Atomic structure and formation mechanism of identically sized Au clusters grown on Si(111)- (7×7) surface

Yaping Wu,¹ Yinghui Zhou,¹ Changjie Zhou,^{1,2} Huahan Zhan,¹ and Junyong Kang^{1,a)} ¹Department of Physics, Fujian Key Laboratory of Semiconductor Materials and Applications, Xiamen University, Xiamen 361005, People's Republic of China ²Department of Physics, Jimei University, Xiamen 361005, People's Republic of China

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Identically sized Au clusters are grown on the Si(111)-(7×7) surface by room temperature deposition of Au atoms and subsequent annealing at low-temperature. The topographical images investigated by *in situ* scanning tunneling microscopy show a bias-dependent feature. The current-voltage properties measured by scanning tunneling spectroscopy indicate some semiconducting characteristics of the Au adsorbed surface, which is attributable to the saturation of Si dangling bonds. These experimental results, combined with the simulated scanning tunneling microscopy images and the first-principles adsorption energy calculations, show that the Au cluster is most likely to have a Au₆Si₃ structure. In the Au₆Si₃ cluster, three adsorbed Au atoms replace the three Si center adatoms, forming a hollow triangle, while the replaced Si atoms and other three Au atoms connect into a hexagon locating within the triangle. The formation mechanism of this atomic configuration is intimately associated with the complicated chemical valences of Au and the specific annealing conditions. © 2010 American Institute of Physics. [doi:10.1063/1.3481483]

I. INTRODUCTION

Recently, low-dimensional nanostructures with potential nanotechnology applications have aroused widespread interests.¹ Design and fabrication of nanodevices become a new inspiring field based on their amazing features that are remarkably different from classical devices.^{2–5} It is believed that artificial low-dimensional metal clusters are promising candidates for next generation nanoelectronics, ultra-highdensity recording, and nanocatalysis.¹ In the past decade, self-organized growth of well-ordered metal clusters on periodic templates of semiconductor surfaces was a favorable choice to obtain artificial nanostructures.⁶ Utilizing the natural template of Si(111)-(7 \times 7) surface, a number of metal nanoclusters with identical sizes and shapes have been successfully fabricated, such as univalent group IA metals (Na),^{7,8} trivalent group IIIA metals (Al, Ga, Tl, and In),^{6,9–13} and even some 3d ferromagnetic metals (Ni, Co, and Fe).^{1,14,15} The continuing development of ultra-high-vacuum (UHV) scanning tunneling microscopy (STM) enables one to explore the properties on the atomic level.¹⁶ Further combination with theoretical simulations, several cluster configurations, and formation mechanisms have been understood. It was found that metals in the same group tended to form a similar cluster structure.^{17,18} Nevertheless, due to the complicated quantivalency of Au as well as the integration of Au and Si atoms, the atomic and electronic structures of Au nanoclusters have been rarely addressed,¹⁹ although the cluster of another IB group element Cu has been demonstrated to contain six Cu atoms, with three on the Si center adatoms and the others on the rest atoms.² The interactions of adsorbed atoms and the substrate are believed to influence the cluster structure and the further growth of metal films. Due to the poor elemental specificity of STM, most of previous works mainly focused on whether the Au atoms react with Si substrate at the initial stage of deposition, and the proposed models of Au/Si interface were controversial.^{19–21} Therefore, the cluster structure and electronic properties, especially the interactions between Au and Si atoms, have not been clarified so far. For the controlled synthesis and device design, it is desirable to investigate the lattice structure and formation mechanism of Au clusters.

In this paper, Au clusters are grown on the clean Si(111)- (7×7) surface at room temperature (RT). By using sophisticated *in situ* STM technology for real-space imaging, the surface structures are systematically characterized at both the positive and negative bias voltages. The current-voltage properties are studied by scanning tunneling spectroscopy (STS). Taking into account the adsorption energies of different structures derived from the first-principles calculations, the experimental atomic configuration of Au clusters is identified. In addition, the cluster structure is confirmed by theoretical simulated STM images and surface Au density measurements. Furthermore, a formation mechanism related to the interactions of Au and Si atoms is unveiled.

