Pb-modified In/Si(100)4×3 magic clusters: Scanning tunneling microscopy and first-principles total-energy calculations

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Using scanning tunneling microscopy and first-principles total-energy calculations, Pb-induced modification of the In/Si(100)4×3 magic cluster arrays has been studied. Cluster modification has been found to occur upon Pb deposition onto Si(100)4×3-In surface held at 330–380 °C and reside in substituting central Si atom in Si_7In_6 cluster of Bunk *et al.* [Appl. Surf. Sci. **123/123**, 104 (1998)] for Pb atom. According to scanning tunneling spectroscopy data, Pb-modified cluster shows up as a semiconductor with a band gap somewhat larger than that of an ordinary cluster. Possibility to fabricate arrays almost completely (up to 95%) built of Pb-modified clusters has been demonstrated.

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I. INTRODUCTION

Self-assembly of ordered nanocluster arrays on solid surfaces has recently been given a large attention because of their unusual physical properties and potential technological applications in nanoelectronics. The most advanced results have been achieved with group-III metals, Al,[1–3] In,[3,4] Ga,[3,5] and Tl (Ref. 6) adsorbed on Si crystalline surfaces. In particular, it has been recognized that Si(100)4×3-In reconstruction is essentially an ordered array of identical-size clusters (i.e., magic clusters).[7–9] Atomic structure of the In/Si(100)4×3 cluster has been a subject of furious debates over the last years[10–17] and most of the recent experimental and theoretical studies have favored the model proposed by Bunk *et al.*[11] in which six In atoms and seven Si atoms form a stable pyramidlike Si_7In_6 cluster [see Fig. 5(a)]. An interesting feature of this system is that upon deposition of additional ~0.05 ML of In, up to 40% of clusters become modified.[7,18,19] Cluster modification involves substitution of Si atom within clusters by In atoms [Fig. 5(b)], which results in changing the cluster electronic properties; hence this modification can be treated as a cluster doping and a modified cluster can be called a doped cluster.[7] Very recently, it has been found that due to its specific dynamical behavior, In-doped In/Si(100)4×3 cluster can be treated as a prototype atomic switch.[19]

Thus, searching ways for controlling structure and properties of the nanoclusters is believed to be very important task for developing nanotechnology. The goal of the present work was to see if the In/Si(100)4×3 clusters could be modified by adsorption of a foreign species. We have tested several species and achieved a success with Pb. It has been found that upon Pb adsorption, up to 95% of clusters could be modified; hence possibility to alter composition, structure, and properties of the magic cluster array has been demonstrated.

II. EXPERIMENTAL AND CALCULATION DETAILS

Our experiments were performed with Omicron scanning tunneling microscope (STM) operated in ultrahigh vacuum (~2.0×10^{-10} Torr). Atomically clean Si(100)2×1 surfaces with a minimal number of defects were prepared using preparation procedure described in Ref. 20. Indium and lead were deposited from Ta-foil tubular effusion cells, both at a rate of about 1.0 ML/min. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed. All STM images were acquired in a constant-current mode at room temperature.

To find the energetically favorable structures among the possible ones, we performed *ab initio* total-energy calculations using the FHI96MD code,[21] in which the Car-Parrinello type of electronic structure calculations[22] was used. The local density approximation (LDA) after Ceperley-Alder[23] in the Perdew-Zunger parametrization[24] for the exchange and correlation was functional and fully separable Hamann[25] pseudopotentials have been employed. The pseudopotentials were constructed using the FHI98PP code[26] and were verified to avoid ghost states and to describe the basic experimental characteristic of bulk materials. The surface has been simulated by a periodic slab geometry with a 4×3 unit cell containing six silicon atomic layers and top In-Si mixed layer. The dangling bonds of the bottom slab layer have been saturated by hydrogen atoms. The hydrogen atoms and bottom layer silicon atoms have been fixed and the rest atoms have been set free to move. A vacuum region of approximately 10 Å has been incorporated within each periodic unit cell to prevent interaction between adjacent surfaces. The energy cutoff of 20 Ry has been applied in all calculations presented.

