Transmission-ion-channeling investigation of Ge adsorbed on the Si(100) surface at submonolayer coverage

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Transmission ion channeling has been used to investigate the bonding geometry of Ge on the Si(100)-2×1 surface at a coverage of 0.6 ML. It is shown that this surface is terminated by asymmetric Ge-Ge dimers with a bond length of 2.6 Å and a tilt of 12°, in agreement with previous results. The structure of the surface is shown to vary with Ge coverage, which is possibly attributable to the strain induced during growth by the 4% lattice mismatch between Ge and Si.

INTRODUCTION

There has been considerable effort expended in order to elucidate the structure of the Ge adsorbed Si(100) surface and to determine how the growth of the Ge layer proceeds. The interest is due not only to the technological importance of Ge heteroepitaxial layers on Si, but also to the fact that, because of the chemical similarity of the two species and a 4% lattice mismatch, this system has become a model for the study of strained-layer growth. For Ge coverage (Θ_{Ge}) approaching 1 monolayer (ML) the surface structure is similar in many respects to that of the heavily studied clean Si(100)-2×1 surface, which is known to reconstruct by a pairing of the first layer atoms into dimers. However, the Ge-Si lattice mismatch does lead to significant differences. Although recent work[1-7] has helped to clarify some of the important issues on this surface, comprehensive information concerning the geometry and dynamics of the Ge adatoms is needed if we are to approach a complete understanding of this system.

Several groups have reported on submonolayer Ge growth on Si(100). The surface has been shown to have elongated islands of asymmetric Ge-Ge dimers as the dominant feature, with symmetric dimers sometimes observed[1,2] at low coverage. Low-energy electron diffraction[3,4] (LEED), scanning tunneling microscopy[3-5] (STM) and other techniques[4,6] have shown that the surface is characterized by strained growth leading to complex structures. A recent x-ray standing-wave (XSW) study[7] by Fontes, Patel, and Comin has addressed the bonding geometry of the Ge adatoms on this surface. They concluded that the Ge adatoms form asymmetric Ge-Ge dimers, and by comparing their data to a two-parameter model for the surface structure, found a dimer bond length of 2.60 Å and a dimer tilt of 12.1°. Their study was for deposition at 500 °C and they reported on coverages below 1 ML.

We have recently applied transmission channeling to this surface in order to determine the bonding site(s) of the adsorbed Ge for deposition at 300 °C and for a coverage of approximately 0.6 ML. This coverage was chosen to maximize the scattering signal from a well-formed Ge overlayer while minimizing possible second layer growth effects. In order to investigate the role that Ge coverage (strain) plays in determining the overlayer structure, we have taken data for a range of coverages, from 0.26 to 0.90 ML. We find that for 0.6 ML, our results for the dimer bond length and dimer tilt are in agreement with the work of Fontes, Patel, and Comin. We also observe that the overlayer strain appears to play an important role in the submonolayer growth process.

EXPERIMENT

Transmission ion channeling has been used in a variety of ways for a number of interface and surface studies on metals and semiconductors.[8] It has been used to determine the *site* of adsorbed atoms on a surface for the case of Ni on chemically cleaned Si,[9] for H and D on clean metal surfaces,[10] and for Sb on the clean Si(100)-2×1 surface.[11] The principles involved in transmission channeling used for surface adsorbate site determination are precisely those involved in the use of channeling for impurity location in bulk crystals, except that the crystal is truncated and the impurity of interest is adsorbed on the clean beam-exit surface. In a typical experiment, scattering energy spectra are obtained at small tilt angles of the ion beam across a low-index crystallographic direction of the substrate. Extracted from such spectra is the scattering yield from the overlayer as a function of tilt angle (an *angular scan;* see Fig. 1). Much can be inferred, qualitatively, about the position(s) of the adatoms directly from the angular scans. Further, a comparison of experimental scans with computer-calculated scans can yield a *quantitative* determination of the impurity site. The code we used to generate the calculated scans[12] is based on the continuum approximation and uses a 25-string Doyle Turner potential, with dechanneling due to multiple scattering with electrons and host nuclei included. A detailed account of our use of transmission ion channeling for semiconductor surface studies has been published elsewhere.[13]

Since the beam-exit surface is studied, transmission ion channeling necessitates thin (~5000 Å), single crystal substrates that can be manipulated and cleaned in ultrahigh vacuum (UHV). We produced thin Si windows within a thick Si frame by a well-known dopant-selective etch.[14] The windows were cleaned *ex situ* by the Shiraki technique and loaded into an UHV (base pressure $<1\times10^{-10}$ Torr) sample preparation chamber having LEED and Auger electron spectroscopy available for sample characterization. The *in situ* oxide desorption was accomplished by heating the sample to 825 °C by irradiation from a thin Ta strip mounted behind the Si window on the sample manipulator and shielded from the sample by a piece of sapphire (to prevent Ta contamination). The pressure during this ~15-min procedure rarely exceeded 1.5×10^{-9} Torr and quickly recovered after the heating. This procedure was typically repeated a few times until the quality of the surface (as determined by LEED) was optimized. This treatment gives rise to a two-domain 2×1 LEED pattern with low background and sharp spots.