II. EXPERIMENTAL AND CALCULATIONAL DETAILS

The experiments are performed with an Omicron (Germany) STM operated in UHV (base pressure of about 1.0 $\times 10^{-10}$ mbar). *P*-type (111)-oriented Si wafer is transferred into the UHV chamber, degassed at 300–400 °C for 10 h, and repeatedly flashed at 1150–1200 °C for 5–10 s by direct current resistive heating to attain an atomically clean Si(111)-(7×7) surface. High-purity Au (99.9999%) is

^{a)}Author to whom correspondence should be addressed. Electronic mail: jykang@xmu.edu.cn. Tel.: +86-592-2185962.

evaporated from a tantalum boat at a rate of 0.125 ML/min $(1 \text{ ML}=7.83 \times 10^{14} \text{ Au atoms/cm}^2).$ 0.04 (3.13) $\times 10^{13}$ atoms/cm²) and 0.06 ML (4.70 $\times 10^{13}$ atoms/cm²) Au atoms are deposited, respectively, on the surface at RT, followed by an 8 min annealing at 120 °C. Electrochemically etched tungsten tip is used for scanning.^{22,23} All STM images are conducted in the constant-current mode at RT with a current of 0.06 nA. Current-voltage characterizations are performed on the clusters as well as clean regions of the surface to detect the changes in local density of the surface states. For validating the STS data, the atomic resolution STM images are acquired and the characterizations are taken simultaneously to ensure an accurate assessment of the spatial position of each *I-V* curve.^{22–24} All the tunneling currents are obtained at the same tip condition corresponding to a tunneling current of 0.06 nA and a bias voltage of -0.8 V.

In order to identify the cluster structure, the adsorption energies and STM images are calculated by the firstprinciples simulations within the framework of the generalized gradient approximation,^{25,26} using the plane-wave density functional theory Vienna Ab Initio Simulation Package.^{27–29} The models are periodically repeated by an atomic slab consisting of four Si layers (200 Si atoms), with n Au atoms adsorbed on the top and 49 H atoms bonded at the bottom. A 12 Å thick vacuum layer is applied for separating the slabs to form a surface. Ionic potentials are described by ultrasoft pseudopotentials, and the plane-wave cutoff energy is set to 330 eV. The surface Brillouin zone is sampled at the Γ point only. Au 5d6s and Si 3s3p are employed as the valence electrons. Structural optimizations are carried out by relaxing all the atomic geometries using the conjugate gradient algorithm.³⁰ The forces on all the atoms are converged within 0.01 eV/Å.

III. RESULTS AND DISCUSSION

A. STM observations

Before annealing, the deposited Au atoms coalesce into a number of irregular clusters distributing evenly on the surface (not shown). Atomic-scale structures within the clusters are difficult to distinguish. Annealing at low-temperature results in clusters with uniform size and shape. Figure 1 shows the typical high-resolution filled-state STM images of the identically sized Au clusters, where "UHUC" and "FHUC" in Fig. 1(a) represent the unfaulted and faulted half unit cells, respectively. It could be found that the cluster forms a big triangle in the center of either half unit cell with an identical threefold symmetry, and the cluster density increases proportionally with the increase of Au deposition. By examining several STM images, about 75% Au clusters are found to accumulate in the FHUCs. According to the Boltzmann distribution $n_{\rm F}/n_{\rm U} = \exp(-\Delta E/kT)$ (where $n_{\rm F}$ and $n_{\rm U}$ are the numbers of clusters in the FHUCs and UHUCs, T the surface temperature, and k the Boltzmann constant),¹² the adsorption energy difference ΔE between the FHUC and UHUC is estimated to be 0.028 eV at RT, much smaller than that of several other elements.^{12,13} It could explain why the previous report did not observe an appreciable preference of Au atoms for a particular half of the 7×7 unit cell.¹⁹



FIG. 1. Filled-state STM images of the Au clusters on Si(111)-(7×7) surface prepared by depositing (a) 0.04 ML (V_{bias} =-1.5 V, 12×12 nm²) and (b) 0.06 ML (V_{bias} =-2.0 V, 14×14 nm²) Au atoms at RT, respectively, followed by an 8 min annealing at 120 °C. The Au clusters locating in the FHUCs and UHUCs are marked as type "F" and "U," respectively.

