Site-Specific Force Spectroscopy and Atom Interchange Manipulation at Room Temperature†

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An atomic force microscope (AFM) under noncontact and nearcontact modes operated at room-temperature (RT) is used for investigations of chemical identifications and lateral atom manipulations of selected single atoms on semiconductor surfaces. Noncontact AFM image can give different contrast between intermixed two chemical species. To make clear the mechanism of chemical identification, we investigated atom selective images and site-specific frequency shifts as a function of tip-sample distance in Sb,Sn/Si(111)-(√3×√3) substrate. Here, we clarified how to construct “Atom Inlay” in more detail. Further, we observed atom interchange manipulation phenomena even in In/Si(111)-(√3×√3) and Sb/Si(111)-(7×7) intermixed systems with not only Si but also In (acceptor element in crystal Si) or Sb (donor element in crystal Si) atoms. [DOI: 10.1380/ejssnt.2006.376]

Keywords: Atomic force microscope; Atom/molecule manipulation; Site-Specific Force Spectroscopy; Atom Interchange; Atom Inlay

I. INTRODUCTION

During the last few years, atomic force microscope (AFM) under noncontact and nearcontact modes has shown a great potential for atom selective imaging [1–3] and manipulating selected single atoms vertically and laterally [4–6]. In this field, the scanning tunneling microscope (STM) has widely shown to be an ideal tool for vertical and lateral manipulation of individual single atoms [7–10] and molecules [9, 11–13], as well as bonds [14–16], opening fascinating new areas of research and pushing our ability for engineering up to the ultimate limits of fabrication [17]. These abilities could be expanded to the nonconductive surfaces, in which it is difficult to operate STM, with AFM under noncontact and nearcontact modes using only the mechanical interaction force acting between the tip apex and the surface.

In this paper, to make clear the mechanism of chemical contrast among different atom species in noncontact AFM image, we investigated atom selective images and site-specific frequency shifts [18, 19] as a function of tip-sample distance in Sb,Sn/Si(111)-(√3×√3) surface with three different intermixed elements. Next, we introduced atom-interchange manipulation phenomenon on Sn/Ge(111)-(c(2×8)) intermixed surface in more detail, and clarified how to construct "Atom Inlay", that is, atom letters “Sn” consisted of 19 Sn atoms embedded in Ge(111)-(c(2×8)) substrate. Here, we clarified how to construct "Atom Inlay" in more detail. Further, we observed atom interchange manipulation phenomena even in In/Si(111)-(√3×√3) and Sb/Si(111)-(7×7) intermixed systems with not only Si but also In (acceptor element in crystal Si) or Sb (donor element in crystal Si) atoms.

II. EXPERIMENTAL

The experiments were performed using a home-built room-temperature (RT) ultrahigh vacuum (UHV) AFM with a base pressure of 5×10−11 Torr shown in Fig. 1. AFM was operated in the frequency modulation detection scheme [20], and constant amplitude mode [21] was used for oscillating low resistivity commercial n-doped silicon cantilevers with a typical spring constant of 48 N/m and first harmonic mechanical resonant frequency of 160 kHz. Before starting the experiments, both cantilever tip apex and sample surface were prepared in situ. Clean Si(111)-(7×7) surface was obtained from a n-type Sb doped single crystal Si wafer by direct current heating, flashing the sample up to 1,200°C with subsequent slowly cooling down from 900°C to room temperature (RT). Clean reconstructed Ge(111)-(c(2×8)) surface was produced from a n-type Sb doped sample with resistivity less than 0.4 Ωcm by successive cycles of Ar ion sputtering.
FIG. 1: Schematic side view of RT-UHV-AFM.

