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STM study of a Pb/Si(111) interface at room and low temperatures

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The coexistence of Si(111)-(1×1)-Pb and $\mathrm{Si_{0.28}Pb_{0.72}}$/Si(111) phases was investigated using scanning tunneling microscopy. Reversible phase transition Si(111)-(1×1)-Pb⇔Si(111)-$c(5\times\sqrt{3})$-Pb at $T_C\approx-30\,°\mathrm{C}$ was observed. Simultaneously, small regions with surface charge ordered states were found on $\mathrm{Si_{0.28}Pb_{0.72}}$/Si(111) indicating a charge density wave phase transition. Both phases were found to be stable in the temperature interval from $T\approx-240\,°\mathrm{C}$ up to T_C. [S0163-1829(99)10243-1]

Phase transitions and ordering in two dimensions (2D) represent an important field of surface physics, both from a theoretical and applied point of view. Recently, the understanding of these processes in metal/semiconductor interfaces has improved due to the growing availability of scanning tunnelling microscopy (STM).[1–3] STM has played a decisive role in revealing that in principle there are two kinds of temperature-driven 2D phase transitions possible. The first type involves the rearrangement of adsorbate atoms at a certain transition temperature T_C, e.g., the transition of a close packed β-$(\sqrt{3}\times\sqrt{3})R30°\Leftrightarrow(1\times1)$ in Pb/Ge(111) at $T_C\approx180\,°\mathrm{C}$,[2] or similarly incommensurate closed-packed $(\sqrt{3}\times\sqrt{3})R30°\Leftrightarrow(1\times1)$ in Pb/Si(111).[3,4] The second type incorporates a symmetry-lowering redistribution of valence charge, resulting in surface charge density waves (CDW's), with a *negligible* lateral displacement of adsorbed atoms. Two illustrative examples of CDW's have been published recently: (1) Pb/Ge(111), where the room-temperature (RT) α-$(\sqrt{3}\times\sqrt{3})R30°$ structure is transformed to the low-temperature (LT) (3×3) ground state at $T_C\approx-20\,°\mathrm{C}$ (Ref. 5) and (2) Sn/Ge(111) with the same structure transformation at $T_C\approx-60\,°\mathrm{C}$.[6] The RT Pb/Si(111) and Pb/Ge(111) overlayer topography and several electronic properties are shared by other structurally similar adsorbate/substrate combinations, such as Al/Si(111) (Ref. 7) or In/Si(111).[8] Therefore, motivation to find the general rules governing the processes in these systems is obvious.

In this paper, we will report on the STM study of two coexisting Si(111)-(1×1)-Pb and Si(111)$-(\sqrt{3}\times\sqrt{3})R30°-$Pb structures [briefly (1×1)−Pb and $\sqrt{3}-$Pb, respectively] in a temperature interval ranging from $T\approx-240\,°\mathrm{C}$ up to RT. The (1×1)-Pb phase undergoes a reversible transition Si(111)-(1×1)-Pb⇔Si(111)-$c(5\times\sqrt{3})$-Pb at $T_C\approx-30\,°\mathrm{C}$. Below T_C, regions with CDW's were obtained in parts of the $\sqrt{3}$-Pb phase. Both phases were found to be stable at temperatures below T_C.

The experiments were carried out in a variable temperature STM (VT STM Omicron, Germany) equipped with low-energy electron-diffraction Auger-electron spectroscopy (LEED-AES) facilities, sample transfer, heating/L-He-cooling capabilities and a UHV water-cooled evaporator of Pb. The Si(111) samples used were in the form of bars, having the following dimensions: $9\times1\times0.3\,\mathrm{mm}^3$. A clean Si(111)-(7×7) surface was prepared by flashing the sample up to $T\approx1250\,°\mathrm{C}$, followed by a subsequent slow cooling to RT. Heating was achieved by passing a direct current through the sample. About 0.6 monolayer (ML) of lead (1 ML is defined as 7.84×10^{14} Pb atoms/cm^2) was evaporated on the clean Si(111)-(7×7) surface at RT. The base pressure in the system was $<5\times10^{-11}$ mbar and during Pb deposition it remained below 1.5×10^{-10} mbar.

