

Artificial nanocluster crystal: Lattice of identical Al clusters

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A two-dimensional artificial crystal, which is made up of artificial atoms—identical Al clusters with nanometer size and spacing, was fabricated by taking advantage of surface-mediated clustering on a growth template. *In situ* scanning tunneling microscopy analysis and first-principles total energy calculations were used to determine the atomic structure of the Al nanoclusters. The Al clusters exhibit more remarkable thermal stability than the In clusters we reported previously. Based on our systematic observations and calculations, the formation mechanism and the high stability of these magic clusters are discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1474620]

Due to quantum confinement effects, the physical and chemical properties of nanoclusters can be very different from those of bulk material. Therefore, nanoclusters are promising for many new and novel important applications in microelectronics, ultrahigh-density recording, and nanocatalysis, etc. Tremendous efforts have been made to fabricate various nanostructures in the last decade. Being influenced by thermodynamic fluctuation and other growth uncertainties, the clusters fabricated with most methods usually have broad size distribution and random spatial arrangement. Since the properties of nanoclusters strongly depend on their size and shape, the inhomogeneity in an ensemble of clusters will smear their special properties. Very recently, some novel approaches have been shown to be promising to make uniformly sized nanoclusters/dots with fairly good spatial distribution by using self-organization in heterogeneous strained thin-film growth^{1,2} and self-assembly in chemical synthesis.³ In many aspects, nanoclusters are artificial atoms.⁴ Therefore, the periodic lattice of the clusters with the same nanometer size and spacing are the artificial nanocluster crystal. This new form of condensed matter provides unprecedented opportunities for exploring the law of physics that nature rarely provides. In a recent work,⁵ we have shown that fabrication of such a kind of artificial crystal is possible. Using the same method, Lai and Wang have independently fabricated two-dimensional lattice of the Ga clusters on the Si(111)-7×7.⁶

In this work, we explore such possibility with Al, the most reactive group III metal. As shown in previous studies, a very strong interaction between Al and Si hinder formation of ordered clusters on the Si(111)-7×7 surface. By carefully controlling the deposition conditions, high quality Al nanocluster crystals could be prepared on Si(111)-7×7 and

exhibit a remarkable thermal stability compared to the clusters that have been made so far.^{5,6} This high stability renders the Al nanocluster array an ideal template for growing magnetic nanostructure.⁷ While the structure of the Al clusters is the exact same as that of the In clusters,⁵ as established by our systemic observation and first-principles total energy calculations, we found that the Al/Si system exhibits different electronic structures.

Our experiments were performed with an OMICRON variable temperature scanning tunneling microscopy (STM) operated in ultrahigh vacuum ($\sim 5 \times 10^{-11}$ Torr).^{5,8} Clean Si(111) substrates were prepared by well-established annealing procedures. A boron nitride crucible was used to produce Al (purity 99.9999%) atomic beams. During deposition, the Al cell temperature is 940 °C, corresponding to a deposition rate of 0.16 monolayer (ML)/min (1 ML = 7.8×10^{14} atoms/cm²). A chemically etched tungsten tip was used as the STM probe. All STM images reported here were recorded at room temperature with a tunneling current of 20 to 50 pA.

As a technologically important metal/semiconductor system, Al/Si(111) has been intensively studied for more than 30 years,⁹ however, neither Al clusters nor their ordered array has been reported. Our study started with room-temperature Al deposition on the Si(111)-7×7 surface. After deposition, we can see many individual Al atoms adsorbed on the top of the Si adatoms as indicated by the white arrows in Fig. 1. Some Al clusters are also observed (the big bright spots in the image). With increasing Al coverage, more clusters will be formed, but the sizes of the clusters are not uniform. At 0.2 ML coverage, a featureless structure consisting of irregular clusters develops, which smears out the 7×7 symmetry of the Si substrate. An ordered identical Al clusters array could be formed only when the substrate temperature is higher than 200 °C, as shown in Fig. 2. We can see that the Al clusters equally occupy both halves of the unit cell of

