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STM observation of Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn at low temperature

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We carefully investigated the α-$\sqrt{3}\times\sqrt{3}$ phase on Si(111) surface covered by 1/3 monolayer of Sn using scanning tunneling microscopy (STM) at room temperature (RT), 70 K, and 6 K, with reflection high-energy electron diffraction (RHEED) at RT and 120 K. While weak streaks of the 3×3 periodicity was observed in RHEED at 120 K, STM showed a long-range ordered $\sqrt{3}\times\sqrt{3}$ phase only, without 3×3 domains, over the whole temperature range investigated. The 3×3 streaks were found to originate from local 3×3 modulations around defects. The present result indicates that there is no phase transition from the $\sqrt{3}\times\sqrt{3}$ to 3×3 on cooling down to 6 K, which contradicts to a prediction from core-level photoemission study and challenges the thermal fluctuation picture for the RT phase.

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Phase transitions in low-dimensional systems have recently attracted a lot of experimental and theoretical interests.[1] One of the most popular systems is $\sqrt{3}\times\sqrt{3}$ phases prepared by 1/3-monolayer (ML) adsorption of Group IV element atoms, Sn or Pb, on elemental semiconductor (111) surfaces, Si(111) or Ge(111).[2,3] Such atoms sit on T_4 sites and create dangling bonds toward vacuum, making the surfaces quasi-two-dimensional metallic systems.[2–5] The striking phenomena were reported on Ge(111)-$\sqrt{3}\times\sqrt{3}$-Pb,[2] Ge(111)-$\sqrt{3}\times\sqrt{3}$-Sn,[3] and Si(111)-$\sqrt{3}\times\sqrt{3}$-Pb (Ref. 6) that these surfaces changed gradually to 3×3 phases when the temperature was lowered below room temperature (RT). The transition on the Ge(111)-$\sqrt{3}\times\sqrt{3}$-Pb surface was proposed to be due to the instability of a low-dimensional electronic system, and its first scanning tunneling microscopy (STM) images presented in Ref. 2 produced a great impact as a direct observation of the surface charge-density wave (CDW). However, further electronic structure investigations by means of photoemission spectroscopy on these systems, especially on the Sn/Ge(111), gave inconsistent results to the CDW picture. The core-level electronic structures of the $\sqrt{3}\times\sqrt{3}$ and 3×3 surfaces were qualitatively quite similar to each other;[4,7] two major components in the Sn $4d$ spectrum were found for both the low- and high-temperature phases, which corresponded to two types of chemical environments for Sn atoms in the 3×3 phase, but were not consistent with a simple T_4 model in the $\sqrt{3}\times\sqrt{3}$ phase at RT. Ultraviolet photoelectron spectroscopy studies were also performed to determine the Fermi surfaces,[4,8,9] but there was little evidence for the CDW transitions. In order to describe these results, it was recently proposed that the transition from the $\sqrt{3}\times\sqrt{3}$ to 3×3 was an order-disorder transition.[4,7] The idea is that the $\sqrt{3}\times\sqrt{3}$ phase is just a disordered state of the 3×3 structure, similar to the famous transition from the $p(2\times1)$ at RT to the $c(4\times2)$ around 100 K on the Si(001) clean surface.[10–13] In the thermal fluctuation model, Sn atoms are considered to sit at two different heights on T_4 sites of the ideal Ge(111) surface, so there is an energy barrier that has to overcome before fluctuations can occur. While the random fluctuation of surface Sn atoms between the two positions leads to the $\sqrt{3}\times\sqrt{3}$ phase at RT, the fluctuation is frozen to produce the 3×3 order by regular occupations of Sn atoms at the up and down positions at low temperature. Thus, at the moment, the transitions on Pb/Ge(111) and Sn/Ge(111) systems are debated in both the CDW and order-disorder pictures.[14–16]

