Observation of a metallic ground state of Sn/Ge(111)-3×3 at 4 K

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The Sn/Ge(111)-3×3 surface was investigated by scanning tunneling microscopy/spectroscopy (STM/STS) at low temperature, for which a triangular Mott-Hubbard ground state was suggested recently. Our detailed STM/STS observation at 77 K combined with *ab initio* calculations unambiguously determines its atomic structure as the one-up two-down model with one third of Sn adatoms lifted upward from the flat $\sqrt{3}\times\sqrt{3}$ layer. The surface is metallic due to the partially filled dangling bonds on the down adatoms. On cooling down to 4 K, another 3×3 phase with a distinct but still metallic electronic structure was observed. The Mott-Hubbard ground state with an undistorted $\sqrt{3}\times\sqrt{3}$ structure is denied.

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I. INTRODUCTION

Recently, there has been a growing interest in metallic monolayers (ML) on semiconductor surfaces as ideal low-dimensional electron systems. Due to the band gap of the substrate, the electrons in these systems are well isolated into one- or two-dimensional (1D/2D) metallic bands. Interesting phenomena, such as the density-wave formation and the electron localization, have been observed, which are closely related to those band structures.[1,2] The ease of real-space observation with atomic resolution in these systems may reveal new physical aspects of 1D/2D metals.

Among them, $(\sqrt{3}\times\sqrt{3})R30°$ ($\sqrt{3}$, hereafter) phases formed by 1/3 ML of Pb or Sn on (111) surfaces of Ge and Si have attracted a great deal of interest because of an intriguing phase transition. These surfaces contain one metal adatom per $\sqrt{3}$ unit, the dangling-bond (DB) electron of which yields a very narrow half-filled band. This band may make the surfaces unstable not only against the electron-phonon interaction leading to the density-wave formation but also against the electron correlation. Indeed, the systems, except Sn/Si(111), commonly undergo phase transitions into 3×3 phases upon cooling,[3–6] whose driving force was a matter of long-standing debate.

This transition was originally attributed to a charge-density-wave transition driven by Fermi-surface nesting.[3,4] However, the absence of any electronic structure change[7,8] and the dynamically fluctuating lattice at room temperature (RT) were later revealed to converge into an order-disorder transition picture.[8–10] The adsorbates thermally fluctuate at RT between vertically shifted positions on the hollow sites but freeze into the 3×3 unit cells with adatoms in up and down positions at low temperature (LT). Although most of the recent studies supported the order-disorder mechanism, the atomic structure of the 3×3 LT phase is currently under debate with two nearly degenerate[11] models of one (two) adatom(s) in the up position among three adatoms within one unit cell, so called the 1U2D (2U1D) model.[12–14] The structural issue is not trivial since the energy differences of the involved models are less than 30 meV and the energetic hierarchy depends sensitively on the strain.[11]

Furthermore, very recently, the 3×3 phase was reported to change into an insulating phase below 30 K on Sn/Ge(111).[15] Structural probes suggested the reappearance of the $\sqrt{3}$ order and the photoelectron spectra were interpreted to evidence a gap opening at LT. A similar insulating phase was also reported on Sn/Si(111) below 70 K.[16] The insulating phase was interpreted as a 2D Mott-Hubbard insulator due to the electron correlation in the narrow metallic band.[17] A 2D Mott insulator on a triangular lattice is very interesting due to the inherent frustration of the spin ordering.[18] Moreover, the present transition into a higher symmetry lattice (from 3×3 to $\sqrt{3}$) is far from being usual since Mott transitions accompany symmetry-breaking structural transformations with only very few exceptions.[19,20] Thus, the nature, structural and electronic, of this phase deserves further attention.

In this paper, we report on an extensive LT scanning tunneling microscopy/spectroscopy (STM/STS) experiment for Sn/Ge(111). We confirm the atomic structure of the 3×3 phase as the 1U2D model at 77 K with the guide of density-functional-theory calculations. The local density of states (LDOS) are detailed to reveal that the metallic property is due to the partially filled DBs on down adatoms. We show that the surface basically keeps its 3×3 order and gapless LDOS down to 4 K. Instead, a bias-specific electronic state change occurs on up adatoms, which can explain the previous observation of the "$\sqrt{3}$-like" structure at LT. This clearly denies the Mott transition scenario[15] but still challenges the present understanding of the ground state of this system.