FIG. 2: (a) Atom selective image of Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) pure phase. The first resonance frequency: $f_0 = 163.853$ kHz, the frequency shift: $\Delta f = -2.0$ Hz, the cantilever oscillation amplitude: $A = 45$ nm, the spring constant: $k = 29.5$ N/m and the image size is 8 nm x 8 nm. (b) The histogram of relative height of Sn and Si adatoms in (a). (c) Atom selective image of Sb,Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) intermixed surface. $f_0 = 169.861$ kHz, $\Delta f = -4.7$ Hz, $A = 36$ nm, $k = 32.9$ N/m and the image size is 8 nm x 8 nm.

tering while heating the sample. During sample preparation, vacuum pressure was kept below $1 \times 10^{-10}$ Torr. Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) and Sn/Ge(111)-c(2 $\times$ 8) surfaces were prepared according to the previous reports [3, 6]. In order to obtain Sb,Sn/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface, at first, Sb was evaporated on the clean Si(111)-(7 $\times$ 7) surface at 600°C and annealed at 600°C for 2 min., and then followed by Sn evaporation and annealing at 650°C for 2 min. In order to obtain In/Si(111)-($\sqrt{3} \times \sqrt{3}$) surface, In was evaporated on the clean Si(111)-(7 $\times$ 7) surface at RT and annealed at 500°C for 5 min., while, to obtain Sb/Si(111)-(7 $\times$ 7) surface, Sb was evaporated on the clean Si(111)-(7 $\times$ 7) surface at 600°C and annealed at 600°C for 2 min. The Si tip apex was carefully cleaned up by Ar ion bombardment for 30 min. with 0.6 keV ion energy, $1 \times 10^{-6}$ Torr of partial Ar pressure. The experiments were conducted at room-temperature (RT). For reproducible site-specific frequency shift measurement using frequency modulation AFM at RT with a lateral precision comparable with that at LT, the atom-tracking technique was introduced [18, 19].

III. RESULTS AND DISCUSSION

A. Chemical identification by noncontact AFM at RT

1. Atom selective imaging of intermixed three elements system

Noncontact AFM image can give different contrast between intermixed two chemical species such as Sb and Si atoms in Si(111)-(5$\sqrt{3} \times 5\sqrt{3}$)-Sb [1], Sn and Ge atoms...
in Sn/Ge(111)-(2 × 8) [2], and Sn and Si atoms in Sn/Si(111)-(√3 × √3) mosaic phase and Sn/Si(111)-(7×7) [3]. Figure 2(a) shows a typical example of atom selective imaging in Sn/Si(111)-(√3 × √3) pure phase (Sn~100% because of Sn~1/3 ML) using noncontact AFM. In this image, we can clearly observe two kinds of bright spots. As shown in Fig. 2(a), we attributed brighter and dim spots to Sn and Si atoms, respectively, because almost all atoms were Sn atoms in pure phase. Then we investigated histogram of Fig. 2(a), as shown in Fig. 2(b), and found that the standard deviation \( \sigma \) of relative height of Sn adatoms is \( \sigma = 2 \) pm, so that our noncontact AFM has vertical resolution less than 2 pm.

To achieve more straightforward chemical identification, we measured site-specific frequency shifts as a function of tip-sample distance (from now on we call SSFS curve) of each Sb, Sn and Si atoms indicated by blue, black and red arrows, respectively, in Sb,Sn/Si(111)-(√3 × √3) inset image of Fig. 4. Here, using atom tracking method, we obtained 40 SSFS curves for each Sb, Sn and Si atoms. Three averaged SSFS curves in Fig. 4 nearly agree each other above 5 Å, so that long range force due to Van der Waals force seems to be dominant above 5 Å [18]. On the other hand, below 5 Å, differences among three averaged SSFS curves increasingly become clear, so that short range chemical force seems to reveal

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**FIG. 3:** Tip-sample distance dependence of atom selective images in Sb,Sn/Si(111)-(√3 × √3) intermixed surface at (a) \( \Delta f = -3.8 \) Hz, (b) \( \Delta f = -4.3 \) Hz and (c) \( \Delta f = -5.3 \) Hz. \( f_0 = 169.861 \) kHz, \( A = 36 \) nm, \( k = 32.9 \) N/m and the image size is 8 nm × 8 nm.