After lead deposition (≈0.6 ML), the sample was annealed for 5 min at $T\approx380\,°\mathrm{C}$ in order to prepare ordered Pb phases.[1] Filled- and empty-state STM images taken at RT (see Fig. 1) revealed a mixture of (1×1)-Pb and $\sqrt{3}$-Pb structures. Statistics of images showed that the $\sqrt{3}$-Pb phase was composed of 28% Si atoms and 72% Pb atoms (Atom identification is explained below). This is not consistent with two widely used designations (1/3 ML$\sqrt{3}\times\sqrt{3}$ and 1/6 ML$\sqrt{3}\times\sqrt{3}$) of the $\sqrt{3}$-Pb phase.[1] These notations, which imply just two possible Pb atom concentrations, do not describe a layer composition unambiguously: The $\sqrt{3}$-Pb layer is in fact a 2D solid solution of Pb and Si adatoms sitting in a hexagonal array of T_4 sites[1,2] and can accommodate a *variable* number of Pb and Si atoms. Depending on initial coverage, an-

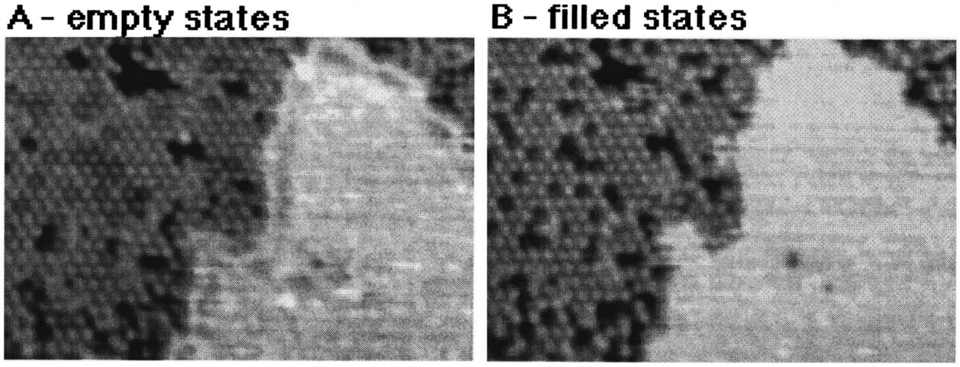

FIG. 1. Selected area of $20\times14\,\mathrm{nm}^2$ displaying the coexistence of flat, smooth (1×1)-Pb islands and a $\mathrm{Si_{0.28}Pb_{0.72}}$/Si(111) solid solution at RT.

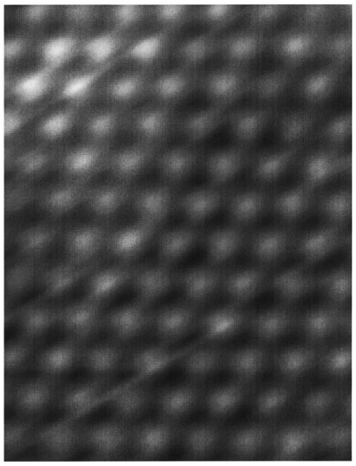

FIG. 2. Detailed structure of a (1×1)-Pb island at RT. Sample bias was set to $U_{\mathrm{Sample}} = +0.12$ V, with a tunneling current $I_{\mathrm{T}} = 0.1$ nA. Image dimensions: 2.9×3.8 nm^2.

nealing temperature, and annealing time, layer composition can be continuously varied from 100% Pb and 0% Si (corresponding to 1/3 ML$\sqrt{3} \times \sqrt{3}$) up to the most stable mosaic structure with 50% Pb and 50% Si (1/6 ML$\sqrt{3} \times \sqrt{3}$).[1,9] Therefore, the notation $\mathrm{Si}_X\mathrm{Pb}_{1-X}/\mathrm{Si}(111)$ as a solid solution, recently introduced by Carpinelli[10] for a similar Pb/Ge(111) interface, appears more adequate. We will follow this designation throughout the paper, with $X = 0.28 \pm 0.05$ in our experiment.

Figure 1, obtained at RT, displays a fraction of a (1×1)-Pb phase island of irregular shape (bright flat region) coexisting with the $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ solution. Surface corrugation at RT (1×1)-Pb is about ten times smaller than that on $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$. Therefore, it was not possible to obtain atomic resolution on both formations simultaneously. While the (1×1)-Pb island in the filled state image appears quite flat all over the area, the empty state image displays a valley running along the inner part of the island border. A detailed island structure (Fig. 2) exhibits a (1×1)-Pb-terminated surface and is aligned with the (7×7) substrate structure (not shown here). The image was taken at a sample bias $U_{\mathrm{Sample}} = +0.12$ V and a tunneling current $I_{\mathrm{T}} = 0.1$ nA. Atomic resolution was not obtained at negative sample biases. A high-resolution image of the $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ structure is presented in Fig. 3. The general rules, as enunciated by Carpinelli[10] for $\mathrm{Ge}_X\mathrm{Pb}_{1-X}/\mathrm{Ge}(111)$ and similar systems, can be easily applied here as well: (1) In the filled-state image Si atoms appear dark, unlike Pb atoms which are bright. This phenomenon is accounted for by a large charge transfer from the Si adatoms to the Pb adatoms.[9] (2) Cumulative neighbor-dependent imaging contrast means that there is an observable contrast difference among Pb adatoms themselves (see the filled-state image), depending on their chemical environment. (3) The imaging contrast between Si and Pb adatoms is less pronounced in the empty-state image. However, the contrast is strongly bias dependent. (4) We have never succeeded in preparing a $\mathrm{Si}_\mathrm{X}\mathrm{Pb}_{1-\mathrm{X}}/\mathrm{Si}(111)$ layer with more than 50% Si atoms $(X > 0.5)$. The layer with equal amounts of Pb and Si $(X = 0.5)$ corresponds to the mosaic structure, which is stable up to relatively high T [600 °C (Ref. 1)].

