Structural properties of Ga clusters on Si(111)

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Using the first-principles molecular-dynamics method in the energy-minimization application, we calculate the detailed geometry of Ga decamers on the Si(111) surface observed by scanning tunneling microscopy (STM). The calculated relative heights of Ga adatoms agree reasonably well with STM data. Our total-energy results support the Ga-Si honeycomblike triangular decamer model proposed by Lai and Wang [Phys. Rev. B **60**, 1764 (1999)] to explain the Ga clusters observed in their STM measurements.

Adsorption of Ga on the Si(111) surface has recently attracted vigorous experimental[1–3] and theoretical[4] investigations. Deposition of 1/3 ML of Ga on Si(111), and subsequent annealing at ~550 °C, were found to lead to the formation of a $\sqrt{3}\times\sqrt{3}R30°$ Ga adlayer, in which Ga adatoms sit at T_4 sites rather than H_3 sites.[5,6] When the Ga coverage was increased to 0.8 ML and the sample was subsequently annealed at 300–500 °C, a 6.3×6.3 incommensurate overlayer structure[7] with an approximate periodicity of 2.4 nm,[8] and closed packed hexagonal aggregates, were observed by scanning tunneling microscopy (STM). Recently, Lai and Wang[9] observed triangular magic Ga clusters on the $\sqrt{3}\times\sqrt{3}R30°$ reconstructed Ga/Si(111) surface when they first deposited 1/3 ML of Ga at room temperature on Si(111), subsequently annealed it at 550 °C, and then deposited an additional 1/6 ML of Ga at 200–500 °C and annealed it for ~10 sec. The numbers of Ga adatoms in these magic clusters were found to be $n(n+1)/2$, where n $(=2, 3, 4, \text{and } 5)$ is the number of adatoms on each side of the triangle. Decamers with $n=4$ were found to be the most abundant among them.[9] To understand the formation of these Ga decamers on Si(111), we have carried out this study.

We use the local-orbital density-functional molecular-dynamics method.[10–12] This method is based on the norm-conserving pseudopotential[13] method with a basis set containing the Bloch sums of s, p_x, p_y, and p_z local orbitals. This method was originated by Sankey and Niklewski,[10] later modified by Tsai, Dow, and Sankey[11] to include charge transfer, and most recently modified by Tsai and Hass[12] to calculate the full charge density and the corresponding potential self-consistently. This method has been shown to work well for semiconductors.[14–16] In this work, we first determine the theoretical lattice constant of the bulk Si crystal to be 5.639 Å, which differs 3.8% from the experimental value of 5.430 72 Å, using a cubic unit cell and sampling the Γ point. This theoretical lattice constant and a repeated four-layer Si slab (i.e., supercell) model with a vacuum region about 10.88 Å wide are then used for our structural models. Our method calculates the charge density self-consistently using Johnson's mixing scheme[17] with a tolerance of $0.000\,000\,1e$ (where e is the magnitude of the electronic charge) for each atom. The Newtonian equation of motion is solved numerically for a time step of 0.62 fs using the fifth-order Gear algorithm.[18] We started the calculations at zero temperature and used a quenching scheme[11,14] to let all atoms settle to their stable or metastable positions, with the criterion that the force acting on each atom is less than 0.1 eV/Å. The uncertainty in the equilibrium or metastable position is estimated to be less than 0.005 Å.

