Nonmetallic nature of In-induced nanoclusters on Si(100)

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We have studied the electronic properties of the nanoclusters formed by In on the Si(100) surface by angle-resolved photoemission spectroscopy. The Si(100)4×3-In surface, composed of Si3In6 nanoclusters, was found insulating with an energy gap of 0.5 eV below Fermi energy. The nanocluster array on this surface induces five different surface states with a characteristic and dominating one within the band gap. The doping of further In onto this surface yields no significant change of the band gap in contrast to the recent scanning tunneling spectroscopy study reporting metallic cluster formation [Phys. Rev. Lett., 91, 026104 (2003)]. The experimental result is fully supported by first-principles calculations, which reveal both the In-doped (Si3In6) and undoped (Si3In6) nanoclusters are insulating with the energy gaps of 0.42 eV and 0.53 eV, respectively.

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Nanoclusters have been shown to possess promising potentials as nanoscale catalysts1 and sensors,2 and also as functional units in nanoscale electronic devices.3 One of the unsolved problems in the applications of nanoclusters is to position them into a desired arrangement. The spontaneous self-assembly is one of the most promising processes, for such positioning and ordering especially over a macroscopic scale.5,7–10 In particular, various nanoclusters have been successfully prepared on solid surfaces by the spontaneous self-assembly such as Cu on Pt(111),5 Si1-xGex on Si(100),4 In on Si(111)7×7,6,7 Ga on Si(111)3×3R30°-Ga,8 and In (or Al) on Si(100).9,10

On the silicon surfaces, while most of the nanoclusters have been found to be insulating, it is remarkable that a certain In nanocluster was reported very recently to be metallized on Si(100).10 The metallic nanoclusters are based on the In-induced cluster array in a 4×3 long-range order, which is formed on Si(100) with 0.5 ML In and a moderate annealing [the so-called Si(100)4×3-In surface]. It is reported that the pristine 4×3-In nanoclusters are insulating but the further In deposition changes the atomic and electronic structures of some nanoclusters (up to 30 percent) into metallic auto-doped nanoclusters.9 In more detail, three different structural models have been suggested for the pristine In nanocluster from scanning tunneling microscopy (STM) (Refs. 11 and 12) and X-ray diffraction.13 Among them, the quantitative structural model from X-ray diffraction is composed of a pyramidlike SiIn6 cluster [see Fig. 1(a)] in each 4×3 unit cell and have been fully supported by the subsequent experimental and theoretical works.9 The indium dopants were suggested to replace two Si atoms in the center of a SiIn6 cluster keeping the bond network within the cluster but to result in a Si3In6 nanocluster [see Fig. 1(b)].10 A first-principles calculation supported the stability of this doped nanocluster structure and the scanning tunneling spectroscopy (STS) indicated the metallic density of states for the Si3In6 nanoclusters in contrast to insulating Si3In6.10

In this Brief Report, we investigate the electronic structures of the Si3In6 and Si3In8 nanoclusters by angle-resolved photoemission spectroscopy (ARPES) and first-principles calculations. The ARPES study found that the 4×3 cluster array is definitely insulating both before and after the doping of In, in contrast to the previous STS study. This result is fully supported by the theory. We further discuss the detailed electronic states of the nanoclusters.

The ARPES measurements were performed using a high-resolution angle-resolved electron analyzer (SES-100, Gamma Data) and He I radiation (hν=21.2 eV) at a base pressure of 4×10−11 Torr. The nominal energy and angular resolution is better than 13 meV and 0.2°, respectively. Indium was deposited by a heated carbon crucible. The evaporation rate was fixed at 0.1 ML/min to maintain the close experimental conditions with the previous STM/STS experiment.10

FIG. 1. Atomic structural models of Si3In6 (a) and In-doped Si3In8 [(b) and (c)] nanoclusters on Si(100), where gray and black circles denote Si and In, respectively.
The atomic and electronic structures were calculated using the Vienna *ab initio* simulation package (VASP) (Refs. 14 and 15) with the ultrasoft pseudopotentials\(^\text{16}\) and the generalized-gradient approximation (GGA) (Ref. 17) for the exchange-correlation energy. For the simulation of the surface, a repeating slab is adopted, where six Si layers plus an additional Si\(_n\)\(_\text{In}_n\) cluster layer and an 8.6 Å vacuum layer are included. The bottom of the slab has a bulklike structure with each Si atom saturated by two H atoms. The 10-Ry cut-off energy in the plane-wave basis and the 4×3 \(k\)-point mesh in the surface Brillouin zone are used.

