Atomic geometry of mixed Ge-Si dimers in the initial-stage growth of Ge on Si(001)2×1

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We have investigated quantitatively the geometry of mixed Ge-Si dimers on a single domain Si(001)2×1 surface by azimuthal scanning core-level photoelectron diffraction. By analyzing Ge 3*d* diffraction patterns from Ge/Si(001) at 0.1 ML coverage using a concentric-shell multiple-scattering algorithm for photon energies of $h\nu = 90$ and 136 eV, the bond length and tilt angle of the mixed Ge-Si dimer are determined to be 2.43 ± 0.10 Å and $31° \pm 2°$, respectively. It is also found that the mixed Ge-Si dimers are substitutional ones rather than ad-dimers. Another significant aspect of this work is that it demonstrates that photoelectron diffraction is able to probe the local environment of an adatom at submonolayer coverage even in the absence of long-range order. [S0163-1829(97)51512-8]

The 2×1 surfaces of Si(001) and Ge(001) have been studied extensively due to their technological importance as well as to a desire to understand in detail the nature of the interesting dimer reconstructions these surfaces present.[1,2] In addition, the heteroepitaxial growth of Ge on a Si(001) surface has been the focus in recent years for the understanding of dimer structure and for gaining insight into interface formation and structure.[3–11] The study of Ge heteroepitaxy on Si(001) serves not only as a model system for the investigation of mechanisms controlling this interface formation, but also as a key to further understanding the Si(001) and Ge(001) surfaces themselves.

One of the most powerful methods of studying these complex systems has been the examination of the surface core-level shifts (SCLS) occurring in high-resolution photoemission measurements. Recent results from high-resolution Ge 3*d* and Si 2*p* SCLS by Patthey *et al.*[9] have shown that there exist mixed asymmetric Ge-Si dimers during the initial stages of growth of Ge on the surface. From their SCLS study, a clear picture emerges for the initial-stage growth of Ge. At very low coverages (<0.2 ML), the predominant growth mechanism is the creation of mixed Ge-Si dimers on the surface with Ge atoms occupying almost exclusively the up-atom position. Thus, the initial-stage growth of Ge on Si(001) surface is not a simple growth of buckled Ge dimers over Si(001) surface as the scanning tunneling microscope (STM) images[8] suggest.

Core-level photoelectron diffraction (PD) has been recognized as a powerful tool for studying surface structure, where the atom specificity allows the discrimination between signals not only from different chemical species, but also from the same species in different chemical environments such as in the form of SCLS.[1,9,12] In PD with such a SCLS resolution, the electron kinetic energy (E_k) is rather low (around 100 eV), where the analysis of PD data should fully take account of multiple scattering (MS), especially that of near-neighbor atoms, as this is known to be very important.

In this paper, we present the results of a full MS analysis of the Ge 3*d* photoelectron-diffraction data from a Ge/Si(001) surface at a 0.1 ML Ge coverage. For such a coverage, the Ge 3*d* spectrum consists almost entirely of a single component, thus implying a single adsorption site.[9] The analysis indicates that, at this coverage, all or most of the Ge atoms are incorporated as asymmetric mixed Ge-Si dimers with Ge atoms occupying the ''up'' site in agreement with Ref. 9. We find that the bond length and tilt angle of the dimers are 2.43 Å and 31°, respectively. The tilt angle found in this study is thus larger than the corresponding angles of 0°–20° reported for Ge dimers at 1 ML coverage on a Si(001) surface.[3–6] We also find that the mixed Ge-Si dimers are substitutional ones rather than ad-dimers. The latter finding is made possible by the use of a single-domain (SD) Si(001)2×1 surface as the substrate.

The PD measurements were carried out at the MAX I storage ring of the MAX-Laboratory Synchrotron Radiation Facility in Lund, Sweden on beam line 41. The end station is equipped with a sample manipulator for polar and azimuthal rotations. The Si(001) wafer used was highly oriented ($\sim \pm 3'$) and preoxidized. The surface was cleaned *in situ* using standard procedures. A SD Si(001)2×1 surface was

