Mixed Ge-Si Dimer Growth at the Ge/Si(001)-(2 × 1) Surface

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The submonolayer growth of Ge on single domain Si(001)-(2 × 1) has been studied using high resolution photoemission by monitoring the Ge 3*d* and Si 2*p* core levels as functions of coverage, electron emission angle, and annealing temperature. It is shown that Ge initially grows as asymmetric mixed Ge-Si dimers with Ge occupying the up atom and Si occupying the down atom sites. Although this growth mode is predominant up to 0.8 monolayer coverage, pure Ge-Ge dimers do occur as well as Ge substitution of second and perhaps deeper layer Si. This interdiffusion is enhanced upon annealing to 600 °C.

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The dimer reconstructions observed on the technologically important clean and adsorbate covered Si(001)-(2 × 1) and Ge(001)-(2 × 1) surfaces have intrigued surface scientists for a long time. The degree of tilting or asymmetry, bond ionicity, ordering, and dynamics of the dimers are important aspects of these surfaces and have generated a great deal of research [1–17]. One of the most powerful ways of studying these complex surfaces in recent years has been through an examination of the surface core-level shifts (SCLS) observed in the high resolution photoemission experiments from these surfaces [6–17]. Despite the wealth of information potentially available from these spectra, however, their interpretation and thus the atomic and electronic structures deduced from such work has been far from unanimous. The growth of Ge on Si(001)-(2 × 1) is a closely related problem as far as the dimer reconstruction it presents [14–22] as well as the interpretation of the SCLS's observed from this system [14–17]. An understanding of the high resolution photoemission spectra from Ge on Si(001)-(2 × 1) is thus fundamental for obtaining a coherent picture of the dimer reconstructions in general as well as their relationships to the photoemission spectra from the clean surfaces. In its own right, the growth of Ge on Si(001)-(2 × 1) has generated a great deal of interest due to the fact that it is a prototype for semiconductor heteroepitaxial growth with considerable importance to electronic and optoelectronic device technologies [23,24]. The growth mode for this epitaxial system is known to be of the Stranski-Krastanov type with pseudomorphic layer-by-layer growth up to several monolayers (ML) coverage [22,25–28]. However, the mechanism of the initial dimer growth and, in particular, the relationship between the dimer structure and the surface core-level photoemission peaks observed from this surface have been subjects of controversy [14–17].

In this Letter, we present high resolution Ge 3*d* and Si 2*p* photoemission results from submonolayer coverages of Ge deposited on single domain Si(001)-(2 × 1) which answer a number of questions concerning both the initial stages of growth and the interpretation of the core-level spectra. From the results presented here, a clear picture emerges in which Ge grows first as mixed asymmetric dimers with Ge occupying the up atom positions and Si occupying the down atom positions. At coverages >0.2 ML, the predominant growth mechanism remains the creation of mixed Ge-Si dimers, although a significant number of pure Ge-Ge dimers do appear along with Ge substitution of second and perhaps deeper layer Si atoms. Upon annealing at 600 °C, the number of dimers created does not change significantly but the ratio of mixed to pure Ge-Ge dimers increases with some Ge atoms diffusing beyond the second layer into the Si substrate.

The existence of mixed asymmetric Ge-Si dimers explains the previous surface core-level results from this system as well as their relationship to core-level studies of clean Si(001)-(2 × 1) and Ge(001)-(2 × 1) surfaces. Scanning tunneling microscopy (STM) images [21] and other studies which show the growth of Ge dimers on Si(001)-(2 × 1) [15,19,20] must thus be reinterpreted in light of these results.

The experiments reported here were performed at the MAX I storage ring of the MAX-laboratory synchrotron radiation facility in Lund, Sweden on beam line 41. This beam line is equipped with a toroidal grating monochromator, a high precision sample manipulator for polar and azimuthal rotations, and an angle resolving hemispherical analyzer for high resolution angle resolved photoemission studies in the energy range of 15–200 eV. For all data presented here the photon energy was 136 eV and the total instrumental energy resolution was 100 meV. A highly oriented ($\pm 3'$) preoxidized Si(001) wafer was used as the starting point for this work. The surface was cleaned *in situ* using standard procedures, and a single domain surface was then prepared by Si evaporation and annealing as described in Ref. [29]. The resulting surface consisted of (2 × 1) and (1 × 2) domains in a ratio of 4:1 as judged by the relative intensities of the low energy electron diffraction (LEED) spots. Ge

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was then deposited onto this surface held at 350 °C at a rate of 0.30 ± 0.03 ML/min using a well outgassed Knudsen cell. Coverage determinations were made using both a quartz crystal thickness monitor and a quantitative evaluation of the Ge $3d$ core-level intensities. For all coverages reported in this study, these estimates agreed to within 15%. In addition, after deposition of 0.8 ML Ge, the LEED pattern showed a reversal of the original 4:1 domain ratio to a 1:2 ratio. Since dimer growth is known to result in domain switching [21,29], this change in domain ratio corresponds to a growth of 0.78 ML of material on the surface, which is very close to the coverage determination established using the thickness monitor and core-level intensities.