**FIG. 4:** Tip-sample distance dependence of frequency shift \( \Delta f \) of selected Sb (blue line), Sn (black line) and Si (red line) atoms indicated by blue, black and red arrows in the inset AFM image. Inset AFM image was obtained at \( f_0 = 169.861 \) kHz, \( \Delta f = -7.3 \) Hz, \( A = 36 \) nm, \( k = 32.9 \) N/m and the image size is 4 nm × 4 nm.
element dependent nature below 5 Å [18]. Among averaged SSFS curves in Fig. 4, Si atom seems to have a deepest minimum, while Sb and Sn seems to have nearly same shallow minimums [22]. This result agrees with the results that maximum covalent bonding force and covalent bond energy of Si atom are larger than those of Sb and Sn atoms, while differences of those values are relatively small between Sb and Sn atoms. Tip-sample distance dependence of SSFS in Fig. 4 can explain tip-sample distance dependence of Figs. 3(a)-(c) [23]. Since the SSFS curves for Si and Sb cross each other at Δf = −10.0 Hz, it is expected that Sn adatoms are imaged brighter than Si adatoms for |Δf| > 10.0 Hz while Sb adatoms are imaged brighter than Sb adatoms for |Δf| < 10.0 Hz. In principle, from such SSFS curves, we can evaluate force parameters of individual atoms at specific-site such as maximum covalent bonding force, covalent bond energy, charge transfer, and atom position that will serve as a "Finger Print" of chemical species at specific-site.

B. Lateral atom-interchange manipulation by nearcontact AFM at RT

1. Atom letters "Sn" consisted of 19 Sn atoms embedded in Ge(111)-c(2×8) surface

Recently, using nearcontact AFM, we found a lateral atom-interchange phenomenon at RT and constructed "Atom Inlay", that is, atom letters "Sn" consisted of 19 Sn atoms embedded in Ge(111)-c(2×8) substrate [6]. Here, we clarified how to construct "Atom Inlay" in more detail.

Figure 5(a) shows noncontact AFM image of Sn/Ge(111)-c(2×8) intermixed surface obtained at frequency shift of Δf_image = −7.0 Hz. Here at the site...
FIG. 8: Noncontact AFM images of Sn/Ge(111)-c(2×8) intermixed surface during process of artificial nanostructuring of "Atom Inlay" by successive imaging and following lateral atom-interchange. $f_0 = 160.450$ kHz, $\Delta f = -4.6$ Hz, $A = 16$ nm, $k = 27.7$ N/m and the image size is $8$ nm×$8$ nm.

indicated by a yellow arrow, we observed single brighter spot, that was a Sn adatom embedded in Ge(111)-c(2×8) surface. Decreasing tip-sample distance by decreasing frequency shift down to $\Delta f_{\text{move}} = -7.2$ Hz, we observed repeated imaging of single Sn adatom, and further we succeeded in breakup of such repeated imaging by increasing frequency shift up to $\Delta f_{\text{image}} = -7.0$ Hz at the fast scan line indicated by blue broken line in Fig. 5(b). White lines of Fig. 5 show the slow scan direction. Then we again observed single brighter spot at frequency shift of $\Delta f_{\text{image}} = -7.0$ Hz as shown in Fig. 5(c). Hence we concluded that the parts of Fig. 5(b) obtained at $\Delta f_{\text{move}} = -7.2$ Hz and $\Delta f_{\text{image}} = -7.0$ Hz correspond to nearcontact and noncontact AFM images, respectively. As can be seen in Fig. 5(b), the embedded Sn adatom (at head of black arrows) was manipulated twice following the tip slow scan when imaging at $\Delta f_{\text{move}} = -7.2$ Hz (high attractive interaction force); and it (at tail of black arrows) was stopped near the line at which the interaction force was released. A possible explanation for this observation is that, after being imaged, the embedded Sn adatom jumped to the next stable adsorption position on the surface following the tip slow scan along the [110] crystallographic direction; the next stable $T_4$ site in this direction should be far enough to allow us to completely image the Sn adatom again. Since this jump occurs after imaging the Sn adatom, a pulling process of the tip on the Sn adatom is inferred. The brighter spot in Fig. 5(a) indicated by a yellow arrow is a Sn adatom embedded in Ge(111)-c(2×8) substrate, so that jump of Sn adatom means interchange with adjacent Ge adatom, as shown in Fig. 6, following the tip slow scan along the [110] crystallographic direction. In a tip-induced movement of an embedded Sn adatom placed in a homogeneously distributed surface potential, one should expect lateral displacements along the fast line scan direction too. These lateral displacements are, however, not observed (Fig. 5(b)); thus, the embedded Sn adatom movement should be confined along the adatom rows by greater diffusion energy barriers in the [112] crystallographic direction than in the [110] one. Then we changed the raster scan method into the vector scan method to interchange the selected Sn adatom with the arbitrarily selected adjacent Ge adatom [6]. Concretely, after imaging the surface under noncontact mode where tip-surface interaction forces do not activate the interchange between Sn and Ge adatoms, the scan size was reduced and the tip fast-scan direction was aligned with the line connecting the centers of the adatoms selected for manipulation. The surface was imaged until the line connecting the centers of the adatoms was reached, and the slow scan was stopped at this position. Successive topographic scans over this line gradually reducing the tip-surface distance lead to the adatom interchange. This process is monitored by a swap in the height signals associated with each adatom type. These line-scans were performed by lifting the oscillating tip up typically 1 Å above the surface on the way back. The surface area was imaged again without perturbing the adatoms. As a re-
result, in spite of inhomogeneous diffusion energy barriers, we achieved the interchange manipulation not only along the [110] crystallographic direction, but also various directions by interchanging Sn adatoms with adjacent Ge adatoms as shown by green arrows in Fig. 7. Only along the [110] crystallographic direction, we succeeded the repeated jumps. Besides, we could not induce the interchange manipulation with the Ge adatoms indicated by black arrows in Fig. 7. These results clearly prove the existence of inhomogeneous diffusion energy barriers.

