

Structure Determination of Surface Magic Clusters

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The structure of a type of surface magic cluster is determined by a combination of scanning tunneling microscopy, density-functional calculations, and dynamical low energy electron diffraction. The diffraction method is applicable because these clusters created through hierarchical self-organization of Ga deposited onto a Si(111)- 7×7 surface have identical size and structure and form an ordered array with exact translational symmetry. The unprecedented detailed structure information provided by the diffraction measurement is consistent with direct microscopic imaging and theoretical calculations.

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Nanostructures on surfaces are of great research interest because of their fundamental interests, novelties, and potential applications [1]. After years of extensive work primarily on the assembly of atoms into various nanostructures on surfaces, researchers have gone beyond the usual growth of surface nanostructures that typically leads to large size dispersion, structure variation, and random spatial distribution. Assembly of nanostructures with specific shapes, sizes, or ordered arrangement in several adsorbate-substrate material systems has been successfully demonstrated. For instance, one- and two-dimensional (2D) nanostructures were created by diffusion-controlled aggregation of adsorbates on surfaces [2], identical-size nanostructures were grown through the formation of surface magic clusters (SMC), which are different from gas phase magic-number clusters for the existence of interaction between the cluster and surface [3–6], and ordered nanostructure arrays were produced on strain-relief surfaces with periodical attractive potential wells [7,8]. Recently, by employing the concept of SMC formation on a periodical template surface, even the growth of perfectly ordered identical-size Ga, In, and Al nanostructure arrays has also been achieved [9–12].

While the fabrication of precise surface nanostructures has made exciting progress, the determination of their atomic structures remains extremely challenging. Until now, experimental information about their structures was obtained primarily by scanning tunneling microscopy (STM). This powerful tool unfortunately has intrinsic limitation in structure determination because it has poor elemental specificity and STM images reflect mainly an object's electronic density of states whose maxima do not always coincide with the positions of its nuclei. Therefore, STM observation alone usually cannot determine the structure of an object.

Recent successful fabrication of ordered SMC arrays on a Si(111) surface provides an exciting possibility of struc-

ture determination that is somehow overshadowed by the excitement in the hierarchical self-assembly of the adsorbates into identical nanostructures and ordered arrays. Only deeper understanding of the subject would lead to the appreciation that such an array is a 2D SMC lattice by itself, and it facilitates the use of diffraction methods for precise structure determination of its constituent SMC. Specifically, dynamical low energy electron diffraction (LEED) [13], which is a crystallographic tool designed for structure determination of surface by including the effects of multiple scattering of incident electrons, can now be applied to determine the structures.

In this Letter, we report the determination of the structure of self-assembled SMCs by combining STM imaging, first-principles density-functional calculations, and dynamical LEED analysis. The results of the LEED analysis provide unprecedented detailed structure information of the SMC, which is quantitatively consistent with theoretical calculations. We also show that the structure of a randomly distributed surface nanostructure can be derived if it exhibits almost identical STM images with its counterpart in a 2D nanostructure lattice.

The experiments were conducted in an ultrahigh vacuum chamber equipped with a STM and a LEED optics, which was connected to a charge-coupled device camera. Deposition of Ga on a Si(111) surface at $\sim 300^\circ\text{C}$ results in almost exclusive formation of a type of SMC on the center of a 7×7 half unit cell (HUC). The empty- and filled-state STM images are shown in Figs. 1(c) and 1(e). Deposition of ~ 0.2 ML of Ga leads to the complete filling of the HUC and the creation of a SMC lattice [Fig. 2(a)]. Since each triangular cluster contains six Ga atoms, as suggested by the six bright spots in Fig. 1(c), we consider two cluster models containing six Ga atoms. Model 1: the Ga atoms sit around the T_4 sites [14,15] while three Si atoms sit atop the substrate-Si atoms as shown in Fig. 1(a). This model, referred to as the Ga_6Si_3 model, has two appealing features. First, the Ga atoms