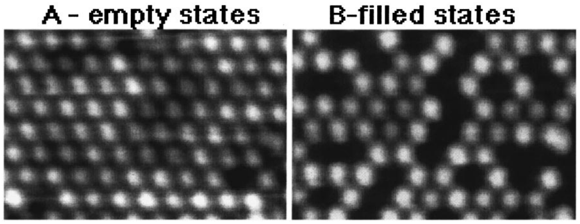

FIG. 3. Detailed structure of $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ at RT. Sample bias (A) $U_{\mathrm{Sample}} = +1$ V and (B) $U_{\mathrm{Sample}} = -1$ V with $I_{\mathrm{T}} = 0.51$ nA. Image dimensions: 7.0×4.8 nm^2.

Following cooling the sample down to $T_{\mathrm{C}} \approx -30\,°\mathrm{C}$, we observed the appearance of a new structure in place of the (1×1)-Pb islands—see Fig. 4. The empty state image reveals an inner island structure in the form of parallel straight rows, while the filled-state image displays a very low corrugation with the rows being hardly noticeable. We observed up to three possible row orientations within one island (not shown here). These were rotated by ±120° with respect to each other, reflecting the existence of three different domains. The parallel rows are directionally aligned with the $(\sqrt{3} \times \sqrt{3})R30°$ arrangement of the neighboring $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ solution. Details of the new phase are shown in Fig. 5. The filled- and empty-state images were taken at $T \approx -240\,°\mathrm{C}$ in order to demonstrate the following: (1) The new phase topography (taken with a positive sample bias) was stable in a wide temperature interval from $T \approx -240\,°\mathrm{C}$ up to T_{C} and (2) at such low temperatures the rowlike arrangement was obtained at *both* polarities of the sample bias. Nevertheless, the rows are also less pronounced in the filled state image and the contrast is continuously weakened with increasing temperature. Each row is composed of round-

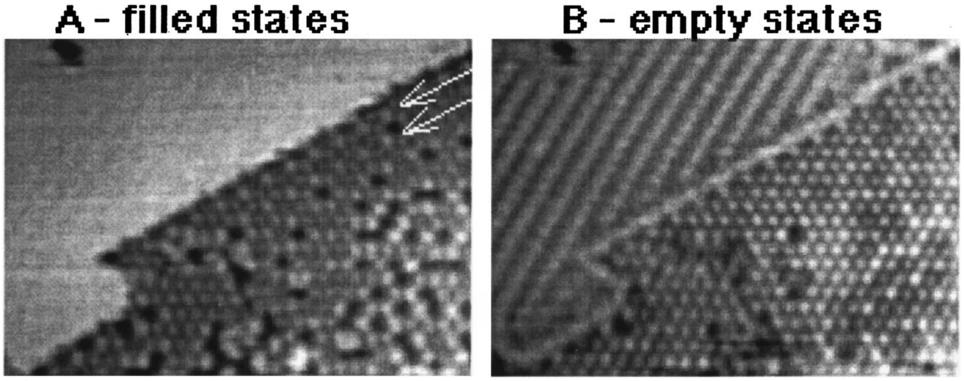

FIG. 4. Selected area of 19×14 nm^2 displaying the coexistence of $\mathrm{Si}(111)\text{-}c(5 \times \sqrt{3})\text{-Pb}$ and a $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ solid solution at $T \approx -35\,°\mathrm{C}$. The two white arrows indicate two rows of brighter Pb atoms, which are arranged with a (3×3) periodicity.

