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Formation of a suprahoneycomb compound of Zn_3 cluster on a Si(111)-(7×7) surface

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A unique suprahoneycomb column of Zn_3 cluster is materialized on a Si(111)-7×7 surface. Zn on a Si(111)-7×7 surface forms a Zn_3 trimer in faulted and unfaulted halves of the 7×7 structure, so that one monolayer takes a honeycomb structure composed of Zn_3 clusters. Further adsorption of Zn undergoes layer by layer growth of the second and third honeycomb layers of a Zn_3 cluster, where the stacked triangular Zn_3 seems to be on top of the underlying Zn_3 cluster with a 60° rotation. Scanning tunneling spectroscopy for the second and third layers suggests that this suprahoneycomb column of a Zn_3 cluster is a semiconductive material with a wide band gap. Interestingly, no fourth of the honeycomb layer but metallic islands grow on the third honeycomb layer. We could say that the honeycomb column of Zn_3 is a supracompound materialized on the Si(111)-7×7 surface by a weak interaction of Zn_3 clusters.

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The lattice matching of a growing layer with an underlying surface has been accepted as a requisite for layer-by-layer growth. In this empirical rule, one tacitly assumes the growth of known materials on the surface. On the other hand, it is well known that such unique macrocompounds as supramolecules, DNA, nonmetal enzymes, etc. are provided by weak interactions between the host and guest molecules. If the adsorbate-adsorbate interaction is optimized or enhanced on a surface by appropriate periodic corrugation of the surface, we could expect the formation of quasicompounds on the surface by regular weak interactions.

Square-shaped 0.8×0.8-nm^2 $(Cu_2)_3$ dots, regularly arrayed on an Ag(110) surface, are a good example,[1,2] where the $(Cu_2)_3$ dots are provided by the interaction of Cu_2 on the Ag(110) surface. (-Ag-O-) strings grow on Ag(110) in the [001] direction, and they array in $p(n\times1)$,[3] but the growth of (-Cu-O-) strings on Ag(110) takes place in the [1-10] direction and make a $(2\times2)p2mg$ array due to weak interaction.[2] A competitive array of (-Ni-H-) and (-Ni-O-) strings on a Ni(110) surface is an evidential example proving the regulation by weak interaction of quasicompounds.[4] So far the deposition of variety of metals was studied on Si(111)-7×7, and it is known that the 7×7 structure is lifted up by forming metal silicides. Some metals, however, adsorb on the Si(111)-7×7 surface without lifting up the 7×7 structure. In such a case, preferential adsorption takes place on the faulted halves on the Si(111)-7×7 surface. In conformity with these facts, the formation of nanoparticles was reported on a 7×7 surface by several groups. An interesting example is the Tl atoms on the Si(111)-7×7 surface. In this case, the formation of a Tl_9 cluster in the faulted halves was supposed, although no atomic resolution of the Tl dot was obtained.[5] In contrast, Zn atoms provide entirely different epitaxial growth on the Si(111)-7×7 surface, as will be reported in this paper; that is, a suprahoneycomb compound of Zn_3 is formed by the layer-by-layer growth mechanism.

Experiments were performed by using a rectangular shape Si(111) wafer (*n*-type, ~0.1Ω) of 1×7×0.3 mm^3. A well-ordered clean Si(111)-7×7 surface was obtained by heating the sample at ~1250 K in an ultrahigh-vacuum (UHV) scanning tunning microscopy (STM) (JSPM-4500S, JEOL) chamber of $\sim2\times10^{-8}$ Pa background pressure. Zn was deposited on a clean Si(111)-7×7 surface by heating a tungsten filament winding around Zn wire. So far, few adsorption studies was reported on Zn in the UHV system because of its high vapor pressure at room temperature.

