Atom-by-Atom Chemical Coordination Effect Observed in Noncontact AFM Topography of Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) Mosaic Phase *

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Using noncontact atomic force microscopy (NC-AFM), we analyzed the height distribution of individual atoms by atomically resolved topography of Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces, discriminated Pb, and substituted Si adatoms atom-by-atom. This successfully revealed the atom-by-atom chemical coordination effect in the height distribution of individual atoms. We found that increasing the number of surrounding nearest-neighbor Si adatoms increases the height of Si adatoms but rapidly decreases the height of Pb adatoms. These coordination effects were qualitatively independent of the tip-sample surface distance. This result agreed with previous results on Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase for only Si adatoms. Pb adatoms, however, showed a strong but opposite dependence on the number of surrounding Si adatoms, and the Sn adatom proved independent of the number of surrounding Si adatoms. Such differences in the chemical coordination in NC-AFM height distribution among the fourth period elements of Si, Sn, and Pb atoms will disclose to differences in charge transfer and related phenomena between intermixed heterogeneous atoms, due to differences in electronegativity and/or their metallic nature.
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I. INTRODUCTION

In the past few years, noncontact atomic force microscopy (NC-AFM) [1, 2] in ultra-high-vacuum environments has evolved from a technique of atomically resolved microscopy [3–5] capable of imaging even insulating surfaces [6–8] to a powerful atomic tool [9]. In some cases it can achieve better spatial resolution than scanning tunneling microscopy (STM) [10–12], vertical and lateral atom manipulations [13–17], chemical discrimination/identification of intermixed atom species [18–20] and site-specific atomic force spectroscopy [19–28]. During this rapid progress, the mechanism of NC-AFM topography has been investigated intensively.

Many surface core-level shifts [29–32] and STM [32–39] experiments have been performed for investigating the large charge transfer effects on (Pb or Sn)/Si(111) and (Pb or Sn)/Ge(111) surfaces. Especially, Jemander et al. quantitatively disclosed the chemical coordination effect in the height distribution of individual Sn atoms on a-Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface as a function of the number of surrounding Si atoms using STM [38]. Then Kaminski *et al.* presented a quantitative theoretical analysis of the atomic and electronic structure, and also STM images of Sn atoms with surrounding Si-substitutional defects on a-Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface using a first-principles density functional theory (DFT)

calculations [39]. On the contrary, there has only been one NC-AFM experiment [18] on the chemical coordination effects in Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase topography. However, only NC-AFM can evaluate chemical coordination effects on atom height in Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase at high precision as a function of the number of surrounding Sn atoms [18]. Strong chemical coordination effects in Si adatom height have been reported, with a decrease of about 10 pm for each increase in the number of surrounding Sn adatoms. In contrast to STM [38, 39], however, no appreciable chemical coordination effect in height of a Sn adatom coexisting with substituted Si adatoms has been reported. For NC-AFM and STM measurements, bond order in the atomic force interaction, and local electronic density of state in the tunneling current, can be changed by the charge transfer between heterogeneous adatoms, respectively. Therefore, in the present study, we investigated the chemical coordination effects in Pb adatom height (another fourth period element) and the coexisting Si adatom height, using the Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase with NC-AFM.

II. EXPERIMENTAL

We used a home-built, room-temperature (RT) ultra-high-vacuum (UHV) NC-AFM, equipped with an optical interferometer for detecting cantilever deflection. Using NC-AFM, the frequency shift of the mechanical resonance of the cantilever, due to the interaction force between the tip apex and sample surface atoms, is detected by frequency modulation (FM) detection [40]. Contamination and the oxide layer of the Si tip were carefully removed by Ar⁺ ion sputtering in UHV. The nominal values of the

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FIG. 1: NC-AFM topography of Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase, obtained in the same region with a frequency shift of (a) $\Delta f = -0.9$ Hz, (b) -1.1 Hz, (c) -1.3 Hz, and (d) -1.7 Hz. The imaging area, mechanical resonance frequency, and oscillation amplitude are $8.2 \text{ nm} \times 6.4 \text{ nm}$, 162.5167 kHz , and $133 \text{ \AA}$, respectively. Each spot corresponds to Pb or Si adatoms.

spring constant, mechanical resonance frequency, and tip-apex radius of the cantilever were ca. 35 N/m , ca. 160 kHz , and 510 nm , respectively. The Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces were prepared as follows. After the Si(111)-(7×7) surface was prepared, Pb was evaporated on the surface, followed by annealing at 500°C .

