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Structural phase transitions of Pb-adsorbed Si(111) surfaces at low temperatures

Kotaro Horikoshi and Xiao Tong
Department of Physics, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Tadaaki Nagao and Shuji Hasegawa
Department of Physics, School of Science, University of Tokyo, 7-31-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
and Core Research for Evolutional Science and Technology, The Japan Science and Technology Corporation,
Kawaguchi Center Building, Hon-cho 4-1-8, Kawaguchi, Saitama 332, Japan

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We found two types of commensurate-incommensurate transition on Pb-adsorbed Si(111) surfaces using reflection high-energy electron diffraction (RHEED) below room temperature (RT); a hexagonal incommensurate (HIC) phase changed to a $\sqrt{7}\times\sqrt{3}$-Pb superstructure around 250 K, and a transient phase between the HIC phase and a striped incommensurate phase changed to a $\sqrt{43}\times\sqrt{3}$-Pb superstructure at 130 K. We constructed a surface structure map in ranges of temperature from 90 K to 500 K and Pb coverage from 0.8 to 1.5 atomic layers including these new phases. We found another structure change where streaks with a 3×3 periodicity began to appear in RHEED just below RT when the $\sqrt{3}\times\sqrt{3}$-Pb phase at 1/3 atomic layer of Pb was cooled. [S0163-1829(99)05039-0]

Metal-induced superstructures of semiconductor surfaces in monolayer (ML) coverage regime have been extensively studied, especially above room temperature (RT). However, below RT, investigation of metal-induced superstructures has been rarely reported. Si(111)-$\sqrt{21}\times\sqrt{21}$-Ag, -6×6-Ag, and Ge(111)-3×3-Pb, -3×3-Sn are rare examples known as low-temperature phases on semiconductor surfaces.[1–3] It is also known that these superstructures indicate novel electronic characters.[2–4] It is thus expected that metal-induced superstructures of semiconductor surfaces below RT will show a variety of interesting electronic properties without drastic reconstructions in atomic arrangements. This is why more investigations on the semiconductor surfaces below RT are needed. In the present paper, we have studied structural changes of Pb-adsorbed Si(111) surfaces in a temperature range from 90 K to 500 K.

The Pb-adsorbed Si(111) surface shows various kinds of phases depending on coverage, temperature and annealing history, which leads to difficulty in understanding their atomic structure and electronic properties.[5–10] Among the various phases on this surface, the incommensurate phase appearing around 1.3 ML Pb coverage and the $\sqrt{3}\times\sqrt{3}$ phase at 1/3 ML have been attracting considerable attention because of their novel electronic properties. Only with about 1-ML Pb adsorption, the incommensurate phase has a metallic character, having an electronic state to pin the Fermi level (E_{F}). This leads to a formation of a very high Schottky barrier of around 1.0 eV.[11] Furthermore, scanning tunneling microscopy observations show that the incommensurate phase is composed of small-sized commensurate $\sqrt{3}\times\sqrt{3}$ domains, which is described as closely packed 30°-rotated compressed Pb(111) layers on bulk-terminated Si(111) surface, and a large quantity of out-of-phase domain boundaries.[12] The configuration of the boundaries changes from a hexagonal network [a hexagonal incommensurate (HIC) phase] to a striped one [a striped incommensurate (SIC) phase] as Pb coverage increases around 1.3 ML.[12] On the other hand, the $\sqrt{3}\times\sqrt{3}$ phase at 1/3 ML is known to have Pb adatoms occupying T_4 sites.[13] The T_4-adatom structures on Si(111) might be expected to undergo a structural change induced by the same mechanism as the transition from $\sqrt{3}\times\sqrt{3}$ to 3×3 superstructures on Pb- and Sn-adsorbed Ge(111) surfaces.[2,3] So, we made reflection high-energy electron diffraction (RHEED) observations on the incommensurate phases (HIC and SIC) around the 1.3 ML Pb coverage and the $\sqrt{3}\times\sqrt{3}$ phase at 1/3 ML in a range of temperature from 90 K to 500 K.

