## Identification of Si and Ge atoms by atomic force microscopy

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We successfully identify individual Ge and Si atoms on intermixed Ge/Si(111)–(7 × 7) surfaces by force spectroscopy using atomic force microscopy at room temperature. Tips with high chemical reactivity show distinct peaks derived from Ge and Si in the histograms of maximum attractive forces. The ratio of the maximum attractive force on Ge to that on Si takes a constant value of 0.84 independently of the tips. We apply the present method to Ge/Si(111)–(5 × 5) surfaces to elucidate the elemental composition of the topmost layer.

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Strained Si-Ge heterojunction structures have attracted much attention due to their potential application to optoelectronics for telecommunications [1,2], high-mobility complementary metal oxide semiconductor devices [3], and electronspin-resonance transistors for quantum computation [4]. This is because Si-Ge has complete miscibility, as shown by its phase diagram, which allows continuous tuning of its band gap and lattice constant between bulk Si and Ge. The good compatibility and resultant lattice mismatch between Si and Ge also make Si-Ge applicable to various low-dimensional systems such as nanoclusters [5–13], nanowires [14–16], 2D wetting layers [17–24], and 3D nanoislands [25–36]. However, it is also known that the intermixing of Si and Ge atoms occurs at the interface between the surface and the bulk during the formation processes. Such a random distribution of relevant atoms would play a crucial role in the reliable operation of the nano- and atomic-scale transistors [37-39].

To date, the detailed local atomic structures and configurations of Si-Ge intermixed surfaces have been extensively studied by scanning tunneling microscopy (STM) and atomic force microscopy (AFM). An interesting issue with regard to the composition of the intermixed surfaces is the possibility of distinguishing Ge and Si atoms. Previous researchers have examined this possibility by STM topography [17,18,21], AFM topography [11,40,41], or current imaging tunneling spectroscopy [19], or by utilizing a third species such as Bi [42,43] or Cl [44] to enhance the STM contrast. On the other hand, the local stoichiometry change at the Si-Ge interface with Ge coverage has also been investigated by reflectance anisotropy spectroscopy [45]. The complete differentiation of the Ge and Si atoms, however, is still a formidable challenge because their chemical properties are so similar, e.g., their radii of covalent bonds (Si 1.17 Å, Ge 1.22 Å) and their covalent bond energies (Si-Si 2.32 eV, Si-Ge 2.12 eV) are nearly identical.

Here, we report the identification of individual Ge and Si adatoms on an intermixed Ge/Si(111) $-(7 \times 7)$  surface by using AFM force spectroscopy. As demonstrated by Sugimoto *et al.* [46], AFM force spectroscopy has the ability to resolve atomic species on a semiconductor surface without disturbance to the bare surface atoms. This method has

already been applied to alloy systems such as Si with Sn, Pb, and/or In, but its viability for use in Si-Ge systems is not unambiguous. In the present study, it is found that AFM tips with high chemical reactivity, meaning tips possessing strong attractive force maxima, are necessary for the reliable chemical discrimination of Si and Ge. In addition, we applied this method to intermixed Ge/Si(111)–(5 × 5) surfaces, where the chemical discrimination of Ge and Si atoms has not previously been performed.

All experiments were carried out with a custom-built frequency-modulation AFM at room temperature. The base pressure was typically less than  $5 \times 10^{-9}$  Pa. In order to obtain force spectroscopies with high sensitivity, we used optical interferometry and soft Si cantilevers. The commercial Si cantilevers were cleaned by Ar ion sputtering to remove native oxide layers. The cantilever-oscillation amplitude was set to be sufficiently large ( $A \sim 100 \text{ Å}$ ) for stable AFM operation. During the experiments, a proper voltage was applied between the tip and sample to compensate the contact potential difference between them. Measurements of force spectroscopies were carried out with atom-tacking and feedfoward systems [47]. Additional details are described elsewhere [48]. Clean Si(111)– $(7 \times 7)$  surfaces are prepared by repeated flashing n-type Si(111) samples to 1250 °C after degassing at 650 °C overnight. Owing to the low pressure of less than  $5 \times 10^{-8}$  Pa during the flashing and the low dopant (Sb) concentration of  $1 \times 10^{18}$  atoms/cm<sup>2</sup> in the Si samples, there are fewer defects such as adsorbed contaminants and intrinsic impurities on the Si(111) $-(7 \times 7)$  surfaces, typically less than 5 defects in a  $20 \times 20$  nm<sup>2</sup> area. Even if we found such defects, we could avoid such regions by changing the scan area and find clean  $10 \times 10 \text{ nm}^2$  regions suitable for our following experiments. Typical terrace width was more than 50 nm. For preparing Ge atoms on the Si(111) $-(7 \times 7)$  surfaces, we used a filament-type evaporator which was wrapped around a small chunk of Ge (purity: 99.999%). A 0.13-0.38 monolayer (ML; 1 ML =  $7.83 \times 10^{14}$  atoms/cm<sup>2</sup>) amount of Ge was deposited on the clean Si(111)– $(7 \times 7)$  surfaces at room temperature while keeping the base pressure less than  $6 \times 10^{-9}$  Pa. Then, we annealed the samples at  $600 \,^{\circ}\text{C}$ typically for 10 minutes.