III. RESULTS AND DISCUSSIONS

To investigate the chemical coordination effects in NC-AFM topography, we first intermixed Pb and Si adatoms, as shown in Figs. 1(a)-(d), and imaged the Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surface on an atomic scale in the same region by decreasing the frequency shift by (a) $\Delta f = -0.9$ Hz, through (b) -1.1 Hz and (c) -1.3 Hz, to (d) -1.7 Hz at RT. At a short tip-sample surface distance, we clearly observed individual atoms, as shown in Figs. 1(c) and (d), while, at a relatively large distance, we obtained a vague image, as shown in Figs. 1(a) and (b). We determined the corresponding atom sites by comparing the atomically resolved images in Figs. 1(c) and (d) atom-by-atom with the somewhat blurred images in Figs. 1(a) and (b) of the same region, and measured the individual atom heights. Figures 2(a)-(d) show the corresponding relative height distribution (histogram of relative height) of individual atoms. Here, we set the z position of the Pb adatom with three nearest-neighbor Si adatoms as a base line (zero relative height). As shown in Figs. 2(b)-(d), at the short tip-sample surface distance, the distributions of Pb and Si adatom relative heights did not separate into two groups. However, at the relatively large distance shown in Fig. 2(a), the relative height distribution separated into two groups, with a nearly equal number of atoms in each group, consistent with the mosaic phase, where the number of Pb and Si atoms is nearly equal. Further, by increasing the Pb content, we

FIG. 2: The histogram of the relative height (relative height distribution) of individual atoms in Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase, corresponding to Figs. 1(a)-(d), respectively. Here, we set the z position of the Pb adatom with three nearest-neighbor Si adatoms as a base line (zero relative height). As shown in Fig. 2(a), at a relatively large distance, the relative height distribution separated into two groups with a nearly equal number of atoms, consistent with the mosaic phase. Further, we found an increase in the number of brighter spots with higher corrugation by increasing the Pb contents. Therefore, we determined the group with higher corrugation in Fig. 2(a) (red) to be Pb adatoms, while the group with lower corrugation (black) was Si adatoms.

found an increase in the number of the brighter spots with higher corrugation [41]. Therefore, we determined the group with higher corrugation in Fig. 2(a) (red) to be Pb adatoms, while the other group with lower corrugation in Fig. 2(a) (black) were Si adatoms. We attributed the individual adatoms in Figs. 2(b)-(d) to Pb (red) and Si (black) adatoms by comparing the corresponding adatom sites in Fig. 1(a) one-by-one with those in Figs. 1(b)-(d), for the same region. Figures 2(a)-(d) clearly show that decreasing the tip-sample surface distance causes the relative height distribution between Pb and Si adatoms to overlap. This means that decreasing the tip-sample surface distance causes the chemical contrast between Pb and Si adatoms to vanish. This agrees with the previous experimental result on Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) surfaces [18].

We investigated the chemical coordination effects by plotting the relative height of Pb (Si) adatoms as a function of the surrounding nearest-neighbor Si (Pb) adatoms, as shown in Figs. 3(a)-(d). Figures 3(a)-(d) clearly show that increasing the number of nearest-neighbor Si adatoms increases the relative height of Si adatoms, while that of Pb adatoms decreases rapidly. In other words, by increasing the number of nearest-neighbor heterogeneous adatoms, the relative height of both Si and Pb adatoms decreases. This result agreed with previous results of Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces [18], as shown in Fig. 4, for Si adatoms. Pb adatoms, however, show a strong but opposite dependence on the number of surrounding Si adatoms. Further, the relative height of the Sn adatom is nearly independent of the number of surrounding Si adatoms, within the experimental error bar, as shown in Fig. 4. Precisely, Fig. 4 is different from

FIG. 3: The relative height of Pb (Si) adatoms in Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase as a function of the surrounding nearest-neighbor Si (Pb) adatoms, corresponding to Figs. 2(a)-(d). Figures 3(a)-(d) clearly show that increasing the number of nearest-neighbor Si adatoms increases the relative height of the Si adatom, while that of the Pb adatom decreases rapidly. These coordination effects are qualitatively independent of tip-sample surface distance, as shown in Figs. 3(a)-(d).