The principal experimental results for normal emission and no annealing are shown in Fig. 1. The data consist of Ge $3d$ and Si $2p$ core levels taken for Ge coverages of 0.1, 0.2, 0.67, and 0.8 ML as well as a Si $2p$ core level taken from clean Si(001)-(2 × 1). For the Si $2p$ core level from the clean surface, the number and energy positions of the peaks present as well as their structural assignments are believed to be well understood [6]. Following the procedure reported in Ref. [6], this level was decomposed into five spin-orbit Voigt functions. The resulting least-squares fit was found to be in excellent agreement with the results of Ref. [6] with the SCLS values never varying by more than 20 meV from those reported in their work. The peak assignments for these core levels are as follows: peaks S and SS correspond to the up and down atoms, respectively, of asymmetric dimers at the surface; peak S' is due to the second layer Si atoms; peak C is probably due to atoms in the third layer; peak B is due to bulk Si.

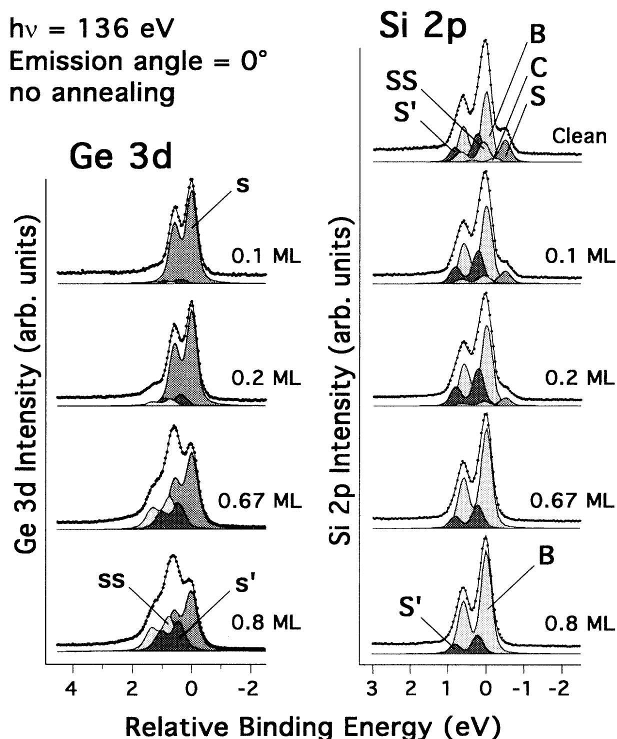

FIG. 1. The Ge $3d$ and Si $2p$ core-level photoemission results for normal emission and no annealing are shown here for coverages of 0.1, 0.2, 0.67, and 0.8 ML Ge/Si(001)-(2 × 1). Also shown at the above right is the Si $2p$ spectrum from clean Si(001)-(2 × 1). Details of the deconvolutions are given in the text.

At a coverage of 0.1 ML, the Ge $3d$ signal is seen to consist almost entirely of one peak (peak s) with the Si $2p$ level showing a significant decrease in the intensities of the signals coming from the up and down atoms of the Si dimers (peaks S and SS, respectively). In addition, the bulk signal B shows a slight widening and increase in its integrated intensity and the small feature C disappears from the spectrum. At 0.2 ML, two additional small peaks appear in the Ge $3d$ signal, one to 400 meV (peak s') and the other to 700 meV (peak ss) higher binding energy with respect to peak s. The Si $2p$ signal at this coverage shows a continuing decrease in the intensities of peaks S and SS and an increase in the peak B intensity. Upon further deposition of Ge, peaks ss and s' continue to grow at more or less equal rates in the Ge $3d$ spectra and the Si $2p$ signal shows a complete absence of the Si dimer related peaks S and SS. At the same time, peak S', due to the second layer Si atoms, decreases in intensity.