Indium adsorbates on Si(100) have been known to form various surface structures such as 2×3, 2×5, and 2×2 phases below 150°C as increasing \(\theta_n\), which are basically composed of one-dimensional In dimer rows.\(^\text{18}\) The 2×2 phase at \(\theta_n=0.5\) ML [Fig. 2(b)] can be transformed into the 4×3 phase built up with the Si\(_n\)\(_\text{In}_n\) nanoclusters [Fig. 2(c)] after annealing above 200°C.\(^\text{18}\) The 4×3 phase was observed with annealing at between 200 and 490°C. Above 490°C, indium begins to desorb and, consequently, the noninteger spots of the 4×3 pattern fade along with the growth of the 2×1 spots from the clean Si(100) surface [Fig. 2(a)]. The surface order of 4×3-In seems to be optimized just below the desorption temperature of In.\(^\text{10}\) The thermal behavior of the 4×3 phase is fully consistent with the previous STM (Ref. 10) and LEED (Ref. 18) observations.

Figure 3 shows the ARPES spectra of the valence bands near Fermi energy for the 4×3-In surface (the Si\(_n\)\(_\text{In}_n\) cluster array) formed at 490°C. The data are taken along the [011] direction. Since the surface is composed of two equivalent but 90°-rotated domains, this measurement probes the overlapped energy bands along \(\vec{\Gamma}-\vec{J}\) and \(\vec{\Gamma}-\vec{J}'\) (see the inset of Fig. 3). There is obviously no photoemission intensity at Fermi energy (binding energy zero) and the highest occupied state (denoted as S1) is located at \(E_n\approx-0.5\) eV at \(\vec{\Gamma}\) (the normal emission). The S1 state shows only little dispersion. That is, the surface is clearly insulating with an energy gap of \(\approx0.5\) eV below a Fermi level. The S1 state is located within the bulk band gap and, thus, we can assign it as due to the Si\(_n\)\(_\text{In}_n\) nanoclusters, which were measured along the [011] direction. The inset shows the surface Brillouin zone. \(\vec{\Gamma}\) corresponds to the normal emission and the angular step between the neighboring spectra is 0.25°.

In order to investigate the change of the electronic states by In doping of the Si\(_n\)\(_\text{In}_n\) nanoclusters, we measured the similar ARPES spectra at a wide range of coverages \(\theta_n\) and annealing temperatures for the further In deposition onto the 4×3-In surface prepared at 490°C. In more detail, In was systematically deposited up to \(\theta_n=2.0\) ML.
of the Si7 In6 nanoclusters do not show any significant change as shown in Fig. 4. The only noticeable change is the reduction temperature. At a low temperature this is likely due to the nanocluster array. This is in clear contrast to the STS observation of the metallization of the Si7In5 nanoclusters by the In doping.

However, a direct comparison of the photoemission and the STS data should be taken carefully since (i) the STS data pick up only very local density of states (DOS) and (ii) the density of the nanoclusters changed by the In doping is not clear at all in the present photoemission and LEED measurements. However, the nonmetallic nature of the In-doped nanoclusters is further confirmed by our first-principles calculations. Figure 5 shows the DOS of the ‘bare’ Si7In6 and ‘doped’ Si3In4 nanoclusters, which are fully relaxed structurally and fully stabilized energetically. For the case of the Si3In4 nanoclusters, a few different structure models were tested including one proposed by the previous work,10 which is shown in Fig. 1(b). However the asymmetric structure shown in Fig. 1(c) is found to be energetically more favorable. Thus, the DOS data shown in Fig. 5 are taken from the new model although the DOS for the original model is not significantly different.

At first, the DOS of a Si7In6 cluster reproduces well the nonmetallic nature and the surface states (S1, S2, S3, S4, and S5) observed for the Si(100)4×3-In surface. Note that the theoretical DOS is broadened by a Gaussian function with a width of 0.1 eV in order to simulate the instrumental resolution and thermal broadening. At the empty states, the lowest unoccupied state E1 locates at a binding energy of −0.3 eV. The calculated band gap is, then, about 0.53 eV, which is fully consistent with the ARPES observation of a band gap larger than 0.5 eV. At second, even after exchanging two Si atoms with In, the filled-state DOS is not varied significantly different.

