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Dynamical nature of the high-temperature Pb/Si(111)-1×1 phase

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Temperature-induced structural change of the Pb/Si(111)-$\sqrt{7} \times \sqrt{3}$ surface has been studied by using *ab initio* molecular dynamics simulations. The ordered $\sqrt{7} \times \sqrt{3}$ surface is found to evolve into a diffusive phase at elevated temperatures. Identified as responsible for the diffusive phase is a low-barrier concerted motion of two Pb atoms, one located on a hollow site and the other on an adjacent on-top site, which leads to an effective hollow-to-hollow Pb diffusion occurring in the background 1 × 1 lattice of the on-top Pb atoms. This diffusion picture explains well the "1 × 1" diffraction pattern with diffuse streaks observed in the high-temperature phase of the $\sqrt{7} \times \sqrt{3}$ surface and is proposed as the common structural and dynamical feature of all the high-temperature Pb/Si(111)-1 × 1 phases evolving from different ordered phases.

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I. INTRODUCTION

Temperature-induced two-dimensional (2D) phase transition is an important subject of broad interest in surface physics.[1] It involves a qualitative change in the structural or electronic property as seen in, for examples, solid-liquid or metal-insulator transitions.[2–4] The driving force underlying a 2D phase transition is mostly our priority concern, but its exploration is often hampered from the very beginning by the lack of correct information on the atomic structures before and after the transition.

One interesting example is the Pb/Si(111) surface exhibiting intriguing 2D phase transitions driven by temperature change. This surface is known as an ideal 2D metal overlayer system because of its abrupt interface due to a negligible mutual solubility between Pb and Si.[5,6] The Pb overlayer forms a variety of structural phases at the coverages of 1.0–1.3 monolayer (ML, defined as one Pb atom per Si), such as the $\sqrt{7} \times \sqrt{3}$, $\sqrt{3} \times \sqrt{3}$, hexagonal incommensurate (HIC), and striped incommensurate (SIC) phases.[7,8] Particularly interesting is that, upon heating at around 270–570 K, these distinct phases all undergo a reversible transition into a 1 × 1 phase in which all domain walls or superstructures disappear.[5–16] Despite many studies, however, the structural and dynamical nature of the high-temperature 1 × 1 phase is not clarified yet.

In one view, the 1 × 1 phase is assigned to an ordered phase with the on-top (T_1) Si sites singly occupied by Pb atoms of 1.0 ML. This picture was based on the persistence of both a sharp 1 × 1 low-energy electron diffraction (LEED) pattern and a pronounced surface photoemission spectrum above the transition temperature[5,6] and also on clear 1 × 1 spot images observed in scanning tunneling microscopy (STM) studies.[9–11] The ordered 1 × 1 phase is in structural harmony with the 1.0 ML trimer model where three Pb atoms in the unit cell are displaced from the ideal T_1 sites to form a Pb trimer (see Fig. 1), which was commonly suggested for the $\sqrt{7} \times \sqrt{3}$ and $\sqrt{3} \times \sqrt{3}$ phases.[9,10] The other picture for the 1 × 1 phase is a disordered (or liquid) phase with diffusing Pb atoms, which was suggested from the diffuse streaks observed in the reflection high-energy electron diffraction pattern.[12,13] In this view, the 1 × 1 pattern reported in the previous LEED and STM studies[5,6,9–11] is interpreted as a result of an averaging process of the atomic motions that is faster than the measuring process.[8,14] The disordered 1 × 1 phase can be compatible with different-coverage structural models for the low-temperature phases, the 1.2 ML model for the $\sqrt{7} \times \sqrt{3}$ phase[17] and the 1.33 ML model for the $\sqrt{3} \times \sqrt{3}$ phase,[14] both containing one more Pb atom per unit cell than the ordered 1 × 1 phase (e.g., see the 1.2 ML model in Fig. 1).

