PHYSICAL REVIEW B, VOLUME 64, 241404(R)

# Self-organized two-dimensional lattice of magic clusters

M. Y. Lai[1] and Y. L. Wang[1,2]*
[1]*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, Republic of China*
[2]*Department of Physics, National Taiwan University, Taipei 106, Taiwan, Republic of China*
(Received 22 September 2001; published 3 December 2001)

Under certain deposition conditions, gallium induces almost exclusive formation of a type of especially stable clusters—magic clusters, on the $7\times7$-reconstructed silicon(111) surface. The cluster has a triangular closed-shell structure and resides on the center of a $7\times7$ half unit-cell. As the gallium coverage is increased, the cluster density increases proportionally, leading essentially to the complete filling of the $7\times7$ half unit-cells and the creation of an unprecedented two-dimensional lattice of magic clusters. A structure model employing three silicon atoms to link six gallium atoms into a configuration with satisfied bonding is proposed to qualitatively account for the cluster's stability.

DOI: 10.1103/PhysRevB.64.241404 PACS number(s): 68.43.Hn, 61.46.+w, 68.35.Bs, 68.37.Ef

Formation of clusters on surfaces has long been a subject of fundamental interest for its relevance to thin-film deposition,[1,2] which is one of the cornerstones of the modern technology. Interests in the subject intensified in the last decade because of its implications to the growth of nanostructures, which is important for the realization of the emerging nanotechnology. When atoms are deposited onto a surface, they diffuse on the surface and aggregate into clusters. Due to the statistical nature in the deposition and diffusion processes, clusters usually have different sizes and random spatial distribution. Such inhomogeneity in an ensemble of clusters tends to smear its interesting properties and therefore is undesirable. Recently, self-organization, rather than random aggregation, of the deposited atoms was observed in certain rare systems.[3–7] Some systems exhibit ''intracluster self-organization'' and result in an ensemble of clusters with uniform size/structure but random spatial distribution.[3,4] While the others exhibit ''intercluster self-organization'' and result in periodic arrays of clusters with different size/structure.[5–7] The existence of these interesting systems raises a scientific curiosity: Is there any system that exhibits such ''intra- and intercluster self-organization'' simultaneously and results in a periodic array of clusters with the same size/structure? Investigations of such a system would provide valuable information for improving our understanding of the self-organized growth,[8–10] which have important implications to the precise fabrication of nanostructures.[11,12]

Here we report a self-organized two-dimensional lattice of magic clusters—a type of especially stable clusters[3,13,14] on the Si(111)-$7\times7$ surface. The magic cluster induced by Ga deposition has a triangular closed-shell structure and resides on the center of a $7\times7$ half unit-cell (HUC). This unprecedented cluster lattice also has an unusual formation process: Increasing Ga coverage leads to linear increase in the cluster density, and the linearity continues until ~80% of the $7\times7$ HUC's are covered. Such essentially ''digitized'' formation of magic clusters without any cluster growth or coalescence is a vivid manifestation of the extraordinary stability of the magic cluster in this particular system. A structure model with a satisfied bonding configuration is proposed to qualitatively account for the cluster's stability.

Our investigation is inspired by the recent observation of magic clusters on the $\sqrt{3}\times\sqrt{3}R30°$ Ga/Si(111) surface,[3] where the deposited Ga atoms interact delicately with Ga and Si adatoms and self-organize into clusters with magic sizes and triangular closed-shell structures. One particular species dominates the system because of its satisfied bonding configuration and the minimized number of dangling bonds on its surrounding $\sqrt{3}\times\sqrt{3}R30°$ adatom lattice. Though the clusters in this system exhibit very strong size/structure preference, they are randomly distributed on the surface. It is therefore tempting to investigate Ga-induced formation of magic clusters on the Si(111)-$7\times7$ surface[15] where the periodic pattern of the reconstructed lattice have the potential to constrain the formation of the clusters and lead to an ordered array of clusters with reduced size dispersion.[7,16]