Figure 1(a) shows an STM feature of a Si(111)-7×7 surface with adsorbed Zn atoms acquired at a bias potential of 3.0 V. Zn formed round-shaped dots in the faulted and unfaulted halves of the Si(111)-7×7 surface, and a corner hole on the Si(111)-7×7 surface was finally surrounded by six uniformly sized round-shaped dots. The round feature of the dots changed to a triangular shape when the bias potential was changed from a positive to a negative value, as shown in Fig. 1(b), which may reflect the empty and occupied states of the Zn cluster, respectively. When the surface was fully covered with the dots, a honeycomb layer composed of Zn cluster dots was established as shown in Fig. 2(a). We can see atom-resolved Zn_2 clusters in an inset STM image in Fig. 1(a), which may be a transient state to the triangular-shaped dots, one in the faulted (*F*) half and the other in the unfaulted (*U*) half. Zn atoms of the Zn_2 clusters look to be located on the center Si adatoms. If this is the case, a triangular dot is composed of three Zn atoms on the center Si adatoms, and the STM feature may reflect a bonding state of the Zn_3 cluster. When the two dots are formed in the adjacent halves of Si(111)-7×7, the center-to-center distance for the two dots is about 1.55 nm, which is nearly twice that of the Si-Si adatoms (0.758 nm) and one-third of the diagonal length of a unit cell (4.66 nm). Taking these facts into account, the three Zn atoms of the Zn_3 cluster are presumed to be attracted toward the center of three Si adatoms, as illustrated in Fig. 3(b), where the Zn_3 dot coincides its center with the center of the triangular half-unit cell. When Zn atoms were removed by heating up at ~520 K, the 7×7 surface was recovered. This fact suggests that the Zn_3 clusters make no such strong Si-Zn bonds with the center Si adatoms of the Si(111)-7×7 surface, although the 7×7

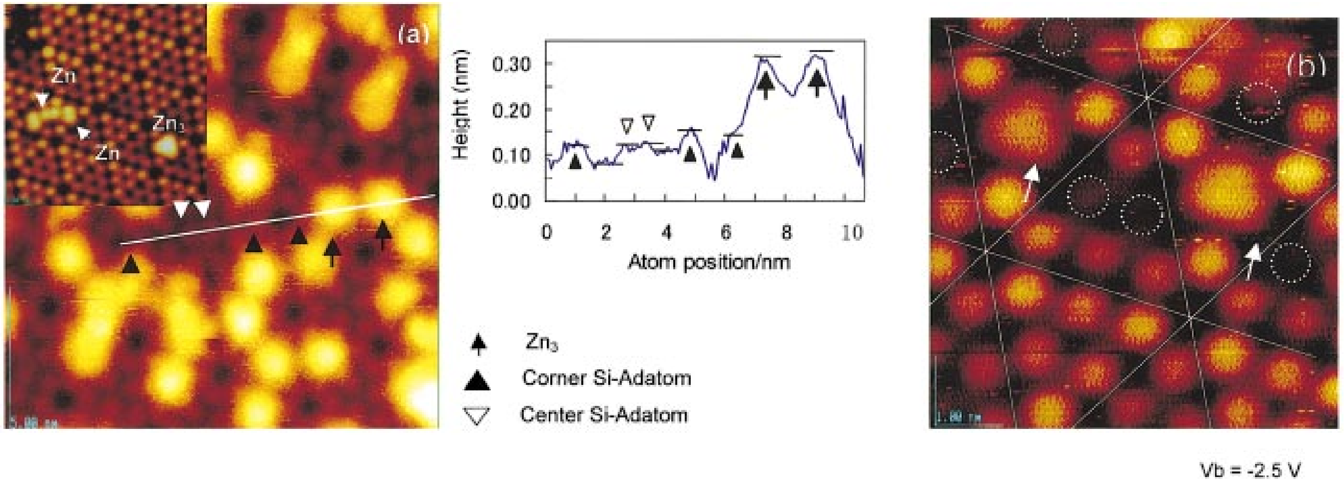

FIG. 1. (Color) A STM image of Zn, Zn_2, and Zn_3 formed in triangular half-unit cells of Si(111)-7×7. (a) An empty-state feature of Zn_3 dots on a Si(111)-7×7 surface (15×15 nm^2) and the corrugation along the line acquired at $V_b=3.0$ V and $I=0.05$ nA. The inserted figure shows an occupied-state image of the Zn_2 clusters and a Zn_3 dot acquired at $V_b=-2.0$ V and $I=0.15$ nA, where the agglomerate Zn_2 species are transient to two Zn_3 clusters. (b) Lowered intensity of the nearest center Si adatoms in the adjacent half unit cells to the Zn_3 clusters at negative bias potential.

structure provides a profitable structure for making a Zn_3 cluster by a mutual interaction of the Zn atoms.