In this paper, we clarify the nature of the high-temperature Pb/Si(111)-1 × 1 phase by exploring the temperature-dependent dynamical behavior of the $\sqrt{7} \times \sqrt{3}$ phase. Our *ab initio* molecular dynamics (MD) simulations show that the 1 × 1 phase is a disordered phase with rapidly diffusing Pb atoms. The main diffusion process responsible for the surface disorder is identified as a concerted motion of a pair of Pb atoms, which results in an effective hollow-to-hollow hopping of a Pb atom. While such hollow-to-hollow hopping is random in direction and thus causes a structural disorder, the Pb atoms occupying the on-top sites remain undisturbed and effectively give rise to a 1 × 1 long-range order, accounting for the 1 × 1 pattern observed in the LEED and STM studies.[7,8,10,11,16]

II. METHOD

Our MD simulations are carried out by employing the VIENNA *ab initio* simulation package[18] with the use of generalized gradient approximation[19] and ultrasoft pseudopotentials.[20] The Si(111) surface is modeled by a periodic slab geometry of four atomic layers with a vacuum spacing of ∼12 Å. Pb atoms are adsorbed on the top of the slab, and the bottom of the slab is passivated by H atoms. The Pb and two topmost Si layers are allowed to relax during the simulations. The electronic wave functions are expanded in a plane-wave basis of 150.6 eV. Similar calculation schemes were successfully used in our previous studies for the Pb/Si(111)-$\sqrt{7} \times \sqrt{3}$ phase.[21,22] For MD simulations, we use a large $5 \times 3\sqrt{3}$ unit cell six times larger than the $\sqrt{7} \times \sqrt{3}$ unit cell (see Fig. 1). One *k* point is used for the $5 \times 3\sqrt{3}$ surface Brillouin-zone integrations. In the MD simulations, the equations of motion are integrated with the Verlet algorithm[23] using a time step of 2 fs. Temperature is

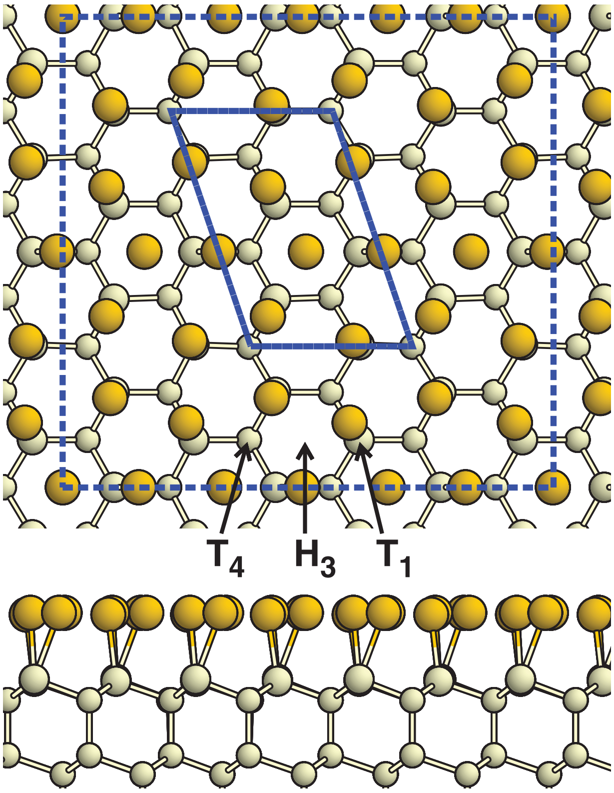

FIG. 1. (Color online) Equilibrium geometry of the 1.2 ML model of Pb/Si(111)-$\sqrt{7} \times \sqrt{3}$. Large and medium balls represent the Pb and first-layer Si atoms, respectively. Small balls represent the rest of Si atoms. Solid lines represent the $\sqrt{7} \times \sqrt{3}$ unit cell and dashed lines the $5 \times 3\sqrt{3}$ supercell used for MD simulations. Arrows indicate three high-symmetry surface sites for Pb adsorption.