Figure 1 presents our methodology. Figure 1(a) shows an AFM topographic image of  $10 \times 10 \text{ nm}^2$  area on an Si(111)–(7 × 7) surface prepared with 0.25 ML of Ge.

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FIG. 1. (Color online) (a) AFM image of the Ge/Si(111)– (7 × 7) surface prepared with 0.25 ML of Ge. (b) Schematic diagram for the (7 × 7) "DAS" model. The shaded region is made up of one unit cell where the faulted half unit cell is the darker shaded region on the right. (c) The  $\Delta f(z)$  curves were acquired on an FH corner adatom (black curve) and a corner hole (green curve) site, which are indicated by the black and green crosses in (a). (d) The converted short-range F(z) curve on a FH corner adatom. The acquisition parameters are the resonance frequency ( $f_0$ ) = 152.913 kHz, the cantilever-oscillation amplitude (A) = 125 Å, the spring constant (k) = 28.2 N/m, the sample bias ( $V_S$ ) = +70 mV, and the frequency shift ( $\Delta f$ ) = -7.3 Hz.

Although there is slight topographic variety at the individual equivalent adatom sites, the chemical identities of the adatoms are not clear, as previously pointed out [41]. As will be seen in Fig. 3 and the Supplemental Material [49], such topographic variations of the adatoms could originate not only from atomic species of adatoms but also from those of back-bond atoms. In order to clarify Si and Ge adatoms, we measured  $\Delta f(z)$ curves on adatom sites in Fig. 1(a). Hereafter, we will show a representative  $\Delta f(z)$  curve [black curve in Fig. 1(c)] obtained at an adatom site indicated by the black cross in Fig. 1(a) to explain a force conversion procedure. Since the  $\Delta f(z)$  curve included not only the short-range chemical force but also the long-range van der Waals force, we measured a  $\Delta f(z)$  curve [green curve in Fig. 1(c)] at a corner hole site [the green cross in Fig. 1(a)] for subtraction of the long-range contribution. After obtaining a short-range  $\Delta f(z)$  curve, we were able to convert it to a short-range F(z) curve by the Sader-Jarvis method [Fig. 1(d)] [50]. Such short-range F(z) curves were acquired on three equivalent faulted half (FH) corner adatom sites with regard to 10 unit cells of the dimer-adatom-stacking fault (DAS)  $7 \times 7$  [Fig. 1(b)], that is, the 30 equivalent FH corner adatom sites in Fig. 1(a). Finally, we analyzed the maximum attractive forces  $(F_{max})$  of 30 F(z) curves in detail as follows.

Figures 2(a)-2(c) show histograms of the maximum attractive forces at the 30 FH corner adatom sites on the Si(111)-(7 × 7) surface prepared with 0.25 ML of Ge. We measured these data sets using tips with different chemical



FIG. 2. (a)–(c) The histograms of maximum attractive forces  $(F_{\text{max}})$  on the 0.25 ML Ge-deposited Si(111)–(7 × 7) surface obtained by changing the tip reactivity. Individual histograms were obtained on the same sample but at different scanning regions. The acquisition parameters are  $f_0 = 152.913$  kHz, A = 125 Å, k = 28.2 N/m,  $V_S = +70$  mV.

reactivities at different regions but on the same sample surface. At this moment, even if the impurities are included in our histograms by chance, we can treat them as deviated points in the histograms since it is known that the maximum attractive forces exerted on Sb become considerably weaker [51]. The average value of the maximum attractive forces increases from Figs. 2(a)-2(c) in that order. It would thus appear that the separation between the two peaks becomes larger as the tips become more chemically reactive; the histograms represent a bimodal distribution. Either of the peaks could originate from Ge adatoms. Therefore, when discriminating the chemical species of atoms that have similar chemical interactions with an AFM tip, we suggest that it is better to use tips with high chemical reactivity (more than 1.5 nN in the present case),