Compared with the Pb or Sn/Ge(111) systems, less attention has been paid to $\sqrt{3}\times\sqrt{3}$ phases induced by Pb or Sn adsorption on the Si(111) surface. These systems may be expected to behave similarly to their isoelectronic counterparts on Ge(111). Actually, a transition from the $\sqrt{3}\times\sqrt{3}$ to 3×3 was observed locally by STM for the Pb/Si(111), but domains of the $\sqrt{3}\times\sqrt{3}$-Pb phase[6] always coexisted with other phases and were not sufficiently large for macroscopic surface analysis such as photoemission spectroscopy. On the other hand, there is no report of a $\sqrt{3}\times\sqrt{3}$-to-3×3 transition on the Sn/Si(111) surface. It is known, however, that the Sn $4d$ core level of the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn surface shows two major components, which is not compatible with the simple T_4 model.[17] According to the thermal fluctuation model, this implies a possibility of a transition to the 3×3 phase at low temperatures, much like the Sn/Ge(111) case. A previous study on Sn/Si(111) showed that the surface remained the $\sqrt{3}\times\sqrt{3}$ phase, without any sign of the 3×3 phase, at 70 K.[17]

In the present study, we have performed detailed STM and reflection-high-energy electron diffraction (RHEED) observations of the Sn/Si(111) surface at various temperatures from RT down to 6 K. We observed the long-range ordered $\sqrt{3}\times\sqrt{3}$ phase only at every temperature investigated, indicating that no phase transition from the $\sqrt{3}\times\sqrt{3}$ to 3×3 occurred even at 6 K. Instead, we found local 3×3 modulations only around defects at temperatures ranging from RT to 6 K, which produced weak 3×3 diffraction streaks in RHEED. The present result indicates that the fluctuation model is not suitable for interpreting two components in the Sn $4d$ core-level photoemission result[17] for the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn phase.

The experiments were carried out using a commercial UHV low-temperature STM-RHEED system (UNISOKU USM501 type) and another variable-temperature RHEED chamber.[18–21] The sample crystals were cut from an n-type

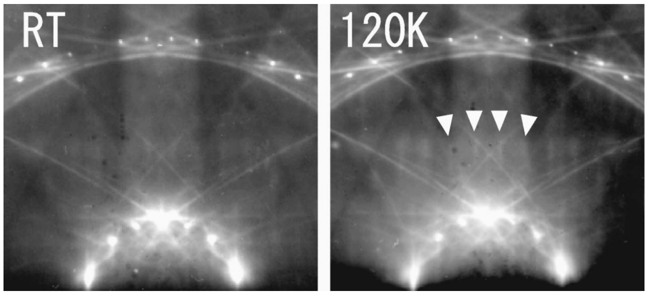

FIG. 1. RHEED patterns of the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn surface at RT and 120 K with accelerating voltage 14 KeV and incidence azimuth$[11\overline{2}]$. White arrowheads indicate 3×3 streaks.

Si(111) wafer (*P* doped, 11∼100 Ωcm) and a *p*-type one-(highly *B* doped). All of the STM images shown here were taken with the former sample, but no difference was observed between the two. The Si(111)-7×7 clean surface was prepared in a standard way ; direct current heating up to 1500 K for a few seconds after mild preheating for about 12 h. Tin was evaporated from an out-gassed alumina-coated W basket. The α phase of Si(111)-$\sqrt{3}\times\sqrt{3}$-Sn was prepared by 1/3-ML deposition of Sn at RT and then annealing up to 750 K for 10 s. The $\sqrt{3}\times\sqrt{3}$ superstructure was checked by RHEED. The STM measurements were carried out at RT, at 70 K, and finally at 6 K. The temperature was measured by a thermocouple attached on the sample stage that was completely surrounded by double radiation shields. All the STM images shown here were taken in constant current mode. Careful RHEED observations were performed at RT and 120 K with the RHEED chamber. During all of our experiments, the pressure was kept at $\lesssim 10^{-10}$ Torr.