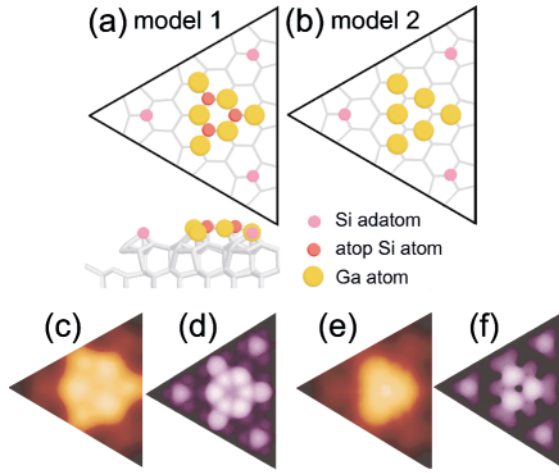


FIG. 1 (color). Models and STM images of a Ga SMC on the unfaulted HUC of the Si(111)- 7×7 surface: (a) Ga_6Si_3 model, (b) Ga_6 model. (c),(d) Empty-state experimental and calculated images ($V_{\text{tip}} = -2.0$ V); (e),(f) filled-state experimental and calculated images ($V_{\text{tip}} = +2.0$ V).

and their surrounding Si atoms form a bonding-satisfied configuration, which could qualitatively explain the extraordinary stability of the SMCs. Second, the three Si atoms could originate from the edge-Si adatoms of a Si(111)- 7×7 HUC [9] before the cluster formation, and there is no need to look for an unnatural source of Si atoms. Model 2: the cluster simply consists of six Ga atoms sitting around the T_4 sites as shown in Fig. 1(b). The validity of this model, referred to as the Ga_6 model, would require the migration of all the edge-Si adatoms to other 7×7 unit cells.

To choose from these two possible models that appear consistent with the STM observations, we performed dynamical LEED analysis. Figure 2(b) shows a normal-incidence LEED pattern, which appears to have characteristic 7×7 diffraction spots. The diffraction pattern is similar to that of the original Si(111)- 7×7 surface [Fig. 2(c)], while detailed inspection reveals distinct differences, as indicated by the arrows in Figs. 2(b) and 2(c). Such differences can be used as indicators for the formation of a SMC lattice.

A series of LEED patterns of the SMC lattice were captured using beam energies from 40 to 150 eV with an interval of 2 eV. Intensities of various diffracted beams were recorded as a function of the electron beam energy (LEED I - V spectra). In total, we used 12 symmetry-inequivalent LEED I - V spectra for the dynamical LEED analysis.

For data analysis, the symmetrized automated tensor LEED package [16], which calculates the intensities of the diffracted beams by combined space methods and a renormalized-forward-scattering perturbation method [13], was employed. Seven phase shifts were used to describe the scattering of a plane wave. The Pendry reliability factor (R_p) was chosen as the indicator for the agreement between the calculated and experimental I - V

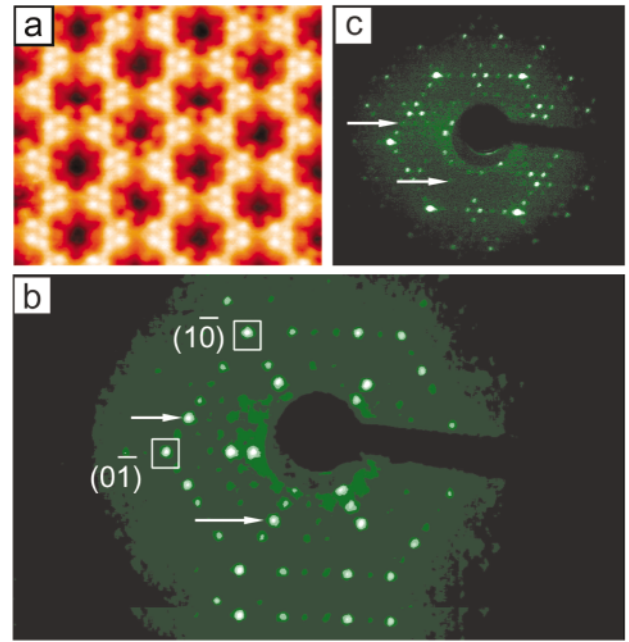


FIG. 2 (color). (a) Empty-state STM images of Ga SMCs on Si(111)- 7×7 surfaces. $V_{\text{tip}} = -1.9$ V. (b),(c) LEED patterns of the Ga SMC lattice and original Si(111)- 7×7 surfaces. Incident beam energy is 60 eV.

