PHYSICAL REVIEW B **72**, 033315 (2005)

Electronic structure of identical metal cluster arrays on Si(111)−7×7 surfaces

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(Received 10 January 2005; revised manuscript received 9 May 2005; published 18 July 2005)

By using first-principles density-functional theory, we calculate the electronic properties of In and Al metal cluster arrays on Si(111), compared with those of the bare 7×7 surface. A systematic trend concerning how the formation of the clusters affects the band structures near the Fermi level is revealed. We show that the formation of the metal clusters does not actually introduce additional metallic states near the Fermi level, but rather makes the surfaces less metallic. Charge redistribution on the surfaces due to the cluster formation is also analyzed. We predict two different two-dimensional electron gases on the metal-covered surfaces, one with connecting metallic regions and one without.

DOI: 10.1103/PhysRevB.72.033315 PACS number(s): 73.22.−f, 73.40.−c

The recent study of identical metal cluster lattices on Si(111)−7×7 substrates[1–9] has not only advanced the control of nanofabrication to ultimate atomic precision, but also provided a new platform for studying next-generation microelectronics such as tuning the Schottky contact, two-dimensional (2D) spintronics, surface superconductivity, and nanocatalysis. However, despite the rapid progress, many of the studies to date have had to rely on empirical knowledge because so far little is known about the electronic properties of the metal cluster arrays and the affected underlying surfaces.

In this regard, indium and aluminum are two of the most commonly fabricated cluster arrays.[8,9] Yet despite the electronic similarity between In and Al, being isovalent, their cluster arrays are qualitatively different. For example, the In clusters occupy mostly the faulted half of the 7×7 unit cell (FHUC), leaving the unfaulted half of the unit cell (UFHUC) empty until all the FHUC sites are depleted. On the other hand, Al clusters occupy simultaneously both halves of the 7×7 cell. The two therefore form two fundamentally different 2D lattices, one being rhomboidal while the other is triangular. The 2D triangular lattice has historically been important for the study of correlated electrons.[10] However, a 2D triangular system with large lattice spacing of several nanometers, 2.7 nm in the present case, has not been possible before due to the inability to fabricate them. Recent first-principles total-energy calculations, combined with high-resolution scanning tunneling microscopy (STM) studies, have determined the atomic structures for both of them.[1] It so happened, however, that Ref. 1 only focused on the structural stability and the STM images. The electronic properties of the clusters, other than the STM images, have never been calculated.

In this paper, we present the first-principles band structures for the In and Al cluster arrays on Si(111)−7×7 surfaces. To assist the analysis, we also calculate the site-decomposed local density of states (LDOS). In addition, we calculate the band structure for the bare Si(111)−7×7 surface for comparison. It appears that the metal clusters do not introduce any electronic states near the Fermi level (E_F). Rather, their formation reduces the number of states near the E_F from that of the bare surface and results in charge redistribution in the real space. The experimentally observed stability of the Al cluster arrays is correlated with the fewer states near the E_F and an opening up of the band gap right above the Fermi level. Moreover, cluster formation leads to two different kinds of 2D electron gases, one with connecting metallic regions and the other without. These findings are expected to have measurable effects, particularly on the surface chemisorption, adatom diffusion,[11,12] and surface electronic transport.

The calculations were carried out using the density-functional theory within the local-density approximation (LDA) and the Vanderbilt ultrasoft pseudopotentials, as implemented in the VASP code.[13] A 7×7 surface cell was used, which consists of the metal clusters, seven layers of Si, and the H atoms used to passivate the back surface. The cutoff energy is 200 eV, and a 4×4×1 *k*-point mesh, including the Γ point, is used to sample the Brillouin zone. All atoms, except for the bottom layer Si and H, are fully relaxed until the forces are less than 0.1 eV/Å.

Figure 1 shows, in a top view, the unit cells of (a) bare and (b) In cluster covered Si(111)−7×7 surfaces.[14,1] On a half unit cell, a bare surface contains six Si adatoms and three Si rest atoms. Upon the chemisorption of an In cluster, the three central Si adatoms (labeled a4–a6) are displaced by about 2.3 Å toward the center of the half cell, as indicated by the arrows in Fig. 1(a). The rest atoms, on the other hand, keep their lateral positions largely unchanged, while rising up by about 0.2 Å. Figure 1(c) shows selectively the distances between In and Si, between two In, and between two Si adatoms. On average, the distance between two In atoms is 4.50 Å, whereas that between an In and an Si is only 2.60 Å. Naturally, the formation of the In-Si bonds has a larger effect on the electronic properties of the clusters.