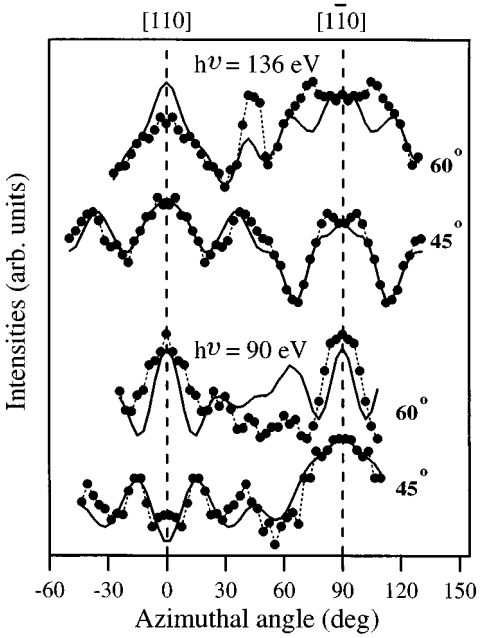

FIG. 1. Azimuthal scans of Ge $3d$ PD experiment (dotted lines) at polar angles of 60° and 45° for $h\nu = 136$ and 90 eV, and MS simulations (solid lines) for the optimized cluster model of Fig. 2.

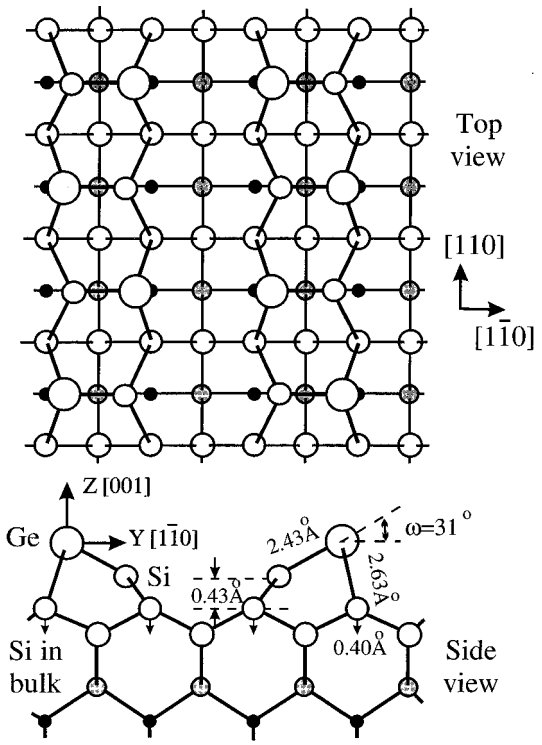

FIG. 2. Top and side views of a model cluster for mixed Ge-Si dimers on Si(001)2×1 surface.

then prepared by Si evaporation and annealing. Ge deposition was accomplished using a well out-gassed Knudsen cell with the Si surface held at 350 °C and a deposition rate of 0.3 ± 0.03 ML/min. Coverage determinations were made using both a quartz-crystal thickness monitor and a quantitative evaluation of the Ge $3d$ core-level intensities. For all data presented here, the photon energies were chosen to be $h\nu = 90$ and 136 eV with a light incident angle of 40° from the sample normal. The PD azimuthal scans were performed by rotating the sample around its normal, and recording the Ge $3d$ intensity every 3° over a range of 135°–180°. The polar detection directions θ were 45° and 60° with respect to the surface normal, in the incident plane, and on the opposite side of the normal from the incoming light. The angular acceptance angle of the analyzer was ±2°. A Ge coverage of 0.1 ML was used for all measurements. The Ge $3d$ spectrum consisted of a single component in accordance with the previous result,[9] thus implying a single adsorption site of Ge.

The full MS scheme used to analyze the PD data is an accurate and efficient concentric-shell algorithm developed by Saldin, Harp, and Chen.[13] In this scheme, we exploit the short-inelastic-scattering length of an electron in a solid, by restricting MS processes to within a finite cluster of atoms centered on an emitter. The efficiency of the scheme follows from the subdivision of the cluster into a series of concentric shells and the separate summation of intrashell and intershell MS. This grouping of atoms into concentric shells speeds the computation and reduces the requirements of computer memory. By means of this scheme, we may carry out PD calculations for E_k's in the range of 50–1000 eV for various experimental geometries.[14,15]

The measured azimuthal PD patterns of Ge $3d$ level from the 0.1 ML Ge/Si(001) sample are shown in Fig. 1 as dotted lines for $h\nu = 136$ and 90 eV with $\theta = 60°$ and 45°. The ordinate is normalized to a fixed intensity variation; the actual variation range is around 15% of the maximum intensities. The zero-azimuth direction [110] corresponds to the direction parallel to the Si-dimer row direction of the SD Si(001)2×1 substrate.