The STM image reflects the corrugation and the local density of states, so it changes with the bias potential. Hamers, Tromp, and Demuth[6] showed early that the tunneling conductance of a clean Si(111)-7×7 surface is less sensitive to the sites of Si atoms when the bias potential is higher than 1.5 V but is sensitive to the sites at negative bias potential. In

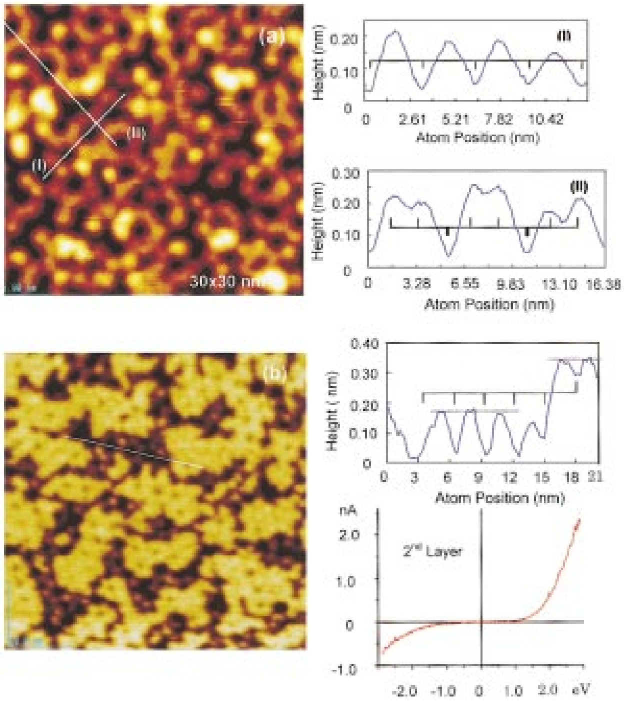

FIG. 2. (Color) Layer-by-layer growth of the first and second honeycomb layers of Zn_3 on a Si(111)-7×7 surface. Periodic honeycomb holes on the two layers are coincident to each other. (a) Honeycomb monolayer established on the Si(111)-7×7 surface and its corrugations along the two lines. $V_b=2.5$ V, $I=0.05$ nA, and 30×30 nm^2. (b) Growth of the second honeycomb layer and corrugation along the line. $V_b=2.5$ V, $I=0.05$ nA, and 45×45 nm^2. The STS for the second honeycomb layer shows a clear band gap.