Figure 1 shows RHEED patterns of the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn surface taken at RT and 120 K. In both patterns, sharp $\sqrt{3}\times\sqrt{3}$ spots can be observed at the 0th and 1st Laue rings.[22] At 120 K, one can also observe weak 3×3 streaks (indicated by arrowheads). This suggests that the 3×3 structure already exists on the surface at 120 K, which contradicts to the previous report in which the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn showed no indication of the 3×3 in the low-energy electron diffraction pattern at 70 K.[17]

Next, detailed STM observations were performed at low temperatures. Figure 2 displays a typical filled-state image taken at 70 K. The results show only a long-range ordered $\sqrt{3}\times\sqrt{3}$ structure, together with some point defects. It is noted, through detailed bias-dependent STM observations, that there are four types of defects labeled *A*, *B*, *C*, and *D* in Fig. 2. These defects were already reported in the previous STM study at RT,[23] and confirmed to have the same bias dependence as our results at 70 K.[24] One can see bright corrugations with a hexagonal arrangement only around defects *A* in Fig. 2. This means that there are 3×3 modulations only at the nearest neighbors of the defects, which is the same at RT.[23] Concerning the defects, it has been also reported that there exist defect density waves on this surface.[25] We found such density-wave-like features only when the defect population is much larger (∼20%) than the present case (∼2%). The details of this issue will be reported elsewhere.[24]

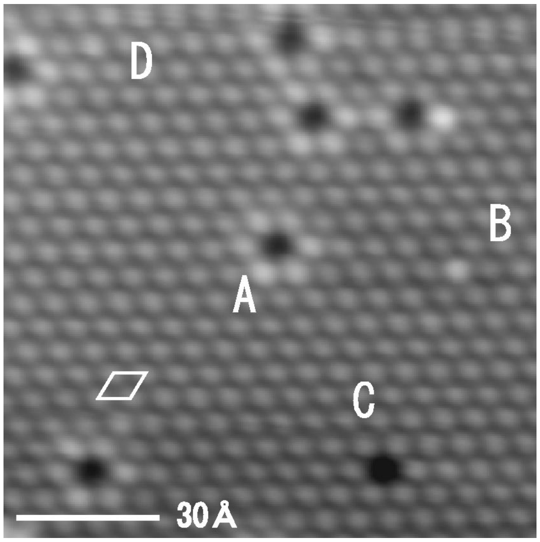

FIG. 2. Filled-state STM image at 70 K with tip bias of 0.8 V and tunneling current of 0.8 nA. Four types of defect were found. The white lozenge indicates the $\sqrt{3}\times\sqrt{3}$ unit cell.

In order to find the relation between the STM images and RHEED patterns, we Fourier transformed (FT) the STM images. STM images and corresponding FT images are shown in Fig. 3 ; typical filled-state images (a) at RT and (b) at 70 K, and (c) a filled-state image of a defect free area at 70 K. In addition to the $\sqrt{3}\times\sqrt{3}$ spots observed in all of the FT images (as indicated by a white arrow in (a)), one can notice very broad features corresponding to the 3×3 periodicity only in (a) and (b). Since such a feature cannot be observed in Fig. 3 (c), it is clear that the 3×3 features in FT images are related to the defects on the surface. We also tried to find the 3×3 correlation in the defect arrangement on this surface using many STM images, but found that the defects aligned completely randomly;[24] the broad 3×3 spots in (a)