After cleaning, Ge was deposited on the samples held at 300 °C from a Knudsen cell with a graphite crucible at a rate of 0.1–0.15 ML/min. The pressure during evaporation remained in the 10^{-10} Torr range, and the samples were allowed to cool slowly (1°/sec) after the evaporation. The temperature of the samples was estimated (±50 °C) from the current passing through the Ta strip by comparison with a calibration curve. The calibration was performed with a thermocouple in contact with a thin window. The LEED patterns after Ge deposition remained largely unchanged except that the background increased slightly on some samples. The samples were then transferred under vacuum to a UHV (base pressure $<10^{-10}$) scattering chamber fitted with three bakeable ion-implanted solid-state detectors. The scattering chamber is connected via a differentially pumped beam line to a 3.5-MV Van de Graaff accelerator. The samples were analyzed with either a 2.0- or 2.5-MeV beam of He^+ ions with an angular divergence of <0.08°. Ge coverages were determined with Rutherford backscattering spectrometry and are accurate to within 10%.

RESULTS AND DISCUSSION

To determine the Ge adatom site(s), calculated Ge scans were arrived at using a χ^2 minimization procedure whereby both adatom positions for the dimer were varied independently in two directions, parallel (in the direction of dimerization) and perpendicular to the surface, in order to give the best agreement between the experimental and calculated scans. Thus positions whereby the dimer atoms are translated perpendicular to the direction of dimerization and the surface normal were not considered. The use of transmission channeling (and many other techniques) for adatom site determination is ultimately limited by a lack of understanding of the vibrational properties of the surface impurity of interest. Some calculations on the vibrations of surface atoms have been performed for the reconstructed Si(100) surface,[15,16] however, little work has been devoted to the study of the vibrational tendencies of Ge adsorbed on Si(100). For this study, we have assumed that both Ge atoms participating in the dimer bond exhibit identical and isotropic vibrations and have taken the magnitude of the two-dimensional root-mean-square thermal vibrational amplitude for the Ge to be $\rho=0.14$ Å. This value is obtained by taking the average of the three Cartesian components of the (weakly anisotropic) amplitude calculated[16] for Si dimers on Si(100) by Alerhand, Joannopoulos, and Mele. It is true that transmission channeling can be used to determine the vibrational amplitudes of surface atoms. However, in cases where the atomic configuration for the calculated best fit to the data varies with the assumed vibrational amplitude, this task can prove difficult or impossible.

Figure 1 shows angular scans across three low-index axial channeling directions for a Si(100) thin window with a Ge coverage of 0.6 ML. Each filled circle represents

