Atomic-scale identification of Ge/Si intermixing on Si(100) at submonolayer Ge coverages

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Abstract

The positions of Ge atoms intermixed in the Si(100) surface at very low concentration are identified using empty-state imaging in scanning tunneling microscopy. A measurable degree of place exchange occurs at temperatures as low as 330 K. Contrary to earlier conclusions, good differentiation between Si atoms and Ge atoms can be achieved by proper imaging conditions.

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Because of their potential applications in high-speed electronic and infrared detection devices and their compatibility with Si processing, heterojunctions and nanostructures formed from SiGe/Si layers have attracted considerable interest in recent years. Many studies have focused on epitaxial growth of Ge or GeSi on Si, in order to realize atomic-level control of interface formation. The early stage of Ge growth on Si(100) exhibits classic Stranski-Krastanov mode behavior (layer-by-layer growth followed by three-dimensional island formation). In this regime a variety of heteroepitaxy phenomena can be quantitatively investigated. Although surface morphology, atomic structure, and surface stress have been extensively studied [1], a direct measurement of the atomic-level stoichiometry of the surface, which has important consequences for device fabrication, has not been achieved.

It is known that Si(100) reconstructs to form rows of dimers to eliminate half of its dangling bonds in order to reduce the surface energy. The surface is under tensile stress along the dimer bond and under compressive stress normal to it. A variety of indirect evidence has been interpreted as suggesting that Ge and Si exchange sites in the (100) surface already at submonolayer Ge coverage [2-4]. Surface free-energy considerations suggest that at one monolayer (ML) coverage, the surface is terminated with pure Ge[2, 5]. Other studies suggest coverage and temperature dependent atomic intermixing promoted by surface defects, with an activation temperature of the order of 670 K [5-9], and in one case as low as 300 K [10]. These unclear and sometimes contradictory results are a consequence of a lack of direct observation of the intermixing at the atomic scale. A real-space, atomic-level elemental identification allows a true determination of the origin of intermixing and the role of intermixing in surface morphology, stress modification, and composition fluctuations in growth.

Scanning tunneling microscopy (STM) is, of course, capable of imaging surfaces on the atomic scale, and has provided many breakthroughs in the Si and Ge surfaces, but distinguishing Ge from Si – the first step in SiGe composition imaging – has not been successful and has been considered extremely difficult because of the electronic and chemical similarities of Ge and Si. A comparison of the surface electronic properties between the intrinsic dimers in Si(100)-2x1 and Ge(100)-2x1 offers some hope, however. Scanning tunneling spectroscopy (STS) spectra of a Ge dimer on Ge(100) [11] and of a Si dimer on Si(100) [12] both show a strong peak (-1 eV and -0.9 eV, respectively) below and a weak peak (+ 0.9 eV and + 0.5 eV, respectively) above the Fermi energy. The strong peaks contribute to typical filled-state images primarily associated with the dimer up-atoms and the backbonds [13]. The weak (empty-state) peaks are produced predominantly by surface dangling-bond (π^*) states primarily associated with the dimer down-atoms. Using the filled-state peaks as references, the relative strength of the empty-state peak in Si is much weaker than that in Ge [11, 12] (i.e., more localized electron states at Ge dimers than at Si dimers), consistent also with theoretical calculations [13]. These spectroscopic comparisons suggest a possibility to distinguish Ge from Si in empty-state imaging. *If Si and Ge appear the same in brightness in a typical filled-state image of a mixed Ge-Si surface,* Ge should be more visible than Si in empty-state images taken at appropriate conditions. There have been few atomic-resolution STM studies on the system using empty-state imaging, most likely because empty-state imaging of Si(100) is more difficult than filled-state imaging. In addition, an empty-state image obtained with conventional conditions is fundamentally not surface-state sensitive [14, 15], and there have been no reports of identification of Ge atoms in or on the Si surface, leading to the belief that it is not possible to distinguish Si and Ge on Si(100) with STM.