III. RESULTS AND DISCUSSION

Si(100)4×3-In surface with identical Si_7In_6 nanoclusters was prepared by saturating adsorption of In on Si(100)2×1 substrate held at about 500 °C [Fig. 1(a)]. When Pb atoms are deposited onto such a surface at a temperature from 330 to 380 °C range, basic 4×3 superstructure is preserved, but some clusters become modified. In particular, in the filled-state STM images, they look more bright

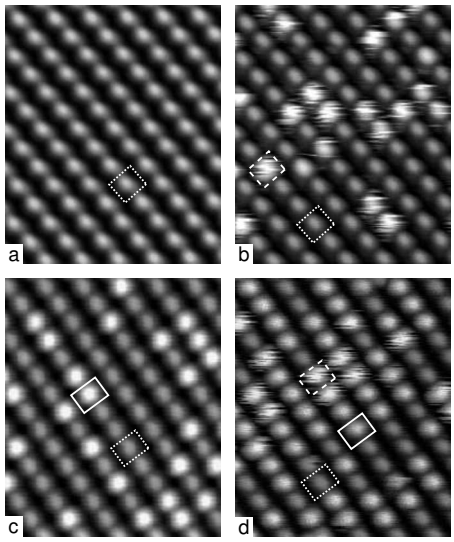


FIG. 1. 120×140 Å^2 filled-state STM images of the In/Si(100)4×3 magic cluster arrays containing (a) only ordinary clusters, (b) ordinary and In-modified clusters, (c) ordinary and Pb-modified clusters, and (d) ordinary, In-modified, and Pb-modified clusters. Ordinary clusters are outlined by dotted frames, In-modified clusters by dashed frame, Pb-modified clusters by solid frame. Magic cluster arrays shown in (a) and (b) are obtained by saturating In adsorption on Si(100)2×1 surface held at 500 and 450 °C, respectively. Magic cluster arrays shown in (c) and (d) are obtained by depositing about 0.3 ML of Pb at 380 °C onto the arrays shown in (a) and (b), respectively.

[Fig. 1(c)]. As their fraction grows with the Pb dose, it is natural to assume that these are Pb-modified clusters. Recall that this behavior is very similar to the case of the cluster modification by adsorption of additional In.[7] However, close examination shows that Pb-modified clusters differ markedly from the In-modified clusters.

Figure 1(d) clearly demonstrates the difference in the filled-state STM appearance of the clusters. Here, Pb was deposited onto the Si(100)4×3-In cluster array which already had contained some In-modified clusters. Hence, the clusters of all three types, namely, (i) original clusters (outlined by dotted frames in Fig. 1), (ii) In-modified clusters (outlined by dashed frames), and (iii) Pb-modified clusters (outlined by solid frame), are present on the resultant surface. One can see that In-modified clusters look fuzzy while Pb-modified clusters are smooth, the clusters of both types looking brighter than original clusters.

Results of a more elaborate examination of the STM appearance of Pb-modified clusters are present in Fig. 2, which illustrates a bias-dependent appearance of the original (outlined by a dotted frame) and Pb-modified (outlined by a solid frame) clusters. All images were taken from the same 77×81 Å^2 region of the surface. Bias voltage applied to the sample is indicated in each image. Experimentally determined bias-dependent STM appearance of the original, Pb-modified, and In-modified clusters is illustrated schematically in Table I. In particular, one can see that in the filled-state STM images at any voltage, all clusters look as single protrusions with modified clusters of both types being brighter than the original one and In-modified cluster looking

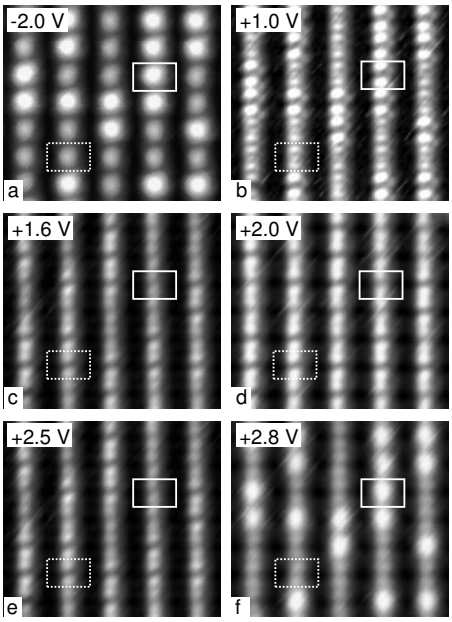
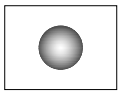
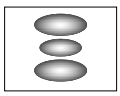
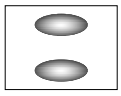
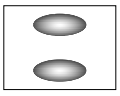
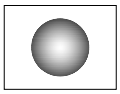
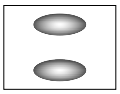
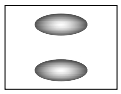
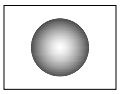
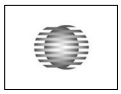
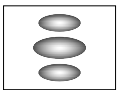
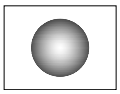