spectra. When searching for the optimum R_p , the simulated annealing scheme [17] with Metropolis criteria [18] was adopted to prevent R_p from being trapped in a local minimum. The lengths of the search steps were randomly generated and gradually reduced as R_p approached the minimum.

In addition to the bulk Si layers, three composite layers with $[102(\text{Si}) + 12(\text{Ga})]/98(\text{Si})/98(\text{Si})$ and $[96(\text{Si}) + 12(\text{Ga})]/98(\text{Si})/98(\text{Si})$ atoms were used for the dynamical LEED analysis of the Ga_6Si_3 and Ga_6 models, respectively. Atoms in the bulk were fixed, while those in the composite layer were allowed to move independently. In the search process, the averaged R_p of the 12 beams started from 0.54 and 0.56 and ended at 0.28 and 0.35 for the Ga_6Si_3 and Ga_6 models, respectively. Both of the optimized R_p were small, suggesting that the simulated annealing scheme was adequate for helping identify the global minima.

Figure 3 shows experimental and calculated spectra of $(\bar{1} 0)$, $(0 \bar{1})$, $(\frac{2}{3} \frac{2}{3})$, and $(\frac{2}{3} 0)$ beams for the optimized atomic configurations of Ga_6Si_3 and Ga_6 models. The spectra for the Ga_6Si_3 model match the experimental data very well for all the beams, while that of the Ga_6 model do not (certain peaks are completely out of phase). Therefore, both the reliability factor and the matching of the peak positions clearly support the validity of the Ga_6Si_3 model.

To further confirm the experimental LEED analysis, we carried out first-principles density-functional calculations using the Vienna *ab initio* simulation package with ultrasoft pseudopotential [19]. The calculation employed

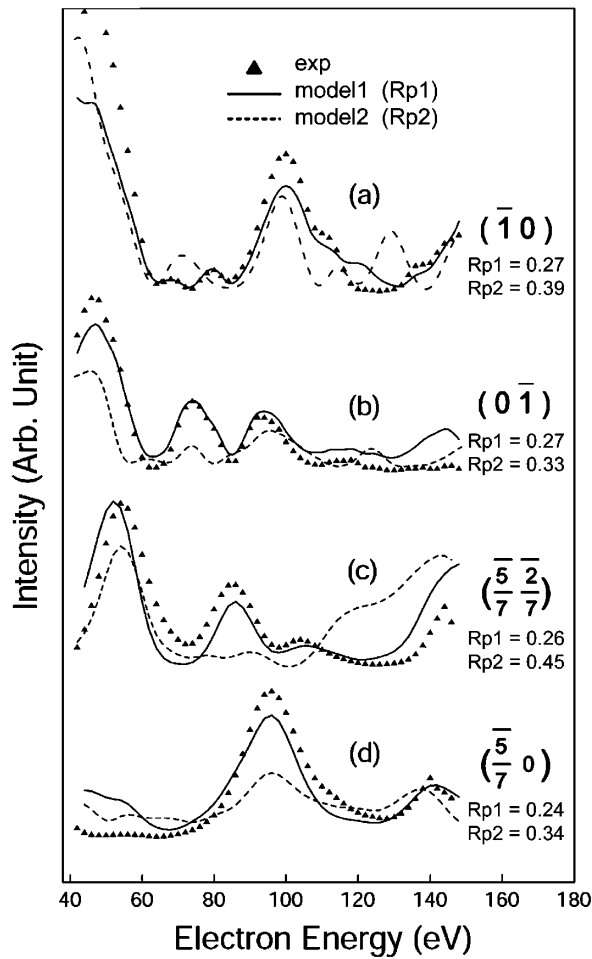


FIG. 3. Experimental LEED I - V data of the Ga SMC lattice and calculated dynamical LEED spectra of the optimized atomic configurations for model 1 (Ga_6Si_3) and model 2 (Ga_6). Four beams: (a) $(\bar{1} 0)$, (b) $(0 \bar{1})$, (c) $(\frac{5}{7} \frac{2}{7})$, and (d) $(\frac{5}{7} 0)$ are shown.