In this Letter, we demonstrate that, contrary to conventional wisdom, Ge/Si intermixing sites can be clearly identified with high-resolution empty-state STM imaging at low biases[14]. We present an atomic-scale characterization of Ge/Si intermixing on the Si(100) surface at submonolayer Ge coverage, and show that Ge/Si place exchange occurs randomly on the terraces, that steps and point defects are not preferential intermixing sites, and that a measurable degree of place exchange occurs at temperatures as low as 330 K. Our studies further the frontier of chemical identification in the Ge/Si(100) system with STM and open opportunities for further real-space investigations of intermixing during growth.

The experiments were performed in an ultrahigh-vacuum scanning tunneling microscope (STM) with a base pressure below $1x10^{-10}$ Torr. The Si substrate was resistively heated, and cleaned in the conventional manner by degassing at 970 K and flashing at 1470 K for ~ 1 minute. Ge was deposited from a resistively heated tungsten wire basket with an intervening shutter, with no detectable radiation heating of the sample. We used Ge coverage between ~ 0.02 and 0.20 monolayer (ML). The substrate temperature during Ge deposition was calibrated with a K-type thermocouple attached to the back side of the substrate. All STM images (filled- and empty-state) were taken at room temperature in the constant-current mode with a tunneling current of ~ 0.1 nA.

Figure 1 shows results of our initial experiments, carried out on a 4 ° vicinal Si(100) substrate. The starting surface, shown in Fig. 1a, consists of narrow terraces almost free of vacancies, presumably because they have diffused to the steps [16] during sample cleaning. We particularly wanted to use a sample on which terrace defects would be negligible because of the current belief that defects are required for intermixing [5]. The clean substrate is nearly single-domain with a typical terrace width of 40 Å. Symmetric-looking dimers are dominant on the

single-domain terraces, except at step edges [17], where dimers are pinned by the local asymmetric geometry into a tilted ("buckled") configuration.

When as little as ~ 0.02 ML of Ge atoms is deposited onto the surface at 500 K, STM as conventionally performed shows the presence of many zigzag rows of buckled dimers (Fig. 1b). The existence of the buckled-dimer rows is correlated with the Ge adsorption, the number increasing with Ge coverage. All of the dimers on the zigzag rows show a similar brightness in filled-state images. The exact position of the Ge atoms in the surface can not be determined from these images.

We obtain visible contrast between the intermixing sites and the rest of the substrate using empty-state imaging at sample biases of less than +1.5 V. The best results, in terms of good contrast and structure clarity, appear at around + 1.0 V, where the image reflects predominantly the Si(100) surface dangling-bond state [14, 15]. Fig. 1c shows an empty-state image of the same surface shown in Fig. 1b at a bias of + 1.2 V. The image reveals many bright dimer-size units that are spatially correlated to the buckled dimer rows shown in Fig. 1b. The rectangular frame in Fig. 1b shows an example, an area consisting of three buckled rows (marked by lines). The same area in Fig. 1c shows three bright units in an offset arrangement in these rows. Such a spatial correlation exists wherever buckled dimers appear on the surface (e.g., ovals in Fig. 1b and Fig. 1c) that are not induced by steps [17] or c-type vacancy defects [18], suggesting that the bright units in the empty-state image correlate to Ge adsorption. The negligible number of clean-surface defects on the vicinal surface (e.g., Fig. 1a) excludes the possibility that intermixing is mediated or controlled by defects.

The intermixing sites are not limited to the flat terraces. We also observe Ge adsorbed at steps that causes a change in dimer buckling in the step area, appearing as bright units shown by

the solid arrows in Fig. 1c. Although the Si dimers at a rebonded step also appear brighter than those on the Si(100) terraces in empty-state images [19, 20], the sites marked by the arrows are brighter yet.