Figure 1(c) also shows that the displaced Si atoms (a4–a6) become fourfold coordinated, three with the In atoms and one with the Si atom directly below. The Si rest atoms (r1–r3) also become fourfold coordinated due to the additional bond with the In atom. On the other hand, the corner adatoms (a1–a3) are not affected by the In. Hence, each In cluster eliminates six Si dangling bonds: three from the Si ada-

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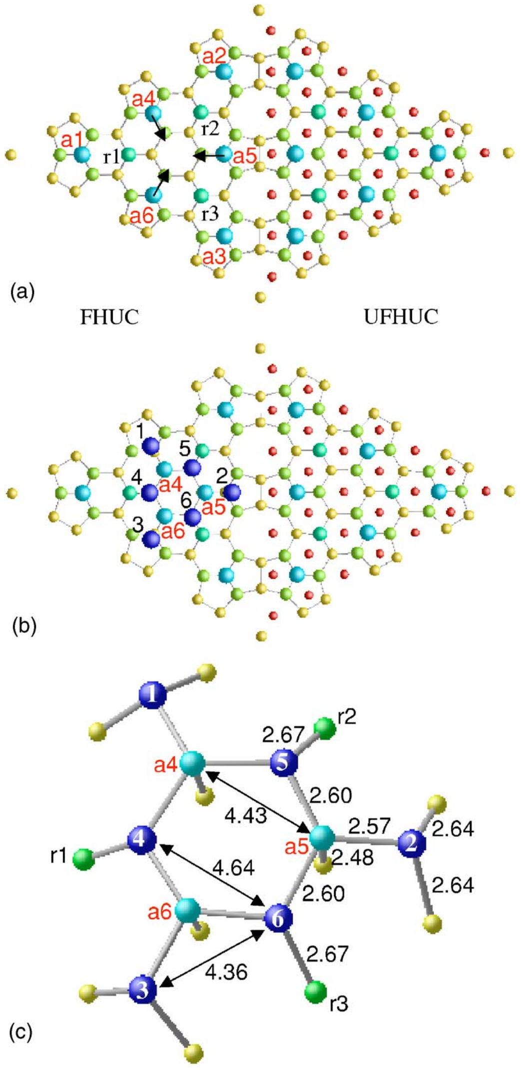

FIG. 1. (Color online) Atomic structures for (a) the bare and (b) the In cluster covered 7×7 surfaces. The 12 large and 6 medium sized balls are the Si adatoms (labeled as a1–a6 in the FHUC) and the rest atoms (labeled as r1–r3 in the FHUC), respectively. The six larger balls in (b) are the In atoms. The directions of the displacements of the a4–a6 Si adatoms upon In cluster formation are indicated in (a) by the arrows. (c) is an enlarged view in which the In cluster atoms are numbered from 1 to 6. The relative distances are denoted in Å. The smallest balls in (c) are Si in the same layer as the Si rest atoms.

toms and three from the Si rest atoms. Also, all six In atoms are threefold coordinated. Indium and silicon have valence three and four, respectively. Hence, from the chemistry point of view, such a bonding in Fig. 1(c) is strongly favored. A closer examination further shows that In (1–3) are 0.3 Å lower than In (4–6). In other words, In (1–3) are more sp^2-like, whereas In (4–6) are more sp^3-like. For Al that is isovalent to In, the structural model in Fig. 1(b) also applies. The only difference is that Alclusters form not only on the FHUCs, but also on the UFHUCs.