We have chosen the $3\sqrt{3}\times3\sqrt{3}R30°$ unit cell as inferred from the STM measurements of Lai and Wang [Fig. 2(a) of Ref. 19] for all our structural models including the 1/3-ML $\sqrt{3}\times\sqrt{3}R30°$ Ga/Si(111) surface model, and sampled only the Γ point in optimizing the surface geometry due to the complexity of this system. The bottom-layer Si atoms are attached with artificial H atoms to saturate their dangling bonds. We first calculate the optimized geometry of the 1/3-ML $\sqrt{3}\times\sqrt{3}R30°$ Ga covered surface. Following the experimental observations, we place the Ga adatoms at the T_4 site. The optimized surface geometry is shown in Fig. 1, in which the empty T_4 site is denoted as T_4'. For the STM observed Ga decamer clusters after additional Ga atoms were deposited on the 1/3-ML $\sqrt{3}\times\sqrt{3}R30°$ Ga-covered surface, we have chosen three structural models. In these three models three Ga adatoms are added to the original nine Ga adatoms of the 1/3-ML $\sqrt{3}\times\sqrt{3}R30°$ Ga-covered surface in the $3\sqrt{3}\times3\sqrt{3}R30°$ unit cell. The top and side views of the fully relaxed atomic arrangement of models (1), (2) and (3) are shown in Figs. 2(a), 2(b), and 2(c), respectively. In Fig. 2(a) Ga adatoms 3, 7, and 9 sitting at the T_4' sites, are the three additional Ga adatoms in the unit cell. Model (2), in which ten of the 12 Ga adatoms form a triangular structure, i.e., a decamer, as shown in Fig. 2(b), was first proposed by Lai and Wang to explain their STM observations.[9] Within the decamer, corner and central adatoms 6, 2, 8, and 11 are located at the original T_4 sites, and side adatoms 3, 4, 5, 7, 9, and 10 are located at the T_4' sites. The three open squares in Fig. 2(b) near the center of the three sides indicate the missing sites originally occupied by $\sqrt{3}\times\sqrt{3}R30°$ Ga adatoms. Model (3) is a modified decamer model, in which the six side adatoms are moved to atop sites near the missing Ga adatom sites marked by the open squares as shown in Fig. 2(c).

Side views of the three models have some common characteristics as those of the original $\sqrt{3}\times\sqrt{3}R30°$ structure

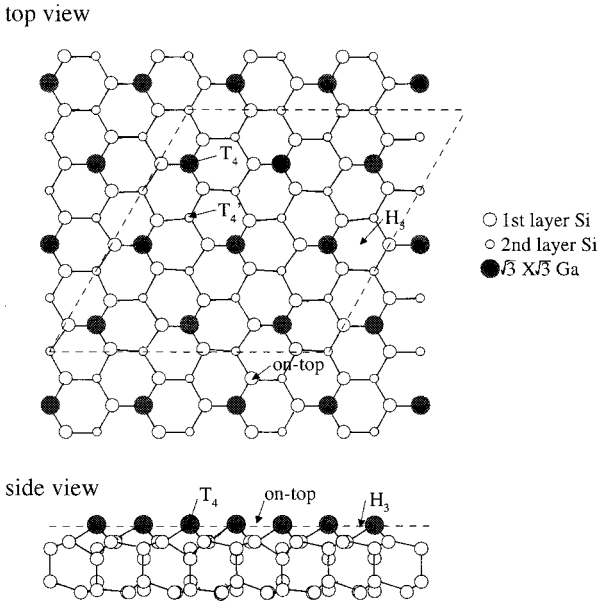

FIG. 1. Top and side views of the optimized Si(111) $\sqrt{3}\times\sqrt{3}R30°$ Ga surface structure. Filled circles denote the Ga adatoms. Larger and smaller open circles in the top view denote surface and second-layer Si atoms, respectively.

with a 1/3-ML Ga coverage (Fig. 1), which were observed previously by Kawazu and Sakama.[20] We find that the second-layer Si atoms beneath the Ga adatoms are depressed substantially by about 0.74 ± 0.01 Å. They in turn depress the neighboring third-layer Si atoms downwards by about 0.62 ± 0.02 Å. The depression of these Si atoms is presumably caused by that Ga adatoms and surface Si atoms tend to conserve their bond length. We also find that surface-layer Si atoms are attracted by the surrounding Ga adatoms and have a lateral shift toward Ga. For model (1), as shown in Fig. 2(a), Ga adatoms 3, 7, and 9 lie higher than those at the original T_4 site except for the central adatom 6. Adatom 6 is approximately in the same plane as those of adatoms 3, 7, and 9. For model (2), as shown in Fig. 2(b), the central adatom 6 lies higher than side adatoms 3, 4, 5, 7, 9, and 10 by about 0.18 Å. Corner adatoms 2, 8, and 11 lie higher than the original T_4-site adatoms by about 0.05 Å, but lie lower than side adatoms by about 0.34 Å. The top view of Fig. 2(b) shows that corner, side, and central Ga adatoms are each coordinated with two, four, and six Ga adatoms, respectively. The height of the Ga adatom is correlated with the number of neighboring Ga adatoms; i.e., the larger the coordination number, the higher the adatom is located. For model (3), as shown in Fig. 2(c), adatoms 3, 5, 4, 7, 9, and 10 are initially placed atop the surface-layer Si atoms. Our energy-minimization calculation results in positions shown in Fig. 2(c); they form three dimers.