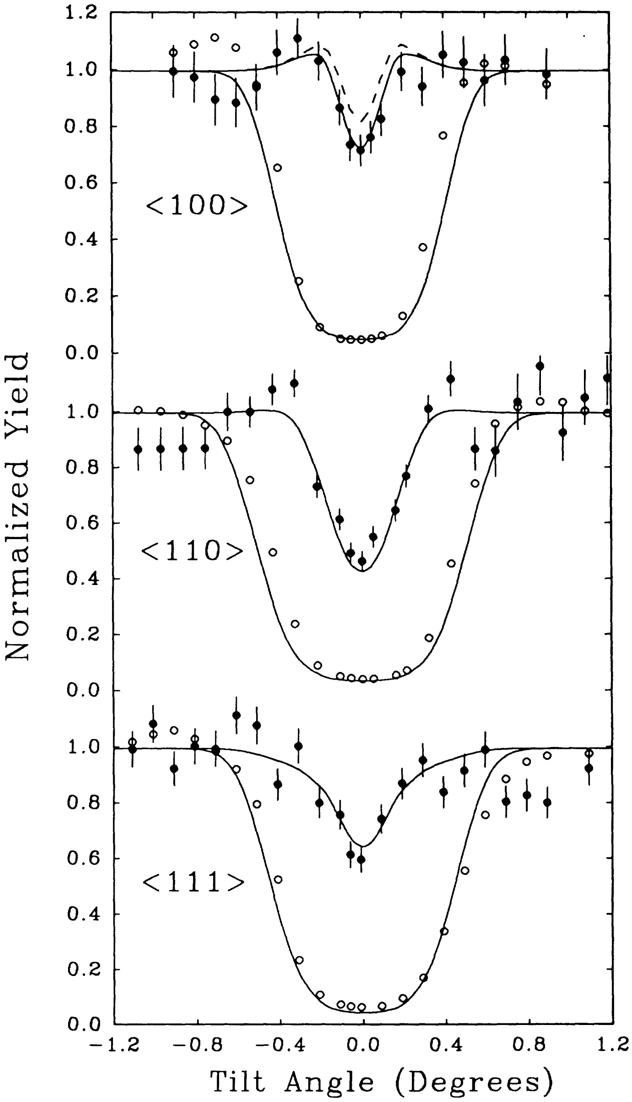

FIG. 1. Angular scans across three low-index axial directions for samples with 0.6 ML of Ge deposited at 300 °C. Filled circles represent the integrated Ge yield and open circles represent the integrated Si yield. The solid lines are calculated scans for a modified bridge site (discussed in text) and a Si-substitutional site. Also shown is the calculated scan for a symmetric dimer (dashed line) with the bulk Ge-Ge bond length. The error bars represent uncertainties due to counting statistics.

the integrated Ge yield (ordinate) from a spectrum taken at a given tilt angle (abscissa) about the axial channel. Likewise, open circles represent scattering from the Si substrate (i.e., a substitutional position) integrated over the thickness of the thin window (~5000 Å). Also shown are calculated angular scans for an asymmetric dimerlike position (upper solid line, discussed below) and for a substitution position (lower solid line). The dashed line (on the ⟨100⟩ scan) is a calculated scan for a symmetric Ge dimer with a bulk Ge-Ge bond length, which is clearly not consistent with the data. The upper solid lines in Fig. 1 are the calculated angular scans which give the best fit to the Ge data. The asymmetric dimer that this represents has a Ge-Ge dimer bond length of 2.6±0.1 Å and a dimer tilt with respect to the surface of 12°±4°. If z is defined as the direction normal to the surface, we find the average z position of the Ge to be 0.25±0.20 Å above the normal bulk-terminated (not reconstructed) surface Si-lattice positions. The vertical dimer atom separation (Δz) is 0.5±0.2 Å and the center of the dimer bond is laterally displaced by 0.07±0.03 Å. The agreement in bond length and tilt angle with the previously mentioned XSW work is surprisingly good and the magnitude of the tilt is consistent with calculated values for reconstructed Si(100) and Ge(100) surfaces.[17,18] The dimer bond length is not in agreement with calculated[17-19] values, which, for Ge (Si) homoepitaxy, consistently predict a Ge (Si) dimer length that is smaller than or approximates the bulk Ge-Ge (Si-Si) bond length of 2.45 Å (2.35 Å). One difference between our results and the findings of Fontes, Patel, and Comin is the slight expansion of the surface (Ge position in z) into the vacuum observed in this study. The calculated Si-host scans in Fig. 1 represent a substitutional site with a vibrational amplitude of 0.14 Å. This is larger than the bulk vibrational amplitude of 0.11 Å calculated with the Debye model for 25 °C. Issues involved in fitting the Si-host data are discussed in Ref. 13.

The uncertainties associated with the site determination were estimated by examining the region bounded by values of the fitting parameters which encompassed all fits below a reasonable χ value. The position with the lowest χ (described above) was near the center of this region. The reduced sensitivity of transmission ion channeling to displacements in z, observed in the off-normal channeling directions (⟨110⟩ and ⟨111⟩), is largely responsible for the size of the uncertainties. Angular scans in these directions probe an average of all projected adatom positions dictated by the two 90° rotated dimer domains and the crystal symmetry, making z displacements difficult to characterize (especially for tilted dimers) with great precision.