the original experimental result [18]. We investigated the reproducibility of Fig. 4 and concluded that within the experimental error bar, the relative height of the Sn adatom is nearly independent of the number of surrounding Si adatoms. A possible driving mechanism of chemical coordination in NC-AFM height distribution is the charge transfer effect due to differences in electronegativity (1.90 for Si, 1.96 for Sn, 2.33 for Pb) [42] and/or the metallic nature, which induces orbital rehybridization [37] and changes the bond order for the atomic force interaction between the tip apex and sample surface atoms. Further, the charge transfer may be compensated through additional back bonding (rebonding) [37]. Thus, the several mechanisms seem to compete with each other. Therefore, ab initio calculation based on the first principle theory is crucial to understand the origin of atom-by-atom chemical coordination in NC-AFM height distribution, dependent on fourth period elements such as Si, Sn, and Pb adatoms.

At a relatively large distance, the relaxation of tip-apex and sample surface atoms [19] is negligibly small. At a short distance, however, the relaxation of tip-apex and sample surface atoms becomes very large because of the strong short-range interaction force. As shown in Figs. 3(a)-(d), however, the relaxation effect does not change the qualitative feature of chemical coordination in NC-AFM height distribution, even at a short distance, but only degrades and eliminates the chemical contrast, as shown in the relative heights in Figs. 2(a)-(d) and 3(a)-(d). We confirmed a similar tip-sample surface dependence of chemical contrast [18] and chemical coordination in NC-AFM height distribution on the Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surface.

Chan *et al.* [43] theoretically deduced the relative height difference of atomic structure as 0.44 Å between a Pb adatom with four nearest-neighbor Si adatoms and a

FIG. 4: The relative height of Sn (Si) adatoms in Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase as a function of the surrounding nearest-neighbor Si (Sn) adatoms [18]. This figure clearly shows that increasing the number of nearest-neighbor Si adatoms increases the relative height of the Si adatom, while the height of the Sn adatom is approximately independent of the number of surrounding Si adatoms, within the experimental error bar.

Si adatom with two nearest-neighbor Si adatoms (four nearest-neighbor Pb adatoms) in Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surface, by first principle ab initio calculation. From Figs. 3(a)-(d), we experimentally deduced the corresponding relative height differences in NC-AFM topography between Pb and Si adatoms as ca. 0.37 Å, at a relatively large distance (Fig. 3(a)) and ca. 0.26 Å at a short distance (Figs. 3(b)-(d)). Therefore, the relative height differences in NC-AFM topography obtained at the relatively large distance are nearly equal to the corresponding theoretical value of atomic structure, within experimental error. Strictly speaking, however, the value obtained by NC-AFM topography is different from that of atomic structure. Therefore, ab initio calculation based on first-principle theory for NC-AFM topography, including the chemical coordination effect, is also needed.

IV. CONCLUSIONS

Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) and Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces have intermixed Pb (Sn) and Si adatoms and order preferentially into kinked lines, hence are called a “mosaic phase.” Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) and Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) pure phase surfaces, however, ideally have no Si adatoms. In mosaic phase surfaces, therefore, substituted heterogeneous Si adatoms will change the atom height of intermixed Pb (Sn) adatoms and also the Si adatom itself, through orbital rehybridization by charge transfer between heterogeneous adatoms, and in return, through rebonding by additional back bonding. For NC-AFM and STM measurements, bond order in the atomic force interaction, and local electronic density of state in the tunneling current, can be changed by the charge transfer between heterogeneous adatoms, respectively, and also affects the atomic corrugation height. Therefore, such atom-by-atom chemical coordination effects in NC-AFM and STM measurements can directly reveal the structural and electronic-structures of individual atoms surrounded by substituted heterogeneous atoms. Until now, however, the dependence of the relative

height of individual atoms on chemical coordination, as a function of the number of surrounding nearest-neighbor atoms, was reported only for Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces using NC-AFM. In the present experiment, we carefully investigated the atom-by-atom chemical coordination effect of Pb/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces using NC-AFM, and compared them with the previous result on Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces. We found that increasing the number of surrounding nearest-neighbor Si adatoms increases the height of Si adatoms, but rapidly decreases the height of Pb adatoms. These coordination effects were qualitatively independent of the tip-sample surface distance. This result agreed with previous results on Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) mosaic phase surfaces for Si adatoms. Pb adatoms, however, showed a strong but opposite dependence on the number of surrounding Si adatoms, and was different than the Sn adatom, which was independent of the number of surrounding Si adatoms.

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