

## Dynamic behavior and phase transition of magic Al clusters on Si(111)-7×7 surfaces

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By means of high-temperature scanning tunneling microscopy, the authors present a direct observation on the dynamic behavior and phase transition of magic Al clusters on Si(111)-7×7 surfaces at high temperature. When the temperature is above 500 °C, fast diffusion of magic Al clusters on Si(111)-7×7 surfaces occurs while the magic cluster phase transforms into  $\sqrt{3} \times \sqrt{3}$ -Al phase on downterraces (the *downstep* side of a terrace). From an Arrhenius plot, the activation energy of magic Al clusters on Si(111)-7×7 surfaces was extracted to be  $2.0 \pm 0.3$  eV. This study supplies important information for understanding the formation and phase transition process of magic Al nanoclusters on Si(111)-7×7 surfaces. © 2006 American Institute of Physics.

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Recently, identically sized cluster arrays of Tl (Ref. 1) as well as Al, Ga, In, Ag, Na, Pb, etc.<sup>2-7</sup> so-called artificial nanocluster crystals, have been fabricated on Si(111)-7×7 surfaces. Such identically sized nanocluster arrays have been considered as promising materials for next generation micro-/nanoelectronics, and also as a perfect template for subsequent deposition of other particles or molecules. For example, when the sample temperature is above 200 °C, two-dimensional (2D) Al nanocluster crystals can form with few defects<sup>2</sup> and have also been used as a template/buffer layer for self-organized Co nanoplatelets.<sup>8</sup>

In our previous study,<sup>9</sup> the thermal stability of the Al nanocluster crystal was investigated systematically. It was found that, above 500 °C, the Al nanocluster crystal begins to transform into a  $\sqrt{3} \times \sqrt{3}$ -Al surface phase with singular triangle shapes on *downterraces* (the *downstep* side of a terrace). On the other hand, similar to the study on dynamic behavior of magic Si clusters on Si(111)-7×7 surfaces<sup>10</sup> as well as Al clusters on Al surfaces,<sup>11,12</sup> studies on the dynamic behavior of metal magic clusters on semiconductor surfaces are also important not only for understanding the formation process of magic clusters, constructing artificial nanostructures, but also for understanding the epitaxial growth and even the phase transition process. However, no such studies have been reported as yet. In this letter, by means of variable-temperature scanning tunneling microscopy (STM) in real time, we present an experimental observation showing the mobility of magic Al clusters on Si(111)-7×7 surfaces grown at high temperature. It was found that when the temperature is higher than 500 °C a phase transition from magic cluster to  $\sqrt{3} \times \sqrt{3}$ -Al phase occurs accompanied by fast jumps of magic Al clusters. From an Arrhenius plot, the activation energy of magic Al clusters on Si(111)-7×7 surfaces was extracted to be  $2.0 \pm 0.3$  eV. The phase transition

process from magic Al clusters to  $\sqrt{3} \times \sqrt{3}$ -Al phase was observed directly.

The experiments were performed with a JEOL 4500 high-temperature STM operated in an ultrahigh vacuum chamber (base pressure  $\sim 1 \times 10^{-8}$  Pa). Samples were heated in STM chamber by direct electric current and the temperature was monitored by an infrared pyrometer. A chemically etched tungsten tip was used to record STM images. Si (111) samples were cleaned briefly by HF acid solution and degassed at  $\sim 600$  °C for several hours in ultrahigh vacuum chamber. Clean Si(111)-7×7 surfaces were obtained by flashing to  $\sim 1100$  °C for several times and annealing at 800 °C for 30 min to decrease defects. An e-beam evaporator was used to grow Al nanoclusters in the STM chamber. All STM images were recorded *in situ* at growth temperature with the constant current mode. A sample bias of 2.5 V and a tunneling current of 0.1 nA were used.