FIG. 2. Set of STM images acquired at various bias voltages from the same 77×81 Å^2 area of magic cluster array containing ordinary clusters (outlined by a dotted line) and Pb-modified clusters (outlined by a solid line). Bias voltages applied to the sample are indicated.

fuzzy. In the empty-state STM images, cluster appearance depends on the bias voltage. At about 1.0 V, original cluster displays three protrusions with the two edge protrusions being brighter than the central one; in In-modified clusters, the central protrusion is brighter than the two edge ones; in Pb-modified clusters, the central protrusion is absent. At 1.0–2.0 V, original and Pb-modified clusters display two edge protrusions (the central protrusion is lacking); In-modified cluster exhibits a single bright protrusion. At higher voltages, original and Pb-modified clusters display two edge protrusions and one central protrusion, respectively.

A set of experiments was performed to elucidate a possible composition of the Pb-modified clusters. Figure 3 shows a fraction of the Pb-modified clusters as a function of the deposited Pb amount at temperatures of 330 °C (open circles) and 370 °C (closed squares). The dotted lines show calculated plots for the cases when modified cluster adopts one, two, three, and four Pb atoms. One can see that experimental data are temperature dependent, which means that not all Pb atoms, deposited onto the surface, actually participate in cluster modification (some Pb atoms could be lost, e.g., due to desorption or agglomeration into islands). Thus, the lower temperature, seemingly, the higher accuracy of the evaluation. Unfortunately, decreasing temperature below 330 °C is inappropriate, because a regular cluster array of sufficient quality cannot be obtained at such low substrate temperatures due to formation of shapeless Pb-associated features. Thus, we have been able to gain in the experiment only an upper estimate which shows that a number of Pb atoms adopted by a modified cluster is not more than three atoms (i.e., either one, two, or three atoms). As for the In atoms, we have not observed any indication that they are displaced from the clusters upon Pb modification (neither

TABLE I. Schematic diagrams illustrating bias-dependent STM appearance of the original, Pb-modified, and In-modified clusters.

	Bias voltages			
		Empty states		
Cluster	Filled states	+1.0 V	+1.5 V	+2.5 V
Original				
Pb doped				
In doped				

In-modified clusters appear, no other known In-associated features[27] are formed).

Besides adsorbate coverage, the coverage of substrate atoms (here, a top Si atom density) involved in reconstruction is also an important characteristics of a reconstruction. To elucidate the top Si atom density in the Pb-doped cluster, we have examined quantitatively Si mass transport caused by Pb adsorption. Note 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 a flat monatomic islands on terrace and an area fraction occupied by these islands is directly linked to the top substrate atom density in the reconstruction.[12,28] For example, an ideal original Si(100)4×3-In surface is characterized by a top Si atom density of 7/12 ML and by an island area fraction of about 42%. Figure 4 shows the change in the island area versus the fraction of Pb-modified clusters. The dotted line is a calculated plot for the case when one Si atom is extracted from every modified cluster and these Si atoms contribute to enhancing island area. One can see that experimental dots are close to the calculated dependence, albeit systematically lower. This deviation reflects that a certain portion of the released Si atoms are trapped at the step edges.

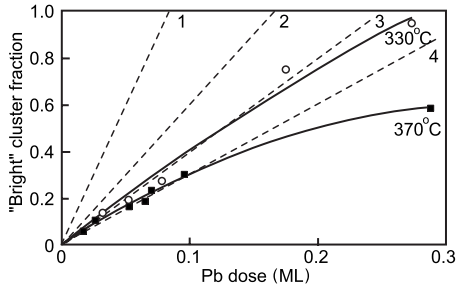


FIG. 3. Fraction of the Pb-modified clusters as a function of Pb dose deposited onto In/Si(100)4×3 magic cluster array at 330 °C (open circles) and 370 °C (closed squares). Dotted lines show calculated plots for the cases when modified cluster adopts extra one, two, three, and four Pb atoms.