Experiments were carried out in an ultrahigh vacuum chamber that was equipped with RHEED and a sample holder available in a temperature range from 90 K to 1500 K. Its base pressure was 5×10^{-10} Torr and less than 1×10^{-9} Torr during Pb deposition. The substrate was an *n*-type Si(111) wafer with nominal resistivity of 48–50 Ω cm at RT and its typical dimension was $25\times4\times0.5$ mm^3. The silicon surface was cleaned by flashing the sample at 1500 K several times and annealing around 1000 K by direct electrical current. Thus a well-defined 7×7 RHEED pattern was observed. The evaporation source of Pb ($5N$ purity) was an alumina-coated W basket. The deposition amount was monitored with a quartz-crystal oscillator. The temperature of the Si wafer below RT was monitored with an AuFe-chromel thermocouple attached to the sample holder, and with an optical pyrometer for high temperatures.

Structural changes on the Pb-adsorbed Si(111) surface observed by RHEED in the present study is summarized in a structure map of Fig. 1. The lead of coverages indicated on the abscissa was deposited onto the clean 7×7 surface at RT, followed by heating up to 570 K for 3 sec, and finally cooled down to the temperatures indicated on the ordinate. The 0.01 ML coverage of Pb corresponded to a frequency change of about 0.3 Hz in our quartz oscillator, which was detected through an analog-to-digital converter by a computer. Such a small change in frequency is reliable when one carefully stabilizes the system (temperature, electronic circuits). The Pb coverage thus determined is consistent with that in Ref. 12.

A 1×1-Pb phase shown in Fig. 2(a) appeared during annealing at 570 K. This structure is thought to be a two-

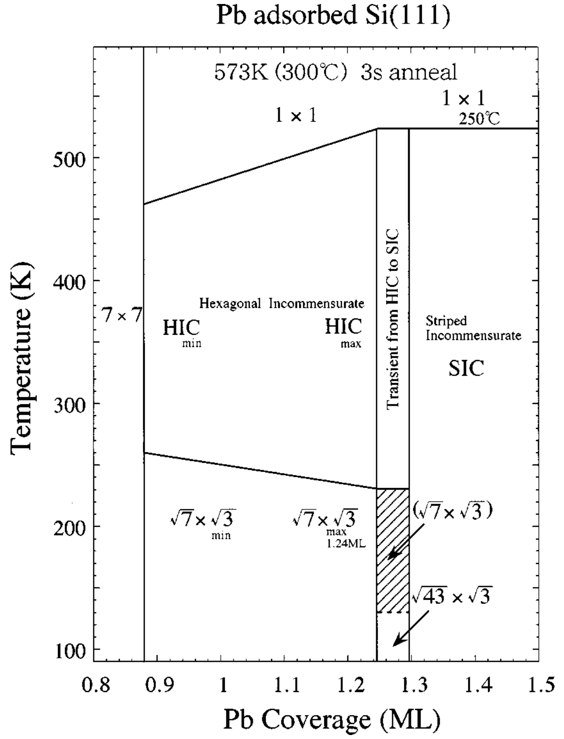

FIG. 1. A structure map, showing the surface phases that appear by Pb deposition.

dimensional liquid phase.[6,14] When this surface was cooled down to RT, two kinds of incommensurate phases appeared depending on Pb coverage as reported in Ref. 12; the HIC phase appeared in a range of coverage less than 1.24 ML, and the SIC phase was added at more than 1.24 ML Pb coverage, and the SIC phase was completed at 1.30 ML. We confirmed these two phases by RHEED.

RHEED patterns in Figs. 2(b) and 2(c) show the HIC phase and the SIC phase, respectively. Streaks at (0.65, 0.65) positions indicated by arrows *A* in Figs. 2(b) and 2(c) correspond to Pb (1, 0) spots,[8,12,14] and streaks at (0.35, 0.35) positions indicated by arrows *B* are attributed to modulation of Pb sites by the corrugation potential.[14] The RHEED pattern in Fig. 2(b) was taken at 1.24 ML, which indicates the sharpest streaks ($\mathrm{HIC}_{\mathrm{max}}$). With more Pb adsorption, the streaks *A* and *B* become broader and more intense without any satellites spots. When the intensity of both streaks become maximum, the streaks *B* split as shown in Fig. 2(c) at 1.30 ML coverage. We discerned that this splitting indicates a completion of the SIC phase according to Ref. 12.