The starting point for modeling the structure of the mixed Ge-Si dimer is shown in Fig. 2. In this model, the Ge-Si dimer cluster sits on top of the Si(001) surface, where Ge atoms occupy the ''up'' sites and Si atom the ''down'' sites, and the adjacent Ge-Si dimer rows are antiphase. We itemize below the reasons for choosing this model. First, the results of Ref. 9 show that the binding energy of the single Ge $3d$ component observed at low coverage suggests such a mixed Ge-Si dimer model. Second, STM images have revealed that two adjacent dimer rows adopt an antiphase configuration.[8] Third, the short inelastic-scattering length of an electron plays an important role in simplifying the cluster models. Since the inelastic length in the present case is on the order of ~6 Å, elastically scattered electrons, originating from a Ge atom, may ''see'' only approximately one adjacent dimer row on either side of its own along the [110] direction (see Fig. 2), and just the two nearest-neighbor dimers on either side of its own in the [110] direction, before losing coherence. Thus, a cluster consisting of two rows with four dimers on each row (termed a $[2\times4]$ cluster), is an appropriate one for our present study.

We carried out PD calculations for the $[2\times4]$ cluster model of Fig. 2 and compared the results with the experimental data using a reliability (R) factor method.[14] During the optimization procedure, we varied the geometry parameters for Ge and Si atoms of the dimers as well as for the Si atoms under the mixed dimers. The MS simulations with the optimized cluster of Fig. 2 are plotted as solid lines in Fig. 1.

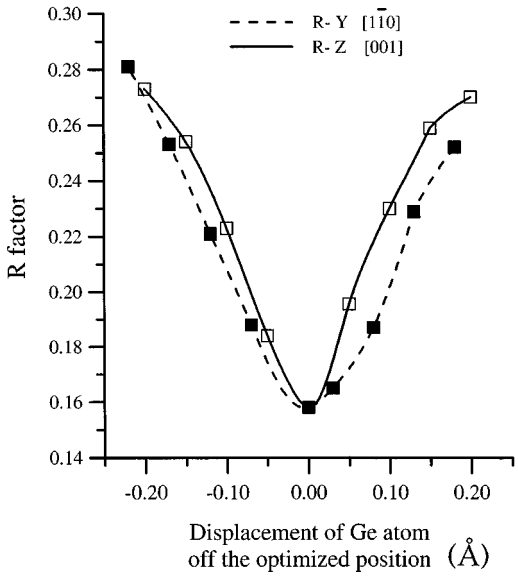

FIG. 3. R factors vs vertical displacement (solid line) and horizontal displacement (dashed line) of Ge atoms in the mixed Ge-Si dimer cluster shown in Fig. 2. Note that two data points overlap at the minimum.

It is seen that the MS calculations match the PD data well, especially for the $\theta = 45°$ scans for both energies. Figure 3 plots R-factor values versus the horizontal and vertical displacements of the Ge atoms from the optimized position, while other structure parameters are kept fixed. From the sharp rise in the R factor from its minimum (optimized) point, one may conclude that the PD is very sensitive to the local environment around the emitters. Also from the R-factor plots, we may determine that the uncertainties of horizontal and vertical displacements for Ge atoms are both conservatively within ~ 0.1 Å.

The optimized cluster, as determined by the R-factor method, yielded a bond length and tilt angle of the mixed Ge-Si dimers of 2.43 ± 0.1 Å and $31° \pm 2°$, respectively. In addition, the bond lengths between Ge and the two nearest-neighbor Si atoms in the substrate were found to be 2.63 ± 0.1 Å as shown in Fig. 2. It is found in our MS analysis that there is almost no lateral relaxation (within 0.02 Å) along both [110] and [$\bar{1}$10] directions for Si atoms (defined as the first-layer Si atoms) just under the mixed Ge-Si dimers, but their vertical shift is 0.40 Å (see Fig. 2) with respect to their bulk position. The Si atoms in the second layer and below are found to be close to their bulk positions. The lateral shift of Ge atoms along [$\bar{1}$10] with respect to the Si atoms just under them is 0.02 Å in a direction to form a shorter mixed dimer bond length. The vertical height between Si atoms formed in the mixed Ge-Si dimers and the first-layer Si atoms is 0.43 Å. The major to minor 2×1 domain ratio is also an adjustable parameter in the simulations and is found to be $\sim 5{:}1$, which is close to 4:1 domain ratio estimated (roughly) by low-energy electron diffraction (LEED) experiment for the sample. The inner potential is also an adjustable parameter and optimized by an R-factor analysis and found to be 1 eV.

