

Doping of Magic Nanoclusters in the Submonolayer In/Si(100) System

V. G. Kotlyar,¹ A. V. Zotov,^{1,2,5} A. A. Saranin,^{1,3,5} E. N. Chukurov,¹ T. V. Kasyanova,^{1,3} M. A. Cherevik,¹
I. V. Pisarenko,¹ H. Okado,⁴ M. Katayama,⁵ K. Oura,⁵ and V. G. Lifshits^{1,2,3}

¹*Institute of Automation and Control Processes, 690041 Vladivostok, Russia*

²*Department of Electronics, Vladivostok State University of Economics and Service, 690600 Vladivostok, Russia*

³*Faculty of Physics and Engineering, Far Eastern State University, 690000 Vladivostok, Russia*

⁴*Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki, Osaka 567-0047, Japan*

⁵*Department of Electronic Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

(Received 12 March 2003; published 11 July 2003)

Si(100)4 × 3-In reconstruction is essentially a superlattice of magic (identical-size) Si₇In₆ nanoclusters. Using scanning tunneling microscopy (STM) observations, we have found that under appropriate growth conditions up to 35% of these clusters can be modified; namely, two Si atoms in the cluster can be replaced by two In atoms, thus forming a Si₅In₈ cluster. This modification can be considered as a doping of the magic cluster, as it changes the electronic properties of the cluster from semiconducting towards metallic. The doped cluster is less rigid than the ordinary one and swings in the electrical field of the STM tip. The atomic structure and stability of the doped magic cluster have been examined using first-principles total-energy calculations.

DOI: 10.1103/PhysRevLett.91.026104

PACS numbers: 68.35.-p, 68.37.Ef, 68.55.Jk

The fabrication and characterization of magic nanoclusters, i.e., the clusters with an enhanced stability at selected sizes, have become exciting areas of research. Very recently, the possibility for the formation of highly ordered superlattices built of magic nanoclusters has been demonstrated [1–3]. The goal has been achieved with group-III metals (Al, In, Ga) deposited onto a Si(111)7 × 7 surface. The forming artificial cluster crystals contain identical nanoclusters, each built of exactly six metal atoms linked by three Si atoms. An overview of the known results on the growth of the group-III metals on a Si(100) surface also reveals a vivid tendency for the magic cluster formation [3]. In particular, the deposition of In onto a heated Si(100)2 × 1 surface results in the formation of identical nanoclusters, whose spatial distribution is random at low In coverages, but they become arranged into the well-ordered Si(100)4 × 3 superlattice at a saturating coverage of ~0.5 ML of In [4,5]. The atomic structure of the In/Si(100) cluster has been a subject of furious debate over the last few years [5–12], and most of the recent experimental and theoretical studies have favored the model proposed by Bunk *et al.* [6], in which six In atoms and seven Si atoms form a stable pyramidlike Si₇In₆ cluster.

In the present study, using scanning tunneling microscopy (STM) analysis and first-principles total-energy calculations, the new fascinating features of the In-Si magic clusters on Si(100) have been revealed. It has been found that under appropriate conditions the Si₇In₆ cluster can be modified; namely, two Si atoms of the original cluster can be substituted by two In atoms, thus forming the Si₅In₈ cluster. This modification can be treated as a *doping of magic cluster*. Scanning tunneling spectroscopy (STS) observations have shown that the doping changes electronic properties of the cluster: the

nondoped cluster exhibits semiconductor properties, while the doped cluster displays metallic properties due to the developing of an extra electron density of states within a forbidden gap.