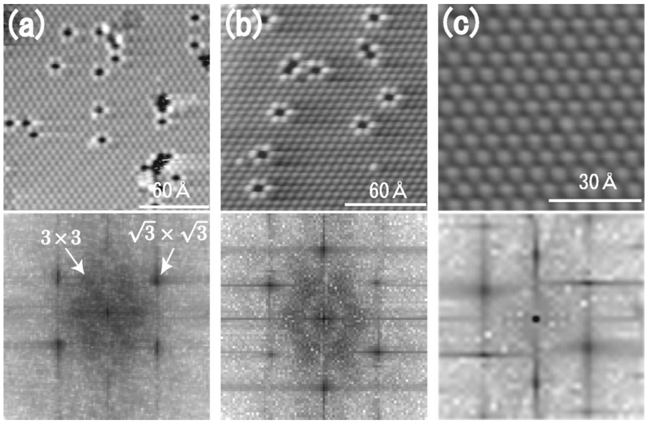

FIG. 3. Filled-state STM images (up) and their Fourier transforms (down), (a) at RT(0.8 V, 0.3 nA), (b) at 70 K(1.0 V, 1.0 nA), and (c) a defect-free area at 70 K (1.0 V, 0.3 nA). White arrows in FT image (a) indicate $\sqrt{3}\times\sqrt{3}$ spots.

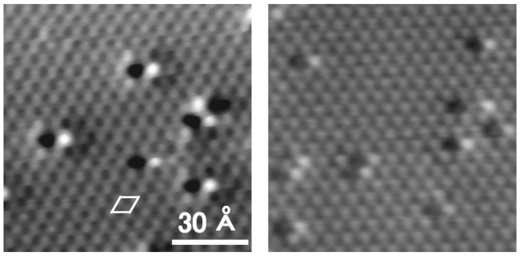

FIG. 4. Filled-state (1.0 V, 0.3 nA) (right) and empty-state (-1.0 V, 0.5 nA) images (left) of the Sn/Si(111) at 6 K. The white lozenge shows a $\sqrt{3}\times\sqrt{3}$ unit cell.

and (b) do not come from the defect arrangement (the details of the defect arrangement analysis will be reported elsewhere).[24] Thus, we can be certain that the 3×3 streaks in the RHEED pattern in Fig. 1 originate from the local 3×3 modulations around the defects (labeled *A* in Fig. 2). Figure 3(a) shows the 3×3 features around defects even at RT, indicating that one could also observe 3×3 streaks in the RHEED pattern at RT in Fig. 1. Actually, one may find very obscure 3×3 streaks in the RT-RHEED image of Fig. 1, which are smeared by more intense background. Consequently, the 3×3 RHEED streaks do not indicate 3×3 domains growing at 120 K. In other words, no phase transition from the $\sqrt{3}\times\sqrt{3}$ to 3×3 occurs at that temperature.

On the other hand, the core-level photoemission study predicted that the transition would occur below 70 K.[17] In order to confirm this issue, we performed STM measurements at 6 K. The results are shown in Fig. 4, which clearly indicate that the surface still maintains the $\sqrt{3}\times\sqrt{3}$ phase even at 6 K. *We find no evidence of a phase transition.*

This result contradicts the proposal from core-level photoemission study by Uhrberg *et al.*[17] First, we shall discuss in detail this discrepancy by comparing the proposed thermal fluctuation model with our results. Within the thermal fluctuation model, the discrepancy may simply be because the temperature of 6 K was not low enough for the transition. If the surface were cooled below 6 K, the 3×3 phase might be observed. If Sn atoms fluctuate between the upper and lower positions at T_4 sites at 6 K with a frequency higher than that of our STM observation, the following relation should hold;

$$\nu_0 \exp\left(-\frac{\Delta}{k_B T}\right) > \nu_{\mathrm{STM}} \tag{1}$$

with $T=6$ K, where ν_0 is the phonon frequency, Δ is an activation energy for the fluctuation between the possible two stable positions of Sn atoms at T_4 sites, and ν_{STM} is the reciprocal number of the time scale for scanning one pixel in our STM images. With a typical phonon frequency of 10^{13} Hz as ν_0 and our experimental STM condition of 10^3 Hz as ν_{STM}, we obtain $\Delta \lesssim 2$ meV. It is noted that recent theoretical calculations suggest a possibility of partial phonon softening in the Sn/Si(111) system.[26] If we take this effect into account, ν_0 should be smaller, so that the resulting activation barrier is less than 2 meV.