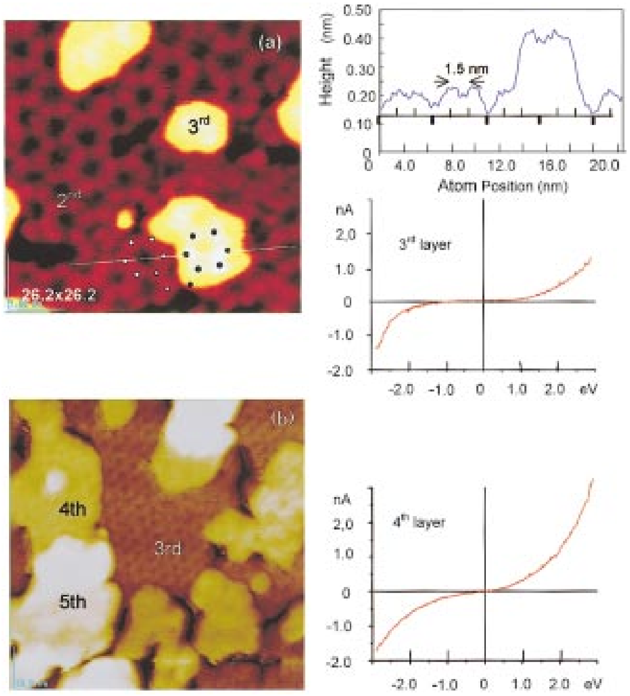

FIG. 3. (Color) (a) The growth of the third honeycomb layer on a perfect second layer and the corrugation along the line. The marks at the step edge of the third layer indicate continuous honeycomb ring structures between the second and third layers, which indicate the stacking of Zn_3 on the top of the Zn_3 of the underlying second layer. $V_b=2.5$ V, $I=0.15$ nA, and 26.2×26.2 nm^2. The STS for the third honeycomb layer has a band gap. (b) Islands grown on the third layer are metallic. $V_b=2.5$ V, $I=0.05$ nA, and 69×69 nm^2.

TABLE I. Corrugation (nm) of atoms along the line in Fig. 1. (*U*) and (*F*) are the atoms on either faulted or unfaulted half.

Si rest atom	Center Si adatom	Corner Si adatom	Bright (Zn) 3 dot	
$-0.04(U)$, $-0.03(F)$	$0.04(F)$, $0(U)$	$0.03(F)$, $0.02(U)$	0.18–0.19	This work
− − −	$0.019(F)$, $0(U)$	$0.034(F)$, $0.015(U)$	− − −	Ref. 7

our experiment, it was known that when a half-unit cell was occupied by a Zn_3 cluster, the neighboring center Si adatoms in the three adjacent halves became dark at −2.5 V of the bias potential, but their intensity was little lowered at a 2.0 V bias potential, as shown in Fig. 1(b). Taking these facts into account, the empty-state image approved at a positive bias potential may reflect the corrugation of surface atoms. The heights of Si adatoms and Zn_3 dots, along the line drawn in Fig. 1(a), are summarized in Table I, where the height is evaluated from the center Si adatom on the unfaulted half (*U*) obtained at a 3.0 V bias potential.

The height of Si adatoms in Fig. 1(a) is in surprisingly good agreement with that obtained by atomic force microscopy (AFM).[7] The height of the Zn_3 dot in Fig. 1(a) is 0.18–0.19 nm from the center Si adatom level (0.21–0.23 nm from the Si rest atom), which is undoubtedly smaller than the size of metallic Zn (~0.27 nm in diameter). The depth of the corner hole of the Si(111)-7×7 area in Fig. 1(a) is about 0.11 nm from the corner Si adatoms. If the three Zn atoms of a Zn_3 cluster would be on the center Si-adatoms in a half-unit cell, the Zn-Zn distance (0.76 nm) is too long to take an attractive interaction among the Zn atoms. Therefore, we presumed that the three Zn atoms move to the center to take an optimum interaction, as illustrated in Fig. 4. It should be pointed out that the depth of hole on the first honeycomb layer in Fig. 2(a) is very close to the height of a Zn_3-dot measured from the corner Si adatom level (0.16–0.17 nm) in Fig. 1(a). Therefore, we can conclude that the first layer is accomplished by the array of Zn_3 clusters one in each faulted and unfaulted halves.

More deposition of Zn brought about a layer-by-layer growth of the second and third honeycomb layers, as shown in Figs. 2(b) and 3(a). Interestingly, the honeycomb holes on the first layer area in Fig. 2(b) have almost equal depth, as observed in Fig. 2(a), that is, the honeycomb holes on the first layer area are not filled with Zn atoms ahead of the growth of the second layer. In contrast, the holes on the second layer area in Fig. 2(b) are undoubtedly shallower than those on the first layer area, that is, the holes on the second layer are about 0.05 nm depth. Taking these facts into account, the second honeycomb layer grows as the honeycomb holes in the first layer are filled with Zn atoms, that is, the honeycomb layer may be guided by filling up the underlying honeycomb holes with Zn atoms. When we compare the bright points of the second honeycomb layer to those on the first layer, the bright points of the second honeycomb layer are on the top of the bright positions of the underlying honeycomb layer, as indicated by guiding spots in Fig. 3(a).