The experiment is conducted in an ultrahigh vacuum (UHV) chamber equipped with a scanning tunneling microscope (STM). Si(111) substrates are cleaned by resistive flashing in UHV until a high quality $7\times7$ reconstruction is observed by the STM. High purity Ga is then deposited onto the surface with a typical deposition rate of 0.1 monolayer (ML) ($1\ \mathrm{ML}=7.8\times10^{14}\ \mathrm{Ga/cm^2}$) per minute. Immediately after the Ga deposition at room temperature, dilute clusters form spontaneously, as shown by the bright areas in Fig. 1(a). The clusters are randomly distributed on the surface, while an individual cluster is mostly confined within a HUC of the Si(111)-$7\times7$ lattice. This indicates that the HUC boundaries made of dimer rows and corner holes are repulsive barriers for the deposited Ga atoms, and the $7\times7$ surface is an effective template for constraining the formation of Ga-induced clusters.[16] The size and shape of the clusters are irregular, suggesting that the cluster formation at room temperature is not a thermal equilibrium process. Thermal annealing of the sample results in significant mass transport and structural reorganization of the clusters. As shown in Fig. 1(b), the size and shape of the clusters become uniform for samples annealed at 300 °C for 10 seconds. The observation reveals that, at an elevated temperature, small or irregular clusters are broken up and sent across the HUC boundaries to form larger and more stable clusters with certain preferred size/structure.

 

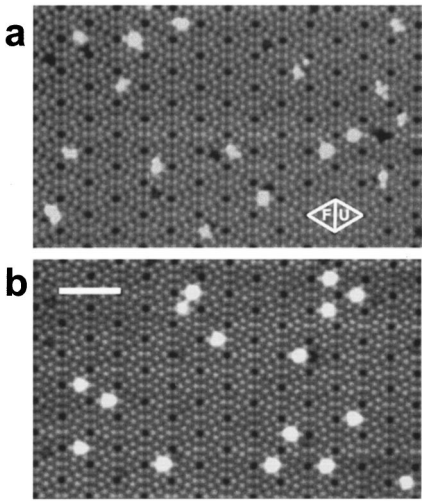


FIG. 1. STM images of cluster formation as Ga is deposited on the Si(111)-(7×7) surface. (a) Clusters prepared at room temperature have irregular size and shape. (0.011 ML of Ga, $V_{tip}=-2.1$ V). The diamond-shaped mark shows a lattice unit with a faulted (*F*) and an unfaulted (*U*) triangular half. (b) Increased uniformity in the cluster size and shape after 10 seconds of annealing at 300 °C (0.017 ML of Ga, $V_{tip}=-2.2$ V). At such low coverage, clusters prefer to form on the faulted than unfaulted HUC's with a preference ratio of ~3:1. Scale bar is 5 nm.

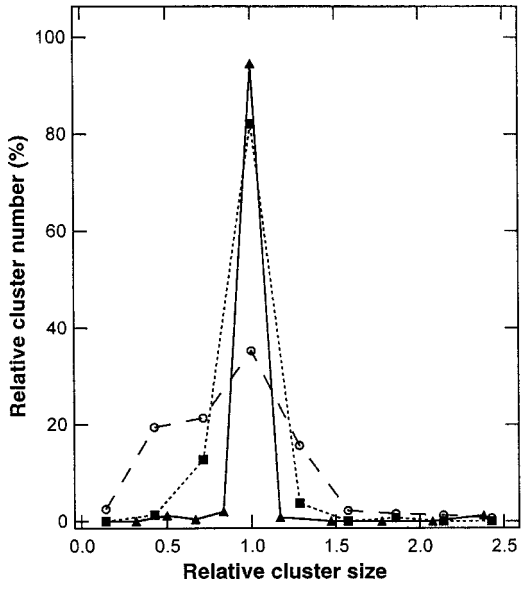


FIG. 2. Normalized size distribution of Ga-induced clusters on the Si(111)-7×7 surface. Different curves depict samples prepared at different conditions: as deposited at room temperature (○), room temperature deposition followed by annealing at 300 °C for 10 seconds (■), deposited at 350 °C (▲). The size of a cluster is measured from empty-state STM images and the cluster size for the data of ▲ (○ and ■) is determined by the number of atoms observed in a cluster (by the area covered by a cluster). The size of the magic cluster is defined as unity.