Seehofer *et al.* observed a 1×1 phase around 0.9 ML coverage at RT while we could observe the HIC phase with faint streaks ($\mathrm{HIC}_{\mathrm{min}}$ in Fig. 1). With Pb coverage between 1.24 ML and 1.30 ML, we identified a transient phase between the HIC phase and the SIC phase, though Seehofer *et al.* identified this coverage range as the SIC phase. This transient phase changed to a different structure by cooling from ones that are obtained from the HIC phase and SIC phase, respectively, as discussed below. Because the broadness and intensity of the streaks *A* and *B* in the HIC phase [Fig. 2(b)] increased between 1.24 ML and 1.30 ML, the HIC phase is considered to change continuously to the SIC phase. So the transient phase is not a new phase, but just a homogeneous mixture of the HIC and SIC phase.

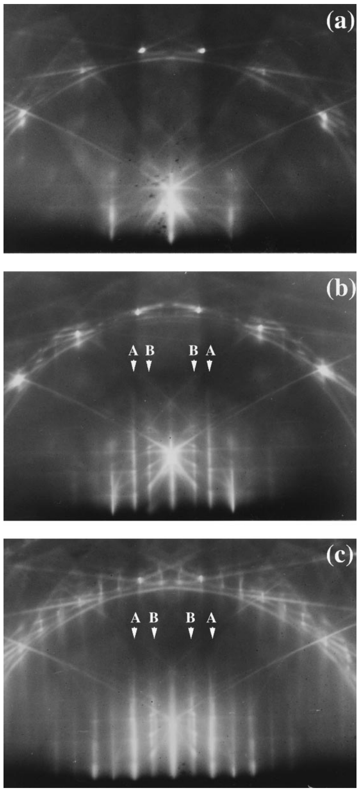

FIG. 2. RHEED patterns taken from the Pb-adsorbed Si(111) surface with an accelerating voltage 15 kV and incidence azimuth $[11\bar{2}]$: (a) 1×1-Pb phase above 520 K, (b) a hexagonal incommensurate (HIC) phase with 1.24 ML Pb coverage at RT, and (c) a striped incommensurate (SIC) phase with 1.30 ML Pb coverage at RT.

When cooled down below RT, the HIC phase changed into a $\sqrt{7}\times\sqrt{3}$ phase shown in Figs. 3(a) and 3(b), which were taken at 100 K with electron beam in $[11\bar{2}]$ and $[1\bar{1}0]$ incidence, respectively. Figure 3(c) is a reciprocal lattice derived from the RHEED patterns. It is a superposition of reciprocal lattices of three equivalent domains rotating each other by ±120°; reciprocal unit vectors b_1^* and b_2^* of the $\sqrt{7}\times\sqrt{3}$ periodicity are represented. Thus, the HIC phase undergoes a commensurate-incommensurate (CI) phase transition to the $\sqrt{7}\times\sqrt{3}$ phase. The transition temperature decreased from 260 K to 230 K with Pb coverage increasing from 0.88 ML to 1.24 ML. The $\mathrm{HIC}_{\mathrm{max}}$ (around 1.2 ML) in Fig. 2 changes to the $\sqrt{7}\times\sqrt{3}$ phase with the sharpest and strongest spot intensity. On the other hand, the $\mathrm{HIC}_{\mathrm{min}}$ (around 0.9 ML) changed to the $\sqrt{7}\times\sqrt{3}$ phase with the broadest and weakest spot intensity. Warming up the $\sqrt{7}\times\sqrt{3}$ surface through the transition temperature up to RT resulted in recovery of the HIC phase, so this CI phase transition was found to be reversible.