Total energies of models (1)–(3) calculated with the single special k point of Cuningham[21] for the hexagonal lattice are $-107.097\,275$, $-107.048\,681$, and $-106.993\,055$ eV/atom, respectively. Model (1) has the lowest total energy. Models (2) and (3) have total energies 0.215 and 0.46 eV per 1×1 cell, respectively, higher than that of model (1). The original triangular decamer model proposed by Lai and Wang[9] has a higher total energy than that of model (1). In other words, this triangular decamer model is not favorable. The physical reasons for this are described in the following. For model (1), each Ga adatom is coordinated with three Si surface atoms. Since the Ga atom has three valence electrons, the Ga adatom has used up all its valence electrons. All Si surface atoms except those coordinated with Ga adatoms 3, 6, 7, and 9 are bonded with three second-layer Si atoms and one Ga adatom, so that they do not have any

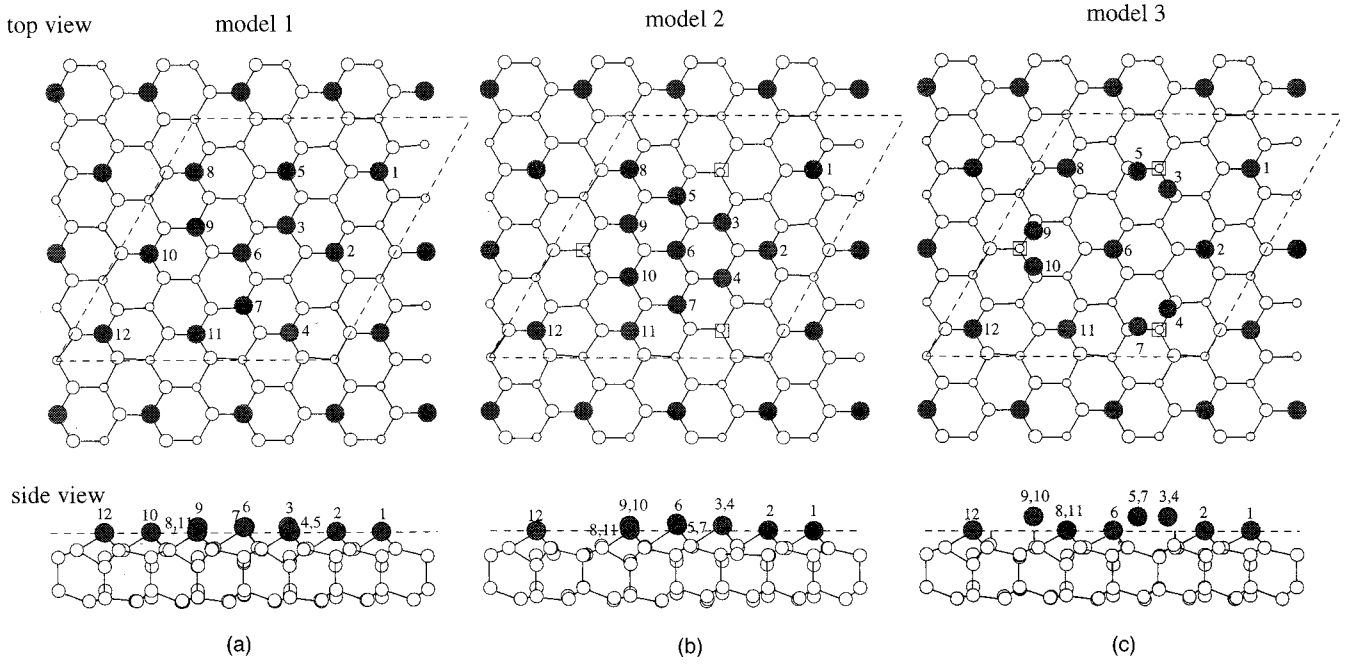

FIG. 2. Top and side views of the optimized surface geometry of decamer models (1)–(3) considered in this study. (a), (b) and (c) correspond to models (1), (2) and (3), respectively. Filled circles denote the Ga adatoms. Larger and smaller open circles in the top view denote surface and second-layer Si atoms, respectively. Open squares in (b) and (c) represent the missing Ga adatoms of the $\sqrt{3}\times\sqrt{3}R30°$ surface.