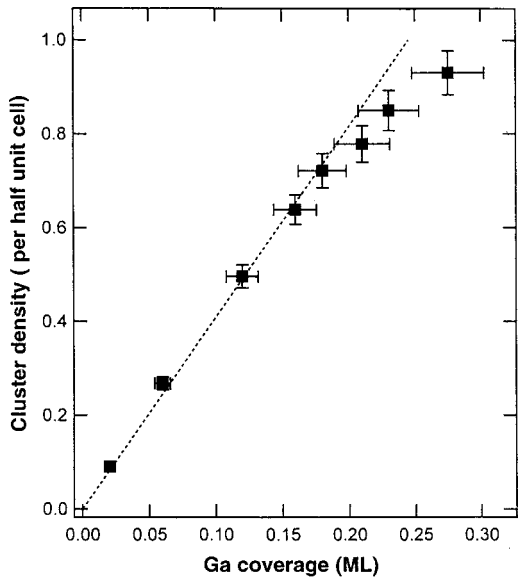


FIG. 3. Density of clusters (mostly magic clusters) as a function of Ga coverage for samples with Ga deposited at 350 °C.

Figure 2 shows the cluster size distribution for samples prepared under various conditions. The curve marked by circles is for samples with Ga deposited at room temperature. Although the cluster size distribution is broad, a peak is discernable, suggesting the existence of a preferred size even for the clusters formed at room temperature. The curve marked by squares is for samples with Ga deposited at room temperature followed by thermal annealing at 300 °C for 10 seconds. It exhibits a single narrow peak, clearly indicating the formation of a type of cluster with enhanced stability—magic cluster. As to be detailed later, these magic clusters have not only the same size but also equivalent bonding configuration. Although the annealing significantly reduces the cluster size dispersion, its temperature is not high enough to transfer all less stable clusters into magic clusters, as evidenced by the small shoulder on the left side of the peak. Further narrowing of the size distribution can be achieved by optimizing the growth condition. By directly depositing Ga onto the Si(111)-7×7 surface at 350 °C, the sizes of the clusters converge essentially to a single value, as shown by the curve marked by triangles. In this condition, 94% of the clusters are the magic clusters. The enhanced stability of the magic clusters is further confirmed by annealing the sample at an elevated temperature. Noticeable disappearance of the magic clusters, which is accompanied by the destruction of the 7×7 surface lattice and the formation of the $\sqrt{3}\times\sqrt{3}R30°$ equilibrium phase,[17] starts only at a temperature beyond ~450 °C.

As Ga coverage is increased under the optimized condition, the density of clusters, most of which are magic clusters, increases proportionally. The linear proportionality continues until ~80% of the HUC's are covered, as shown by the curve in Fig. 3. Although simple, the linear proportionality covering such a wide range (~0.2 ML of adatom coverage) reflects the unusual cluster formation in this system, especially when it is compared with the nucleation and growth of clusters in most systems. Usually, the linear pro-

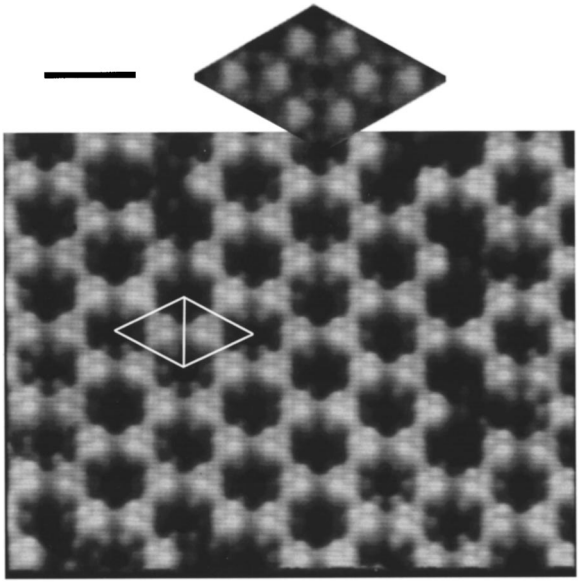

FIG. 4. Empty-state STM image ($V_{tip}=-1.9\,V$) of a two-dimensional lattice of Ga-induced magic clusters grown on the Si(111)-7×7 surface at 350 °C. A lattice unit containing two clusters is marked on the image. The inset shows the filled-state image ($V_{tip}=2.1\,V$) of the magic-cluster lattice. Scale bar is 3 nm.