When depositing an appropriate amount of Al (around 0.24 ML, 1 ML=one adsorbed atom per substrate atom)<sup>2,3,9</sup> at high temperature (above 200 °C) on Si(111)-7×7 surfaces, large-scaled 2D Al nanocluster crystals can form. Each nanocluster consists of six Al atoms.<sup>2,13</sup> In order to study the dynamic behavior of Al nanoclusters on Si(111)-7×7 surfaces, underdosed Al (<0.2 ML) was deposited at 400, 450, 500, 515, and 520 °C, respectively, and several tens of successive STM images were observed *in situ* at the growth temperature. As a representative, four successive STM images extracted from a movie of magic Al clusters on Si(111)-7×7 surfaces at 520 °C are shown in Figs. 1(a)–1(d). It can easily be seen that these Al clusters are mobile and can diffuse on the Si(111)-7×7 surfaces at high temperature. For example, comparing Figs. 1(a) and 1(b), 9 clusters [marked by magenta circles in Fig. 1(a)] disappeared and 10 clusters [marked by green circles in Fig. 1(b)] appeared at some new sites. Some clusters even hopped far away from the original sites and left the perfect Si(111)-7×7 surface behind. From Figs. 1(a)–1(d), no fractional magic cluster or cluster aggregation (except for near defects,

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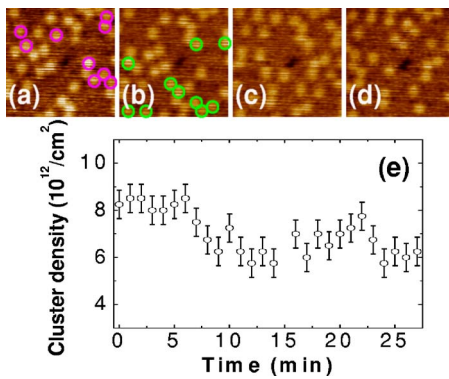


FIG. 1. (Color online) Time evolution of Al nanocluster arrays after growth at 520 °C, which was extracted from a STM movie: (a) 0 min, (b) 1 min, (c) 2 min, and (d) 3 min after growth. Sample bias: +2.5 V, tunneling current: 0.1 nA, and scanning size:  $20 \times 20 \text{ nm}^2$ . (e) Total cluster density ( $d_t$ ) as a function of time.

i.e., vacancies) was observed during the cluster diffusion. Phenomenally, similar to Si magic clusters on Si(111)- $7 \times 7$  surfaces,<sup>10</sup> Al clusters act as “surface molecularlike magic clusters” during the diffusion process. It seems that the Si(111)- $7 \times 7$  surface only supplies a periodic foundation for magic Al clusters.

By comparing consecutive STM images in the same region, we are able to count the total cluster density ( $d_t$ ) and mobile cluster density ( $d_m$ ). As shown in Fig. 1(e), the density of total clusters decreases with time at 520 °C, which did not occur below 500 °C. If we neglect the multijumps between two consecutive STM images,<sup>14</sup> the jump frequency ( $\gamma$ ) of each Al cluster may be roughly calculated by  $\gamma = (d_m/d_t)(1/t_w)$ , where  $t_w$  is the time interval between two consecutive STM images. In our experiments,  $t_w = 60 \text{ s}$ . We have measured  $\gamma$  from 400 to 520 °C. As for thermally activated motion,  $\gamma = \gamma_{\text{eff}} \exp(-E_d/k_B T)$ , where  $\gamma_{\text{eff}}$  is the attempt frequency,  $E_d$  is the activation energy,  $k_B$  is the Boltzmann constant, and  $T$  is the sample temperature. From the Arrhenius plot shown in Fig. 2, we obtained the  $E_d \sim 2.0 \pm 0.3 \text{ eV}$  with  $\gamma_{\text{eff}} \sim 10^{10} \text{ s}^{-1}$ . The activation energy is slightly lower than that of the average value of magic Si clusters on Si(111)- $7 \times 7$  surfaces (1.96–2.64 eV);<sup>10</sup> however, it is much higher than that of single atoms on both semiconductor and metal surfaces, such as Pb on Si(111)- $7 \times 7$  surfaces<sup>15</sup> (0.64 eV) and Al on Al(111) surfaces (0.04 eV).<sup>11</sup>  $\gamma_{\text{eff}}$  is lower than the values of  $10^{11}$ – $10^{12} \text{ s}^{-1}$  expected for the bare attempt frequency of individual single atom hops, which is easy to understand due to the cooperative motion of the whole cluster or multiadatoms. The high value of the activation energy suggests that large-scaled Al

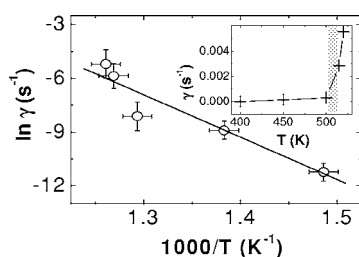


FIG. 2. Arrhenius plot for the diffusion of magic Al clusters on the Si(111)- $7 \times 7$  surfaces measured from 400 to 520 °C. The inset shows the jump frequency as a function of temperature with a linear y scale.