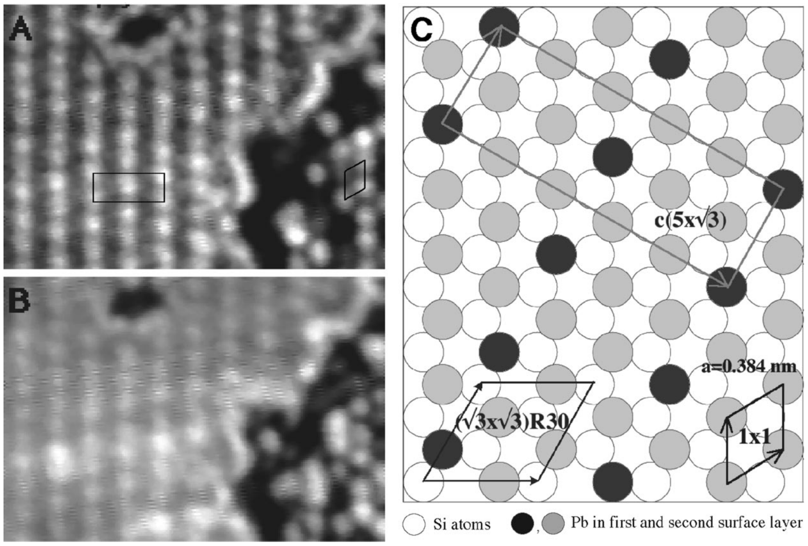

FIG. 5. Empty-state (A) and filled-state (B) image of Si(111)-$c(5\times\sqrt{3})$-Pb at $T\approx -240\,°\mathrm{C}$. The rectangular $c(5\times\sqrt{3})$ and $\sqrt{3}\times\sqrt{3})R30°$ unit cells are indicated in the left and right part, respectively. Sample bias (A) $U_{\mathrm{Sample}}=+1$ V and (B) $U_{\mathrm{Sample}}=-1$ V with $I_T=0.16$ nA. Image dimensions: $10.3\times 7.1\ \mathrm{nm}^2$. (C) represents the model of atomic arrangement: the white balls denote the last layer of Si atoms in an ideal unreconstructed Si(111) surface; the grey balls denote Pb in the first surface layer; and the dark balls represent protruding Pb atoms forming the rows.

shaped single protrusions that are equally spaced $\sqrt{3}a(a=0.384$ nm), which is the same distance as among neighboring adatoms in $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$. Since the protrusions are visible in the same positions at both polarities, we attribute them to the sp_z orbitals of single Pb atoms. The distance between neighboring rows equals $5a/2$. The island border is sharp, with an atomic arrangement different from that of the inner island parts.

The rectangular $c(5\times\sqrt{3})$ unit cell of this phase is drawn in Fig. 5(c) together with the (1×1) and $(\sqrt{3}\times\sqrt{3})R30°$ unit cells. The white balls denote the top layer of Si atoms in an ideal unreconstructed Si(111) surface. The gray balls correspond to Pb atoms in the second surface layer and the dark balls represent the protruding Pb atoms of the first surface layer forming the rows. The position of the gray balls is mere speculation and we expect charge redistribution to affect their displacement. It is possible to find non-rectangular cells (reflecting hexagonal substrate basis) such as (5×5) or $(\sqrt{3}\times 5\sqrt{3})R30°$, both with 60° between translation unit vectors. Since the area of these cells is larger, we prefer the $c(5\times\sqrt{3})$ designation.

We would like to draw attention briefly to the structure of the $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ solution below T_C (Fig. 4). We assume that at LT Si atoms appear considerably darker than Pb atoms (as at RT). On closer inspection, in the direction of the two white arrows, there are two rows of brighter Pb atoms, which are arranged with a (3×3) periodicity. Close resemblance to systems with CDW's at LT (Refs. 6 and 5) is obvious. Small regions $\approx 10\ \mathrm{nm}^2$ with (3×3) ordering can be easily found on the surface, in particular in the vicinity of Pb-rich islands. Locally, there are just Pb atoms on Si(111) here ($X=0$). Indications of (3×3) ordering were noticed, even on large areas of the $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ phase. This, however, requires further study. Temperature-dependent observations in real time are necessary to determine the transition temperature T_C of Si(111)-(1×1)-Pb⇔Si(111)-$c(5\times\sqrt{3})$-Pb, and T_C of CDW transition on $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$.

We summarize the results as follows: a Pb/Si(111) system was prepared with the (1×1)-Pb and $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ phases coexisting. RT STM studies confirmed the general predictions made by Carpinelli[10] for structurally similar systems. There is a phase transition Si(111)−(1×1)−Pb⇔Si(111)−$c(5\times\sqrt{3})$−Pb at $T_C\approx -30\,°\mathrm{C}$, resulting in a row-like ordered structure. Simultaneously, regions with charge ordered states were found on $\mathrm{Si}_{0.28}\mathrm{Pb}_{0.72}/\mathrm{Si}(111)$ indicating a charge density wave transition. To conclude, further studies focusing on the phase transition dynamics in real time are desirable.

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