a plane wave basis set with an energy cutoff of 130 eV and Γ -point in the Brillouin zone sum. In addition to two clusters and six Si adatoms, a slab geometry containing six bilayers of a $\text{Si}(111)$ - 7×7 unit cell with 49 H atoms passivating the bottom 1×1 Si dangling bonds and a vacuum layer of 10 Å were used in the calculation.

According to our calculations, the total energy of the Ga_6Si_3 model is 4.5 eV lower than that of the Ga_6 model per cluster if the three atop-Si atoms are assumed to diffuse to the favorite sites of other 7×7 unit cells, confirming the validity of the Ga_6Si_3 model. Besides, the total energy of the Ga_6Si_3 model is 1.79 eV per cluster lower than that of a variant Ga_6Si_3 model derived from exchanging the corner-Ga atoms with the atop-Si atoms in the Ga_6Si_3 model, supporting the fact that the three Si atoms inside the clusters come from the original edge-Si adatoms. As shown in Table I, the Ga_6Si_3 model's atomic structures determined by the dynamical LEED analysis are quantitatively consistent with those from theoretical calculations. The bond lengths between any pair of Ga and Si atoms are very close, from 2.42 to 2.54 Å. An atop-Si atom (invisible from the STM imaging) stands 2.41 Å above a substrate-Si atom. The length of this Si-Si bond is close to that of the bulk Si-Si bond (2.35 Å), indicating that the Ga atoms of a Ga_6Si_3 cluster do not exert too much stress on the atop-Si atoms. The edge- and corner-Ga atoms are both slightly lower than the atop-Si atoms, with height differences of 0.26 and 0.60 Å, respectively. The result that edge-Ga atoms are higher than the corner-Ga atoms is qualitatively consistent with the empty-state STM images. We note that similar height differences were also observed in In and Al SMCs on the $\text{Si}(111)$ - 7×7 surface [10,11]. This seemingly "universal" height difference could be qualitatively rationalized as follows. The corner-Ga atom is located approximately at the geometric center of the triangle formed by one atop-Si and two substrate-Si atoms while the edge-Ga atom at that of the triangle formed by two atop-Si and one substrate-Si atoms. Since the two triangles have similar size and slope, the vertical position of the edge-Ga atom is expected to be higher than the corner one.

The dynamical LEED analysis indicates the SMC is an equilateral triangle where the lateral distance between two edge-Ga atoms is 4.32 Å, while that between the edge- and corner-Ga atoms is 4.21 Å. The filled-state STM image of the SMC [9] also appears as an equilateral triangle. However, the empty-state STM image [Fig. 1(a)] looks like a deformed equilateral triangle with the three

TABLE I. Structure data of Ga SMC. De-e and De-c represent the distances between two edge-Ga and between edge-Ga and corner-Ga. Ga(c), Ga(e), and Si(a) are corner-Ga, edge-Ga, and atop-Si. dZ is the height relative to atop-Si.

	De-e (Å)	De-c (Å)	Bond	Length (Å)	Atom	dZ (Å)
STM	5.6	4.3				
Dynamic LEED	4.32	4.21	Ga(c)-Si	2.46, 2.46, 2.50	Ga(c)	-0.60
			Ga(e)-Si	2.48, 2.48, 2.52	Ga(e)	-0.26
			Si(a)-Ga	2.48, 2.48, 2.50	Si(a)	0.00
<i>Ab initio</i> nuclei	4.24	4.11	Ga(c)-Si	2.47, 2.47, 2.42	Ga(c)	-0.62
			Ga(e)-Si	2.44, 2.44, 2.54	Ga(e)	-0.27
			Si(a)-Ga	2.44, 2.44, 2.42	Si(a)	0.00
PCD	4.72	4.41				