Experiments were performed with Omicron STM operated in an ultrahigh vacuum (~1 × 10⁻¹⁰ Torr). Atomically clean Si(100)2 × 1 surfaces with a minimal number of defects were prepared using the surface preparation procedure described in Ref. [13]. Indium was deposited from a Ta foil tube at a rate of about 0.1 ML/min. In most cases, the samples were heated by radiation from the tungsten heater located at the sample back. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

As illustrated in Fig. 1(a), a saturating adsorption of In on Si(100) at ~500 °C produces a 4 × 3 superlattice of the In-Si clusters having identical size and shape. Deposition of In onto this surface at the lower temperature of ~450 °C results in the surface structure shown in

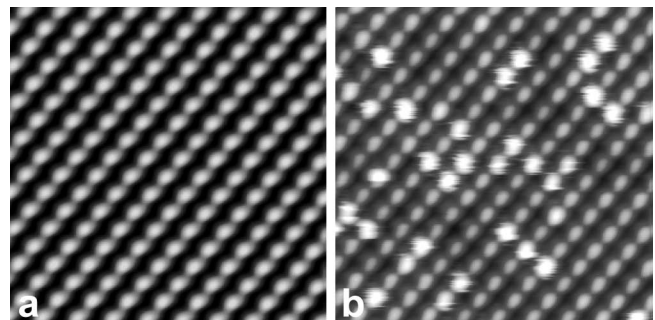


FIG. 1. The 170 × 170 Å² filled state ($V_t = +1.8$ V) STM images of the Si(100)4 × 3-In surface formed (a) upon adsorption of ~0.5 ML of In at 500 °C and (b) upon subsequent In deposition at 450 °C. Formation of “bright” clusters is clearly seen.

Fig. 1(b). One can see that the basic 4×3 superstructure is preserved, but some clusters show up brighter. At the early stages of In deposition, the fraction of the “bright” clusters grows linearly with the dose but eventually reaches the saturation of $\sim 35\%$ (Fig. 2). The slope of the initial linear dependence provides an upper estimate for the number of the additional In atoms incorporated in the bright cluster. The slope of the plot for In adsorption at 440°C yields the value of two additional In atoms per the bright cluster (see Fig. 2). The increment rate of the bright cluster fraction is lower (hence, the seeming number of In atoms per cluster is greater) both at lower and at higher temperatures. At lower temperatures ($\sim 300\text{--}400^\circ\text{C}$), this is a consequence of the fact that besides the bright cluster formation some In are accumulated in various In aggregates, like meandering chains or shapeless clusters. At higher temperatures (above $\sim 450^\circ\text{C}$), In desorption becomes noticeable. Upon annealing above $\sim 480^\circ\text{C}$, the bright clusters can be completely eliminated from the surface.

There are two alternative ways for the transformation of the ordinary In-Si cluster to the bright one, namely, (i) just by adding extra In atoms and (ii) by replacing some Si atoms by In atoms. The latter case would inevitably involve Si redistribution, as upon Si substitution for In some Si atoms become liberated. It has been recently demonstrated for numerous adsorbate/substrate systems that when a forming adsorbate-induced reconstruction incorporates a fraction of the top atomic layer of the substrate, the surface develops into the two-level system of flat monatomic islands on terrace (Fig. 3) and the area fraction occupied by these islands S is linked to the top substrate atom density in the reconstruction [here, the top Si atom density of the $\text{Si}(100)4 \times 3\text{-In}$ phase, $\Theta_{\text{Si}}^{4 \times 3}$] by the expression

$$\Theta_{\text{Si}}^{4 \times 3} = \Theta_{\text{Si}}^{2 \times 1} - S, \quad (1)$$

where $\Theta_{\text{Si}}^{2 \times 1}$ is the top Si atom density of the original clean $\text{Si}(100)2 \times 1$ surface; ideally this is one monolayer

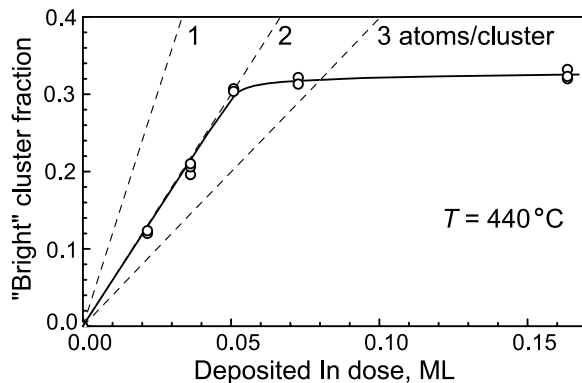


FIG. 2. Fraction of “bright” clusters versus deposited In amount. Dashed lines show calculated plots for the cases when each bright cluster adopts an extra one, two, and three In atoms.