FIG. 3. (Color online) Histograms of topographic heights and maximum attractive forces measured at FH corner adatom sites on the intermixed Ge/Si(111)–(7 × 7) surfaces prepared with Ge deposition amounts of 0.13 ML [(a) and (b)], 0.25 ML[(c) and (d)], and 0.38 ML [(e) and (f)]. The data sets related to a Ge deposition amount of 0.25 ML are the same as in Fig. 2(c). Insets of (a) and (b), (c) and (d), and (e) and (f) show the AFM topographic images of the measured area before and after the chemical identification, where Ge and Si adatoms are indicated with blue and red circles, respectively. The acquisition parameters of (a) and (b) are  $f_0 = 151.729$  kHz, A = 133 Å, k = 27.5 N/m,  $V_S = +500$  mV, and  $\Delta f = -6.5$  Hz. The acquisition parameters of (c) and (d) are  $f_0 = 152.913$  kHz, A = 125 Å, k = 28.2 N/m,  $V_S = +70$  mV, and  $\Delta f = -10.6$  Hz. The acquisition parameters of (e) and (f) are  $f_0 = 151.730$  kHz, A = 147 Å, k = 27.5 N/m,  $V_S = +500$  mV, and  $\Delta f = -7.0$  Hz.

because otherwise the tails of peaks will become convoluted in the histogram, as shown in Figs. 2(a) and 2(b). The dispersions of the peaks are determined by the precision of the force measurements on adatoms.

Next, in order to determine which peak is involved with Ge, we altered the amounts of Ge deposited onto the Si(111)– $(7 \times 7)$  surface and then observed the samples with highly reactive tips. The results of the histograms of maximum attractive forces measured on the samples with Ge deposition amounts of 0.13 ML, 0.25 ML, and 0.38 ML are represented in Figs. 3(b), 3(d), and 3(f), respectively. It is apparent that the individual histograms are bimodal, exhibiting two peaks respectively composed of weaker and stronger maximum attractive forces. The ratio of the atom counts in the peak composed of weaker maximum attractive forces to the total number increased almost proportionally as the amount of Ge coverage was augmented; it changed from 23% in Fig. 3(b) to 57% in 3(d) to 77% in 3(f). This strongly indicates that the left side peaks in Figs. 3(b), 3(d), and 3(f) arise from Ge adatoms. As shown in the insets of Figs. 3(b), 3(d), and 3(f), the Ge (blue circles) and Si (red circles) adatoms identified by the present method were overlaid on the AFM topographic images [insets of Figs. 3(a), 3(c), and 3(e)]. It can be seen that these adatoms are randomly distributed on the Si(111)– $(7 \times 7)$ surface.

It is known that the maximum attractive force on an Si adatom can be altered from 0.5 nN to 2.5 nN depending on the chemical reactivity of the tip [52]. The chemical identification method using AFM force spectroscopy, however,

is robust against the different tip reactivity because it utilizes a normalization procedure with regard to the maximum attractive forces of target and reference adatoms [46,53]. Thus, using the mean maximum attractive forces of the target Ge ( $F_{max, Ge}$ ) and reference Si ( $F_{max, Si}$ ), the values of the interaction ratios ( $F_{max, Ge}/F_{max, Si}$ ) are estimated as 0.85 [Fig. 3(b)], 0.83 [Fig. 3(d)], and 0.84 [Fig. 3(f)]. Because the ratio is independent of the tip states, we take the average value of 0.84. Compared to those of other elements such as Sn (0.77), In (0.72), and Pb (0.59) [46], the value for Ge is higher, making it more difficult to distinguish Ge from Si adatoms by a tip with less chemical reactivity, e.g., lower than 1.5 nN, on an Si adatom site.

Figs. 3(a), 3(c), and 3(e) show the histograms of topographic heights measured from corner holes with regard to identified Ge and Si adatoms. Clearly, the histograms stemming from Ge and Si lie one on top of another, demonstrating the difficulty of distinguishing them solely by AFM topography. We infer that the ambiguity of the height difference between Ge and Si adatoms is due to their chemical similarities and resultant intermixing; some of the Si atoms at the back-bond sites could be replaced with Ge atoms [49].