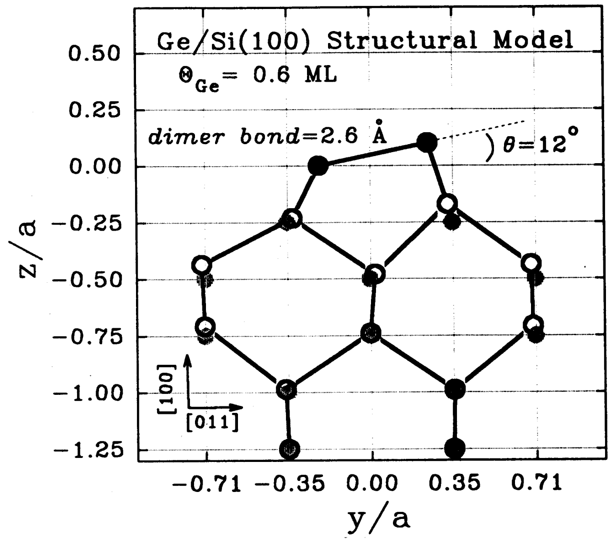

FIG. 2. Structure of Ge overlayer. Filled circles represent Ge adatoms and shaded circles represent bulk-terminated Si positions. The open circles represent Si atoms displaced from bulk positions due to the surface reconstruction. The Si positions were estimated using the Keating model (see discussion in text) and are qualitatively only (a=5.430 Å).

The above structure is summarized in Fig. 2. Since transmission channeling determines the adatom positions relative to the bulk lattice, some information about subsurface lattice distortions can be inferred. Using our experimentally determined Ge positions (represented by filled circles), the positions of the subsurface Si atoms shown in Fig. 2 (open circles) have been estimated with the well-known Keating model.[20] In this model, the elastic energy (E_K) is given by a sum of bond stretching and bond bending contributions,

$$E_K = \sum_{i,j} \alpha_{ij}(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij} - d_{ij}^2)^2 + \beta \sum_{i,j,k} (\mathbf{r}_{ij}\cdot\mathbf{r}_{ik} + \tfrac{1}{3} d_{ij} d_{ik})^2 , \qquad (1)$$

where the first sum is over all bonds and the second over all bond pairs. Here $\mathbf{r}_{ij}$ is the vector from atom i to atom j and d_{ij} is the nominal bond length (d_{ij} can represent a Si-Si bond or a Si-Ge bond). This model assumes tetrahedral bonding and is therefore not expected to exactly reproduce all atomic positions. However, since the bond stretching term dominates, the model can give a qualitative idea of the magnitude and direction of the subsurface atomic displacements. Using five atomic Si layers, doubly periodic boundary conditions, and with the Ge atoms fixed at experimentally determined positions, subsurface Si atomic positions were found by minimizing Eq. (1). We have used for our parameters[21,22] α_{ij}=0.201 (0.180 for the Si-Ge interface) and β=0.0183 and have demanded that the lowest Si layer be bulklike. A 2×1 overlayer symmetry was assumed.

The Ge dimer geometry was also investigated allowing for asymmetric vibrational amplitudes. If the vibrational amplitude is allowed to vary independently for each axial direction, we find large and anisotropic vibrations give the best fit. In this case, ρ_{100}=0.19 Å, ρ_{110}=0.45 Å, and ρ_{111}=0.29 Å are the two-dimensional vibrational amplitudes for the respective directions. For the dimer bond length, we get 2.35 Å, nearer the bond length for bulk Ge. The quality of the fits is improved since three more parameters are introduced; however, the dimer tilt becomes very large (31°), leading to unphysical subsurface distortions. Because of this and the large vibrational amplitudes (especially in the ⟨110⟩ direction), we do not consider this geometry as feasible.

Shown in Fig. 3 is the minimum yield (ratio of the in-

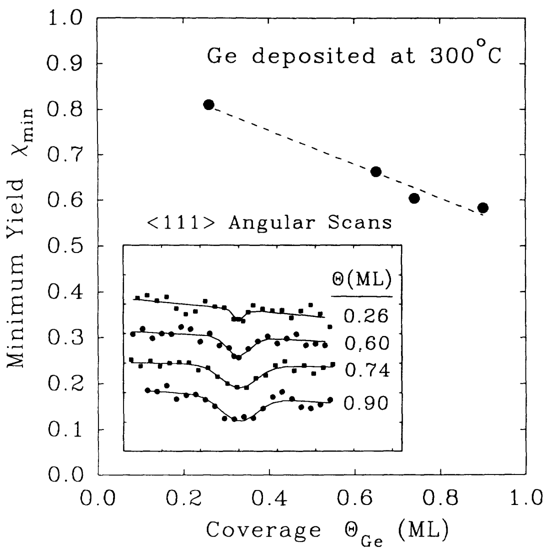

FIG. 3. Dependence of overlayer structure on coverage. Shown is the minimum yield (solid circles) as a function of Ge coverage in the ⟨111⟩ direction. The dashed line is a linear regression. In the inset are the raw ⟨111⟩ angular scans with solid lines (fits to a line minus a Gaussian) to guide the eye.