brightest edge spots protruding outwardly obviously. Specifically, the lateral distance between the two brightest edge spots is as large as 5.6 Å. Since this large lateral separation is independently observed by other researchers [20] and in the Al SMC [11], it is unlikely to be an experimental error. To understand its origin, we study the partial charge density (PCD) distribution of the SMC as calculated by density-functional theory. The calculated STM images in Figs. 1(d) and 1(f) are in qualitative agreement with experiment [Figs. 1(c) and 1(e)]. The distance between the charge density maximum associated with two edge-Ga atoms is 4.35 Å, slightly larger than the distance (4.2 Å) between the two nuclei. If one chooses the “apparent separation” between two edge-Ga atoms as the lateral distance between two corresponding highest points of the PCD contour surface whose charge density is 50% of maximum charge density, then the apparent separation increases to 4.72 Å, still significantly smaller than 5.6 Å of the experimental empty-state STM image. We speculate the apparent lateral expansion on the experimental STM image is due to the convolution effect between the finite-sized STM tip and the constant-PCD contour, which translate a step height into a broader slope, leading to unusually large separation between the two brightest spots. However, more studies are needed to clarify the mystery quantitatively.

It is interesting to note that the above analysis not only determines the structure of Ga SMCs on a Si(111)-7 × 7 surface, but also clarifies the structure of a type of randomly distributed SMC in another system. As mentioned above, a type of triangular SMC exhibiting three atoms on each of its sides was observed on the Si(111)/Ga-√3 × √3 surface [3], as shown in Fig. 4(a). The empty- and filled-state STM images of such random SMCs are very similar to those of the SMCs in the 2D lattice [Fig. 4(b)], as shown by the height profiles across these two clusters in Fig. 4(c). The similarity in STM images strongly suggests that these two SMCs are of the same type. Therefore the structure of the Ga SMC determined in this work provides strong evidence to support the Ga₆Si₃ model proposed previously and excludes the Ga₆ model for the “side = 3” SMC observed on the Si(111)/Ga-√3 × √3 surface.

In conclusion, we have combined STM direct imaging, dynamical LEED, and first-principles density-functional calculations to provide the first precise structure determination of self-assembled nanostructures in an adsorbate-substrate system where a 2D lattice of SMCs has been successfully created. STM imaging is used to show the existence of identical-size SMCs and the formation of 2D SMC lattices. Dynamical LEED allows the precise structure determination of the SMC lattice and its constituent SMC. First-principles density-functional calculations further confirm the experimental results. In principle, the methodology we have developed for the structure determination of Ga-induced SMCs on Si(111)-7 × 7 surfaces

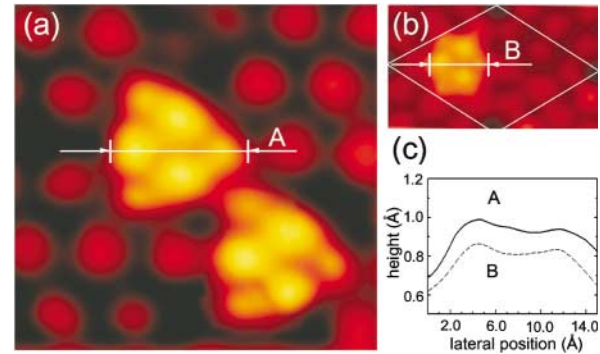


FIG. 4 (color). (a) STM image of side = 3 surface magic cluster observed on the domain boundaries of a Si(111)/Ga-√3 × √3 surface. (b) STM image of Ga SMC in the 2D lattice. (c) STM tip-height profiles of the two clusters ($V_{\text{tip}} = -2.2$ eV).

can be applied to determine the structure of other SMCs. The detailed structure information provides an important cornerstone for our further understanding of the physical and chemical properties of the SMCs and facilitates the reliable use of *ab initio* calculations for predicting some of its properties that are accessible to experimental methods.

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