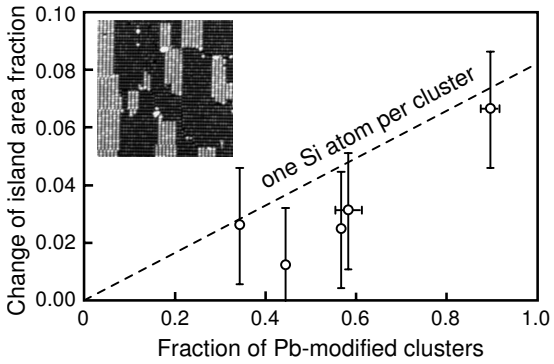


FIG. 4. Change in the island area as a function of the fraction of Pb-modified clusters. The dotted line is a calculated plot for the case when one Si atom is extracted from every modified cluster. Inset shows a large-scale (600×600 Å^2) STM image illustrating developing two-layer system of 2D islands on terraces due to Si mass transport induced by Si(100)4×3-In reconstruction formation.

Thus, results of the experimental evaluation can be summarized as follows. Upon Pb modification, a cluster (i) adopts either one, two, or three Pb atoms, (ii) plausibly loses one Si atom, and (iii) preserves original number of In atoms. Bearing these findings in mind, we have constructed a set of possible models for the Pb-modified cluster and have tested their stability using total-energy calculations. It is worth noting that we have considered atomic configurations which symmetry reproduces the symmetry of the cluster STM images. To compare the structures having different number of silicon and lead atoms, we have used the surface formation energy defined as[17]

$$\Omega = E(N_{\mathrm{Si}}, N_{\mathrm{In}}, N_{\mathrm{Pb}}) - N_{\mathrm{Si}}\mu_{\mathrm{Si}} - N_{\mathrm{In}}\mu_{\mathrm{In}} - N_{\mathrm{Pb}}\mu_{\mathrm{Pb}},$$

where $E(N_{\mathrm{Si}}, N_{\mathrm{In}}, N_{\mathrm{Pb}})$ is the total energy of the system, N_{Si}, N_{In}, and N_{Pb} are the number of Si, In, and Pb atoms, and μ_{Si}, μ_{In}, and μ_{Pb} are the energies per atom in bulk Si, In, and Pb, respectively. The only atomic configuration has been found to be more stable (by 0.3 eV per 4×3 unit cell) than ordinary Si_7In_6 cluster. This configuration is shown in Fig. 5(c) together with the models for ordinary Si_7In_6 [Fig. 5(a)] and In-doped Si_6In_8 [Fig. 5(b)] clusters. It contains one lead atom

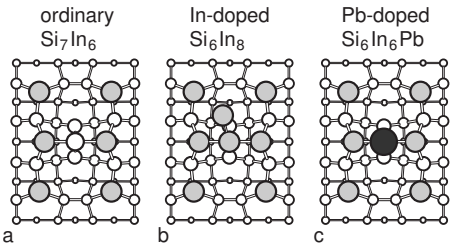
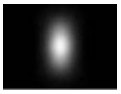
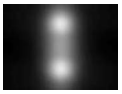
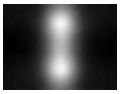


FIG. 5. Structural models of the (a) ordinary Si_7In_6 cluster, (Ref. 11), (b) In-doped Si_6In_8 cluster (Ref. 19), and (c) Pb-doped Si_6In_6Pb cluster. Si atoms are shown by white circles, In atoms by light gray circles, and Pb atom is shown by dark gray circle.

TABLE II. Simulated STM images of the orignal and Pb-modified clusters.

	Bias voltages			
	Filled states	Empty states		
Cluster	−2.0 V	+1.0 V	+1.5 V	+2.5 V
Original				
Pb doped				

substituting central silicon atom, thus forming symmetric Si_6In_6Pb cluster. Other considered configurations (including those with two and three Pb atoms) have the formation energy by, at least, 0.1 eV greater than ordinary Si_7In_6 cluster. As a test for the validity of the chosen configuration, we have conducted simulation of the STM images at several bias voltages. The results are summarized in Table II, which shows simulated filled-state (−2.0 V) and empty-state (+0.5, +1.5, and +2.5 V) STM images for the Si_6In_6Pb cluster (as well as for the ordinary Si_7In_6 cluster, given for comparison). One can see that simulated STM images nicely reproduce all principal features of the experimental STM images (see Fig. 2 and Table I). It is worth noting that simulated STM images of the other considered configurations were in apparent inconsistency with the experimental STM images.