II. EXPERIMENTAL

The experiment was performed using a commercial LT scanning tunneling microscope (UNISOKU, Japan).[22] The Ge(111) wafer (n type, 10–50 Ω cm) was cleaned through cycles of Ar^+ sputtering and annealing at 850 °C as checked by low-energy-electron diffraction (LEED). Sn was evaporated from an effusion cell. After each evaporation, the sample was annealed to ~300 °C to form a well-ordered $\sqrt{3}$ surface. dI/dV spectra and maps were taken by using the

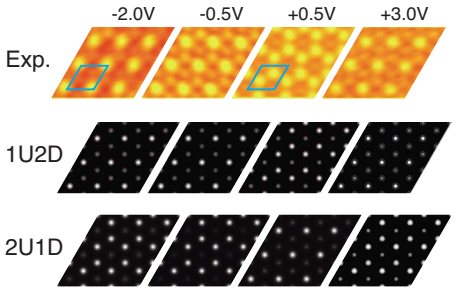

FIG. 1. (Color online) (Top) A collection of STM images of Sn/Ge(111) at 77 K taken from the same surface area with the sample bias indicated. The 3×3 unit cells are indicated. The tunneling current were 200, 90, 80, and 200 pA from left to right, respectively. (Middle and bottom) The simulated STM images at corresponding biases based on the 1U2D and 2U1D models (Ref. 21). The contrast of each image is adjusted to optimize the clarity.

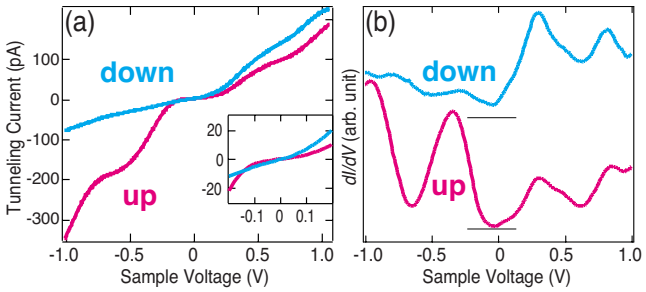

FIG. 2. (Color online) Typical STS (a) I-V and (b) dI/dV-V curves on the up and down Sn atoms taken at 77 K. The dI/dV curves are shifted for clarity, with the zero value of dI/dV marked by solid lines. The inset in (a) enlarges the curves around the zero bias. These spectra are averaged for two sites to reduce the noise level but the spectral shapes are robust among a large number of adatoms probed.

lock-in technique with an external sinusoidal modulation of 25 mV at 1 kHz.

III. RESULTS AND DISCUSSION

First, we examine the detailed bias dependence of the STM images at 77 K. This is very important for the LT phase transition as discussed below. Selected ones are shown in the top panel of Fig. 1. The surface exhibits a 1U2D pattern (one bright and two dark protrusions per unit cell) in filled states down to the sample bias (V_s) of −3.0 V. However, in empty states, the opposite 2U1D pattern is observed in the low-bias region. This result is in accord with the previous reports.[4,23] Another contrast inversion occurs at a higher empty-state bias beyond 2.0 V resulting in a strong 1U2D pattern at 3.0 V, which was not probed previously. This is apparently a strong electronic effect, which makes it difficult to identify the up and down adatoms.

In order to determine the atomic structure, we perform *ab initio* density-functional-theory calculations using the VASP code,[24,25] which incorporates ultrasoft pseudopotentials[26] and generalized-gradient approximation for the exchange-correlation energy.[27] The surface is simulated by a repeated slab model in which eight Ge layers and a vacuum layer corresponding to ten atomic layers are included. The bottom-most Ge bilayer of the slab is fixed at a bulklike structure with its DBs passivated by hydrogen atoms. The 13 Ry cut-off energy in the plane-wave basis and a 8×8 k-point mesh in a 3×3 surface Brillouin zone are used. We follow the Tersoff-Hamann scheme[28] to simulate STM images.

