known phenomenon. However, it is less likely judging from the irregularity of the boundaries of the dark area. On the top of some clusters, there exist bright spots, which may be due to incomplete reconstructions.

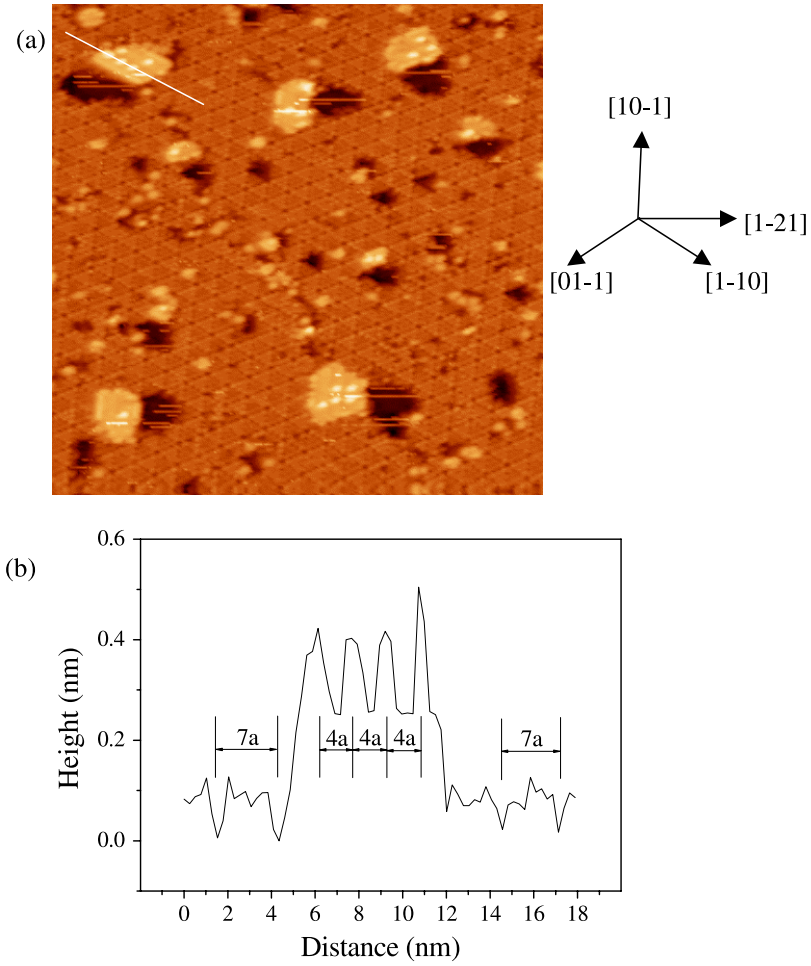

Figure 2. (a) Filled-state STM image (50×50 nm^2) of Au adatoms on the Si(111)-(7×7) surface deposited at 460 °C (sample bias: -1.2 V, tunneling current: 0.4 nA). (b) A height profile along a line in (a).

We note that deposition of 0.07 ML at temperatures as high as 390 °C do not create any patches of another reconstruction, e.g. ($\sqrt{3} \times \sqrt{3}$)–Au. This contrasts with the previous report of the formation of the Si(111)-($\sqrt{3} \times \sqrt{3}$)–Au reconstruction by deposition of 0.2 ML at 280 °C. Therefore, it is suggested that the energy barrier of the formation of the ($\sqrt{3} \times \sqrt{3}$)–Au reconstruction depends upon the Au coverage. It is speculated that the increased coverage of Au reduces either or both of the diffusion barrier and the formation barrier of the ($\sqrt{3} \times \sqrt{3}$)–Au reconstruction.

When the substrate temperature is high enough, Au adatoms may destabilize the Si(111)-(7×7) surface and induce new reconstructions such as 5×2 or $\sqrt{3} \times \sqrt{3}$. In this study, the Au adatom-induced Si(111)-(5×2) reconstruction started to appear at 460 °C deposition as shown in figure 2(a). In addition to small clusters gathering together, several islands as big as a few (7×7) unit cells occurred. These granular islands were always accompanied by holes with similar areas. Unlike the dark areas around the clusters in figure 1(c), these holes were located at one side of the islands. On top of the islands there existed bright spots oriented in a

row along the $\langle 1\bar{1}0\rangle$ directions. The distances between the bright spots are $4a$, $6a$ or $8a$ (a is a lattice constant of Si(111) and equals 0.384 nm). A height profile along the line in figure 2(a) is displayed in figure 2(b). The orientation of the white spots and the distance between the white spots are indicative of the Si(111)-(5 × 2)–Au reconstruction [11].