To see how Pb-induced modification of the Si(100)4×3-In clusters affects their electronic properties, we have conducted scanning tunneling spectroscopy (STS) measurements on ordinary and Pb-modified clusters. The results of the STS evaluation are shown in Fig. 6. One can see that Pb-induced modification results in a certain increasing

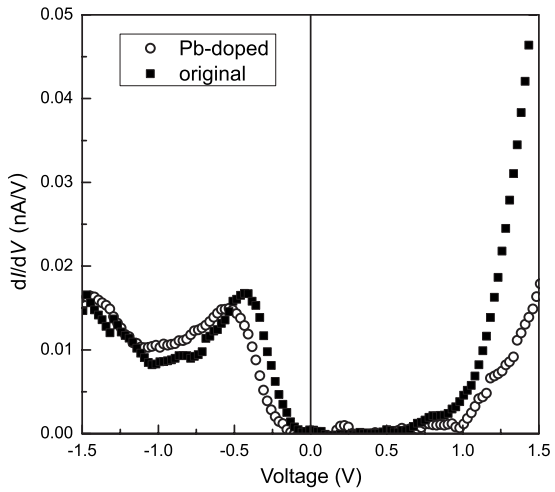


FIG. 6. STS spectra taken from the original (closed squares) and Pb-doped (open circles) In/Si(100)4×3 magic clusters.

FIG. 7. 525×390 Å^2 filled-state STM image of the In/Si(100)4×3 magic cluster array which is almost completely (by ~93%) built of Pb-modified clusters. The array was prepared by saturating Pb adsorption at 330 °C.

band gap with preserving all other spectral features essentially unchanged. This effect is opposite to that produced by In doping,[7] in which case an additional electron density of states develops within a band gap.

As a final remark concerning Pb-modified Si(100)4×3-In clusters, we would like to outline a remarkable possibility to fabricate arrays almost completely (up to 95%) built of Pb-modified clusters. As an example, such an array formed upon saturating adsorption of Pb at about 330 °C is shown Fig. 7. Recall that this is opposite to the case of In-induced cluster modification, where a fraction of In-modified clusters has never exceeded the value of 40%. This difference possibly stems from the fact that according to total-energy calculations In-doped Si_6In_8 cluster is less stable by ~30 meV than the ordinary Si_7In_6 cluster,[19] while Pb-modified Si_6In_6Pb cluster is, in contrast, more stable by ~300 meV. Possibility to produce monodispersed Pb-modified cluster arrays makes them a convenient object for investigating by surface integrating methods, such as photoelectron spectroscopy, which can tell us more about physical properties of the system.

IV. CONCLUSION

Using scanning tunneling microscopy observations and first-principles total-energy calculations, effect of Pb adsorption on the composition, structure, and properties of the In/Si(100)4×3 magic cluster arrays has been studied. It has been found that upon Pb adsorption at 330–380 °C, a certain portion of clusters in the array become modified (at 330 °C up to 95% of clusters become modified). Pb-modified clusters display bias-dependent STM appearance qualitatively different from that of the ordinary Si_7In_6 (Refs. 11 and 12) and In-doped Si_6In_8 (Refs. 7 and 19) clusters. Experimental evaluation of the cluster composition reveals that Pb-modified cluster plausibly preserves all In atoms, loses one Si atom, and adopts one, two, or three Pb atoms. First-principles total-energy calculations demonstrate that among various possible structural models of the Pb-modified cluster, the most stable is the configuration in which the central Si atom in the ordinary Si_7In_6 cluster is substituted for Pb atom.

Simulated STM images from such a structure nicely reproduce all principal features of the experimental bias-dependent STM images. According to scanning tunneling spectroscopy data, Pb-modified cluster shows up as a semiconductor with a band gap somewhat larger than that of an ordinary cluster.

ACKNOWLEDGMENTS

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