To further investigate surface electronic states of the Au clusters, a series of filled- and empty-state STM images are taken at different bias voltages of -2.0, -1.5, -0.8, -0.5, +0.5, +1.0, +1.3, and +1.8 V on the same surface area with a cluster in the FHUC, as shown in Figs. 2(a) and 2(b). The height profiles along line AB-CD (marked only on the STM images acquired at -2.0 and +0.5 V) are displayed accordingly in Figs. 2(e) and 2(f). At the bias voltage of -2.0 V, the cluster appears as a large and bright triangle. Its size and brightness decrease gradually as the voltage reduces from -2.0 to -0.5 V, while the shape is almost unaltered. The green and red arrows in Figs. 2(a) and 2(e) point to the cluster itself and the closest Si center adatom in neighboring UHUC, respectively. It is seen from the height profiles that the height of the cluster decreases with decreasing bias voltage, with respect to that of Si corner adatom in the FHUC (denoted by the black arrow). The height of the closest Si center adatom in neighboring UHUC is seriously suppressed, leaving only a small dark dot below -1.5 V. This phenomenon, however, is not observed in empty-state STM images in Fig. 2(b). Herein, the height suppression is caused by the charge redistribution rather than Au adsorption on top or the substitution by Au atoms. In the empty-state images, the green, blue, and pink arrows represent the three sites at the triangular Au cluster: the center, the corner (close to Si center adatom), and the side (close to Si corner adatom), respectively, as shown in Figs. 2(b) and 2(f). It is found that the height of the center is lower than that of the other two sites regardless of bias voltage. At the bias voltage of +0.5 V, the Au cluster degenerates into a dim region, whose center is about 1.34 Å lower than the Si corner adatom, indicating that



FIG. 2. (a) Filled- and (b) empty-state STM images of a Au induced cluster in the FHUC at bias voltages of -2.0, -1.5, -0.8, -0.5, +0.5, +1.0, +1.3, and +1.8 V. The black, green, and red arrows at -2.0 V image indicate the Si corner adatom in FHUC, the center of the cluster, and the closest Si center adatom in the neighboring UHUC, respectively. The green, blue, and pink arrows at the +0.5 V image indicate the center of the cluster, the site close to Si center adatom, and the site close to Si corner adatom, respectively. (c) Simulated filled- and (d) empty-state STM images of a Au₆Si₃ cluster in the FHUC, with the same bias voltages used in the experiments. The clean Si(111)- (7×7) unit cell is also simulated for comparison. [(e) and (f)] The corresponding height profiles along line AB-CD (marked only on the STM images acquired at -2.0 and +0.5 V).

the metallic surface states of the Au cluster are weaker than those of the Si adatoms. It is also worth noticed that, at the +1.0 V bias voltage, the cluster splits into three equivalent small pellets, forming a triangle with the average height almost equal to that of the Si corner adatom. The distance among the pellets is about 6.38 Å, slightly smaller than the ideal spacing among Si center adatoms. When the voltage is raised to +1.3 V, the cluster becomes brighter while the boundary of the three pellets becomes vague. Interestingly, as the bias voltage further increases to +1.8 V, the triangle turns upside down, with other three brighter pellets emerging, presenting protrusions of approximately 0.28 Å [indicated in Fig. 2(f)] than the Si corner adatom. The distance among the pellets is 6.03 Å, about 1.67 Å lower than the ideal spacing among Si rest atoms. Obviously, these pellets do not exactly locate on top of the Si rest atoms, but shift toward the center. At any voltage, the three surrounding Si corner adatoms [denoted by the black arrow in Figs. 2(a) and 2(b)] are always clearly recognizable and almost intact, suggesting that they are not involved in the formation of the cluster.