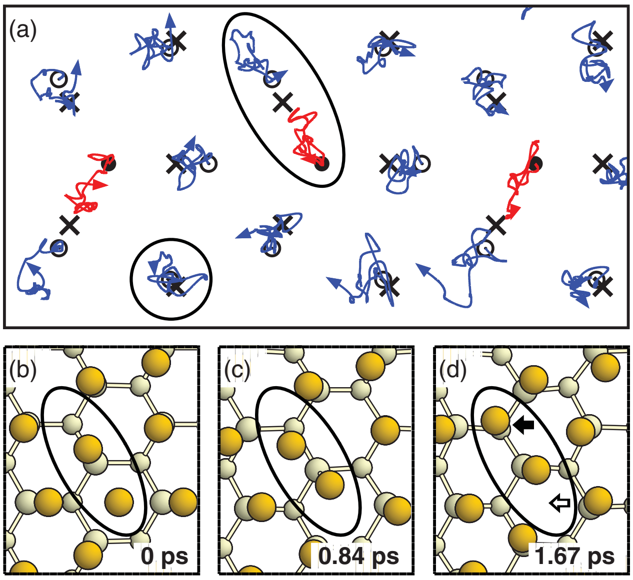

FIG. 2. (Color online) Atomic motions in an MD simulation for 5 ps at 400 K. (a) In-plane trajectories of the Pb atoms. Blue (black) lines represent the Pb atoms initially located on the T$_1$ site. Red (dark gray) lines represent the Pb atoms initially located on the H$_3$ site. Crosses represent the bulk positions of the first-layer Si atoms. Ellipse (circle) indicates a representative diffusive (vibrational) motion. (b)–(d) Successive snapshots showing the atomic details of the diffusive motion marked with the ellipse in (a). In (d), empty and filled arrows indicate the hollow positions of Pb before and after the diffusion, respectively.

controlled by a Nosé-Hoover thermostat[24,25] for the canonical ensemble.

III. RESULTS

Figure 1 shows the 1.2 ML model for the $\sqrt{7} \times \sqrt{3}$ phase that was taken as an initial geometry for our MD simulations. This model features one extra Pb atom added on a H$_3$ (or T$_4$) hollow site in the ideal 1.0 ML $\sqrt{7} \times \sqrt{3}$ model with all T$_1$ sites saturated by single Pb atoms. This model was proposed in a x-ray study of Kumpf *et al.*[17] and has been supported by density functional theory (DFT) calculations as an energetically sound structural model, well reproducing the measured STM images and surface band structures.[15,21,22,26] This model also reproduces the intriguing 1×1 pattern appearing in the Fermi surface of the $\sqrt{7} \times \sqrt{3}$ surface, when taking into account the effect of triple domains existing in the $\sqrt{7} \times \sqrt{3}$ samples.[21,22,27]

Figure 2 shows the result of the MD simulations performed at 400 K. Since this temperature is sufficiently higher than the experimental transition temperature ($T_C \sim 270$ K),[8,10,11] our MD simulations could well represent a high-temperature phase. The lines shown in Fig. 2(a) display the in-plane trajectories of the Pb atoms for a MD run of 5 ps. The motion of the Pb atoms can be categorized into two. One is the local vibration of the Pb atoms on T$_1$, as marked with a circle in Fig. 2(a). The other is a concerted diffusion involving a pair of Pb atoms, as enclosed with an ellipse in Fig. 2(a), where the motion of one Pb atom is closely related with the motion of the other, as will be given in detail below. We found that these two types of motions continue in our extended MD run up to 15 ps. Unlike the local vibrations of the ontop Pb atoms, the diffusions involving a hollow Pb atom disturb the lattice structure of the Pb layer: due to the directional irregularity, such diffusions break the $\sqrt{7} \times \sqrt{3}$ periodicity and drive the Pb overlayer disordered. In contrast with the mobile Pb atoms, the substrate Si atoms are found static with only small vibrations during the simulation, indicating that the Pb/Si(111) system forms a disorder/order interface.

The snapshots shown in Figs. 2(b)–2(d) display the structural changes in the course of a concerted diffusion of two Pb atoms marked with an ellipse in Fig. 2(a). Initially, one Pb atom is on a H$_3$ hollow site and the other on a nearby T$_1$ site [see Fig. 2(b)]. The Pb atom on H$_3$ moves to the T$_1$ site, pushing the host Pb atom on T$_1$ toward an adjacent, empty hollow (T$_4$) site [see Fig. 2(c)]. Finally, the Pb atoms reach another locally stable configuration with one on T$_1$ and the other on T$_4$ [see Fig. 2(d)]. Since this concerted diffusion preserves the Pb occupation of the T$_1$ site, its net effect is a hollow(H$_3$)-to-hollow (T$_4$) hopping of a single Pb atom, as illustrated by empty and filled arrows in Fig. 2(d). The Pb atom on the new hollow (T$_4$) site is of course subject to another concerted diffusion in the same way, being the source of Pb atoms drifting in the Pb layer through effective