Another important finding in this simulation is that the [$\bar{1}$10] axis in Figs. 1 and 2 is the direction along the Si-dimer rows of the substrate major domain. This means that the direction of mixed Ge-Si dimer row is the same as that of the substrate Si-dimer rows, indicating that the Ge-Si mixed dimers are not ''ad-dimers'' but ''substitutional dimers.'' Then, the long rows of islands seen by STM (Ref. 8) are likely to be Si-dimers (and Ge-Si dimers in some contents) formed from Si atoms expelled from the substrate by substitution with Ge atoms.

A question may be raised of the validity of using a single $[2 \times 4]$ cluster to represent statistically all the different types of mixed dimer distributed at the level of substrate dimers. In fact, similar cluster models, for $[M \times N]$ clusters (M rows with N dimers in each row), where M is chosen from 1 to 4 and N from 2 to 6, have also been considered in our analysis. The MS results from these clusters produce similar PD patterns at all directions except those corresponding to grazing electron emergence. This fact indicates that the dominant factor in the diffraction patterns at high-electron take-off angles is the local environment around the emitters. In other words, when compared to the local structure, i.e., the bond lengths and angles of the nearest-neighbor atoms, the PD pattern is less sensitive to whether there is a neighboring row of mixed dimers or not. Thus for simplicity, we may pick a two-dimer-row cluster. However, such simplifications may somewhat limit our efforts to explore all aspects of the surface geometry. An alternative way of overcoming this might be to assume models with all kinds of dimer formations and to weight them differently, but this would introduce more parameters in the simulation and would not increase the accuracy of the structure determination although a better fit might be reached.

Other possible models that have been considered in the MS analysis are (1) pure Ge dimers on the surface and (2) the switching of the Ge and Si positions in the mixed dimer model, i.e., Ge in a ''down'' site and Si in the ''up'' position. All these models result in significantly larger R factors ($R > 0.3$). Therefore, we may rule out the possibility of the appearance of these structures on the surface, at least in significant populations.

The present study reports on the geometry of the Ge/Si(001) heteroepitaxy at its low coverage of 0.1 ML, compared with several reports on the geometry of Ge/Si(001) heteroepitaxy at full monolayer coverage.[3–6] It is worthwhile to comment on the results for 1 ML. The results of theoretical studies[5,6] are consistent with each other, the bond lengths (Ge-Ge) being both 2.39 Å and buckling angles being 17° and 16.3°. The results of experiments[3,4] are inconsistent, the bond length (Ge-Ge) being 2.51 and 2.60 Å and buckling angles being 0° and 12°, respectively. However, in the above four studies, no possibility of Ge-Si mixed dimers is considered, which causes reconsideration of the studies. The presence of Ge-Si mixed dimers for a Ge(1 ML)/Si(001) heteroepitaxy has recently been proven.[7,9] Furthermore, substitutional intermixing of Ge with substrate Si up to the fourth layer is shown to be present,[7,16] which would further affect the interpretation of experiments.[3,4] Theoretical study for the mixed Ge-Si dimers is called for in comparison with the present result.

A displacive adsorption of Ge on Si(001) at submonolayer coverage has been suggested by Tromp[10] in view of the re-

sults of several studies such as low-energy electron microscopy and surface stress-induced optical deflection. The present result confirms this displacive adsorption and further shows that Ge atoms displace the ''up'' site Si atoms with those geometrical parameters already determined. The fact that displacive adsorption may have wide significance in heteroepitaxy on semiconductor surfaces and the kinetics of displacive adsorption must be studied although this has not been considered to be important so far.[11]

In summary, we have reported a quantitative investigation by photoelectron diffraction of the structure of mixed Ge-Si dimers on a Si(001)2×1 surface at 0.1 ML Ge coverage. Using a multiple scattering analysis of the PD data taken at $h\nu=90$ and 136 eV, the bond length and tilt angle of the mixed dimer were determined to be 2.43 ± 0.1 Å and $31°\pm2°$, respectively. These results are consistent with and extend a prior photoemission study which first showed the existence of such mixed Ge-Si dimers at low Ge coverage.[9] The present result also shows that the Ge-Si dimers are formed by substitution of the ''up'' site of Si of each substrate Si-dimer with Ge, suggesting that the narrow islands seen by STM (Ref. 8) are essentially Si-dimer rows. This fact of substitutional adsorption must be taken into account in understanding heteroepitaxy on semiconductor surfaces. Another significant aspect of this work is that it demonstrates that, unlike conventional LEED or surface x-ray diffraction, which may be used only for ordered surfaces, core-level PD is able to probe the local environment of an adatom at submonolayer coverage, where no long-range order of the adatoms may be present.

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