Is this small value of the energy barrier for the fluctuation plausible? To our knowledge, there has been no theoretical study to estimate the barrier for the fluctuation on the $\sqrt{3}\times\sqrt{3}$-Sn surface. So we have to compare the present result with other well-known fluctuation systems, such as Si(001)-2×1 (Refs. 10–13) and Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag (Refs. 27, 28) surfaces. It has been reported that these surfaces also give order-disorder phase transitions below RT, and the activation barriers have already been reported by theoretical calculations. For the clean Si(001) surface, the $2\times1\rightarrow c(4\times2)$ transition occurs around 100 K and the activation barrier for the flip-flop motions of tilted Si dimers is ~130 meV.[29] For Si(111)-$\sqrt{3}\times\sqrt{3}$-Ag, it has been known that the Ag trimers show rotatory vibrations between two equivalent configurations with an activation barrier of ~100 meV,[27,28] which is frozen around 150 K. These examples imply that the activation barrier for thermal fluctuation between two stable atomic configurations on Si surfaces is typically ~100 meV. This is much larger than the barrier estimated here for the $\sqrt{3}\times\sqrt{3}$-Sn, by about two orders of magnitude. Thus, it is unlikely that thermal fluctuation on the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn still survives at 6 K. In other words, the thermal fluctuation model is not suitable for the Si(111)-$\sqrt{3}\times\sqrt{3}$-Sn surface ; the Sn atom thermally vibrates around a single stable position at the T_4 site, not between two stable positions of different heights. The Sn atom is frozen at a single-height position on each site at low temperature, maintaining the $\sqrt{3}\times\sqrt{3}$ periodicity.

Here, it is worth comparing the present LT-STM observations with those for the Si(001)-2×1 clean surface. STM images of the Si(001) show symmetric dimers at RT, asymmetric dimers at ~100 K, and symmetric dimmers again below ~10 K.[30,31] While the change between RT and ~100 K is well described by freezing of flip-flop motion of Si asymmetric dimers, the origin of the symmetric dimers observed below ~10 K remains very controversial because this phenomenon cannot be described by the conventional thermal fluctuation picture. Several explanations such as quantum fluctuation[29] and STM tip influence[32] are proposed for that. Here, we discuss our results with these models. In the quantum fluctuation model, Sn atoms are expected to tunnel through the energy barrier between the up and down positions. The model is only suitable for light elements, but not for heavy elements such as Sn; the calculated tunneling probability and the resulting fluctuation frequency are too low. Concerning the tip influence, it has been reported that Si dimers on the Si(001) can be observed below 10 K to be either symmetric or asymmetric depending on the tip bias or tunneling current; the dimers looks symmetric when the tip is very near the sample surface, suggesting a strong tip influence. So in order to check the possible tip influence on the $\sqrt{3}\times\sqrt{3}$-Sn surface at 6 K, we performed STM measurements at tip bias ranging from -3.0 to $+5.0$ V and tunneling current from 0.25 to 2.0 nA that ranged wide enough to cover the tunneling conditions for observing both of symmetric and asymmetric dimers on Si(001). All the STM images showed the $\sqrt{3}\times\sqrt{3}$ structure only, indicating that we can rule out the extrinsic tip influence during the STM scanning.

From the experimental results and discussions described so far, we can conclude that the Si(111)-α-$\sqrt{3}\times\sqrt{3}$-Sn phase does not show a transition to the 3×3 phase on cooling. Because of the single stable height of Sn atoms at T_4 sites, there should be only one chemical environment for Sn atoms on the surface. But, this is not compatible with the two major components found in Sn $4d$ core-level photoemission results.[17] One needs to find an alternative explanation for the two components other than the fluctuation model between two stable positions. One may need to consider more seriously contributions from Sn atoms diffusing into the subsurface region and/or those at defects.

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