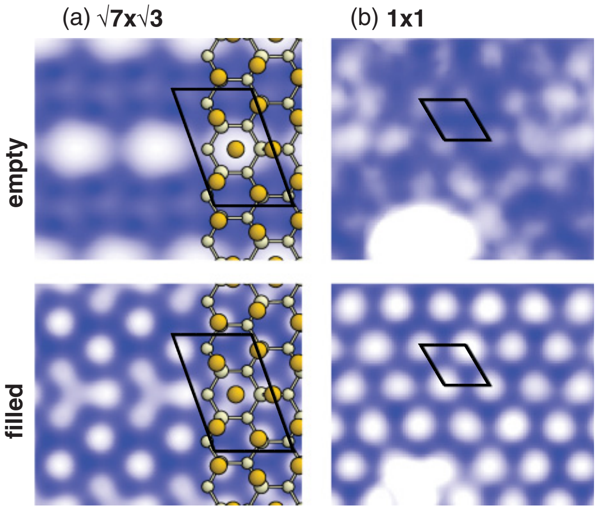

FIG. 3. (Color online) Simulated constant-current STM images: (a) $\sqrt{7}\times\sqrt{3}$ and (b) 1×1 phases. The empty-state (filled-state) images were obtained by integrating $\rho(r,E)$ from E_F to $E_F+1.0$ eV ($E_F-1.0$ eV) at $\rho = 1\times10^{-3}$ e/Å^3.

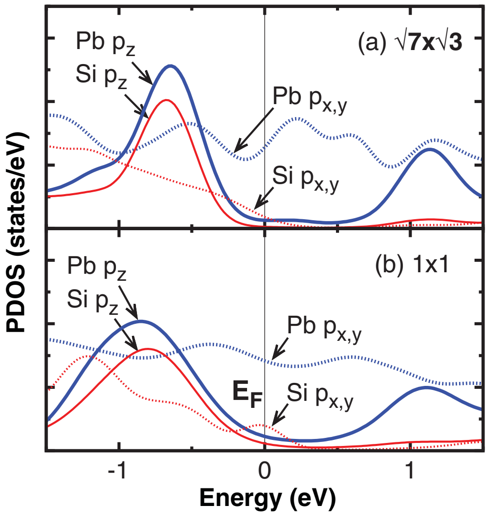

FIG. 4. (Color online) PDOS's for the Pb and Si p orbitals: (a) $\sqrt{7}\times\sqrt{3}$ and (b) 1×1 phases. The projection for the Si p orbitals was done for the topmost Si layer.

hollow-to-hollow motions. At 400 K, such a concerted diffusion takes a short time of ∼2 ps and occurs frequently with a rate of 4.8×10^{25} cm^{-2}s^{-1}. We found in our static calculations that the energy barrier for the concerted diffusion is as low as ∼0.1 eV. In the present diffusion picture, while relatively few Pb atoms on the hollow sites are diffusive with fast hoppings, the majority of Pb atoms stay around the on-top sites, thus giving rise to a long-range 1×1 order. This qualitatively explains why a clear 1×1 diffraction pattern was observed at above $T_C\sim270$ K in previous LEED studies.[7,8]

It is interesting to see the effect of the diffusing Pb atoms on high-temperature STM images. Figure 3 shows the simulated constant-current STM images for the ordered $\sqrt{7}\times\sqrt{3}$ phase and the high-temperature (400 K) 1×1 phase. Here, the high-temperature images were obtained by averaging the STM images for the atomic structures taken at every 1 ps in the 15 ps MD run. Dominant in the ordered $\sqrt{7}\times\sqrt{3}$ phase are the features of the extra Pb atoms adsorbed on H_3, i.e., Y-shape patterns in the filled-state image and round protrusions in the empty-state image, which are in good agreement with previous experimental and theoretical images.[15,16] In the high-temperature images, on the other hand, the image of the diffusive Pb atoms is dispersive. The 1×1 pattern arising from bright dots on the T_1 sites is noticeable at both polarities with weak diffusive adatom features, and the clarity of the 1×1 pattern depends on the polarity [see Fig. 3(b)]. The simulated images are found to well reproduce the experimental features reported in high-temperature STM measurements,[10,11,16] providing a microscopic support for the present diffusion picture. The bright spot present on the bottom of the images in Fig. 3(b) reflects only an exceptional diffusion event. It represents a vertical protrusion of a hollow Pb atom by ∼2 Å off the Pb layer. This structure was predicted before as a metastable Pb configuration on the hollow site,[22] and its large atomic protrusion leads to the very bright STM spots.