B. STS measurements

Figures 3(a) and 3(b) show the *I-V* curves measured at five typical points, as marked in Fig. 3(a). Point (1) denotes

the Si center adatom in the FHUC of clean Si(111)- (7×7) surface. Point (2) denotes the corresponding position when a Au cluster adsorbs in the FHUC. Points (3) and (4) denote the positions in UHUC similar to points (1) and (2), respectively. Point (5) represents the site as the pink arrow marked in Fig. 2(b). The normalized numerical differential curves ((dI/dV)/(I/V)) are plotted correspondingly to visualize abrupt changes in the differential tunneling conductance,^{31–33} as shown in Figs. 3(c) and 3(d). Both curve (1) in Fig. 3(c) and curve (3) in Fig. 3(d) exhibit two surface states²⁷ at about +1.0 and -0.6 V, marked by the red and blue arrows, respectively. They are derived from the partially filled Si adatom dangling bonds,¹⁷ resulting in the metallicity of clean Si(111)- (7×7) surface.¹ For point (2), there is no obvious surface state between 0 and +1.0 V, responsible for the brightness degeneration of the cluster at +0.5 V [Fig. 2(b)]. Simultaneously, the dangling bond state at the negative region moves toward the higher voltage value. These I-V characteristics of point (2) suggest that the Au cluster saturates the dangling bond states of Si(111)-(7 \times 7) surface, ending with an energy gap around the Fermi level with weak semiconductor behaviors. Compared to point (2), the state density on top of point (5) is much lower at the negative voltage region, whereas there is an additional peak at a positive voltage around +1.7 V. Generally, higher state density is asso-



FIG. 3. (a) Filled-state STM image of the Au cluster taken at $V_{\text{bias}} = -0.8$ V. The arrows mark some typical points: (1) and (2) are the Si center adatom in FHUC of the clean Si(111)-(7×7) surface and the corresponding position with a Au cluster adsorbing in the FHUC, respectively; (3) and (4) are the positions in UHUC similar to points (1) and (2), respectively; (5) is the location near the Si corner adatom. (b) *I*-V curves taken at these typical points. [(c) and (d)] Corresponding normalized numerical differential curves.

ciated with brighter STM image, so point (2) is brighter than point (5) at the negative voltages and lower positive voltages, but darker as the bias voltage exceeds +1.7 V. That could explain why the Au cluster appears as a triangle at the voltages from -2.0 to +1.3 V [Figs. 2(a) and 2(b)], but changes to an inverted triangle when the bias voltage reaches up to +1.8 V [Fig. 2(b)]. As for the numerical differential *I-V* curve of point (4) [Fig. 3(d)], the surface dangling bond state at the negative voltage region is greatly eliminated. This may be the cause of the serious height suppression of the closest Si center adatom in neighboring UHUC in filled-state STM images [Fig. 2(a)]. From the evolution of the surface states on top of points (2), (4), and (5), it is speculated that there could be charges transfer from the closest Si center adatom in neighboring uncovered UHUC to the Au cluster in the FHUC, which helps to further stabilize the cluster.

C. First-principles energy calculations and STM simulations

According to the structural information provided by the STM images and STS measurements, four possible atomic configurations of Au cluster in the FHUC are constructed as in Fig. 4: (a)(1) is a three Au atom cluster (Au₃) with each Au atom on top of one Si center adatom, (b)(1) is a four Au atom cluster (Au₄) forming a tripod, with the outer three Au atoms bonding to three Si rest atoms, respectively, (c)(1) is the configuration proposed in Ref. 19 (similar to Cu cluster model), where six Au atoms form a ringlike aggregation (Au₆), with three sitting on top of the Si center adatoms and the other three bonding to the Si rest atoms, and (d) three adsorbed Au atoms (label 1) replace the three Si center adatoms and other three Au atoms (label 2) connect into a hexagon (Au₆Si₃) locating within the triangle.