dangling bond. The Si surface atom coordinated with Ga adatoms 3, 6, 7, or 9 has already been bonded with three second-layer Si atoms and another Ga adatom. Thus, the bond between this Si atom and the Ga adatom 3, 6, 7, or 9 is weaker and has a larger bond length. That is why Ga adatoms 3, 6, 7, and 9 lie higher than other Ga adatoms. For model (2), the dangling bonds of the three Si surface atoms located near to the open squares shown in Fig. 2(b) are not saturated. For this model, the three Si surface atoms surrounding adatom 6 are coordinated with three second-layer Si atoms and three Ga adatoms. Their coordination number, 6, is two more than enough for Si with four valence electrons. Thus, it is expected that the bond between adatom 6 and its three neighboring Si surface atoms are the weakest and has the longest bond length. This is the reason why central adatom 6 lies higher than other adatoms. For side adatoms, two neighboring Si surface atoms have a coordination number of 6 and the third has a coordination number of 4. For corner adatoms, one neighboring Si surface atom has a coordination number of 6 and the other two have a coordination number of 4. Thus it can be expected that the height of the Ga adatom decrease with the order of central, side, corner, and original T_4-site adatoms as described previously. Model (3), as shown in Fig. 2(c), has the same three Si dangling bonds as model (2). The formation of three Ga dimers renders this model more favorable than model (2). The nearest-neighbor Ga-Ga distance of 3.84 Å is about twice the atomic radius of the Ga atom of about 2.0 Å. Since the orbitals of valence electrons of an atom extend beyond its atomic radius, there is an overlapping between orbitals of neighboring Ga adatoms. Thus the triangular decamer of model (2) may form weak metallic bonding. Our total-energy results indicate that this weak metallic bonding is not important enough to render model (2) more favorable.

Based on a recent STM study of an incommensurate Ga-covered Si(111) surface and earlier x-ray standing-wave measurements,[3] which suggested that the apparent Ga clusters might actually be a Ga-Si graphite-like clusters, Lai and Wang proposed a modified triangular decamer model.[19] This modified model differs from model (2) [Fig. 2(b)] by the addition of six Si adatoms located at atop sites, so that Ga and Si adatoms form a honeycomblike or graphitelike clusters. These Si adatoms are coordinated with one Si surface atom and three Ga adatoms, so that they do not introduce any new dangling bond. Their presence provides additional bonding for Ga adatoms that stabilizes the aggregation of Ga adatoms into the triangular decamer. The top and side views of the relaxed geometry of this modified model is shown in Fig. 3. The top view shows that the six Si adatoms are located approximately at atop sites with lateral deviations within 0.133 Å, and that the side and corner Ga adatoms have about 0.15-Å lateral deviation from T_4' or T_4 sites. The side view shows that the central Ga adatom (adatom 6) of the decamer lies highest among the Ga adatoms, and is higher than the $\sqrt{3}\times\sqrt{3}R30°$ Ga adatoms by about 1.11 Å. The Si adatoms lie lower than the central Ga adatom by about 0.20 Å. Side Ga adatoms 3, 4, 5, 7, 9, and 10, which are bonded with two Si adatoms and three Si surface atoms, are higher than the $\sqrt{3}\times\sqrt{3}R30°$ Ga adatoms by about 0.60 Å. Corner Ga adatoms 2, 8, and 11, which are bonded with a Si adatom and three Si surface atoms, are higher than $\sqrt{3}\times\sqrt{3}R30°$ Ga