Figure 2 shows a set of images on a well-oriented Si(100) surface (~ 0.03 ° miscut) with ~ 0.20 ML of Ge deposited at 330 K. In addition to ad-dimer-row islands, most of which are in the form of diluted-dimer rows [15], the filled-state image (Fig. 2a) also shows rows of statically buckled dimers in the substrate(arrow), like those in the vicinal surface(Fig. 1b). The corresponding empty-state image (Fig. 2b) shows bright units associated with the buckled rows, at least one per row. We can show that these bright units are, in fact, buckled dimers (e.g., arrow in Fig. 2c) with their down ends more visible [14] when imaged at the surface-state-sensitive bias [21]. Because they show a similar bias dependence as the bright units shown in the vicinal surface (Fig. 1c), we conclude that the bright buckled dimers in Fig. 2c are signatures of Ge/Si intermixing. This interpretation is also consistent with the observation of dense Si ad-dimer islands on the same surface (Fig. 2d). Fig.2d shows two kinds of dense ad-dimer rows, one without buckling (upper arrow) and the other with zigzag buckling (lower arrow). Si ad-dimers in an isolated dense row island should appear symmetric without buckling [22], while Ge ad-dimers in a dense row island would buckle to form a zigzag pattern [21]. The coexistence of both types of dense ad-dimer rows on the surface supports our conclusion that an adatom substrate-atom exchange has occurred, and that the Si islands on the surface form from the displaced Si atoms. Notice that the intermixing shown in Fig. 2 occurs at substrate temperature as low as 330 K, much lower than had been anticipated.

Because a Si atom takes the place of an adsorbed Ge atom during place exchange, we can calibrate the amount of deposited Ge by simply measuring the ad-dimer islands in an area on a

terrace and therefore also the percentage of intermixed dimers (i.e., the bright buckled dimers). We estimate the latter (for the surface shown in Fig. 2c) at about 10 % (~ 0.003 ML) of the total Ge coverage (i.e., all the ad-dimers counting both Si and Ge) in the area.

Similar to the double steps shown in vicinal Si(100) (Fig. 1c), Ge/Si intermixing sites at single atomic steps appear brighter than other step-edge dimers in low-bias empty-state imaging, but are not visibly different in brightness from terrace intermixing sites. Neither A nor B-type single atomic steps preferentially favor Ge incorporation.

We have shown that we can distinguish Ge/Si intermixing sites on the Si surface. Why are Ge-containing dimers more visible than substrate Si dimers in low-bias empty-state images? X-ray standing wave measurements [23] and theoretical work [24] suggest that the asymmetry (i.e., dimer height displacement and buckling angle) of pure Ge dimers on Si(100) mimics Ge dimers on the intrinsic Ge(100) surface. This conclusion is consistent with the expectation we start with, based on comparison between clean Ge(100) and Si(100) STS results [11, 12], that Ge dimers appear brighter than substrate Si dimers. Although a larger asymmetry for Ge dimers on Si(100) than for Ge dimers on Ge(100) has also been calculated [25], such an asymmetry simply leads to more charge transfer from down-ends of the Ge dimers to the up-ends, making for even greater visibility of Ge in low-bias empty-state imaging. If intermixing results in a Ge-Si mixed dimer, we need to consider whether in this case the dimer is still brighter than a substrate Si dimer. Photoemission experiments suggest that for small Ge coverage, the predominant growth mechanism is the creation of Ge-Si mixed dimers, with Ge atoms occupying the up-ends of the dimers and Si atoms occupying the down-ends[3]. Recent photoelectron diffraction [26] studies follow this route and suggest that the tilt angle for a mixed dimer (~ 31 °) is significantly larger than that of an intrinsically buckled Si dimer (~ 18 ° [15]) on the surface. Therefore, compared

with substrate Si dimers, a mixed dimer has larger charge transfer from the down atom (Si) to the up-atom (Ge). The increase in empty states located at the down atom (Si) should make the mixed dimer also more visible than a substrate Si dimer. The differences between Ge-Ge dimer and Ge-Si dimer are, however, too small to allow us to distinguish between them.

Low-bias empty-state imaging has general advantages over filled-state imaging in distinguishing subtle differences in the electronic properties between adsorbates and Si: (1) the density of states available in the empty-state imaging of Si(100) is much less than the density of states available in the typical filled-state imaging [12], therefore, any modest tunneling intensity modulation at particular sites (e.g., Ge intermixing sites) on the surface is easier to differentiate from the background intensity in a low-bias empty-state image than in a typical filled-state image; and (2) these empty-state images have greater surface-state sensitivity [14, 15]. It would be valuable to perform STS on Ge-containing dimers at intermixing sites of the Si(100) surface, and perhaps use pattern classification techniques [27] to distinguish the details between the two types of Ge-containing dimers. Nevertheless, to be able to identify the atomic intermixing sites on the surface is certainly the first step.