A similar STM simulation was recently reported, which simply categorized the images into filled- and empty-state conditions.[23] However, the above mentioned bias dependence, which exhibits the transition between 1U2D and 2U1D patterns even in the same bias polarity, requests a more careful and detailed comparison with experiments. The total-energy calculation itself is not too helpful in identifying the structure since the energy differences between different models is marginal (smaller than 20 meV per unit cell) and close to the accuracy of the calculation. The simulated STM images for the 1U2D and 2U1D models are presented in Fig. 1. While the simulation with the 1U2D model nicely reproduces the whole characteristic bias-dependent STM images, especially the double contrast inversion, the 2U1D model produces a totally opposite contrast for the entire bias range. This is because the up and down atoms have electronic states with almost opposite characteristics as explained below. Thus, the atomic structure of the 3×3 phase is unambiguously identified as the 1U2D model. The above bias dependence was observed even around defects, which reveals the common atomic structure all over the surface, contrary to the previous knowledge.[29]

Within the STM images, the bright protrusions in high biases of both polarities correspond to the up adatoms, reflecting more or less the geometry. However, near the Fermi level (E_F), a charge transfer occurs from the DBs of down adatoms to the up ones, which is actually the origin of the up-and-down structural distortion. This reconstruction mechanism is very similar to the old Haneman model for clean Si(111)-2×1, where the charge is transferred from the DB of the lifted-down atom to that of the lifted-up atom, breaking the sp_3 symmetry.[30] The filled (empty)-state DB LDOSs are, thus, highly localized on up (down) adatoms. This explains the contrast inversion at the low-bias range ($-0.5\sim0.5$ V). The DB states are clearly identified in the STS spectra shown in Fig. 2(b). The strong peaks observed at the vicinity of zero bias (±0.3 V) in dI/dV are unambiguously attributed to DB states.[8] This is further confirmed by the dI/dV map at the corresponding bias ($V_s\sim-0.3$ V) for the filled DB state [Fig. 5(b)]. A clear 1U2D pattern is seen in Fig. 5(b) indicating larger DB LDOSs on up adatoms. All these spectroscopic results are fully reproduced in the theory while the energy gap between the filled and empty DB states are underestimated as about half of the measured value. It is well known that density-functional-theory calculations usually underestimate the gap size. However, the agreement between the calculations and the experiments is excellent for the present system in band dispersions,[23] STS spectra, and STM images. This indicates that the electron correlation effect is not substantial for the 3×3 phase. However, this may not be the case for the very low-temperature ground state as discussed below.

Since there are two down adatoms in a unit cell to provide electrons, a single up-adatom DB can be fully occupied

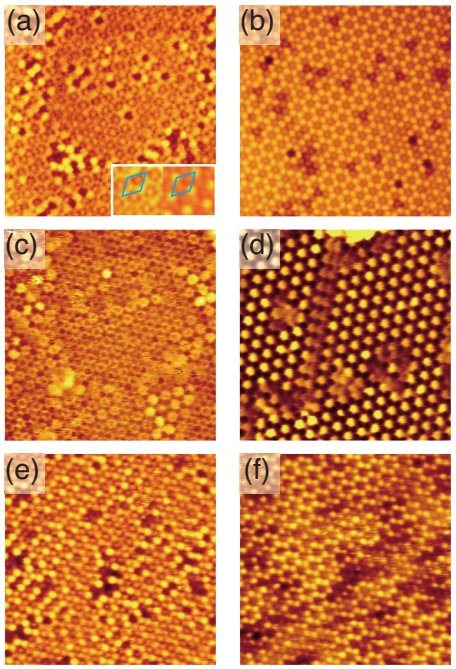

FIG. 3. (Color online) (a) Filled- and (b) empty-state STM images (170×170 Å^2) of Sn/Ge(111)-3×3 taken at 4 K. The tunneling condition (V_s,I) is (−1.0 V, 200 pA) for (a), and (0.5 V, 100 pA) for (b). (c) The dI/dV map at (−0.3 V, 100 pA) shows a weaker 1U2D pattern than (d) the corresponding image taken at 77 K. (e) and (f) show filled- (−1.0 V, 200 pA) and empty- (0.5 V, 100 pA) state STM images of a defect-rich surface at 4 K, respectively. (a)–(c), (e), and (f) were taken on the same surface areas, respectively. The inset of (a) compares the filled-state STM images (−1.0 V, 200 pA) taken at 4 (left) and 77 K (right) with 3×3 unit cells indicated.