Figure 4 shows the projected density of states (PDOS) for the Pb and Si p orbitals obtained for the ordered $\sqrt{7}\times\sqrt{3}$ phase and the high-temperature (400 K) 1×1 phase. The high-temperature PDOS's were obtained by averaging the calculated PDOS's for the atomic structures taken at every 1 ps in the 15 ps MD run. The $\sqrt{7}\times\sqrt{3}$ surface features the Pb p_z and Si p_z orbitals at about 0.7 eV below E_F and the Pb $p_{x,y}$ orbital at E_F and above, indicating interface Pb-Si covalent bondings and inplane Pb-Pb bondings with metallic surface character, repectively, as was discussed before.[22] We find that the overall PDOS feature of the $\sqrt{7}\times\sqrt{3}$ phase persists in the disordered 1×1 phase with only small peak broadenings due to the thermal fluctuation, which indicates that the disorder driven by the concerted diffusions little affects the surface electronic structure. It is worth pointing out that the high-temperature STM images shown in Fig. 3(b), in which the 1×1 pattern appears somewhat fuzzy in the empty state, reflect well the bias dependence of the orbital characters found in Fig. 4(b). The Pb-Si bonding character (containing both Pb p_z and Si p_z orbitals) is dominant in the filled states, and thus the Pb atoms staying on the on-top sites can produce bright spots in the filled-state STM image, forming a clear 1×1 pattern. On the other hand, the empty states represent the Pb-Pb bondings (or antibondings) involving not only the Pb atoms vibrating on the on-top sites but also the Pb atoms hopping between the hollow sites, which leads to somewhat diffusive 1×1 pattern on the empty-state STM image.

Finally, let us examine the temperature dependence of the diffusion property of Pb. Figure 5 shows the mean-square displacement of Pb atoms as a function of time,

$$d_{\rm ms} = \langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle,$$

analyzed from the MD simulations carried out at different temperatures (100, 200, 300, and 400 K). While $d_{\rm ms}$ increases linearly with time with small deviations at 400 K, its linear behavior degrades with larger fluctuations at lower temperatures. The linearity of $d_{\rm ms}$ with time is an indication of a random evolution from its original position in the diffusive

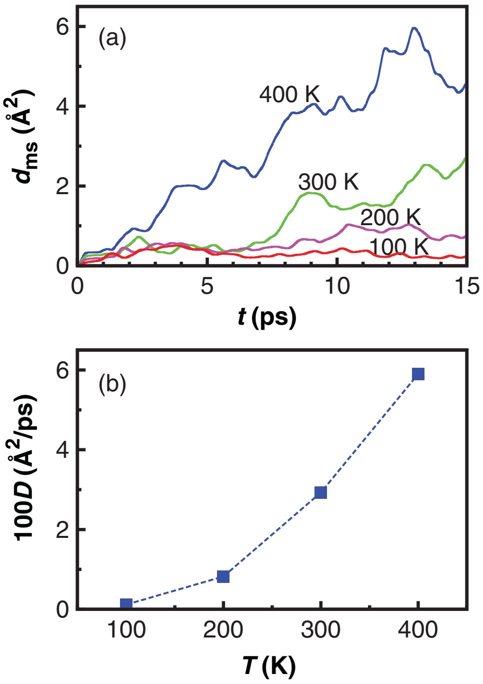

FIG. 5. (Color online) Temperature dependence of Pb diffusivity: (a) mean-square displacement d_{ms} and (b) self-diffusion coefficient D of Pb atoms.