In summary, we have confirmed Si and Ge intermixing for Ge deposited on Si(100), and have identified the atomic intermixing sites with scanning tunneling microscopy using high-resolution low-bias empty-state imaging. The atomic intermixing occurs randomly on the surface; steps and point defects are not preferential sites for the place exchange. Intermixing occurs at temperatures as low as 330 K, suggesting that intermixing is more likely to happen in Ge/Si growth than previously expected. Such information will allow us to establish quantitative values of interaction energies and kinetic barriers for interface formation, and should also be extremely useful for developing processes for controlled growth of SiGe heterojunctions.

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the upper terrace may be buckled because of the gradual relaxation of the strain at kinks, and the corresponding two rebonded atoms from the lower terrace are usually at different heights (see Fig. 1a). These two rebonded atoms may induce static buckling within their dimer row on the terrace, which can easily be recognized in a filled-state image (e.g., Fig. 1a).

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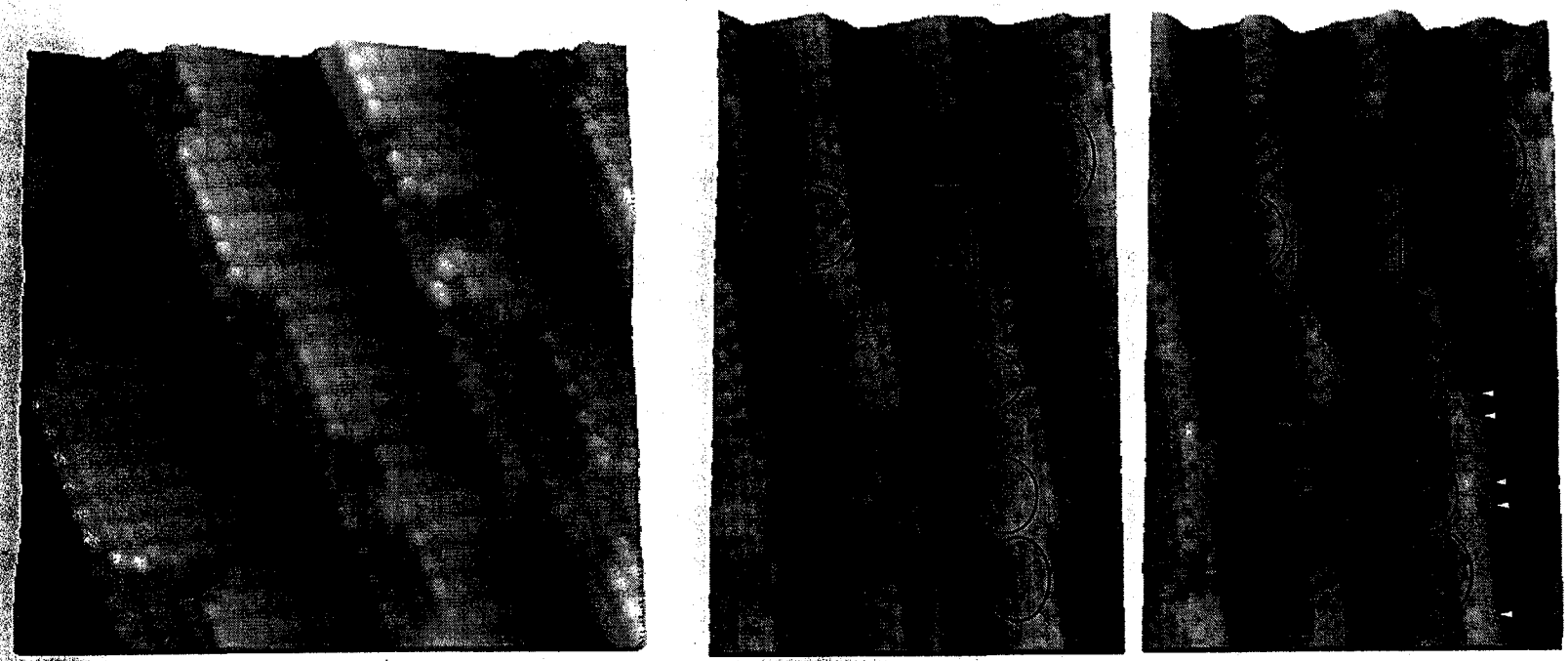
Figure Captions