On the other hand, the transient phase in the coverage range between 1.24 ML and 1.30 ML exhibited another phase transition below 130 K, where the transient phase changed into a structure shown in Figs. 4(a) and 4(b). These RHEED patterns were taken at 100 K with electron beam in $[11\bar{2}]$ and $[1\bar{1}0]$ incidence, respectively. Figure 4(c) is its reciprocal lattice derived from the RHEED patterns. This phase has also three domains. Reciprocal unit vectors of a

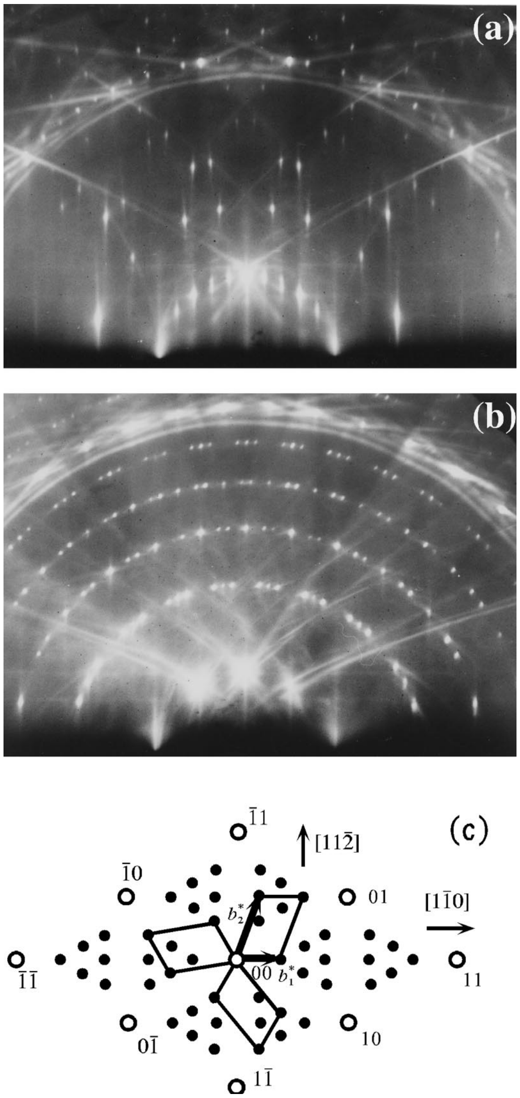

FIG. 3. RHEED patterns of the Si(111)-$\sqrt{7}\times\sqrt{3}$-Pb surface taken at 100 K. The incidence azimuths are (a) $[11\bar{2}]$, and (b) $[1\bar{1}0]$, respectively, and (c) a reciprocal lattice deduced from the RHEED patterns.