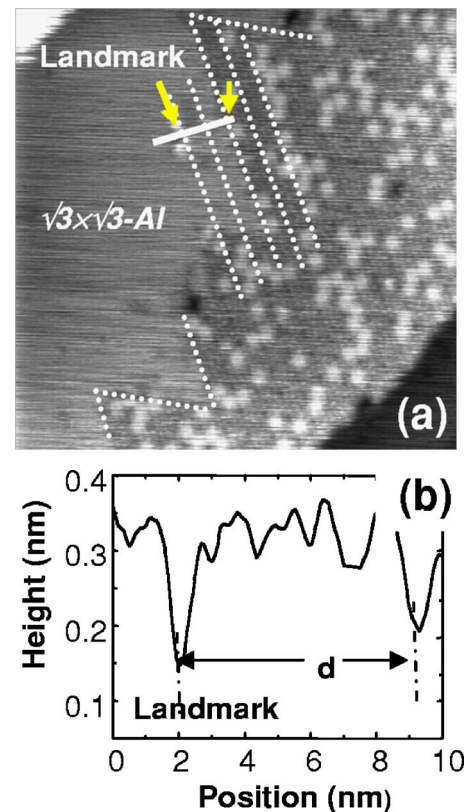


FIG. 3. (Color online) (a) STM images near the phase boundary between  $\sqrt{3} \times \sqrt{3}$ -Al and magic cluster phases at 520 °C, sample bias: +2.5 V, tunneling current: 0.1 nA, and scanning size:  $61.8 \times 61.8 \text{ nm}^2$ ; the dash lines are used to guide the eyes. The block arrows show the landmark and phase boundary. (b) Cross section of the straight solid line in (a).

nanocluster arrays could not be formed by the cluster diffusion process at a temperature lower than 500 °C within a short time.<sup>16</sup> In other words, instead of cluster diffusion, atom diffusion process should be responsible for the formation of Al nanocluster arrays. When depositing Al on Si(111)- $7 \times 7$  surfaces, Al atoms can diffuse relatively freely and prefer to stay at the energetically favorable sites. Finally magic clusters form in the attractive potential wells when the Al deposition amount is over a critical value, which is probably similar to the case of Na on Si(111)- $7 \times 7$  surfaces.<sup>6</sup> Comparing to Al nanocluster jumping as a whole in the cluster diffusion process, it seems more plausible that Al cluster diffuses via disassembly of Al clusters followed by adatom diffusion, until reassembly happens in a different potential well. From this point of view, the activation energy  $E_d$  represents the sum of binding energy between adatoms in one magic Al cluster and the hopping energy of Al adatoms to overcome the periodic barriers of Si(111)- $7 \times 7$  surfaces. The honeycomb surface structure should be a thermodynamically quasiequilibrium condition at high temperature.

The inset of Fig. 2 shows the temperature dependence of the jump frequency with a linear y scale. When increasing the sample temperature over 500 °C, the jump frequency increases dramatically. Notably, it is also above 500 °C (Ref. 9) that the 2D Al nanocluster crystal begins to transform into a  $\sqrt{3} \times \sqrt{3}$ -Al surface phase (the flat surface phase as shown in Fig. 3) with singular triangle shapes on downterraces. The identification of  $\sqrt{3} \times \sqrt{3}$ -Al has been done in our previous study<sup>9</sup> and also by others.<sup>2,3,17</sup> As shown in Fig. 3(a), the straight and sharp boundaries between nanocluster phase and