Figure 8 shows successive noncontact AFM images of Sn/Ge(111)-c(2 × 8) intermixed surface during artificial nanostructuring process of "Atom Inlay" by successive imaging and following lateral atom-interchange. As a result, as shown in Fig. 9, we constructed "Atom Inlay", that is, atom letters "Sn" consisted of 19 Sn atoms embedded in Ge(111)-c(2 × 8) substrate [6]. Figure 10 shows models of preceding [7, 24] and present lateral atom manipulation. Present novel artificial nanostructuring using mechanical atom manipulation method has several significant differences from conventional ones as follows: (1) "AFM" which can be applicable even to insulating materials was used instead of STM. (2) "Selective Atom Manipulation" that selectively manipulated two kinds of atom species such as intermixed Sn and Ge atoms was used instead of conventional atom/molecule manipulation method. (3) "Lateral Atom Interchange Manipulation" phenomenon that can interchange two kinds of atom species such as adjacent Sn and Ge atoms was discovered and used for creating nanostructure. (4) "Atom Inlay" - embedded atom letter "Sn" - that is a novel artificial nanostructure was created at RT. Such chemical discrimination and following novel atom manipulation/assembly method as shown in Fig.8 may enable us to search and create complex nanomaterials and nanodevices with novel functions consisting of many atom species even on insulating substrate at RT.

To investigate universality of atom interchange manipulation phenomenon, we proceeded atom interchange manipulation experiments on In/Si(111)-(√3 × √3) intermediate phase (~ 50%<In<~ 100%) and Sb/Si(111)-(7 × 7) intermixed surface. As a result, as shown in noncontact AFM image of Fig. 11(a), we succeeded in chemical identification of In and Si adatoms, because dominant brighter spots in intermediate phase were In atoms. We also succeeded in atom interchange manipulation between selected In and Si adatoms enclosed by dotted open white rectangles as shown in noncontact AFM images of before (Fig. 11(a)) and after (Fig. 11(b)) atom interchange manipulation. Besides, as shown in noncontact AFM image of Fig. 12(a), we succeeded in chemical identification of Sb and Si adatoms, because dominant brighter spots in (7 × 7) surface were Si atoms. We also succeeded in atom interchange manipulation between Sb and Si adatoms enclosed by dotted open white rectangles as shown in noncontact AFM images of before (Fig. 12(a)) and after (Fig. 12(b)) atom interchange manipulation. (1) Hence we achieved atom interchange manipulation experiments using not only Ge(111) substrate, but also Si(111) substrate. (2) Besides we achieved atom interchange manipulation experiments using not only Ge(111)-c(2 × 8) reconstructed surface, but also In/Si(111)-(√3 × √3) intermediate phase and Si(111)-(7 × 7) reconstructed surfaces with different surface reconstructions. (3) Further, we also achieved atom interchange manipulation experiments using not only embedded Sn atom, but also embedded In atom that is acceptor element in crystal Si, and Sb atom that is donor element in crystal Si. Therefore, atom interchange manipulation phenomenon occurs in various semiconductor substrates, various reconstructions and various chemical species, and seems to be universal phenomenon. To understand why In adatom is brighter than Si adatom, while Sb adatom is dimmer than Si adatom, both theo-
interchange manipulation.