The adsorption energy E(n) of Au cluster is defined as $E(n) = [E_{ad}(n) - E_{si}]/n - E_{Au}$, where $E_{ad}(n)$, E_{si} , and E_{Au} stand for the total energies of the surface with *n* adsorbed Au at-



FIG. 4. [(a)–(c)] Top views of the possible Au₃, Au₄, and Au₆ structural models and the simulated empty- and filled-state STM images. (d) Top view of the proposed Au₆Si₃ model of the Au cluster on the Si(111)-(7×7) surface.

oms, the clean Si(111)-(7×7) surface, and the isolated Au atom, respectively.¹⁸ Within these four cluster models, the adsorption energy E(n=6) of Au₆Si₃ shows the lowest value of -3.358 eV/atom, about 0.479, 0.326, and 0.310 eV/atom lower than that of Au₃, Au₄, and Au₆, respectively, indicating that the Au₆Si₃ cluster is more stable than the other three configurations.

From the perspective of Au-Si bonding, the atomic structure of Au₆Si₃ cluster exhibits a characteristic of the valence. It is well known that the tetravalent Si adatoms and rest atoms are of partially filled, resulting in the dangling bonds on the Si(111)- (7×7) surface. As a transitional group element, Au is likely to be in a 3+ valence state when reacting with nonmetallic atoms. Hence, in the Au₆Si₃ structure, each Au atom bonds to three nearby Si atoms, and each Si atom bonds with one Au corner atom [label 1 in Fig. 4(d)], two Au edge atoms [label 2 in Fig. 4(d)], and one Si atom below it. Consequently, the Au₆Si₃ model is the most optimal configuration for fully saturating the surface dangling bonds and forming the stable clusters. Although Au and Cu both belong to the IB group, they show different valences when combining with the atoms of other elements. It may interpret the significant difference between the Au and Cu clusters. In addition, structural relaxation result of Au₆Si₃ model shows that the six Au atoms and three replaced Si atoms are not exactly on a plane. The Au edge atoms [label 2 in Fig. 4(d)] and the three Si atoms are about 0.29 and 0.28 Å higher than the Au corner atoms [label 1 in Fig. 4(d)], respectively. Instead of precise threefold symmetry, the Au-Si bond lengths range from 2.47 to 2.58 Å, while the Si-Au-Si angles vary from 84.7° to 112.7°. As mentioned above, Au is inclined to be in a 3+ valence state when bonding to Si atoms. However, different from the exact trivalence of group IIIA metals (such as Al and In), Au contains much more complexity in the chemical valence, which may be responsible for the destroyed threefold symmetry of Au-Si bonds.

Based on the Au₆Si₃ model and the cluster density estimated from STM images, the densities of Au atoms on the surface are measured to be 3.09×10^{13} atoms/cm² for 0.04 ML deposition and 4.59×10^{13} atoms/cm² for 0.06 ML deposition, which are, respectively, consistent with the actual deposition densities of Au atoms $(3.13 \times 10^{13} \text{ and } 4.70 \times 10^{13} \text{ atoms/cm}^2)$. The agreement between the measured and the actual deposition densities of Au atoms also reasonably supports the Au₆Si₃ cluster configuration.