Figure 2 shows the calculated band structures for the bare, one In cluster, and two Al clusters covered Si(111)-7×7 surfaces, respectively. Energy zero corresponds to the position of the E_{F}. Calculation of atomic site-decomposed local density of states (not shown) allows us to mark the various states in Fig. 2 according to their atomistic origins. Taking the bare surface in Fig. 2(a) as an example, states below -0.6 eV are Si σ bonding states, whereas states above $+0.4$ eV are Si σ^* antibonding states. There are seven states in the narrow energy range between -0.6 and -0.5 eV, which are the six Si rest atom dangling bond (DB) states plus one state from the corner hole atom. On the other hand, there are 12 states between -0.3 and 0.3 eV, which are the Si adatom DB states. Only the three lowest adatom DB states (below $E_{\mathrm{F}}=0$) are occupied with five electrons. For the In and Al cluster covered surfaces, we observed that, while the number of the Si adatom DB states decreases from 12 for bare surface to 9 for In cluster to 6 for Al clusters due to passivation by the clusters, both the number of the electrons (namely five per cell) and the number of the bands below the E_{F} (namely $n=3$) do not change.

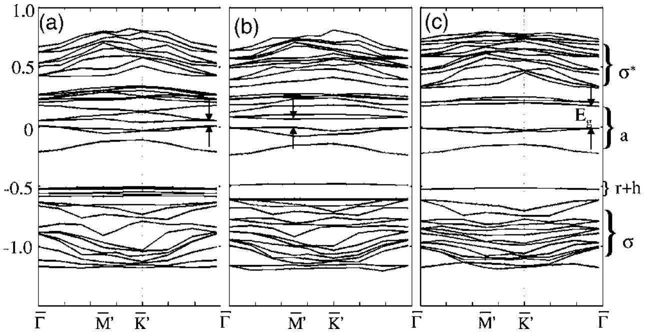

FIG. 2. Band structures for (a) the bare, (b) the In cluster, and (c) the Al clusters covered 7×7 surfaces. Energy zero is at the E_{F}. For clarity of discussion, we have indicated where these states are originated, as revealed by a site decomposed LDOS analysis. The symbols σ and σ^* denote the near-band-edge bonding and antibonding states, whereas r, h, and a denote the DB states of the rest atoms, the corner hole atom, and the adatoms. The surface energy gap, discussed in the text, is also indicated.

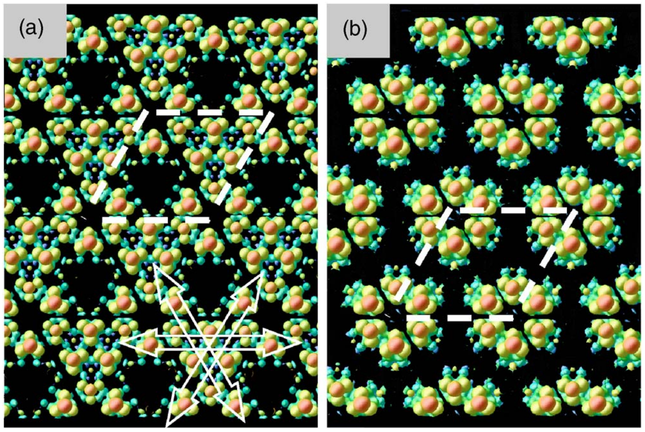

FIG. 3. (Color online) Isosurface of the integrated charge density from $E_{\mathrm{F}}-0.1$ eV to E_{F} for (a) the In clusters and (b) the Al clusters. In (a), these states form a connected network, but in (b) no such connectivity exists. The dashed rhombuses indicate the 7×7 unit cell and the arrows in (a) indicate the directions along which surface current may flow.

TABLE I. The counting of Si dangling bonds (DBs) and DB electrons for the bare, In, and Al cluster covered Si(111)7×7 surfaces and the relationship between them.

Notations	Descriptions	Bare surface	In cluster	Al clusters	Remarks
DB1	Adatom DBs	12	9	6	
	Passivated ones	0	3	6	12−DB1
DB2	Rest atom DBs	6	3	0	
	Passivated ones	0	3	6	6−DB2
DB3	Corner hole DB	1	1	1	
E1	Total DB electrons	19	13	7	DB1+DB2+DB3
E2	On the rest atom DBs	12	6	0	E2=2×DB2
E3	On the corner hole DB	2	2	2	E3=2×DB3
E4	Left on the adatom DBs	5	5	5	E4=E1−(E2+E3)