intermixed surface (a) before and (b) after lateral atom-interchange manipulation. $f_0 = 166.709$ kHz, $\Delta f = -4.8$ Hz, $A = 30$ nm, $k = 31.1$ N/m and the image size is 6 nm $\times$ 6 nm.

FIG. 12: Noncontact AFM images of Sb/Si(111)-(7 $\times$ 7) intermixed surface (a) before and (b) after lateral atom-interchange manipulation. $f_0 = 174.538$ kHz, $\Delta f = -5.8$ Hz, $A = 42$ nm, $k = 33.7$ N/m and the image size is 8 nm $\times$ 8 nm.

retical investigations and SSFS curve studies are needed.

IV. CONCLUSIONS

In conclusion, we proved that we can discriminate intermixed two atom species in Sn/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) pure phase, In/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) intermediate phase and Sb/Si(111)-(7 $\times$ 7) reconstructed surfaces in addition to the previous Si(111)-(5$\sqrt{3}$ $\times$ 5$\sqrt{3}$)-Sb [1], Sn/Ge(111)-c(2 $\times$ 8) [2], Sn/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) mosaic phase and Sn/Si(111)-(7 $\times$ 7) [3] reconstructed surfaces. Hence, we achieved chemical identifications by atom selective imaging on various surface reconstructions using not only Ge(111), but also Si(111) substrates. Besides, we achieved chemical identifications by atom selective imaging between two atom species of (Sn, Si), (In, Si), (Sb, Si), and (Sn, Ge). Therefore, chemical identifications by atom selective imaging is possible in various intermixed semiconductor substrates, various reconstructions and various chemical species, and seems to be universal phenomenon. To make clear the mechanism of chemical identification, we investigated atom selective images and site-specific frequency shifts as a function of tip-sample distance in Sb,Sn/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) intermediate phase with three different intermixed elements. The latter that we call SSFS curve enables us to identify chemical species more decisively, because from such SSFS curves, we can evaluate force parameters of individual atoms at specific-site such as maximum covalent bonding force, covalent bond energy, charge transfer, and atom position that will serve as a “Finger Print” of chemical species at specific-site. Then, we clarified how to construct ”Atom Inlay” in more detail. Further, we observed atom interchange manipulation phenomena even in In/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) intermediate phase and Sb/Si(111)-(7 $\times$ 7) intermixed systems. Hence we achieved atom interchange manipulation experiments using not only Ge(111) substrate, but also Si(111) substrate. Besides we achieved atom interchange manipulation experiments using not only Ge(111)-c(2 $\times$ 8) reconstructed surface, but also In/Si(111)-(\(\sqrt{3} \times \sqrt{3}\)) intermediate phase and Si(111)-(7 $\times$ 7) reconstructed surfaces with different surface reconstructions. Besides, we achieved atom interchange manipulation experiments using not only embedded Sn atom, but also embedded In atom that is acceptor element in crystal Si, and Sb atom that is donor element in crystal Si. Therefore, atom interchange manipulation phenomenon occurs in various semiconductor substrates, various reconstructions and various chemical species, and seems to be universal phenomenon. Such chemical discrimination and following novel atom manipulation/assembly method may enable us to search and create complex nanomaterials and nanodevices with novel functions consisted of many atom species even on insulating substrate at RT.

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