026104-2

($1 \text{ ML} = 6.8 \times 10^{14} \text{ cm}^{-2}$), but actually somewhat lower (typically $0.98\text{--}0.99 \text{ ML}$) due to the presence of missing-dimer defects. Evaluation of the STM images have revealed that when the $4 \times 3\text{-In}$ surface is free of bright clusters, the islands occupy an area fraction of 0.40 ± 0.02 which corresponds to the top Si atom density $\Theta_{\text{Si}}^{4 \times 3} = 0.58 \pm 0.02 \text{ ML}$. Note this result coincides with the value of $7/12 \text{ ML}$ predicted by the Bunk’s model [6]. In the case of $4 \times 3\text{-In}$ surface with $\sim 35\%$ of bright clusters, the area fraction occupied by islands has been found to be 0.46 ± 0.02 ; hence the mean top Si atom density is $0.52 \pm 0.02 \text{ ML}$ [14]. One can calculate that this means that from every bright cluster 2 ± 1 Si atoms are removed.

Recent STM observations have revealed that the ordinary In-Si cluster has a bias-dependent STM appearance [4,7]: It shows up as a single round protrusion in the filled state images, as a pair of oval protrusions in the empty state images at $\sim 2 \text{ eV}$ bias and as three oval protrusions in empty state images at $\sim 1 \text{ eV}$ bias. Our STM observations of the bright clusters at various bias voltages have shown that the bright cluster has an STM appearance similar to that of the ordinary cluster. It also displays a single round protrusion in the filled states and three oval protrusions in the empty states at $\sim 1 \text{ eV}$ bias but with enhanced apparent height (brightness) of the central part of the cluster [Fig. 4(a)]. In the empty states at $\sim 2 \text{ eV}$ bias [Fig. 4(b)], an intense bright protrusion develops at the location of the central depression typical for the ordinary cluster. These results imply that the bright cluster plausibly preserves the basic structure of the ordinary cluster and the main modifications concern the central part of the cluster.

Taking the Bunk’s structure [see Fig. 5(a)] as a basal model, consider a possible atomic arrangement of the bright cluster. The most plausible model is shown in Fig. 5(b). In this model, in agreement with the experimental results the two Si atoms in the ordinary cluster [labeled Si3 and Si3’ in Fig. 5(a)] are replaced by two In atoms [labeled In3 and In3’ in Fig. 5(b)].

To examine the atomic structure and stability of the modified cluster, we carried out the calculations, in which the first-principles molecular-dynamics scheme proposed

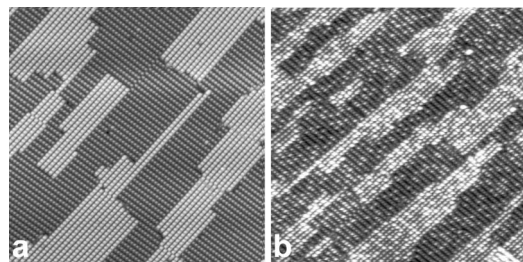


FIG. 3. The $750 \times 750 \text{ \AA}^2$ filled state ($V_t = +1.9 \text{ V}$) STM images showing development of the two-level system of monatomic islands on the terrace for the $\text{Si}(100)4 \times 3\text{-In}$ surface (a) without and (b) with “bright” clusters. The area fraction occupied by islands is 0.40 ± 0.2 in (a) and 0.46 ± 0.02 in (b).

