

Gold adsorption induced surface alloying on Si(111)- $\sqrt{3}\times\sqrt{3}$ -Pb surface

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The formation of surface Au/Pb alloys on a Pb-induced Si(111)- $\sqrt{3}\times\sqrt{3}$ surface is investigated using scanning tunneling microscopy (STM). Two types of alloy islands, compact and loose islands, have been observed. The former shows a long-range ordered 3×3 -Au/Pb reconstruction corresponding to an Au_{0.57}Pb_{0.43} alloy, while the latter is not totally disordered with a short-range ordered structure. Based on the atomic structure of the substrate around the compact islands, Si atoms are excluded in the formation process of the Au/Pb surface alloys. © 2009 American Institute of Physics. [doi:10.1063/1.3262950]

The fundamental understanding of metal alloying on semiconductor surfaces is important not just for pure scientific interest, but also for technological development.^{1,2} In the case of gold on a homogenous Si(111)- 1×1 -Pb surface, it has been found that there exist nanoring arrays of 8×8 -Au/Pb and 4×4 -Au/Pb alloys upon thermal annealing.³ The Pb/Si(111) system has been considered as a model system for an unreactive interface due to the negligible mutual bulk solubility.⁴ With a Pb coverage of 1/3 ML, a perfect Si(111)- $\sqrt{3}\times\sqrt{3}$ -Pb (1/3 ML-R3 or β -R3 phase) reconstruction is known to form, where the Pb atom is located at the T₄ site.⁵ As the Pb coverage decreases, Si atoms gradually take the position of Pb, leading to a $\sqrt{3}\times\sqrt{3}$ -Pb (R3 in the following) phase. By the time the Pb coverage is reduced to 1/6 ML, the surface changes into a R3 mosaic phase (or γ phase), consisting of a mixture of equal numbers of Pb and Si adatoms sitting in the T₄ sites.⁵ These exposed Si adatoms may influence on the formation of surface alloys, and therefore it is interesting to study the atomic arrangement of Au/Pb alloys when Au adsorbs on Si(111)- $\sqrt{3}\times\sqrt{3}$ -Pb.

In this paper, a recently observed Si(111)- 3×3 -Au/Pb reconstruction has been studied by means of scanning tunneling microscopy (STM). Two types of alloy islands were observed, the long-range ordered (LRO) island and the short-range ordered (SRO) island. This phenomenon of local ordering effect was attributed to reaction of Au with the exposed Si atoms on the substrate.

The experiments were carried out in an ultrahigh vacuum system equipped with an Omicron variable-temperature STM and molecular beam epitaxy. The procedure for preparing clean 7×7 reconstructed Si(111) (with a resistivity of 2 Ω cm and a miscut angle of 0.05°) was described in detail elsewhere.⁶ About 1.5 ML Pb was deposited at a deposition rate of 0.25 ML/min from a pyrolytic boron nitride crucible onto the Si(111)- 7×7 substrate at room temperature (RT). Thermal annealing of the sample at 300 °C for one hour or two followed by cooling down to RT resulted in a uniform Si(111)- $\sqrt{3}\times\sqrt{3}$ -Pb structure. At a substrate temperature of 120 °C, gold was then evaporated onto the $\sqrt{3}\times\sqrt{3}$ -Pb surface from a Knudsen cell held at 1110 °C with a calibrated deposition rate of 0.07 ML/min. All the STM images were taken at RT.

Figure 1(a) displays a typical STM topographic image of the R3 phase prepared using the procedure mentioned above. For the R3 phase, it is known that surface Pb and Si atoms are relatively indistinguishable at a sample bias of 1 V, while at other voltages there is an apparent contrast difference between them. Vacancies appear as real holes in STM images at any sample bias voltage, and thus atom identification can be obtained using a comparison between two images acquired at the typical sample voltages of -1 and 1 V. In the filled-state image Si adatoms appear dark, unlike the bright Pb atoms, as illustrated in the diagram of Fig. 1(b). This phenomenon is attributed to a significant charge transfer from Si adatoms to Pb adatoms.⁴ The imaging contrast between Si and Pb adatoms is indeed less pronounced in the empty-state image [see Fig. 1(c)]. However, the contrast is strongly bias dependent. Statistics of a large number of recorded images show that the replacement of Pb by Si occurs randomly and the $\sqrt{3}\times\sqrt{3}$ -Pb phase, as shown in Fig. 1, consists of 17% Si atoms and 83% Pb atoms.