The topographic filled- and empty-state STM images of the four relaxed models are further simulated using the theory of Tersoff and Hamann.³⁴ Typical simulated images of Au₃, Au₄, and Au₆ are shown in Figs. 4(a)-4(c). The Au₃ cluster appears as three pellets arranged in a triangle pattern at the bias voltage of +1.8 V [Fig. 4(a)(2)], which is different from the experimental observation that an inverted triangle emerges at that voltage. In addition, the apparent height of the cluster is even lower than that of the Si corner adatom at -1.5 V [Fig. 4(a)(3)], also inconsistent with the experimental results. For the Au₄ structure, there is no depression in the cluster center in empty-state images [e.g., Fig. 4(b)(2)], although the filled-state images [e.g., Fig. 4(b)(3)] have some similarities with the experimental ones. As to the Au₆ model, the states of the cluster are nearly cleared at the bias voltage of -0.8 V [Fig. 4(c)(3)] and the image at +1.8 V [Fig. 4(c)(2)] resembles to that of the Au₃ structure [Fig. 4(a)(2)]. It is evident that the experimental STM images cannot be reproduced by these three models.

For the Au₆Si₃ cluster adsorbed Si surface, the biasdependent STM images are calculated with the comparison of clean Si(111)- (7×7) surface, as shown in Figs. 2(c) and 2(d). In the filled-state images [Fig. 2(c)], the cluster appears as a bright triangle, whose size and brightness decrease as the voltage reduces. The closest Si center adatom of neighboring uncovered UHUC is significantly darkened in all filled-state STM images, compared to that of the clean Si(111)- (7×7) surface. On the other hand, in the simulated empty-state STM images [Fig. 2(d)], the cluster center is depressed regardless of the bias voltage. In the +0.5 V image, the cluster changes into a dim region, with the height is much lower than that of the Si adatoms. At the bias voltages of +1.0 and +1.3 V, it distinctly splits into three equivalent parts occupying each corner of the triangular pattern, respectively. As the voltage is raised to +1.8 V, other three brighter pellets emerge, and the cluster pattern changes to an inverted triangle instead. Obviously, the simulated STM images of Au_6Si_3 model in Figs. 2(c) and 2(d) are in remarkable qualitative agreement with the experimental results in Figs. 2(a)and 2(b), which further demonstrates the rationality of Au₆Si₃ cluster configuration.

The discrepancy of the cluster configurations in our experiment and that proposed in Ref. 19 mainly induced by the low-temperature annealing. Before annealing, the mobility of Au atoms are spatially limited by the substrate, so they directly adsorb on Si(111)-(7×7) surface, integrating into irregular-shaped clusters without the Si atoms. However, in the process of low-temperature annealing, the basic morphology of Si(111)-(7×7) surface is still held, while the positions of Au atoms are optimized by overcoming the kinetics barriers. Synchronously, promoted by the thermal effects, some activated Si center adatoms react with the Au atoms to further stabilize the cluster structure. Consequently, the Au clusters with uniform shape and size are grown.

IV. CONCLUSIONS

Au clusters with identical sizes are prepared on the Si(111)- (7×7) surface by room temperature deposition followed by an annealing at about 120 °C. In situ STM and STS are used to characterize the structural and electronic properties at both the positive and negative bias voltages. According to counting statistics, the adsorption of Au clusters displays a preference for the FHUCs. The saturation of Si adatom dangling bonds leads to the semiconducting characteristics of cluster adsorbed surface. Moreover, the Au cluster in the FHUC empties the surface dangling bond state of the closest Si center adatom in neighboring UHUC at about -0.6 V, causing a serious height suppression of the closest Si center adatom in the filled-state STM images. First-principles adsorption energy calculations show that the Au clusters tend to grow into the Au₆Si₃ structure, in which three adsorbed Au atoms replace the three Si center adatoms, forming a hollow triangle, while the replaced Si atoms and other three Au atoms connect into a hexagon locating within the triangle. Using this structural model, the simulated biasdependent STM images are well consistent with the experimental observations. The formation mechanism of this atomic configuration is related to the characteristic of the chemical valence of Au as well as the interactions of Au and Si atoms under certain annealing conditions. These investigations are of significant importance in understanding the initial growth stages of Au adsorption on Si(111) surface and offer some references for the controlled fabrication of lowdimensional nanoclusters and the design of nanodevices.

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