026104-2

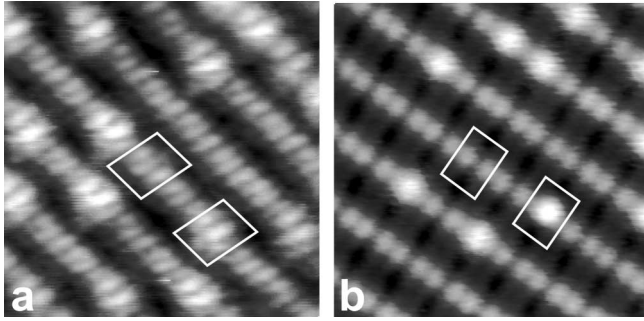


FIG. 4. High-resolution ($80 \times 80 \text{ \AA}^2$) empty state STM images of the $\text{Si}(100)4 \times 3\text{-In}$ surface with “bright” clusters acquired (a) at $V_t = -1.0 \text{ V}$, $I = 0.01 \text{ nA}$; (b) at $V_t = -2.0 \text{ V}$, $I = 0.16 \text{ nA}$. The ordinary and bright clusters are outlined.

by Car and Parrinello [15] was used. The mixed Si-In layer was placed on top of the slab formed by five Si atomic layers (each one containing 12 Si atoms) with dangling bonds on the other side of the slab being passivated with H atoms. Norm-conserving pseudopotentials including s and p nonlocal terms were employed to describe the electron-ion interaction. The nonlocal part of the pseudopotential was treated by the Kleinman-Bylander procedure [16]. The energy cutoff for the plane-wave expansion was set to 10 Ry.

As a starting point, we have calculated the structural parameters of the ordinary Si_7In_6 cluster which appear to be in a reasonable agreement with the x-ray diffraction data [6] and in a good agreement with the results of the recent calculations [12](see Table I). In the same table, the calculated bond lengths in the bright Si_5In_8 cluster are also listed. One can see that the most essential difference between the two clusters is that the interatomic distance In3-In3' is noticeably greater than the Si3-Si3' one which is a natural sequence of the elimination of the direct bonding between Si3 and Si3' when these atoms are replaced by trivalent In atoms. Other bond lengths remain essentially unchanged.

Several other possible structures have also been tested, including (i) the asymmetric Si_5In_8 cluster in which Si1

TABLE I. Experimental and calculated bond lengths in Å in the $\text{Si}(100)4 \times 3\text{-In}$ ordinary Si_7In_6 and “bright” Si_5In_8 clusters.

Atoms	Si_7In_6 cluster			Si_5In_8 cluster
	Expt. [6]	Calc. [12]	This work	This work
Si1-In1	3.00	2.66	2.67	2.66
Si1-Si3	2.28	2.34	2.39	
Si1-In3				2.55
In1-Si2	2.75	2.61	2.62	2.63
In2-Si2	2.74	2.57	2.60	2.61
In2-Si4	2.54	2.66	2.63	2.62
In2-Si5	2.75	2.58	2.60	2.63
Si3-Si3'	2.53	2.38	2.45	
In3-In3'				3.29

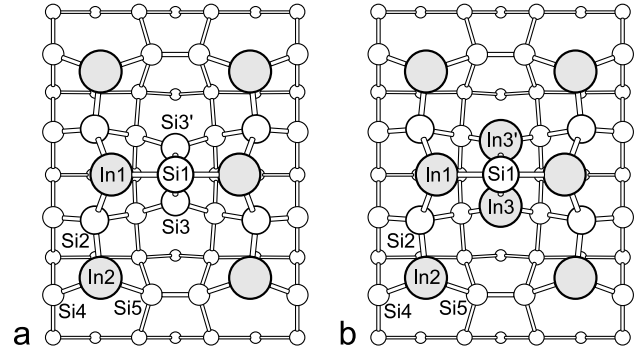


FIG. 5. (a) Structural model of the ordinary Si_7In_6 cluster as proposed by Bunk *et al.* [6]. (b) Plausible structural model of the “bright” cluster. Si3 and Si3' atoms are replaced by In3 and In3' atoms, thus forming the symmetric Si_5In_8 cluster. Si atoms are shown as white circles, and In atoms as grey circles.