To obtain ordered Au/Pb alloy phases, submonolayer of Au was deposited onto Si(111)- $\sqrt{3}\times\sqrt{3}$ -Pb with a substrate temperature held at 120 °C. Figure 2 shows representative topographies and structures of Au adsorption on the Pb-terminated Si(111)- $\sqrt{3}\times\sqrt{3}$ surface. At the Au coverage of 1/3 ML, there are two types of two-dimensional (2D) islands on the terraces of the substrate: the LRO island and the SRO island, as shown in Fig. 2(a). About 35% of the substrate is

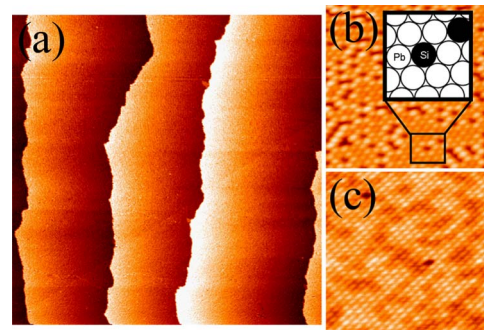


FIG. 1. (Color online) (a) A topographic STM image, 500×500 nm², obtained with $V_s=-1.5$ V and $I=0.02$ nA, showing a homogenous Si(111)- $\sqrt{3}\times\sqrt{3}$ -Pb surface. High resolution STM images (30×30 nm²) acquired from the same region, using (b) $V_s=-1$ V and (c) $V_s=1$ V. Inset illustrates the local atomic structure.

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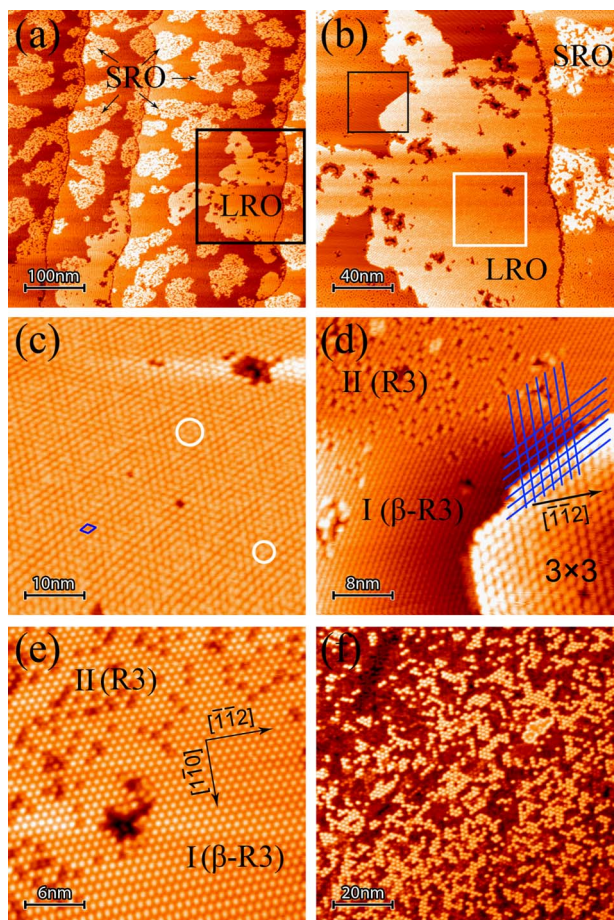


FIG. 2. (Color online) STM images recorded at a sample bias $V_s = -1.5$ V and a tunneling current $I = 0.02$ nA for different coverages of Au grown on Si(111)- $\sqrt{3} \times \sqrt{3}$ -Pb. (a) 1/3 ML Au deposited on the substrate at 120 °C. (b) The zoom-in STM image of the closed-packed island in the square region in (a). (c) The zoom-in STM image of the 3×3 -Au/Pb island in the white square region in (b). The parallelogram indicates the 3×3 unit cell, and the white circles highlight hexagonal and three-pointed star configurations. (d) Zoom-in STM image ($V_s = -1$ V, $I = 0.02$ nA) of the LRO island edge in the black square region in (b). (e) High resolution STM image ($V_s = -0.02$ V, $I = 0.05$ nA) acquired from the substrate near the LRO island. (f) Image of the surface following the deposition of 2/3 ML of Au at 120 °C.