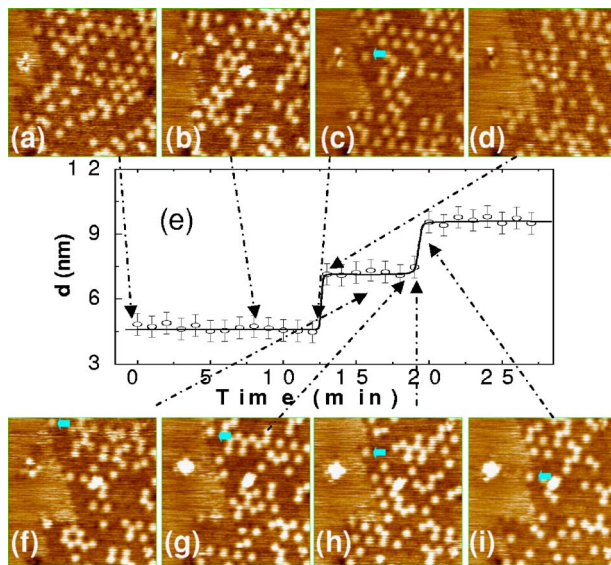


FIG. 4. (Color online) [(a)–(d) and (f)–(i)] Time evolution of phase transition at 520 °C, which was extracted from a STM movie. The time interval is 60 s between two successive STM images, sample bias: +2.5 V, tunneling current: 0.1 nA, and scanning size:  $36.1 \times 36.1$  nm<sup>2</sup>; turquoise block arrows [in (c) and (f)–(i)] mark the kinks with magic Al clusters. (e) Perpendicular distance between the landmark and phase boundary [ $d$ , as defined in Fig. 3(a)] as a function of time.

$\sqrt{3} \times \sqrt{3}$ -Al phase follow the main symmetry directions of the Si(111)- $7 \times 7$  substrate and unit cell edges.

The phase transition process was observed directly at high temperature *in situ*, as shown in Fig. 4(a)–4(d) and 4(f)–4(i).  $\sqrt{3} \times \sqrt{3}$ -Al phase appears at first near the step edge and grows up at the expense of Al nanoclusters. The phase transition occurs only at the kinks rather than at straight phase boundaries along the main Si(111)- $7 \times 7$  directions. Interestingly,  $\sqrt{3} \times \sqrt{3}$ -Al phase grows up row by row with the width of Si(111)- $7 \times 7$  unit cell, as shown in Fig. 4(e). Additionally, Al adatoms should be able to jump onto Al- $\sqrt{3} \times \sqrt{3}$  surfaces, however, there are no nucleation positions. Near the landmark where a vacancy exists, large Al mound formed sometimes, which is due to some Al atoms that were trapped there.

According to the dynamic process aforementioned, the phase transition process can be understood. When the temperature is above 500 °C, some magic Al clusters are broken into Al adatoms, and some of them transform into  $\sqrt{3} \times \sqrt{3}$ -Al phase, which usually nucleates on the dnterraces. By consuming Al adatoms disassembled from magic Al clusters,  $\sqrt{3} \times \sqrt{3}$ -Al phase grows up near the kinks. Due to the consumption of Al cluster near phase boundaries on dnterraces, Al clusters have a tendency to jump from up- to dnterraces, which should be responsible for the retraction of Al nanocluster crystals with annealing time on upterraces observed in our previous study.<sup>9</sup> The decrease of cluster density with annealing time at 520 °C [see Fig. 1(e)] can be under-

stood according to the dynamic process as well. Aside from transforming into  $\sqrt{3} \times \sqrt{3}$ -Al phase, some Al adatoms that disassembled from Al nanoclusters could be evaporated into the vacuum, part of them deposited again and formed magic clusters or  $\sqrt{3} \times \sqrt{3}$ -Al phase; however, some of them did not return to the sample surface. Moreover, the disassembled Al adatoms could diffuse quite fastly on the surface at such a high temperature, which cannot be easily observed by STM at high temperature.

In summary, we report a study on the dynamic behavior of magic Al clusters on Si(111)- $7 \times 7$  surfaces at high temperature in *real time* by means of hot STM. When the temperature is higher than 500 °C, the magic cluster phase transforms into  $\sqrt{3} \times \sqrt{3}$ -Al phase which was found to be accompanied by the fast diffusion of magic Al clusters. From the Arrhenius plot, the activation energy of magic Al clusters on Si(111)- $7 \times 7$  surfaces was extracted to be  $\sim 2.0 \pm 0.3$  eV. The phase transition process from magic Al cluster to  $\sqrt{3} \times \sqrt{3}$ -Al on dnterraces was observed directly.

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