FIG. 4. ARPES spectra at \( \bar{\Gamma} \) (the normal emission) of Si(100)4×3-In before and after doping In by \( \theta_{\text{In}} = 1.0 \, \text{ML} \) at between 230 and 460°C. The spectra near Fermi energy are magnified in the inset.

at between 200°C and 460°C. In the previous STM/STS experiment,10 In-doped Si3In4 nanoclusters were observed at 400–450°C. The LEED pattern indicated that the 4×3 surface periodicity is maintained even after such a deposition in consistency with the STM study. However, as the deposition time increases, the LEED spot intensity shows a tendency of weakening [see Fig. 2(d)]. This may indicate the formation of the doped nanoclusters randomly on the surface, or at least the random adsorption of In, as the STM study observed. In the case of electronic states, at all deposition temperatures and \( \theta_{\text{In}} \)’s investigated, the surface states of the Si3In4 nanoclusters do not show any significant change as shown in Fig. 4. The only noticeable change is the reduction (enhancement) of the S1 state at a low (high) deposition temperature. At a low temperature this is likely due to the adsorption of extra In onto the Si3In4 nanoclusters, since the S1 state is localized in the Si trimer on top of a Si3In4 nanocluster, as explained below, which could be a preferential adsorption site. What is more important is that the In-doped surfaces are still insulating; as shown in the inset of Fig. 4, there is still no photoemission intensity at Fermi energy and no significant change of the valence-band maximum. Although Fig. 4 shows the ARPES data only along the normal emission, the same behavior is observed over the whole angular range and surface Brillouin zone. Thus, we can clearly conclude that the In doping does not change significantly the electronic structure of the 4×3 Si3In4 nanocluster array. This is in clear contrast to the STS observations including one proposed by the previous work,10 which is shown in Fig. 1(b). However the asymmetric structure shown in Fig. 1(c) is found to be energetically more favorable. Thus, the DOS data shown in Fig. 5 are taken from the new model although the DOS for the original model is not significantly different.

At first, the DOS of a Si3In6 cluster reproduces well the nonmetallic nature and the surface states (S1, S2, S3, S4, and S5) observed for the Si(100)4×3-In surface. Note that the theoretical DOS is broadened by a Gaussian function with a width of 0.1 eV in order to simulate the instrumental resolution and thermal broadening. At the empty states, the lowest unoccupied state E1 locates at a binding energy of −0.3 eV. The calculated band gap is, then, about 0.53 eV, which is fully consistent with the ARPES observation of a band gap larger than 0.5 eV. At second, even after exchanging two Si atoms with In, the filled-state DOS is not varied substantially [Fig. 5(b)] as observed in the present experiment (Fig. 4). Furthermore, the lowest unoccupied state E1 is also almost invariant making the energy gap of 0.53 eV roughly unchanged. The only noticeable change of the electronic states by the In doping is the appearance of a new empty state E2 with a binding energy of −0.6 eV. In the previous STS experiment, a new empty state was observed at −0.4 eV for the doped nanoclusters although the finite DOS at a Fermi energy does not match with the calculation. One difference between the present calculation and the STS measurement is that the theory deals with an array of the clusters while the STS probes an isolated cluster. However, since the dispersion of the band (that is, the overlap of the corresponding wave function between the neighboring clusters in the array) is marginal, this difference would not affect the present conclusion.

FIG. 5. Density of states of the (a) Si3-In6 [Fig. 1(a) and 1(b)] Si3In4 [Fig. 1(c)] nanocluster arrays calculated by first-principles calculations.

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In a simple picture, the electron counting can also explain the nonmetallic nature of the Si$_7$In$_6$ and the Si$_3$In$_8$ nanoclusters. The number of electrons of the Si$_7$In$_6$ and the Si$_3$In$_8$ nanoclusters are even; 46 (28 from Si+18 from In) and 44 (20 from Si+24 from In), respectively. In a similar sense, we cannot exclude that In-doped nanoclusters are, in fact, Si$_6$In$_7$ or Si$_4$In$_9$ with odd electron numbers to explain their origins are quite different.

The calculation further reveals that, although the DOS’s of the Si$_7$In$_6$ and the asymmetric Si$_3$In$_8$ nanoclusters happen to be very similar, their origins are quite different.$^{20}$ In the Si$_7$In$_6$ cluster, S1, S2-S3, S4-S5, and E1 are originated from the Si trimer at the top of the pyramid, the bonds between the top-most In atoms and its neighboring Si atoms of the Si-In dimers, the backbonds between the top Si atom and the second-layer Si atoms, and the antibonding state between the top Si atom and its neighboring In atoms, respectively. In the asymmetric Si$_3$In$_8$ cluster, on the other hand, S1, E1, and E2 are characterized by the bond between the substituted In and the substrate Si atoms, the empty orbitals of the substituted In atoms, and the empty orbitals of the second-layer In atoms, respectively.

In conclusion, we found that the Si(100)4×3-In surface with Si$_7$In$_6$ nanoclusters is insulating with five different electronic states at 0.5–2.0 eV below a Fermi level. There is no evidence of the metallization of the nanoclusters by further In doping in contrast to a recent STS observation. A further study is required to identify the chemical and atomic structure of the extra bright protrusions or clusters observed by STM for In doping on Si(100)4×3-In.

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