covered by the SRO island, while the ratio of occupied area of the SRO island to that of the LRO island is about 35%:8% \approx 4.4. Most of the LRO islands are attached to the step edge connecting to the upper terrace, while the spatial distribution of the SRO islands is relatively random. The irregular domain boundaries originate from the random replacement of Pb and Si on the substrate. Both 2D islands are about 3 Å high as measured from the substrate, which is not the monolayer height for either Au (2.36 Å) or Pb (2.86 Å). The phase diagrams of Au–Pb, Au–Si, and Pb–Si indicate that Au/Pb alloys are easier to be formed than the other two at the temperature of 120 °C.⁷ On the other hand, considering that no 2D ordered Au/Si alloys exist, we thus propose that the 2D islands formed upon deposition of Au onto the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Pb substrate are of 2D Au/Pb alloy. Si atoms on the second layer of the surface are unlikely to be incorporated into the surface alloy because too much energy would be required to break the Si–Si back bonds.

A zoom-in image of a LRO island, Fig. 2(b), was obtained from the region marked with a black square in Fig.

2(a). The top surface of the island displays a semi-ordered lattice structure consisting of some orientational dots, as shown in Fig. 2(c). More interestingly, these dots may form some interesting configurations, such as hexagons and three-pointed stars highlighted by the white circles. The center-to-center distance of the nearest neighbor dots is measured to be 1.14 nm. This is nearly three times of the surface lattice constant of the Si(111) surface (3.84 Å). Therefore, this superstructure has a (3×3) periodicity with a close-packing direction along $[\bar{1}\bar{1}2]$. Although it does not belong to either Au- or Pb-induced reconstructions on Si(111), this periodic arrangement indicates a strong dependence on the substrate structure. The SRO island has a similar 3×3 reconstruction in local regions, however, the alloys show a SRO structure.

To find out why LRO and SRO islands can coexist on the substrate, a close-up view was taken as shown in Fig. 2(d), which is a region near the island edge marked by the black square in Fig. 2(b). The lower right corner of the image, Fig. 2(d), has a LRO island with the 3×3 -Au/Pb alloy structure, while the rest of the image exhibits the structure of the Si(111)- $\sqrt{3} \times \sqrt{3}$ -Pb substrate. The substrate in the vicinity of the 3×3 -Au/Pb island is noted to have a perfect 1/3 ML-R3 structure, and further away from the island, the substrate has the normal, Si(111)- $\sqrt{3} \times \sqrt{3}$ -Pb, structure. A grid is overlaid onto the image to identify the positions of the dots within the 3×3 alloy in relation to the atomic positions of the substrate. It can be seen that each dot of the 3×3 superstructure is located in the hollow site of the underneath Pb atoms of the substrate. In this case, the substrate can be divided into two types: region I and region II. Region I is a perfect 1/3 ML-R3 structure, while region II is a typical R3 phase with a Pb coverage of 1/6–1/3 ML. The LRO islands are observed exclusively on the fully Pb-covered substrate of region I, while in region II, SRO islands are observed. Since thermal annealing of Pb/Si(111) systems can lead to rapid movement and redistribution of excessive Pb atoms on the surface, Pb atoms near the step edge on the lower terrace can obtain sufficient energy to jump over the step edge, and then aggregate on the upper terrace. This is why there are sufficient Pb atoms to form the perfect 1/3 ML-R3 phase on the upper terrace, and consequently leading to the formation of the LRO 3×3 structure. On the substrate of region II, there are some dark vacancies representing the replaced Si atoms. These Si atoms tend to form strong bonds (3.65 eV/bond) to the adsorbed Au adatoms.⁸ Therefore, the key reason to interrupt the order of Au/Pb alloy is the bare Si atoms on the R3 surface.

Another STM image, Fig. 2(e), taken at -0.02 V and a tunneling current of 0.05 nA clearly shows the substrate structure near the LRO island edge. Apart from the dark holes due to real vacancy defects, some less bright spots in region II appear in very low bias voltages instead of the vacancies. However, region I on the lower right corner is filled with the bright atoms. These bright spots are the Pb atoms of the R3 substrate, while the less bright spots are the replaced Si atoms. The lattice constant of the R3 phase is measured to be $\sqrt{3}$ times of that for Si(111), and the unit cell is rotated by 30°.