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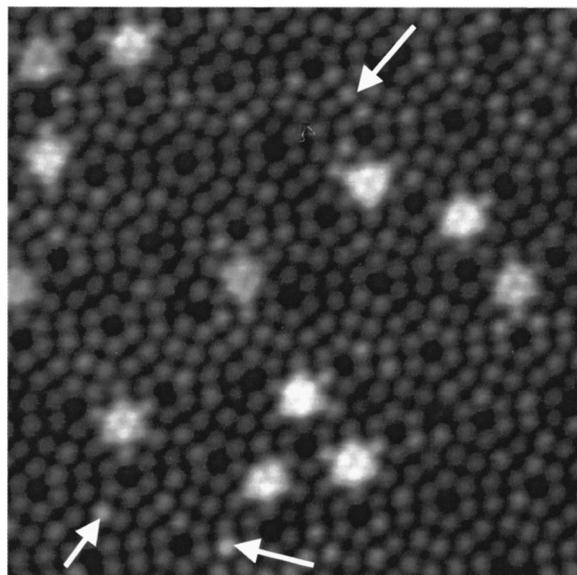


FIG. 1. STM image (18 nm \times 18 nm) of the Si(111)-7 \times 7 adsorbed with 0.05 ML Al. The white arrows indicate the Al atoms adsorbed on the top of Si adatoms. Sample bias voltage $V_s = +2.0$ V.

Si(111)-7 \times 7 forming a characteristic honeycomb structure. Considering each cluster as an artificial atom, this periodic lattice of the same sized clusters represents a new artificial crystal, and the geometry of this “lattice” is the same as that of the Si(111)-7 \times 7.

High-resolution STM image [Fig. 3(a)] shows that the Al cluster appears triangular and resides at the center of each half of the Si(111)7 \times 7 unit cell. Each cluster contains six white spots, the three on the edge are brighter than those at the corner. The STM image of the Al cluster is more or less similar to that of the Ga cluster observed by Lai and Wang⁶ as well as by us, it is quite different from that of the In cluster,⁵ where the three spots on the edges of the triangle appear darker at the empty state.

First-principles total energy calculations were performed to investigate the atomic structure and formation mechanism

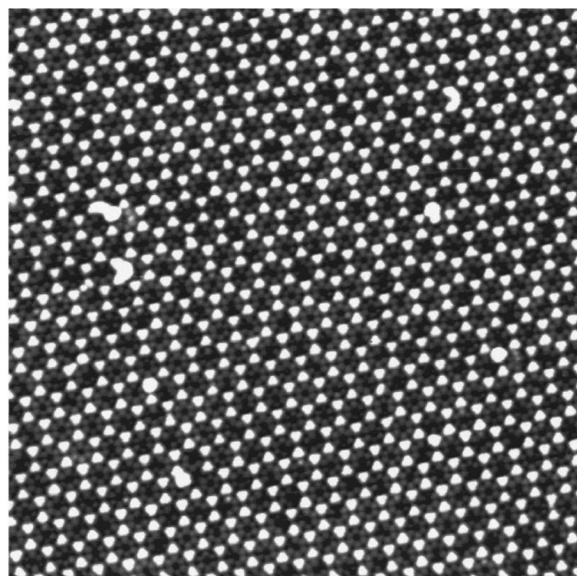


FIG. 2. Perfectly ordered Al nanocluster array at ~ 0.25 ML Al coverage, the STM image was obtained at $V_s = -2.0$ V with image size of 50 nm \times 50 nm.

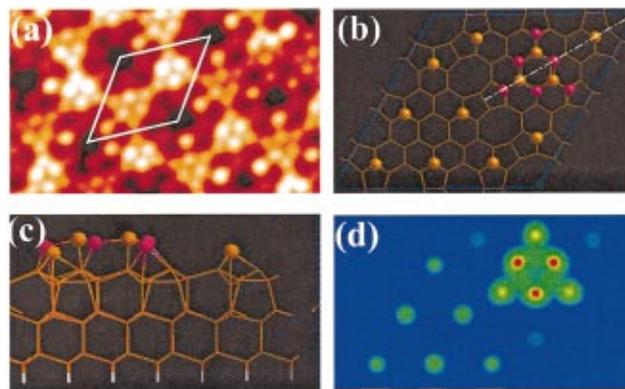


FIG. 3. (Color) (a) Atomically resolved STM image (9 nm \times 5.5 nm) of the Al clusters recorded at V_s of +1.1 V. (b) Top view of the proposed atomic structure of the Al₆ cluster on Si(111)-7 \times 7. The pink balls are Al atoms and the yellow balls are Si adatoms. (c) Side view of the Al₆ cluster along the white dashed-dotted line in (b). (d) Calculated empty state STM image (for positive bias +1.1 V with respect to the Fermi energy) for the atomic structure in (b). The color code indicates the image height: blue/green being low and red/yellow being high.