This fact may indicate that Zn_3 clusters of the second layer are stacked on the top of the underlying honeycomb Zn_3 clusters, and that the honeycomb column composed of Zn_3 clusters is materialized on the Si(111)-7×7 surface. We presumed that such an unusual stacking is conducted by rotating the Zn_3 cluster 60° as illustrated in Fig. 4.

As summarized in Table II, the height of the first layer is ~0.17 nm from the center Si adatoms, but the height of the second, third, and fourth layers is ~0.21 ± 0.01 nm. The apparent height of the first layer depends on the Si level adopted, and the height of the first layer measured from the rest Si atom is 0.20–0.21 nm. As we presumed above, if the three Zn atoms of the Zn_3 cluster contract to the center of the 7×7 half-unit cell, the level of the first layer goes down a little.

It is known that the honeycomb holes become shallower and shallower in a sequence of the first, second, and third layers are increased. It should be pointed out that no fourth honeycomb layer is attained on the third layer, but Zn islands are grown as shown in Fig. 3(b). Accordingly, we presumed that the holes on the third layer are too shallow to regulate the growth of the fourth honeycomb layer on it, so that the deposited Zn forms islands on the third layer, as observed in Fig. 3(b).

We could say that the honeycomb layers of the Zn_3 cluster formed on Si(111)-7×7 is a novel matter which is materialized by the weak interaction of Zn atoms and Zn_3 clusters. As far as we know, this is the first example of a supercompound of cluster materialized on the surface by weak interaction, and we can say that this is a kind of suprahoneycomb compound. The suprahoneycomb of a Zn_3 cluster is entirely different from the interference fringe pattern observed on the Pd-deposited Si(111)-7×7 surface in Ref. 8. The scanning tunneling spectroscopy (STS) of the Zn_3 suprahoneycomb layers has a clear wide band gap, as shown in Fig. 2(b) (second layer) and Fig. 3(a) (third layer), where the STS was measured at the bright points of the corresponding honeycomb layers. In contrast, the Zn islands grown on the third

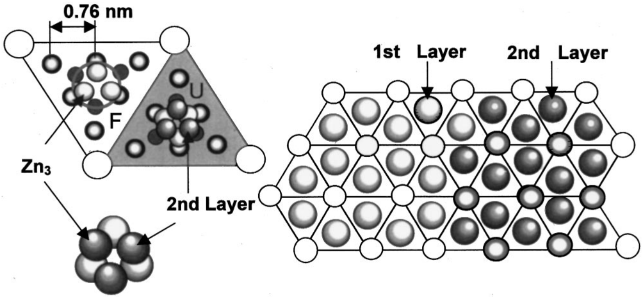

FIG. 4. A model of the Zn_3 cluster formed on a Si(111)-7×7 surface and the coincident growth of the second honeycomb layer by stacking the Zn_3 cluster on top of the underlying Zn_3 site by rotating 30°.

TABLE II. Corrugation for the $(\mathrm{Zn})_3$ dot and the step height of honeycomb layers (nm) evaluated from empty-state images.

Center Si adatom	Corner Si adatom	$(\mathrm{Zn})_3$ dot	First	Second	Third	Fourth
$0.01(F)$, $0(U)$	$0.03(F)$ $0.02(U)$	0.18–0.19	0.17	0.22	0.20	0.21

layer is undoubtedly metallic, as shown in Fig. 3(b). These results also indicate that the honeycomb layers provide a compound materialized by the weak interaction of a Zn_3 cluster on Si(111)-7×7. The suprahoneycomb compound of Zn_3, found in this paper, is explicitly different from the adsorption of Tl atoms (speculated to be Tl_9 clusters) in the faulted half of the Si(111)-7×7 surface reported in Ref. 5. They showed that a Tl_9 cluster-adsorbed Si(111)-7×7 surface is metallic due to STS, and no growth of the second layer was observed. The details of the electronic structure as well as the position of Zn atoms will be studied by angle-resolved spectroscopic experiment and a surface x-ray-diffraction study.

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