When the substrate temperature increased to 565 °C, the Au deposition lead to more and larger island–hole pairs in comparison to those at 460 °C deposition as shown in figure 3(a). These islands and holes are elongated and more regular in shape. Furthermore, rows of bright spots are clearly seen not only on the islands but also in the holes. The islands and holes typically include two parallel edges which are parallel with the sides of a half (7 × 7) unit cell, i.e. along the $\langle 1\bar{1}0\rangle$ directions. There are three equivalent $\langle 1\bar{1}0\rangle$ directions, all of which were found as the two parallel edges of the islands. From the orientations of the rows of the white spots, the distances between the white spots and the LEED pattern, we know that the Si(111)-(5 × 2)–Au reconstruction is formed both on the islands and in the holes. The edges of the islands and holes parallel to the rows are linear; while those crossing the rows are zigzag. This is in agreement with the fact that the growth of the (5 × 2) domains along the $\langle 1\bar{1}0\rangle$ direction where the (2×) period occurs has stronger driving force and the growing rates of different rows are different [12]. The out-of-phase boundary (marked by a white arrow) seems to have little influence on the growth of the island–hole pairs since the island–hole pairs can either cross it or lie along it.

On the other hand, the formation of the Si(111)-(5 × 2)–Au reconstruction at a step is quite different from that on a terrace. At a step shown in figure 3(b), only holes with (5 × 2) reconstruction in the upper terrace were found instead of the typical island–hole pairs occurring on a terrace. Figure 3(c) displays a height profile along a line in figure 3(b). From the height profile, we found that (i) the holes in the upper terrace were higher than the lower terrace, and indeed had the same heights as the islands on the lower terrace; (ii) the height difference between an island and its paired hole on the lower terrace was the same as that between the lower and upper (7 × 7) terraces across a step (i.e. a distance between two Si bilayers, 0.31 nm). These demonstrate that the Si(111)-(5 × 2)–Au reconstruction on the island is a single Si(111) step higher than that in the hole. The holes at the step are also elongated, but the directions of the two parallel long edges are only oriented in two of the $\langle 1\bar{1}0\rangle$ directions, not along the direction of the step (which is also one of the three equivalent $\langle 1\bar{1}0\rangle$ directions). These holes can grow at either side of the step. For example, they can either penetrate into the upper terrace or stick out towards the lower terrace. In addition, we have also found holes which were not paired by an island. There were more such holes near the step than distant from the step.

Similar island–hole pairs have also been reported with 0.2 ML Au deposited at 280 °C on the Si(111)-(7 × 7) where both the islands and the holes displayed Si(111)-($\sqrt{3}$ × $\sqrt{3}$)–Au reconstruction [5]. The formation of the ($\sqrt{3}$ × $\sqrt{3}$) island–hole pairs was attributed to the lower Si atom density in the ($\sqrt{3}\times\sqrt{3}$) reconstruction than in the (7 × 7) reconstruction [5]. We accept their explanation on the ($\sqrt{3}$ × $\sqrt{3}$) island–hole pairs formation, and similarly ascribe the (5 × 2) island–hole pairs' formation in the terrace in this study to an imbalance in surface Si atom density between the (7 × 7) and (5 × 2)–Au reconstructions. It is well known that the Si atom density in the Si(111)-(7 × 7) reconstruction is 2.08 ML with the dimer–adatom-stacking fault structure [13]. Several models have been proposed for the Si(111)-(5 × 2)–Au reconstruction [14–16], although its structure has not been finally resolved [17]. The Si atom densities range from 1.3 to 1.7 ML in the proposed (5 × 2)–Au reconstruction models. All of these numbers are lower than that in the Si(111)-(7 × 7) reconstruction. Therefore, we expect that some tenths of ML of Si atoms are released when the (7 × 7) reconstruction changes into the (5 × 2) reconstruction. Furthermore, we note that while some unpaired holes existed without islands, none of the unpaired islands were found. This suggests that the (5 × 2) reconstruction