With increasing Au coverage, the 3×3 superstructure gradually becomes disordered. As the coverage increases to 2/3 ML, all LRO islands disappear, replaced by more SRO islands exhibiting rather complicated local ordering as shown

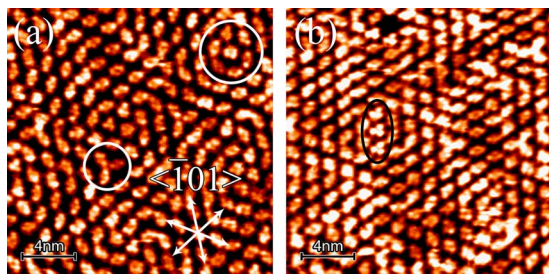


FIG. 3. (Color online) STM images of the LRO 3×3 superstructure showing the orientation feature and finer details of the Au/Pb alloys. Tunneling parameters are (a) -0.25 V, 0.05 nA and (b) -0.3 V, 0.05 nA, respectively.

in Fig. 2(f). In such cases, the composition ratio of Au:Pb is more than 2:1 due to less than $1/3$ ML Pb existing in the R3 phase. At the substrate temperature of 120 °C, Au_2Pb , AuPb_2 , and AuPb_3 alloys can be formed based on chemical stoichiometry.⁷ It means that ordered Au/Pb alloys on the $1/3$ ML-R3 substrate can be found for an Au coverage less than $2/3$ ML. Once the Au coverage is higher than $2/3$ ML, the alloy islands become disordered due to the excessive Au atoms which may need to bond to the exposed Si atoms on the surface. In other words, the LRO island is formed as a result of direct interaction between Au and Pb atoms on the $1/3$ ML-R3 phase. Considering the case that an ordered nanoring array of Au/Pb alloy spontaneously forms on a Pb-terminated Si(111)- 1×1 surface,³ we can also conclude that the Pb-rich alloy yields a more ordered structure than the Au-rich alloy.

Finally, to gain further understanding of the Au/Pb alloy structures, atom resolved STM images were taken from the LRO island. Each principal dot of the 3×3 superstructure was resolved into three or four sub features at very low bias voltages as shown in Fig. 3. Since the underneath substrate is a perfect $1/3$ ML-R3 phase, we can infer that a unit cell of 3×3 superstructure should consist of nine Si atoms, three Pb atoms, and three or four Au atoms. However, the unit cell with four gold atoms is in the majority of the Au/Pb alloys observed in any region of the surface. For instance, in Figs. 3(a) and 3(b), 97.7% of the unit cells can be described by four-atom parallelogram (or rhomboid), while only 2.3% exhibit a shape of equilateral triangle. Judging from a large number of recorded images we estimated that in the LRO Au/Pb alloys, the composition ratio of Au and Pb is statisti-

cally 57:43 [e.g., in Fig. 3, $\text{Au:Pb}=(97.7\% \times 4 + 2.3\% \times 3):3$], which corresponds to $\text{Au}_{0.57}\text{Pb}_{0.43}$. Three equivalent orientations of $\text{Au}_{0.57}\text{Pb}_{0.43}$ are found, with a rotation angle of 120° between them. Therefore the pattern is attributed to a superstructure of rotationally equivalent domains. Along the closed-packed $\langle \bar{1}01 \rangle$ directions of the 3×3 superstructure, the nearest neighbors of Au atoms in one principal dot are 5.27 Å apart. Several unit cells of $\text{Au}_{0.57}\text{Pb}_{0.43}$ alloy in the same orientation are grouped into a small domain, and the connected domains form the LRO island. $\text{Au}_{0.57}\text{Pb}_{0.43}$ alloy was found primarily at lower-symmetry orientations, as could be expected based on the structure of the substrate.

In summary, we have shown that the coexisting LRO and SRO Au/Pb alloy islands with varying Au:Pb composition ratios are formed on Si(111)- $\sqrt{3} \times \sqrt{3}$ -Pb following the deposition of Au at 120 °C. The degree of ordering depends on how many Si atoms are exposed on the substrate. The LRO islands consist of many small domains of $\text{Au}_{0.57}\text{Pb}_{0.43}$ alloy, which undergoes a significant degree of surface alloying. Although the complication of Au/Pb alloys has been reported many times during the past two decades, this research provides a unique insight into the system and points to the direction of further studies of the Au/Pb alloy system.

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