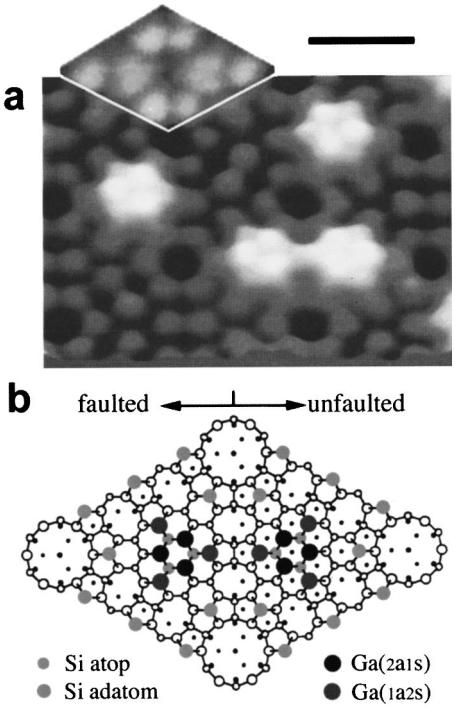


FIG. 5. Detailed structure of the Ga-induced magic clusters on the Si(111)-7×7 surface. (a) Empty-state STM image ($V_{tip}=-2.0\,V$) of four clusters. Inset is filled-state image ($V_{tip}=2.2\,V$) of a pair of clusters surrounded by six corner Si adatoms. Scale bar is 2 nm. (b) Model for clusters on faulted and unfaluted HUC's of the 7×7 structure (see Ref. 15). Small circles and dots are substrate Si atoms. Ga($2a1s$) denotes Ga bonded to two atop Si and one substrate Si while Ga($1a2s$) bonded to one atop Si and two substrate Si.

portionality between the cluster density and adatom coverage, which is observed in the pure nucleation regime, terminates at an adatom coverage on the order of 0.001 ML.[1,2] Above this coverage, the linearity is gradually lost due to the growth in the size of the clusters. In contrast, the self-organization process in this system proceeds essentially through a unique ''digitized'' formation of magic clusters without any cluster growth or coalescence.

The unusual self-organization process allows us to fill almost the entire Si(111) surface with the Ga-induced magic clusters. Figure 4 shows the STM image of a periodic array of magic clusters formed by the deposition of ~0.25 ML of Ga at 350 °C.[18] The honeycomb cluster array has a diamond-shaped unit cell that contains two clusters, one on the faulted and the other the unfaulted HUC. Each cluster contains $6.0\pm0.8$ Ga atoms, as determined from the quotient of the Ga coverage and cluster density. Although the corners of the clusters appear to be almost connected in the empty-state image, they are clearly separated in the filled-state image, as shown in the inset of Fig. 4. Based on the same size and shape as well as the fixed orientation of the constituent clusters shown in Fig. 4, the cluster array exhibits the plane symmetry of p6mm ($C_{6v}$). [To be exact, it has $p3m1$ ($C_{3v}$) symmetry if the stacking sequence of underlying Si structure is also taken into account.] To our knowledge, such a precise two-dimensional lattice of magic cluster is unprecedented. It is also an elegant manifestation of the unique self-organization process in this system.

The information in the STM images provides important clues for us to speculate on the atomic structure of the magic cluster, which can help us understand the origin of its extraordinary stability on a HUC of the Si(111)-7×7 surface. Figure 5(a) shows an atomically resolved empty-state STM image of four magic clusters, two on the faulted and the others on the unfaulted HUC's. Irrespective of the different stacking sequences of their underlying Si structures, these clusters do not exhibit significant difference in our STM imaging studies. The cluster is approximately triangular and resides at the geometric center of a HUC. It covers the area originally occupied by the three edge Si-adatoms of the 7×7 structure and is surrounded by the three corner Si-adatoms. The observation suggests that three edge Si-adatoms are involved in the formation of the cluster. From the empty state image, the cluster appears to contain six atoms. The ones on the edge are brighter than those on the corner. The distance between two edge atoms is 0.56 nm while that between the edge and the corner atoms is 0.43 nm. Both are much larger than the lattice parameter (0.384 nm) of the Si(111) surface, indicating that there is no direct bonding among the six observed atoms in the cluster. While the empty-state image distinguishes the edge atoms from the corner atoms clearly, the corresponding filled-state image presents the cluster as a featureless triangle (edge length = 0.88 nm), as shown in the inset of Fig. 5(a). In this filled-state image, the cluster and the corner Si adatoms are clearly separated and the edges of the clusters are as far as 0.57 nm away from the centers of the corner Si adatoms. The observation indicates that the corner Si adatoms are not part of the cluster.