and In3 atoms exchange their sites, (ii) the symmetric Si_6In_7 cluster, i.e., the ordinary cluster in which the Si1 atom is substituted for the In atom, and (iii) the asymmetric Si_6In_7 cluster, i.e., the ordinary cluster in which the Si3 atom is substituted for the In atom. In order to have the possibility to compare structures having different compositions, we have used the surface formation energy defined as [12]

$$\Omega = E(N_{\text{Si}}, N_{\text{In}}) - N_{\text{Si}}\mu_{\text{Si,bulk}} - N_{\text{In}}\mu_{\text{In,bulk}}, \quad (2)$$

where $E(N_{\text{Si}}, N_{\text{In}})$ is the total energy of the Si-In system, N_{Si} and N_{In} are the numbers of Si and In atoms, and $\mu_{\text{Si,bulk}}$ and $\mu_{\text{In,bulk}}$ are the energies per atom in bulk Si and In, respectively. The calculations have shown that the structure of the symmetric Si_5In_8 cluster [Fig. 5(b)] is the most stable with the energy gain of 0.14 eV with respect to the asymmetric Si_5In_8 cluster and of about 0.55 eV with respect to both symmetric and asymmetric Si_6In_7 clusters which appear to have close energies.

By analogy with the bulk crystals, the discussed modification of the cluster composition can be treated as a *cluster doping*. Customary doping of semiconductor crystals results in an appearance of the electron energy levels within the band gap, and hence leads to the change of crystal electronic properties. The effect of the doping on

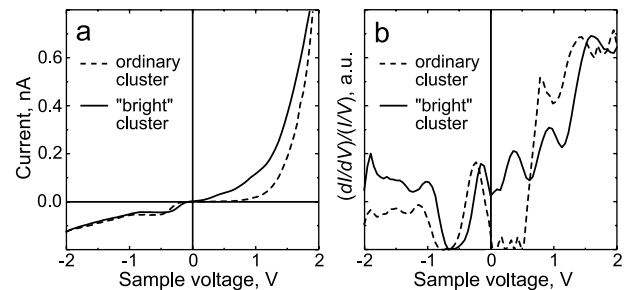


FIG. 6. STS data for the ordinary (dashed line) and “bright” clusters (solid line): averaged (a) I - V and (b) $(dI/dV)/(I/V)$ - V spectra acquired at a constant tip-sample separation.

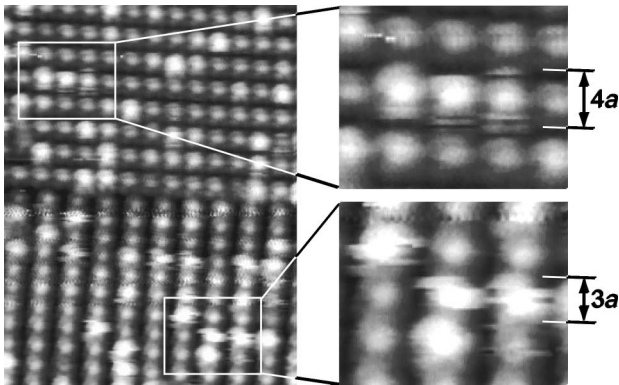


FIG. 7. Filled state STM images of the Si(100) 4×3 -In surface with “bright” clusters acquired at 110 K. Two orthogonal domains separated by atomic step is seen. One can see that swinging of the bright cluster occurs mainly along the $4a$ -periodicity direction.

electronic properties of the In-Si clusters has been checked using STS. Figure 6 presents I - V and $(dI/dV)/(I/V)$ - V STS spectra from the nondoped (ordinary) cluster and doped (bright) cluster. One can see that the ordinary Si_7In_6 cluster shows up in STS spectra as a semiconductor with a band gap of ~ 0.6 eV. The cluster doping results in developing an extra electron density of states at around $+0.4$ eV, i.e., within the band gap of the nondoped cluster. Thus, doping of the cluster changes its properties from semiconducting towards metallic, just as for bulk semiconductors.