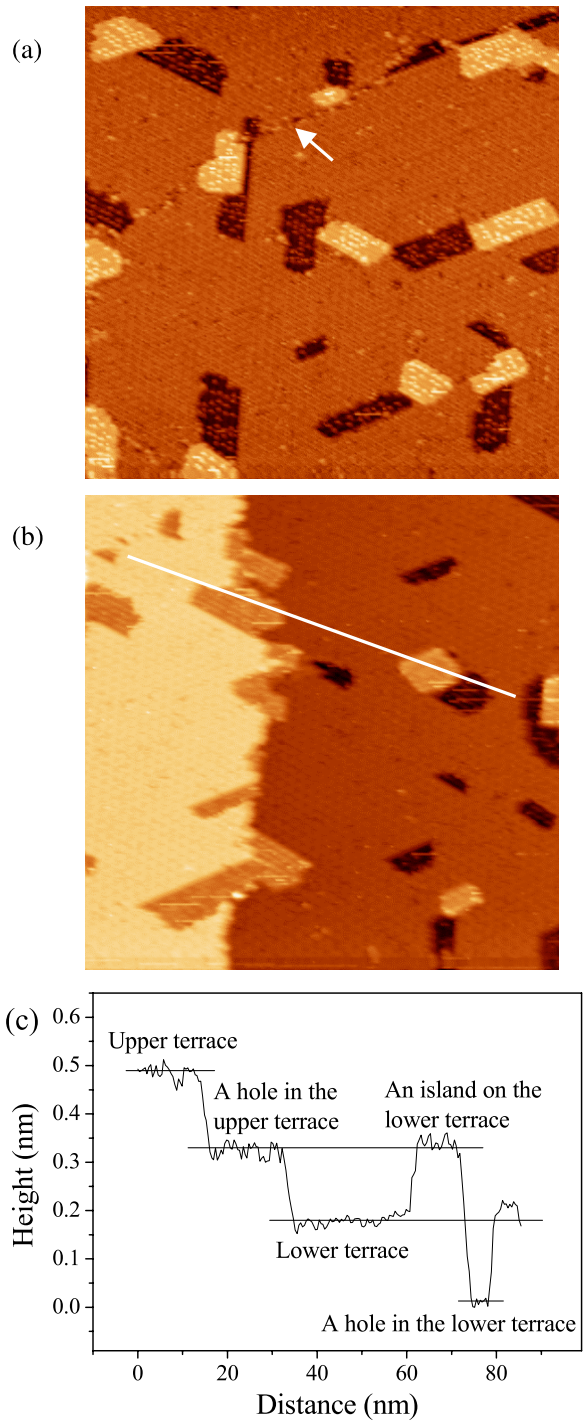

Figure 3. STM images (100×100 nm^2) of Au adatoms on the Si(111)-(7×7) surface deposited at 565 °C; (a) on a terrace (sample bias: -1.3 V, tunneling current: 0.3 nA), (b) at a step (sample bias: 1.3 V, tunneling current: 0.05 nA). (c) A height profile along a line in (b).

occurs initially to form a hole. The Si atoms released during the hole formation either diffuse into a step and are accommodated there (which is more likely to happen when the hole is close to a step), or are used in building up a (5 × 2)–Au island close to the hole (which is more likely to happen when the hole is far from a step).

A formation of a (5 × 2) island follows a hole formation. The height profile in figure 3(c) indicates that the island is one step higher than the hole. Like the Si(111)-(7 × 7) reconstruction across a step, the plane immediately below the (5 × 2) surface layer on the island should be an unreconstructed Si(111)-(1 × 1) bilayer (Si atom density: 2 ML) rather than the original (7 × 7) reconstruction layer. Therefore, the Si atoms used to form the (5 × 2) reconstruction on the island come from those released Si atoms from (i) the paired hole (some tenths of ML) and (ii) the original Si(111)-(7 × 7) reconstruction (0.08 ML) which has the same area as the island. The area ratio of the island to the hole depends on the Si atom density in the (5 × 2) reconstruction. However, the determination of the Si atom density in the (5 × 2) reconstruction from the island and hole area ratio is accurate only when those released Si atoms are totally used to form the island.

4. Conclusions

We studied the influence of the substrate temperature on submonolayer Au adsorption on the Si(111)-(7 × 7) surface using STM. Clusters formed at temperatures ranging from RT to 390 °C. With increasing temperature, they grew in size, exhibited a coalescence tendency, and incorporated surrounding substrate Si atoms. At 460 °C deposition, characteristic island–hole pairs started to appear at terraces together with clusters. More and larger island–hole pairs occurred at the 565 °C deposition with negligible clusters. These islands and holes displayed Si(111)-(5 × 2)–Au reconstruction and were elongated with long edges parallel to $\langle 1\bar{1}0\rangle$ directions. At a step, only (5 × 2) holes existed rather than the island–hole pairs. Profile measurements showed that the height difference between an island and its paired hole was equal to an Si(111) step height; and the holes in the upper terrace had the same height as the islands on the lower terrace. The formation of the (5 × 2) reconstruction as island–hole pairs resulted from a lower Si atom density in the (5 × 2) reconstruction than in the (7 × 7) reconstruction.

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