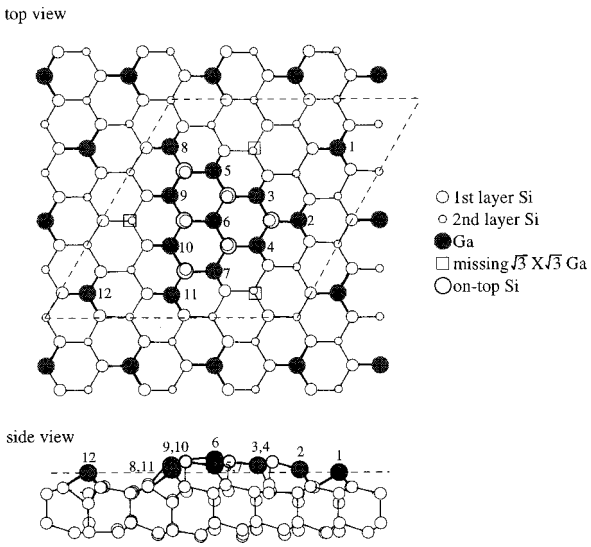

FIG. 3. Top and side views of the modified triangular Ga decamer model proposed by Lai and Wang. Six additional Si adatoms are denoted by the largest open circles. Filled circles denote the Ga adatoms. The second largest and smaller open circles in the top view denote surface and second-layer Si atoms, respectively. Open squares represent the missing Ga adatoms of the $\sqrt{3}\times\sqrt{3}R30°$ surface.

adatoms by about 0.23 Å. The empty-state STM image of Lai and Wang showed that the side and central Ga adatoms appear to be higher than the corner Ga adatoms by 0.2 and 0.7 Å, respectively.[19] However, the filled-state STM image could not resolve height differences for the Ga adatoms, though the center of decamer appeared to be higher than the surrounding atoms by 1.2 Å.[19] Our calculated relative heights of the Ga adatoms in the decamer seem to agree reasonably well with STM observations, especially in the order of heights. The empty-state STM image and the depth profile passing through one of the corner adatoms and the central adatom of Lai and Wang did not show the Si adatom between them. These STM measurements had a tip bias of 2.5 V. Our analysis of the orbital components for the eigenstates within 2.5 eV above the Fermi level shows that the components of Si-adatom orbitals overall are smaller than those of the Ga adatoms. Since the size of the Ga atom is much larger than that of the Si atom, the contribution of the Si adatom to the STM image might be overshadowed by surrounding Ga adatoms and was not resolved in the STM measurements.

The modified decamer model of Lai and Wang[19] has six additional Si adatoms. We find that the influence of these Si adatoms on the bonding between the bottom-layer Si atoms and artificial H atoms is not negligible due to our use of a thin four-layer supercell model. Thus we do not have a common footing on which to compare free energies of this model and models (1)–(3), and to determine whether this model is more stable. This model and model (2) are the only two models considered which are compatible with STM images. Since our total-energy results show that model (2) is not favorable, this model is more likely to account for the triangular Ga decamer observed by STM. The necessity of the six additional Si adatoms to stabilize the Ga decamer is further supported by STM observations that the triangular Ga

decamers are always oriented with their three sides along the $[11\bar{2}]$, $[1\bar{2}1]$, and $[\bar{2}11]$ directions. From Fig. 3 we can see that if Ga adatoms 2, 8, and 11 are moved to the sites marked by the open squares, Ga adatoms form a similar triangular decamer with its three sides along the $[\bar{1}\,\bar{1}2]$, $[\bar{1}2\bar{1}]$, and $[2\bar{1}\,\bar{1}]$ directions. Without the six Si adatoms, both orientations have similar energies and should have an equal likelihood of being observed by STM. With the Si adatoms, the rotated orientation will be less favorable because the Si adatoms bonded to Ga adatoms 2, 8, and 11 are not atop the surface-layer Si atoms, and are not energetically favorable. That is why Si adatoms are crucial to account for the absence of the rotated decamer in STM images.

In summary, using the first-principles molecular-dynamics method in the total-energy minimization application, we obtain an optimized geometry of the triangular Ga decamer models proposed by Lai and Wang to explain their STM images and two other possible models. The calculated relative heights of the Ga adatoms in the decamer agree reasonably well with STM data. Our total-energy results support the most recent model of Lai and Wang[19] for the observed triangular Ga decamer, in which the aggregation of Ga adatoms is stabilized by Si adatoms that form a Ga-Si honeycomblike cluster. The earlier model proposed by Lai and Wang[9] is found to be the least favorable among the structural models considered in this study.

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