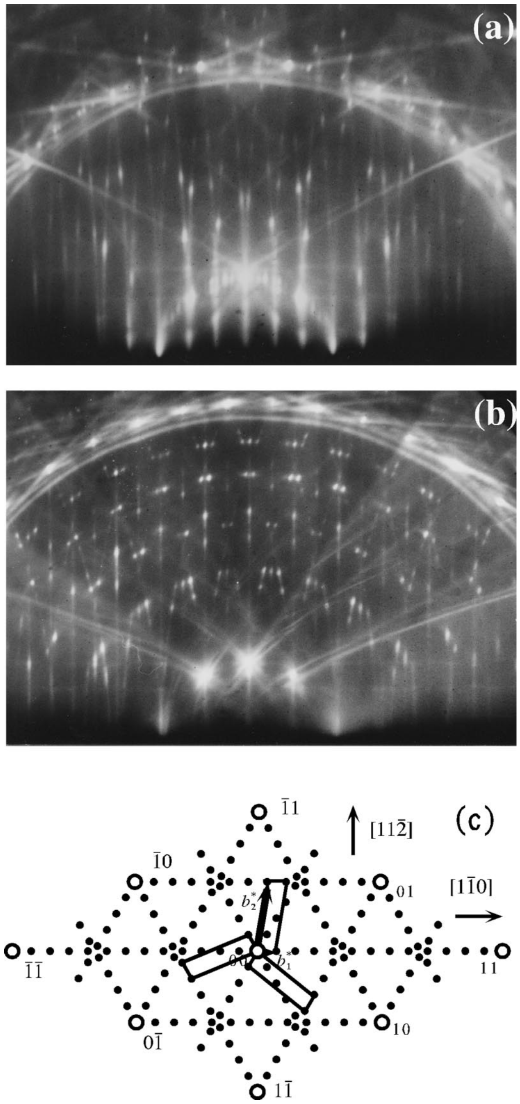

FIG. 4. RHEED patterns of the Si(111)-$\sqrt{43}\times\sqrt{3}$-Pb surface at 100 K. The incidence azimuths are (a) $[11\bar{2}]$, (b) $[1\bar{1}0]$, respectively. (c) A reciprocal lattice deduced from the RHEED patterns.

$\sqrt{43}\times\sqrt{3}$ periodicity are represented in Fig. 4(c). Thus, there is another CI phase transition from the transient phase between the HIC and the SIC to the $\sqrt{43}\times\sqrt{3}$ structure below 130 K. With warming up through the transition temperature of 130 K, the $\sqrt{43}\times\sqrt{3}$ structure changed into the $\sqrt{7}\times\sqrt{3}$ structure, and subsequently, returned to the transient phase at 230 K. So, this CI phase transition was found to have different sequences in structural change between cooling and annealing processes.

We have already observed the $\sqrt{43}\times\sqrt{3}$ phase by low-temperature STM.[15] Its images with atomic resolution clearly show a characteristic ordering in the superstructure; the long-range order along the $[11\bar{2}]$ direction is good, while the order along the $[1\bar{1}0]$ direction is frequently disturbed. The streaks in RHEED patterns in Fig. 4 comes from this kind of anisotropy in ordering.

We also found that additional Pb deposition onto the $\sqrt{7}\times\sqrt{3}$-Pb surface (1.24 ML coverage) kept at 115 K caused a change to the SIC phase at 1.30 ML via the $\sqrt{43}\times\sqrt{3}$-Pb structure. With less than 0.05 ML deposition, the surface superstructure completely changed into the $\sqrt{43}\times\sqrt{3}$, and even after interruption of the deposition, this structure stably remained.

Now, we summarize the phases found here in Fig. 1. The fluid phase (1×1-Pb), incommensurate phases (HIC and SIC), and the commensurate phases ($\sqrt{7}\times\sqrt{3}$ and $\sqrt{43}\times\sqrt{3}$ structures) were confirmed depending on both the Pb coverage and substrate temperature. The SIC phase did not undergo any phase transition by cooling. This suggests that the dense arrangement of Pb atoms on Si(111) suppresses the CI transition, because Pb atoms in the SIC phase arranged on the Si surface more compressively than those in the HIC and transient phases.[12] For the HIC phase and the transient phase, Pb atoms have room to rearrange due to lower compression. But, we have to make more investigation into the driving force of the CI phase transitions.

A RHEED pattern of the $\sqrt{3}\times\sqrt{3}$ phase at 1/3 ML Pb coverage is displayed in Fig. 5(a). This phase appears through 2/3 ML Pb desorption by annealing at 700 K after 1

ML Pb deposition on the clean 7×7 surface. This surface is known to be composed of Pb adatoms occupying T_4 sites on the bulk-truncated Si surface in a hexagonal array.[13] When this $\sqrt{3}\times\sqrt{3}$ phase was cooled down just below RT, streaks with a 3×3 periodicity began to appear as shown in Figs. 5(b) and 5(c), which were taken with electron beam in $[11\bar{2}]$ and $[1\bar{1}0]$ incidence, respectively, at 100 K. Faint streaks appear, at (0, 1/3) and (0, 2/3) on a line connecting (0, 0) and (0, 1) bulk spots in Fig. 5(b). Also in Fig. 5(c), faint two streaks appear with equal intervals between superstructure spots of $(\bar{1}/3, 2/3)$ and $(2/3, \bar{1}/3)$. The streaks with the 3×3 periodicity were very weak just below RT, and became slightly brighter on the temperature decreasing, but we could not observe strong 3×3 spots as observed on the Ge(111) surface.[2,3]