This interesting observation can be quantitatively understood using the electron counting model (see Table I): On a bare 7×7 unit cell, there are 12 Si adatoms, 6 rest atoms, and 1 corner hole atom. There are, therefore, DB1+DB2+DB3=12+6+1=19 nominally singly occupied dangling bonds with E1=19 electrons.[15] As indicated in Fig. 2(a), however, the DB states of the rest and corner hole atoms are significantly lower in energy than the DB states of the adatoms, by 0.3–1.0 eV, and are hence doubly occupied. This takes away E2+E3=2×(DB1+DB2)=2×(6+1)=14 electrons. There are, therefore, E4=E1−(E2+E3)=19−14=5 electrons left in the adatom DB states and only the three lowest states are occupied. In the case of the In cluster, LDOS analysis shows that the three central Si adatoms (a4–a6) and three rest atoms (r1–r3) are passivated by the newly formed In-Si bonds in Fig. 1(c), thus the corresponding states moving significantly down in energy. The In dangling bonds, on the other hand, are typically higher in energy than those of Si, so we can ignore them. Therefore, DB1=12−3=9, DB2=6−3=3, and DB3=1 is unchanged, with E1=19−6=13. The rest and corner hole atoms (i.e., DB2 and DB3) take away E2+E3=6+2=8 electrons. This leaves the adatom DBs with E4=E1−(E2+E3)=13−8=5 electrons. In the case of the Al clusters, there is no rest atom left other than the corner hole atom. Thus, DB2=0, E2=0, and DB3=1 with the only state in Fig. 2(c) near $\varepsilon=-0.5$ eV. The number of the Si adatom DBs is also reduced to DB1=12−6=6 with E1=19−(2×6)=7. Two of the electrons will occupy the corner hole states (E3=2). This also leaves the adatom DBs with E4=E1−(E2+E3)=7−(0+2)=5 electrons. In other words, irrespective of the number of the clusters on the surface (0, 1, or 2), the number of electrons in the Si adatom DB states remains five per unit cell. Because the number of the Si adatom DB states decreases from 12 (bare) to 9 (In cluster) to 6 (Al clusters), the nominal electron number density increases from 5/12 to 5/9 to 5/6 per Si adatom.

The electronic structure near the E_F determines many of the physical properties of the surfaces. We notice that in all three cases, energy dispersion near the E_F is small, less than 0.1 eV. Hence, one can expect that the associated states are highly localized on the Si adatoms. There is an energy gap (E_g) between the third and fourth Si adatom DB band for each case in Fig. 2. This gap increases with the number of the adsorbed clusters from noticeably less than 0.1 eV for the bare surface to about 0.1 eV for the In cluster to about 0.2 eV for the Al clusters. The larger gap for the Al clusters suggests that one can passivate this surface relatively easily, either by chemisorption of electrically active radicals or by hydrogen with one extra electron per 7×7 unit cell. A larger gap along with fewer near-gap states, even in the absence of complete passivation, is often in accord with a more stable surface for semiconductors. Indeed, it has recently been shown that the Al clusters covered surfaces are considerably more stable than the bare surfaces, as well as being chemically much less reactive.[16]

Figure 3 shows the integrated real-space charge distribution for the states near the E_F. Depending on the type of clusters and their real-space number density, there exist now periodic regions on the surfaces where electrical conduction through current flow is forbidden. For one In cluster per 7×7 cell, surface conduction can still take place via a *diffusion* through the channels highlighted in Fig. 3(a). For two Al clusters per 7×7 cell, however, the electrical forbidden regions double in size to percolate. In this case, conduction may only take place via a *tunneling* through the Si dangling bond states.

In summary, we have calculated the electronic structures for the In and Al identical cluster arrays on Si(111)-7×7 surfaces. Our results show that the metal clusters, despite their apparent metallicity, do not actually introduce any states near the Fermi level. Instead, LDOS analysis shows that the formation of the cluster arrays serves to *reduce* the density of states near the E_F. We predict real-space charge redistribution among the remaining Si dangling bonds and charge depletion from certain parts of the surface regions, noticeably from where the metal clusters reside. This leads to two different kinds of 2D electron gases on the metal covered Si(111)-7×7 surfaces, one with connecting metallic regions and one without. We expect these results to enlighten the future studies of the metal cluster arrays.

Work at IOP was supported by the NSF and MOST of China. S.B.Z. was supported by the BES and OER, U.S. Department of Energy, under Contract No. DE-AC36-99GO10337.

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