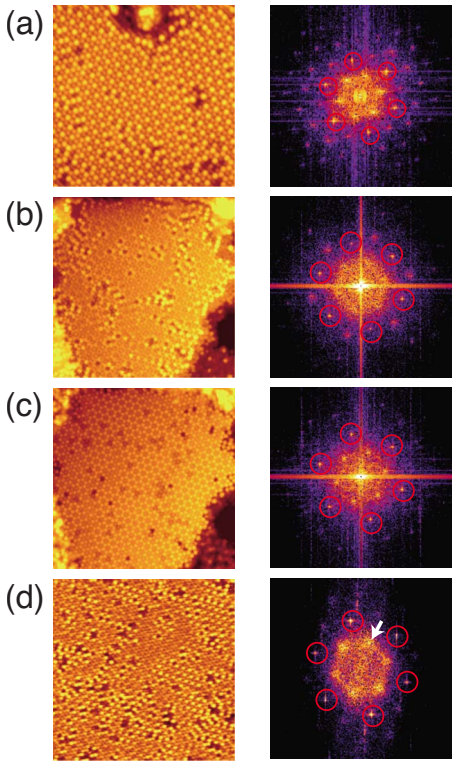

FIG. 4. (Color online) STM and corresponding Fourier transform images of Sn/Ge(111)-3×3 at (a) 77 and [(b) and (c)] 4 K, and those of (d) the defect-rich surface at 4 K. The tunneling conditions for (a)–(d) are (−0.7 V, 70 pA), (−1.0 V, 200 pA), (1.0 V, 200 pA), and (−1.0 V, 200 pA), respectively. The $\sqrt{3}$ features in the Fourier transform images are marked by circles and the 3×3 features are located closer to the center as indicated by the arrow in (d).

while the down adatoms are not fully emptied but quarter filled.[11] The down adatoms, thus, should be metallic. This is confirmed experimentally by the significant density of states (DOS) at E_F in Fig. 2(b) on down adatoms, in clear contrast to up adatoms. This contrasting behavior is also obvious in the corresponding I-V curves [see the slopes at E_F in the inset of Fig. 2(a)]. A very recent study suggested that the two down adatoms are inequivalent in STM images, which would explain the complex line shape of the Sn core-level photoelectron spectra.[31] This asymmetric feature in the STM images for the down adatoms within a 3×3 unit cell is also observed here in the filled state (see Fig. 1) as a slight height (contrast) difference. However, this difference is marginal compared with the overall STM corrugation and no difference was found in the STS spectra between these inequivalent down adatoms. This small contrast difference exhibits little temperature dependence, not affecting the following discussions.

Next, the ground state is investigated by further cooling. Figure 3(b) shows an empty-state STM image taken at 4 K. The same low-bias 2U1D pattern as that at 77 K is evident all over the surface. One can confirm that the 3×3 translational symmetry is preserved in contradiction with Ref. 15. The origin of the discrepancy is discussed further below. The persistent 3×3 ordering even at 4 K occurs throughout the whole surface and this ordering is a significantly long-range one. This is clearly evidenced by the Fourier transform analysis of the large area STM images as shown in Fig. 4. The 3×3 features in the Fourier-transformed STM images are evident at all temperatures down to 4 K and at all bias voltages, and are even independent of the defect density. These features are blurred at 4 K, which may be due to the reduced coherence of the 3×3 order.

However, in contrast to the persistent 3×3 ordering, there is a certain temperature-dependent change within a limited bias range of filled states, $V_s=-0.1--1.5$ V. Figure 3(a) displays filled-state STM images at 4 K and $V_s=-1.0$ V of the same surface area as Fig. 3(b). The 1U2D contrast observed at 77 K becomes weak except around defects and has a different shape as shown in more detail in the inset. However, this temperature-induced change does not indicate the recovery of the $\sqrt{3}$ symmetry and is observed only in a limited bias range. Note also that the previous STM data suggesting the low-temperature $\sqrt{3}$ phase were also taken at this bias range.[15] The significantly reduced contrast between up and down adatoms must be the reason why the $\sqrt{3}$-like phase was observed in the previous filled-state STM study.[15] This previous work did not present any empty-state image, where we find little change in the 3×3 contrast. We also scanned the temperature and found that the above change occurs from 20

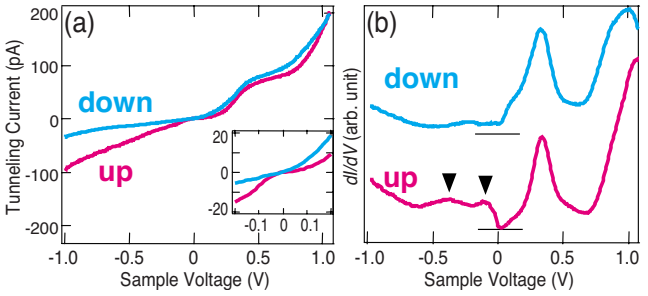

FIG. 5. (Color online) Typical STS (a) *I-V* and (b) dI/dV-V curves taken at 4 K on the up and down adatoms away from defects in Figs. 3(a) and 3(b). The dI/dV-V curve on the up adatom drastically loses its weight around −0.3 V in comparison with that at 77 K. Yet, the metallic nature is clearly identified in both *I-V* and dI/dV-V curves on the down adatoms.