motion of a particle, and its slope defines the self-diffusion coefficient (D), a typical quantity for atomic transport,[28]

$$d_{\mathrm{ms}} = 6Dt \quad \text{for} \quad t \to \infty.$$

The D values obtained by the linear fit to d_{ms} data are shown in Fig. 5(b). D is almost zero at 100 K, indicating that the system can be regarded as the ordered $\sqrt{7} \times \sqrt{3}$ phase at this temperature. D is fairly small at 200 K (still below the experimental $T_C \sim 270$ K), but it increases rapidly with temperature and reaches $\sim$0.06 Å^2/ps at 400 K. This amounts to about 30% of the bulk diffusion coefficient of liquid Pb ($D_b = 0.22$ Å^2/ps) measured at just above the melting temperature $\sim$600 K,[29] thus being considered sufficiently large to put the Pb layer in a disordered state. The temperature dependence of D is fitted well by the Arrhenius behavior $D = D_0\exp(-E_D/k_BT)$ with a prefactor of $D_0 \sim 0.45$ Å^2/ps. We found that the estimated activation energy for diffusion (E_D) is $\sim$0.07 eV, which indeed compares well with the aforementioned $\sim$0.1 eV found in our static calculations.

The order-to-disorder picture for the $\sqrt{7} \times \sqrt{3} \leftrightarrow 1\times1$ phase transition would also be valid for the temperature-induced 1×1 phase transitions found in the $\sqrt{3} \times \sqrt{3}$, HIC, and SIC phases. The HIC (SIC) phase consists of the $\sqrt{3} \times \sqrt{3}$ domains separated by hexagonal (striped) domain walls of the "almost" $\sqrt{7} \times \sqrt{3}$ phase,[7] manifesting that the $\sqrt{7} \times \sqrt{3}$ and $\sqrt{3} \times \sqrt{3}$ phases underlie all the low-temperature phases undergoing the transition into the 1×1 phase. Moreover, the basic structure proposed for the $\sqrt{3} \times \sqrt{3}$ phase[30] is the 1.33 ML model,[14] which corresponds to the the ideal 1 ML model with additional 0.33 ML Pb atoms on the hollow sites. Therefore, the $\sqrt{3} \times \sqrt{3}$, HIC, and SIC phases can be commonly viewed as a mixture of the 1.0 ML Pb atoms on the on-top sites and the 0.2–0.33 ML Pb atoms on the hollow sites. These surfaces are likely subject to the same concerted diffusions involving the hollow Pb atoms as in the $\sqrt{7} \times \sqrt{3}$ surface, reaching a similar disordered 1×1 phase. In an early photoemission study for the $\sqrt{3} \times \sqrt{3} \leftrightarrow 1\times1$ transition, Le Lay *et al.*[6] reported that a pronounced surface state at about 0.9 eV below E_F persists after the transition and used it as an evidence for an order-to-order transition. The presence of a common surface state in both phases, however, cannot be used as an evidence that the transformed phase is ordered. As shown in our PDOS calculations above, the Pb p_z and Si p_z orbitals at about 0.7–0.8 eV below E_F constitute a strong surface state in both the ordered $\sqrt{7} \times \sqrt{3}$ phase and the disordered 1×1 phases (see Fig. 4), being consistent with the experimental report.[6] It is because the structural origin of the common surface state is the direct Pb-Si bonding that has no relation with the nature of the disorder.

IV. SUMMARY

In conclusion, the present DFT study verifies the high-temperature Pb/Si(111)-1×1 phase as a disordered phase where some of Pb atoms are thermally diffusing from a metastable hollow site to another on the background of an approximate 1×1 lattice of the Pb atoms on the stable on-top sites. This constitutes a key structural and dynamical picture commonly underlying the high-temperature evolutions of the $\sqrt{7} \times \sqrt{3}$ phase, the $\sqrt{3} \times \sqrt{3}$ phase, and their mixed phases.

Note added. We find in a recently published ARPES study[31] that the disordered Pb/Si(111)-1×1 phases formed at about 300 K (just above the experimental $T_C \sim 270$ K) were interestingly assigned to a liquid state, based on that the temperature-dependent correlation length analysis of Pb-related LEED spots fits well to a 2D melting theory.

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