The changes in the Ge $3d$ and Si $2p$ core levels as functions of coverage in the submonolayer regime can be explained in a straightforward way based on some simple considerations and existing studies of the Si(001)-(2 × 1) [1–7,9,12,13] and Ge(001)-(2 × 1) [4,9–14] clean surfaces and of Ge deposited on Si(001)-(2 × 1) [14,15,18–22]. At the lowest coverages studied, the existence of a single component in the Ge $3d$ spectrum and the decrease in the intensity of peak S in the Si $2p$ spectrum strongly suggest a single Ge adsorption site corresponding to the up atom position. At higher coverages, the Ge $3d$ spectra reveal that this original single component s is the lowest binding energy component by several hundred meV of a multiple component structure. Core-level studies from the clean Ge(001)-(2 × 1) surface show the existence of a bulk and two surface components [9–12]. Although there are inconsistencies among these studies concerning the details of the high binding region of the Ge $3d$ signal, there is almost universal agreement from experimental [9–12] and theoretical [13,14] studies that the sharp component to 500 meV lower binding energy compared to the bulk peak is due to the up atoms of asymmetric dimers at the surface. This feature has also been observed in experimental [15] and theoretical [14] work of 1 and 2 ML Ge/Si(001)-(2 × 1), although in Ref. [15] it was assigned to both atoms of a covalently bonded dimer. This conclusion was refuted by subsequent comments in favor of the up atom assignment, however [16,17]. Cho, Jeong, and Kang [14] have recently calculated Ge $3d$ SCLS's for the Ge/Si(001)-(2 × 1) surface using the final state pseudopotential theory of Pehlke and Scheffler [13]. This

theory has been successfully applied to calculations of the SCLS's appearing in the spectra of clean Si(001)-(2 × 1) and Ge(001)-(2 × 1) [13]. In Ref. [14], they find that 1 ML Ge/Si(001) exists as asymmetric dimers on the surface with the up atom signal occurring to 540 meV lower binding energy than the down atom signal.

In light of these considerations, we thus conclude that the dimers which are known to appear in the earliest stages of growth are mixed Ge-Si asymmetric dimers with Ge in the up atom positions and Si in the down atom positions. In this case, the dimers observed in STM images of submonolayer Ge on Si(001)-(2 × 1) are not Ge-Ge dimers as normally assumed but consist primarily of mixed Ge-Si composition. The possibility of mixed dimers was, in fact, postulated by Cho, Jeong, and Kang in Ref. [14] on the basis of their total-energy calculations. The decrease in the Si down atom signal (peak SS) in the Si $2p$ spectra at coverages of 0.1 and 0.2 ML may at first glance seem inconsistent with the growth of mixed Ge-Si dimers, since the number of Si down atoms should not be decreasing at this coverage. However, the chemical environment of the Si down atoms participating in the mixed Ge-Si dimers is certainly different than for the clean surface. Since the Si $2p$ spectra at these coverages also show a widening and slight increase of the bulk signal, it seems likely that some of the signal coming from the Si down atoms move to lower binding energy and become mixed in with the bulk signal.

At the higher coverages studied, the Ge $3d$ signal shows the growth of two components (ss and s') to higher binding energy very similar to photoemission results from the clean Ge(001)-(2 × 1) surface [9–12]. Although a previous experimental study on Ge/Si(001)-(2 × 1) indicated only one peak to higher binding energy [15], it was found that the Ge $3d$ spectra shown in Fig. 1, combined with those taken at electron emission angles of 45° and 70° discussed below, could not be fit with only one additional peak but required a second component in the high binding energy region. The Si $2p$ spectra at coverages of 0.67 and 0.8 ML show a complete absence of the dimer related peaks S and SS and a significant decrease of the signal coming from the second layer Si atoms (peak S'). A natural interpretation of this evolution is that one of the peaks ss or s' in the Ge $3d$ spectra is due to Ge atoms in the down atom position and the other to a substitution of second or possibly deeper layer Si. This interpretation is consistent with previous findings in that the down atom and second layer atoms for the clean surface have been found to yield signals in the high binding region of the Ge $3d$ spectrum [9–14]. The splitting between the low and the high binding components in the work presented here is somewhat larger than for the clean Ge(001)-(2 × 1) surface. However, this result was also predicted by Cho, Jeong, and Kang [14] in their comparisons between core levels from 1 and 2 ML Ge/Si(001)-(2 × 1) and the clean surface.

In an attempt to determine which of the peaks ss or s' is due to the down atoms of the pure Ge-Ge dimers and which is due to Ge in the second or deeper layers, we measured the Ge $3d$ signal from the 0.67 and 0.8 ML coverages at electron emission angles $\theta = 0°$, 45°, and 70°. The ss/s' peak intensity ratio was found to increase by 39% for the 0.67 ML case and 16% for the 0.8 ML case in going from the $\theta = 0°$ bulk sensitive measurements to the $\theta = 70°$ surface sensitive measurements suggesting that peak s' arises from deeper layers than peak ss. On the basis of these results we tentatively assign peak ss to the down atoms of pure Ge-Ge dimers at the surface and peak s' to Ge in deeper layers. This assignment is consistent with several results from the clean surface [9,11–14] and, in particular, the results of Landemark [9], which are the highest resolution measurements to date on this surface, assign the down atoms to the highest binding energy component and second layer Ge to the component to slightly lower binding energy. The substitution of second layer Si by Ge is also indicated by the decrease in the relative intensity of peak S' in the Si $2p$ spectra at higher coverages. However, since diffraction effects can play a role in the polar angle behavior of core-level intensities and the fine details of peak assignments may be different for the Ge/Si(001)-(2 × 1) than for the Ge(001)-(2 × 1) clean surface, this assignment must be regarded as tentative on the basis of these results.