tegrated yield in the channeling direction to the yield in a random direction) for ⟨111⟩ angular scans as a function of Θ_{Ge}. In the inset the raw data (angular scans) are shown, which clearly display a systematic broadening and deepening with coverage. These scans are very sensitive to changes in the average Ge adatom position with respect to the substrate. From this trend, it can be concluded that our data are not consistent with identical and perfectly formed dimer rows throughout this range of coverage, which would show absolutely no dependence on Θ_{Ge}. Instead, our results indicate that submonolayer Ge growth is complicated by a dimer geometry that changes with coverage or a coverage-dependent mixture of adatom sites. For example, the data are consistent with a reduction in the dimer tilt with increasing coverage, the presence of a coverage-dependent fraction of a Ge site other than a dimer site (perhaps at defects) or a mixture of dimer geometries which varies with coverage. This is supported by several recent results. For instance, as opposed to a termination consisting of a uniform Ge-dimer overlayer, it has been shown that the surface is characterized by a complex $2\times N$ structure,[2–5,22,23] where N varies with Ge coverage. In this picture, at low coverage, the surface is riddled with missing dimers, which, with increasing coverage, order to form missing dimer rows perpendicular to the dimer strings, eventually giving $N\approx 11$ at 1 ML (2×11 surface structure). Further work has suggested that the submonolayer growth proceeds through a displacive adsorption process,[4] whereby Ge dimers replace Si dimers on the terraces, freeing Si dimers to participate in growth at step edges. Additionally, it has been shown that Ge dimers grow on Ge-terminated Si (second layer growth) long before the initial Ge ML is complete [by 0.8 ML by STM (Ref. 2)], and a core-level photoemission study[6] has shown evidence for a small component of second layer growth at coverages as low as 0.3 ML. In order to minimize the influence of such mechanisms, for our determination of the Ge dimer geometry, we have focused on a coverage near 0.6 ML. Here we expect that the vast majority of the dimers will be surrounded by other Ge-Ge dimers and reside on Si. At lower coverage it is possible that the Ge dimers have been dissociatively adsorbed and reside largely in the top, dimerized Si layer or that the fraction of nonideal dimer sites is appreciable. At higher coverage there exists the possibility of significant second layer growth.

CONCLUSIONS

Transmission ion channeling has been used to determine the bonding geometry of Ge-Ge dimers on the Si(100)-2×1 surface. The Ge-Ge bond length (2.60 Å) and dimer tilt (12°) are found to be in agreement with a previous XSW study.[7] However, the bond length is longer than theoretical predictions. As in the XSW study, we assume an isotropic vibrational amplitude. Structural studies on heteroepitaxial systems often proceed under the assumption that all adatoms occupy locally identical positions, with no dependence on coverage. We have shown that this situation is not realized for this system. It is possible that our site determination has been influenced slightly by mechanisms such as second layer growth, a mixture of dimer geometries, or our treatment of the vibrational amplitude. We have, however, taken care to minimize such effects. Further work on this system should include a thorough characterization of the Ge-Ge bond length with coverage by a very sensitive technique, such as surface-extended x-ray adsorption fine structure. Additionally, studies such as this would be facilitated by a precise measurement of the adatom vibrational amplitude.

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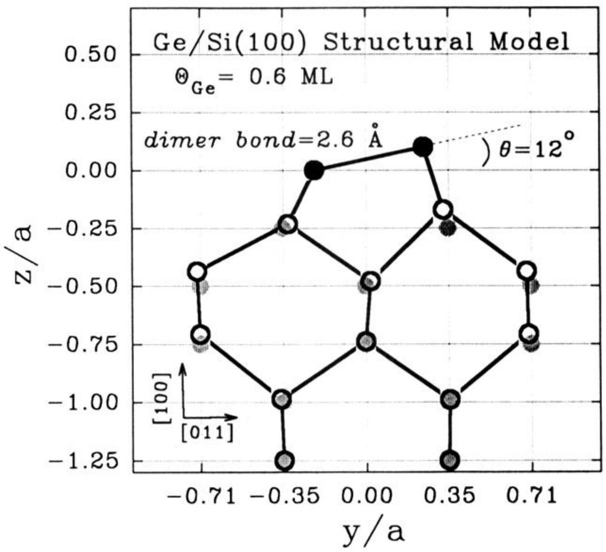

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