The T_4-adatom structure might be commonly expected to undergo a structural change from the $\sqrt{3}\times\sqrt{3}$ to the 3×3 periodicity.[2,3] We guess that the observed structural change on the Pb-adsorbed Si(111) surface is due to the same mechanism as on the Pb- and Sn-adsorbed Ge(111) surface.[2,3]

In summary, we discovered new surface superstructures on the Pb-adsorbed Si(111) surface around 1.3 ML coverage below RT, $\sqrt{7}\times\sqrt{3}$ and $\sqrt{43}\times\sqrt{3}$ phases. The $\sqrt{7}\times\sqrt{3}$ phase resulted from a reversible CI transition from the HIC phase by cooling below 260 K–230 K. The $\sqrt{43}\times\sqrt{3}$ phase resulted from another CI transition from a transient phase between the HIC and SIC phases by cooling below 130 K. This phase transition had different structural changes between the cooling process (transient phase $\rightarrow\sqrt{43}\times\sqrt{3}$) and the warming process ($\sqrt{43}\times\sqrt{3}\rightarrow\sqrt{7}\times\sqrt{3}\rightarrow$transient phase). We constructed a structure map from these observations in a temperature range from 90 K to 500 K. We also found that the $\sqrt{7}\times\sqrt{3}$ changed to the $\sqrt{43}\times\sqrt{3}$ phase at 115 K by additional Pb deposition.

For the $\sqrt{3}\times\sqrt{3}$ phase at 1/3 ML coverage, we observed the other structural change by cooling just below RT, in which streaks with a 3×3 periodicity began to appear in RHEED. This change might be the phenomenon similar to that on Pb- and Sn-adsorbed Ge(111) surfaces.[2,3]

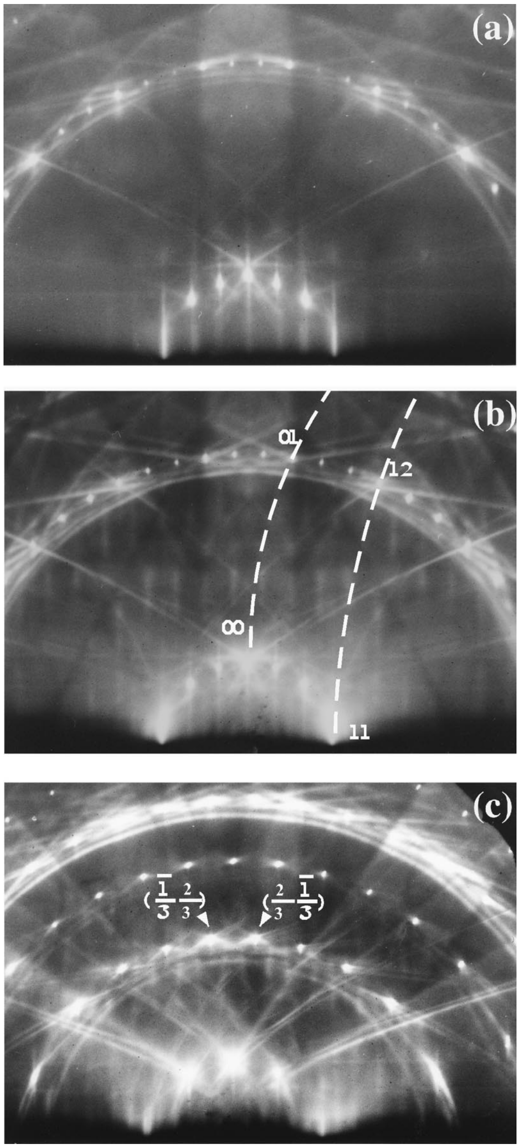

FIG. 5. (a) A RHEED pattern of the Si(111)-$\sqrt{3}\times\sqrt{3}$-Pb structure at 1/3 ML coverage, taken at RT in incidence azimuth $[11\bar{2}]$. (b),(c) RHEED patterns of the Si(111)-3×3-Pb phase, taken at 100 K. The incidence azimuths are (b) $[11\bar{2}]$, and (c) $[1\bar{1}0]$, respectively.

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