Finally, we applied our chemical identification method using AFM to Ge/Si(111)– $(5 \times 5)$  surfaces (wetting layer). We prepared the surfaces by using approximately 3 ML of Ge deposition and subsequent annealing at 600 °C for 10 minutes, and the resulting surfaces typically contained 7 × 7 and 5 × 5 regions [Fig. 4(a)]. In the previous STM studies, random distribution of the topographic heights of adatoms was



FIG. 4. (Color online) AFM topographic images of the Ge/Si(111) surface prepared with Ge deposition amounts of about 3 ML showing (a) the coexistence of  $(5 \times 5)$  and  $(7 \times 7)$  reconstructed surface phases and (b) the largely formed  $Ge/Si(111)-(5 \times 5)$ surface (wetting layer). (c) Schematic diagram for the  $(5 \times 5)$ "DAS" model. The shaded region is made up of one unit cell where the faulted half unit cell is the darker shaded region on the right. Histograms of (d) topographic heights and (e) maximum attractive forces measured at FH adatom sites on the intermixed Ge/Si(111)– $(5 \times 5)$  surface with a less reactive tip. Insets of (d) and (e) show the AFM topographic images of the measured area before and after the chemical identification, where Ge and Si adatoms are indicated with blue and red circles, respectively. The acquisition parameters are  $f_0 = 151.736$  kHz, A = 137 Å, k = 27.5 N/m,  $V_S = +500 \text{ mV}, \Delta f = -6.5 \text{ Hz}.$ 

observed on the equivalent sites on the Ge/Si(111)–(5 × 5) surfaces [18,19]. While this result was attributed to the coexistence of Ge and Si atoms on the topmost surface layer [18], recent calculations had suggested that the compressive strain due to the lattice mismatch between the Ge surface and the Si substrate tended to cause the 5 × 5 topmost layer of Ge [35] and even that the totally segregated Ge surface could cause the random corrugation in STM image [22]. In the present study, to determine whether Si atoms were present on the topmost layer, we carried out force spectroscopy on equivalent FH corner adatom sites around the center of the 5 × 5 area, as shown in

Fig. 4(b). Since Ge/Si(111)– $(5 \times 5)$  also has corner hole sites [Fig. 4(c)], we were able to follow the same procedures as in the case of Ge/Si(111)– $(7 \times 7)$ . The histogram was composed of 66 maximum attractive forces and indicated a bimodal distribution [Fig. 4(e)]. The interaction ratio of the mean maximum attractive force of the peak composed of weaker maximum attractive forces to that of the peak consisting of stronger maximum attractive forces was estimated to be 0.86, which is similar to the interaction ratio of 0.84 in Ge/Si(111)– $(7 \times$ 7). Therefore, the peaks composed of weaker and stronger maximum attractive forces were derived from Ge (blue) and Si (red) adatoms, respectively [Fig. 4(e)]. Unfortunately, as found in the magnitude of the maximum attractive forces in Fig. 4(e), we eventually had a tip with sufficiently low reactivity that we could no longer see a distinct peak separation. Accordingly, there were bins of unidentified adatoms (black) around 1.23 nN. The identified Ge and Si adatoms are indicated with blue and red circles, while unidentified adatoms are represented with black ones [inset of Fig. 4(e)]. We found that it was much more difficult to prepare highly reactive tips of more than 1.5 nN reactivity on the Ge/Si(111)– $(5 \times 5)$ surfaces than on the Ge/Si(111)– $(7 \times 7)$  surfaces. This was because the surface adatoms, where the foremost tip atoms were replaced by mild contact, were mainly dominated by Ge atoms. It is well known that the contribution from the atomic species terminating the tip apex to the maximum attractive force is as significant as the tip structure and the relative orientation of the tip with regard to the surface [46]. Actually, the Ge occupancy, which is defined as the number of Ge atoms divided by the number of total measured sites, reached 86%, resulting in a high possibility of acquiring less reactive tips. As shown in the inset of Fig. 4(e), our results support the previous claim that Ge and Si atoms coexist and are randomly distributed in the topmost surface layer. On the other hand, the discrimination between Ge and Si adatoms is still difficult only by the histogram of AFM topographic heights, as shown in Fig. 4(d) and its inset.

In summary, we were able to experimentally identify Ge and Si adatoms on the Ge/Si(111)– $(7 \times 7)$  surfaces by AFM force spectroscopy, while the discrimination of these adatoms based on AFM topographic heights was very difficult. It was found that the reactive tips showed a bimodal distribution in the histogram of maximum attractive forces. The origins of the peaks in the histograms were determined by changing the deposition amount of Ge. Our results showed that the calibrated interaction ratio of Ge to Si became 0.84, which would make practical use of chemical identification of unknown atoms on other Si-Ge intermixed surfaces. We then applied our method to Ge/Si(111)– $(5 \times 5)$  surfaces and found that a small number of Si adatoms were randomly distributed even on 3 ML Ge-deposited surfaces. In general, it is worth mentioning that the similarity of chemical properties of the atoms to be identified by AFM causes two difficulties; one is that they show a similar magnitude of maximum attractive forces when using less reactive tips, and the other is that they do not show clear topographic height differences if they can be intermixed. The chemical identification by AFM should be useful for further studies of the intermixing process on the surfaces or for the investigation of atomic-scale transistors in Si-Ge alloy systems.

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