K. This transition temperature is consistent with the previous report and the defect density of the present surface is comparable to those of the previous experiment.[15]

The temperature-induced change was manifested in the electronic structure. Figures 5(a) and 5(b) show typical STS spectra on the up and down adatoms [dark and bright, respectively, in Fig. 3(b)] at 4 K. While other spectral features are more or less intact, the intensity of the filled DB state on up adatoms is greatly reduced and splits into two small peaks compared with that at 77 K. This LDOS reduction is also obvious in the *I-V* curves and the dI/dV map of the surface at V_s=−0.3 V [Fig. 3(c)]. The 1U2D contrast in the LDOS map becomes much weaker than that at 77 K [Fig. 3(d)]. However, as shown in Fig. 5, the metallicity of the surface is preserved; the finite LDOS (and the slope of *I-V*) at E_F on down adatoms exhibits little change without any sign of the gap opening. No difference in the STS spectra was found among the down adatoms although the inequivalent down adatom feature is obvious in the inset of Fig. 3(a) as that at 77 K. This is in sharp contrast to the claim of the previous photoemission study.[15] However, we notice the significant reduction and broadening of the DB state also in the photoemission spectra.[15] Thus the gap opening claimed in that study might simply be due to the reduced intensity of the DB state near E_F. The conservation of the DOSs at E_F and the change of the filled DB state are not consistent with the Mott transition picture at all. In summary, the present results clearly rule out the possibility of the recovery of the $\sqrt{3}$ symmetry and the Mott (or any other gap opening) transition at LT.

At the present stage, the origin of the change of the 3×3 phase at LT observed here is not clear. A glass transition,[32] which was proposed on the related system of Pb/Ge(111), is not the case because the surface keeps a clear 3×3 ordering [Fig. 3(b)]. We scanned the surface at various sample biases from −1.5 to 3.0 V and tunneling currents from 30 to 200 pA, which yields consistent results. We can, thus, rule out a tip effect.[33] The influence of defects is also not likely since "the modified 3×3 phase" does not develop near the defects. The defect effect can be seen more clearly on a defect-rich surface in Figs. 3(e) and 3(f). This surface has ~25% increased defect population from that in Figs. 3(a) and 3(b). The 1U2D pattern remains more widely in the filled-state STM images [Fig. 3(e)] although the empty-state images were essentially independent of the defect concentration [Figs. 3(b) and 3(f)]. Thus, the present LT transition is thought to be intrinsic to the surface and the modified 3×3 structure could be the ground state of the defect-free surface. On the other hand, the coexisting domains of two different 3×3 phases can reduce the spatial coherence and could weaken the 3×3 features of the LEED pattern in the previous study as also shown in the Fourier-transformed STM images of Fig. 4.[15]

The previous[11,34] and the present total-energy calculations indicate that the energy gain of the 1U2D model is only marginal (13 meV) from the flat $\sqrt{3}$ structure, which is close to the accuracy limit of the calculation. From the transition temperature of 20 K, we think that there exists another 3×3 structure, which has a proximal energy difference from the 1U2D model. This phase may have a slightly different geometry, which is not clearly determined by the calculation due to such a small energy difference. On the other hand, although the Mott-Hubbard model is denied, the previous theory suggested the possible importance of the electron correlation and the spin ordering,[17] which is out of the scope of the calculation scheme used here. Further theoretical study is thus highly required to investigate the ground states of the present system with such extra degrees of freedom.

IV. CONCLUSIONS

We have investigated electronic and atomic structures of Sn/Ge(111)-3×3 with STM/STS. The detailed bias dependence of the STM images and the *ab initio* calculations identify the 1U2D model as the atomic structure at 77 K. The surface changes into another 3×3 surface with the split dangling-bond state but keeps the intact metallicity at 4 K. The Mott-Hubbard transition picture of this surface is ruled out. The 3×3 structure found here should be energetically very close to the 1U2D structure while it is not easily reproduced in the density-functional calculations. The spin ordering and electron correlation may be important to understand this intriguing 2D metal.

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