Fig.1 STM images of Si(100) miscut 4 degrees toward the [110] direction. (a) Filled-state image of clean Si(100). (b) Filled-state image after 0.02 ML Ge deposition at 500 K, showing zigzag buckled dimer rows (frames and ovals) on the terraces. (c) Empty-state image of (b), showing bright units correlated to the buckled dimer rows (frames and ovals). The big arrow points to a c-type defect, which is always bright in empty-state imaging. The solid arrows point to the Ge adsorption sites at step edges. The short lines point to zig-zag dimer rows and the corresponding Ge-Ge or Ge-Si dimers (bright units). Sample biases: (a-b) - 2 V; (c) + 1.2 V.

Fig. 2 Filled-state (a and d) and empty-state (b and c) images of ~ 0.20 ML Ge deposited at 330 K on a well-oriented Si(100) surface (0.03 degree miscut). (b) Ovals highlight the intermixing sites. (c) The buckled Ge-containing dimers at intermixing sites appear brighter and larger than the rest of substrate dimers (e.g., the dimer in the right oval is marked by an arrow). (d) Straight Si (upper big arrow) and zigzag Ge (lower big arrow) dense-dimer-row islands appear on the same surface. Most of islands are diluted-dimer rows. Sample biases: (a) -1.8 V; (b) + 1.3 V; (c) +1 V; (d) - 2.0 V.



a b c

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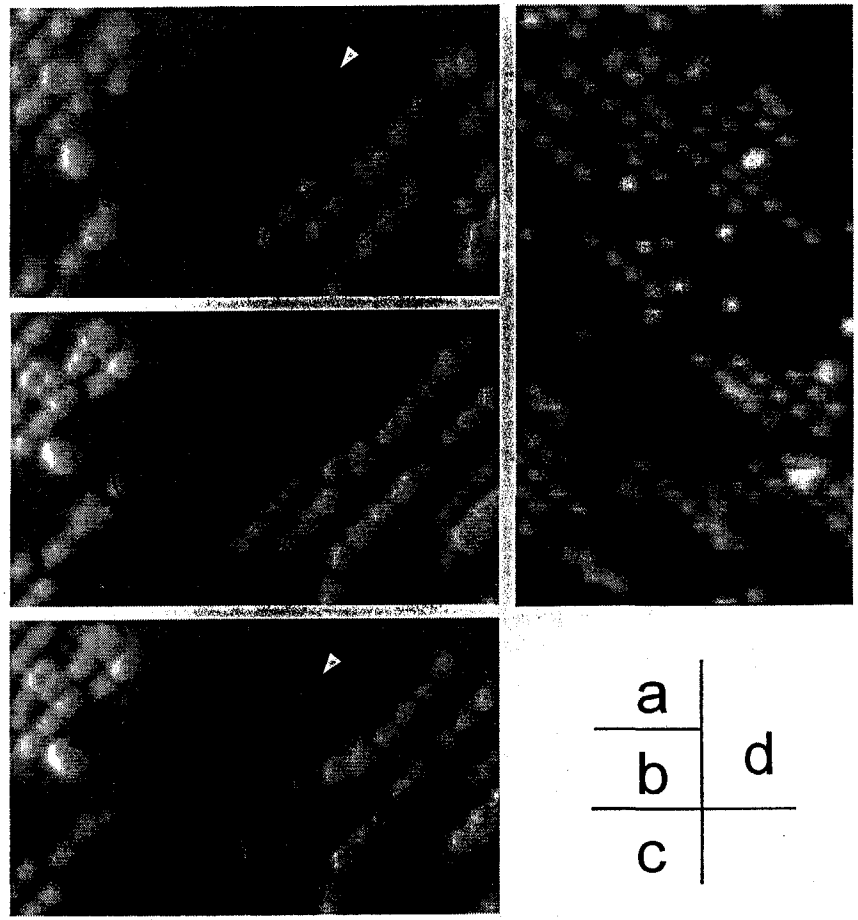

Fig. 2 **Qin *et al.***