One can notice in Fig. 1 that in contrast to the ordinary clusters the bright clusters display a fuzzy STM appearance which reflects their instability during STM imaging. To distinguish between the tip effect and the thermally activated motion, we have cooled the sample to low temperatures. As one can see in Fig. 7 showing the filled state STM image of the surface at 110 K, the bright clusters are still seen fuzzy indicating that this instability is due to the tip effect. Observation of this motion only with a positive voltage applied to the tip sounds also supportive of this conclusion. As for the intrinsic properties of a bright cluster, this kind of behavior seems to reflect that it is more compliant compared to an ordinary cluster. An ordinary Si_7In_6 cluster is believed to have a rigid structure due to a direct bond between Si_3 and Si_3' atoms. Upon substitution of these Si atoms by In atoms in the Si_5In_8 cluster, this bond no longer exists. Remarkably, the bright clusters indeed swing mainly along this direction, as one can conclude from comparison of bright cluster images in the two orthogonal 4×3 domains separated by an atomic step (Fig. 7). Here, with the direction of the STM tip scanning from left to right, the observed swinging of the bright clusters is along the $4a$ periodicity direction.

In conclusion, it has been found that magic Si_7In_6 clusters constituting the Si(100) 4×3 -In superlattice can

be modified: namely, two Si atoms in a cluster can be replaced by two In atoms, thus forming Si_5In_8 clusters. This modification, which is essentially cluster doping, alters the mechanical and electronic properties of a cluster: the cluster becomes less rigid and its electronic properties change from semiconducting towards metallic. Using first-principles total-energy calculations, stability of the Si_5In_8 cluster has been proved and its atomic structure has been evaluated.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, by the Russian Foundation for Fundamental Researches (Grant No. 02-02-16105), by Program “Universities of Russia” (Grant UR.01.01.035), and by Russian National Program (Grants No. 40.012.1.1.1151 and No. 40.072.1.1.1178).

-
- [1] M. Y. Lai and Y. L. Wang, Phys. Rev. B **64**, 241404 (2001).
 - [2] J. L. Li, J. F. Jia, X. J. Liang, X. Liu, J. Z. Wang, Q. K. Xue, Z. Q. Li, J. S. Tse, Z. Zhang, and S. B. Zhang, Phys. Rev. Lett. **88**, 066101 (2002).
 - [3] V. G. Kotlyar, A. V. Zotov, A. A. Saranin, T. V. Kasyanova, M. A. Cherevik, I. V. Pisarenko, and V. G. Lifshits, Phys. Rev. B **66**, 165401 (2002).
 - [4] A. A. Baski, J. Nogami, and C. F. Quate, Phys. Rev. B **43**, 9316 (1991).
 - [5] A. A. Saranin, A. V. Zotov, V. G. Lifshits, J. T. Ryu, O. Kubo, H. Tani, T. Harada, M. Katayama, and K. Oura, Phys. Rev. B **60**, 14372 (1999).
 - [6] O. Bunk, G. Falkenberg, L. Seehofer, J. H. Zeysing, R. L. Johnson, M. Nielsen, R. Feidenhans'l, and E. Landemark, Appl. Surf. Sci. **123/124**, 104 (1998).
 - [7] A. V. Zotov, A. A. Saranin, V. G. Lifshits, J. T. Ryu, O. Kubo, H. Tani, M. Katayama, and K. Oura, Phys. Rev. B **57**, 12492 (1998).
 - [8] O. Bunk, G. Falkenberg, J. H. Zeysing, R. L. Johnson, M. Nielsen, and R. Feidenhans'l, Phys. Rev. B **60**, 13905 (1999).
 - [9] M. Shimomura, T. Nakamura, K. S. Kim, T. Abukawa, J. Tani, and S. Kono, Surf. Rev. Lett. **6**, 1097 (1999).
 - [10] P. J. E. Reese, T. Miller, and T. C. Chiang, Phys. Rev. B **64**, 233307 (2001).
 - [11] T. M. Schmidt, J. L. P. Castineira, and R. H. Miwa, Appl. Phys. Lett. **79**, 203 (2001).
 - [12] N. Takeuchi, Phys. Rev. B **63**, 245325 (2001).
 - [13] K. Hata, T. Kimura, S. Ozawa, and H. Shigekawa, J. Vac. Sci. Technol. A **18**, 1933 (2000).
 - [14] A similar value ($\Theta_{\text{Si}}^{4 \times 3} = 0.51 \pm 0.02$ ML) was obtained in our recent work [5], where the presence of bright clusters was not taken into account. As a result, an erroneous structural model of the cluster was proposed.
 - [15] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
 - [16] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).