of the Al clusters. A pseudopotential plane-wave method¹⁰ with local density approximation was used. The supercell for modeling the Si(111)-7 \times 7 surface contained 298 silicon atoms and 49 hydrogen atoms at the bottom saturating the Si dangling bonds. A single k point was used in the integration with a plane-wave cutoff energy of 100 eV. Similar techniques have been used by one of the authors with success in the calculation of adsorption on Si(001) surface.¹¹ Using this approach, the optimized structure of the Si(111)-7 \times 7 surface is in excellent agreement with previous *ab initio* calculations.^{5,12}

Starting from the STM observation and coverage measurement, we calculated the formation energies of the Al₃Si₃ and Al₆ clusters on Si(111) with the initial configurations similar to the In₆ cluster.⁵ The optimized structure is the Al₆ model as demonstrated in Figs. 3(b) and 3(c). In this model, six three-fold-coordinated Al form a triangle and three Si adatoms originally on the edge are displaced toward the triangle center considerably [Fig. 3(b)]. For the Al atoms at the corners of the triangle, the bond lengths are 2.487 Å, 2.487 Å, and 2.435 Å, whereas the bond angles are 92.6°, 122.7°, and 122.7°, respectively. For the Al atoms on the edges, the bond lengths are 2.471 Å, 2.471 Å, and 2.551 Å with the bond angles of 115.5°, 121.0°, and 121.0°, respectively. Each of the three Si adatoms originally on the edge now bonds to three neighboring Al atoms and one Si atom under it. The Si–Al bond lengths are 2.471 Å, 2.471 Å, and 2.435 Å, whereas the bond angles are 115.3°, 112.8°, and 112.8°, respectively. The vertical positions of these three Si adatoms are also changed considerably. They are 0.81 Å higher than the Al atoms at the corners of the triangle. So, in this model, the three Si adatoms originally on the edge and the three Si rest atoms become four-fold coordinated. The simulated STM image based on this conformation is shown in Fig. 3(d). The agreement between the theory and the experiment [Figs. 3(a) to 3(d)] is very good.

Although the STM images are different, the structure models for both Al and In clusters are essentially the same,⁵ except that the Si–In bond lengths are larger than the Si–Al bond lengths because the In atom has a larger covalent radius.

lent radius. So, it is reasonable to use the same mechanism to explain the formation and ordering of the Al clusters. In the case of In, the corner In atoms appear brighter in the empty state STM image, whereas the edge Al atoms look brighter for the Al cluster. The reason for this is that the corner In atoms extrude more out of the surface while the corner Al atoms are more sp^2 like, one can see this from the bond angles for these two atoms.^{5,13} The higher stability of Al clusters is due to the tighter bonding between Al and Si atoms. According to our calculations, the binding energy (total energy minus atomic energy) of Al_6 on Si(111) is 5.86 eV/cell lower than that of In_6 . Giving such high energy, it is not difficult to understand why the fabrication of the ordered Al nanocluster array has been less successful. The details about theoretical calculations and comparison between In, Ga, and Al clusters will be published elsewhere.¹³

In this work, high quality Al nanocluster crystals have been fabricated on the Si(111) 7×7 by the method we proposed previously. The atomic structure and formation of the Al clusters are investigated by *in situ* STM analysis of clusters and first-principles total energy calculations. The very stable Al nanocluster crystal provides unprecedented opportunities for exploring the new physical phenomena. This sta-

bility, together with the significant removal of the Si dangling bonds, makes this crystal a promising template for growing magnetic (Fe, Co, etc.) nanostructures and quantum devices based on the advanced Si technology.

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