Based on the above observations, the magic cluster in the present system is very similar to the type of $Ga_6Si_3$ magic cluster observed in our previous study of Ga on the $\sqrt{3}\times\sqrt{3}$ $R30°$ Ga/Si(111) surface.[3] Thus, we are tempted to propose an atomic model [Fig. 5(b)] for the magic cluster appearing on either the faulted or unfaulted HUC. The model represents a triangular cluster with three Si atoms surrounded by six Ga atoms. The Si atoms, which are most likely the original edge Si adatoms on a $7\times7$ HUC, occupy three atop sites of the Si(111) surface and act as media to link the Ga atoms to form the triangular cluster. The Ga atoms whose lateral positions appear to be approximately on the $T_4$ sites have special bonding configurations. The edge Ga atoms are bonded to two atop Si atoms inside the cluster and one substrate Si atom outside the cluster, while the corner Ga atoms are bonded to one atop Si atom and two substrate Si atoms. Since the edge Ga atoms have one more bond to the atop Si atoms than the corner Ga atoms have, their vertical position is likely to be somewhat higher than that of the corner Ga atoms, qualitatively consistent with the image in Fig. 5(a). To be particularly emphasized is that the chemical bonds of the atoms in our model are completely satisfied and the number of dangling bonds on a HUC is drastically reduced from nine to three by the formation of such a $Ga_6Si_3$ cluster.[19] Therefore, this model provides good qualitative explanations for the extraordinary stability of the magic cluster and its strong size selection.

In conclusion, we have observed an unprecedented example of a self-organized nanostructure array with identical constituents and atomically precise lateral periodicity by the deposition of Ga on the Si(111)-$7\times7$ surface. The interesting self-organization process of the magic-cluster lattice, which proceeds through the ''digitized'' formation of magic clusters on a template surface with periodic attraction basins, reveals a pathway for the growth of precise nanostructure arrays on surfaces. In principle, a similar pathway leading to the creation of lattices of identical nanostructures might also be found in other material systems. Such lattices are particularly desirable for the study of interesting quantum properties, e.g., the coherent quantum coupling among their constituent nanostructures.

We gratefully thank Dr. J. -C. Lin and Dr. K. Liu for stimulating suggestions. This work was partly supported by the National Science Council (NSC 89-2112-M-001-040) of Taiwan, Republic of China. M. Y. L. was supported by a postdoctoral fellowship provided by Academia Sinica.

*Email: ylwang@po.iams.sinica.edu.tw

[1] H. Brune, Surf. Sci. Rep. **31**, 121 (1998).
[2] J. A. Venables, G. D. T. Spiller, and M. Hanbücken, Rep. Prog. Phys. **47**, 399 (1984).
[3] M. Y. Lai and Y. L. Wang, Phys. Rev. Lett. **81**, 164 (1998); M. Y. Lai and Y. L. Wang, Phys. Rev. B **60**, 1764 (1999).
[4] Ing-Shouh Hwang, Mon-Shu Ho, and Tien T. Tsong, Phys. Rev. Lett. **83**, 120 (1999).
[5] D. D. Chambliss, R. J. Wilson, and S. Chiang, Phys. Rev. Lett. **66**, 1721 (1991).
[6] H. Brune, M. Giovannini, K. Bromann, and K. Kern, Nature (London) **394**, 451 (1998).
[7] L. Vitali, M. G. Ramsey, and F. P. Netzer, Phys. Rev. Lett. **83**, 316 (1999).
[8] Q. Xie, A. Madhukar, P. Chen, and N. P. Kobayashi, Phys. Rev. Lett. **75**, 2542 (1995).
[9] J. Tersoff, C. Teichert, and M. G. Lagally, Phys. Rev. Lett. **76**, 1675 (1996).
[10] G. Springholz, V. Holy, M. Pinczolits, and G. Bauer, Science **282**, 734 (1998).
[11] D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990).
[12] G. P. Lopinski, D. D. M. Wayner, and R. A. Wolkow, Nature (London) **406**, 48 (2000).
[13] W. D. Knight *et al.*, Phys. Rev. Lett. **52**, 2141 (1984).
[14] M. Brack, Sci. Am. **277**, No. 6, 30 (1997).
[15] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).
[16] K. Cho and E. Kaxiras, Surf. Sci. **396**, L261 (1998).
[17] J. Nogami, S. Park, and C. F. Quate, Surf. Sci. **203**, L631 (1988).
[18] Typically, ~10% of the surface area is covered by defects, which consist of mostly HUC's without any cluster, some with clusters of different sizes, and a few larger islands on the boundaries between degenerate $7\times7$ domains.
[19] The dangling bonds in the corner holes are not included in the counting.