Lin *et al.* [15] have also reported Ge $3d$ and Si $2p$ spectra from Ge deposited on Si(001)-(2 × 1). In their work, these authors report that the Ge $3d$ signal is composed mostly of one low binding energy peak for coverages below 1 ML, with a second peak occurring to 0.63 eV higher binding energy at higher coverages. From the results of their work, they postulate the existence of symmetric dimers at this surface, a result now in conflict with the majority of the work on this and related surfaces. In view of the results presented in this Letter, the work of Lin *et al.* can be explained by supposing a miscalibration of the Ge deposition, a possibility already considered by Rowe and Wertheim [16], and by Cho, Jeong, and Kang [14]. It seems likely that at the lower coverages in their study, Lin *et al.* actually observed the single site Ge signal due to the up atoms of the mixed Ge-Si dimer growth reported here. The higher binding energy peak which they observed at greater coverages can then be interpreted as an unresolved two peak structure due to down atoms of pure Ge-Ge dimers and second layer Ge atoms.

The question of Ge diffusion into Si(001)-(2 × 1) during epitaxial growth is a critical one for the development of abrupt semiconductor heterojunctions and remains unresolved [12,14–21]. In order to study this issue, we report here the effects on the Ge $3d$ core levels of annealing the 0.67 and 0.8 ML covered surfaces at 600 °C. As can be seen in Fig. 2, significant changes occur in the shapes of the core levels upon annealing. Although there is an apparent increase in the peak s signal due to this annealing, a determination of the normalized peak intensities shows that peak s increases by only ~10% with the major part of the change in peak shape due to a decrease in the peak ss intensity by ~45% and the peak s' intensity by ~30%. We

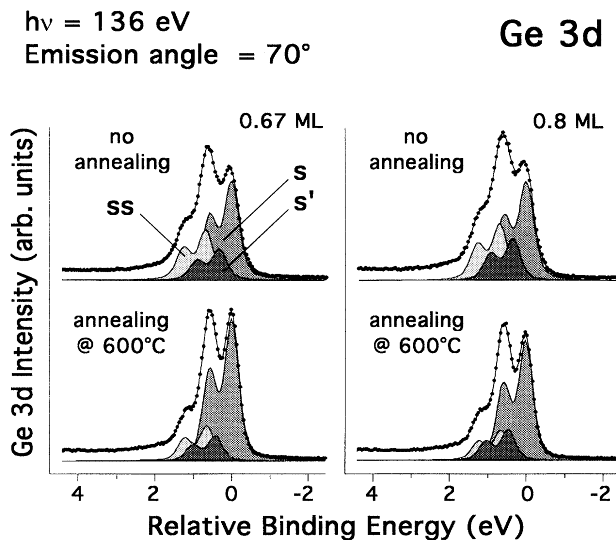

FIG. 2. Shown in this figure is a comparison of Ge $3d$ spectra for an unannealed surface and one annealed to 600°C for Ge coverages of 0.67 and 0.8 ML.

thus conclude that upon annealing the number of dimers created on the surface remains roughly the same. However, the decrease in the Ge down atom signal, whether this be peak *ss* or s', indicates that the ratio of mixed Ge-Si to pure Ge-Ge dimers increases. The overall decrease of both the down atom and second layer Ge signals indicates that annealing to 600 °C results in a further interdiffusion into deeper layers of the Si substrate in agreement with the work of Sasaki *et al.* [18].

In conclusion, the high resolution Ge $3d$ and Si $2p$ photoemission core levels presented here for submonolayer coverages of Ge deposited on single domain Si(001)-(2×1) show the creation of mixed Ge-Si asymmetric dimers in the early stages of growth. This novel growth mechanism is not in conflict with the results of existing studies although STM images as well as other results for this surface must be reinterpreted in light of these results. At coverages >0.2 ML, pure Ge-Ge dimers do occur along with Ge substitution of second and perhaps deeper layer Si atoms although mixed dimers predominate up to 0.8 ML coverage. Annealing to 600 °C results in an increase in the ratio of mixed Ge-Si to pure Ge-Ge dimers with further interdiffusion of Ge into deeper Si layers.

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