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Photoemission measurement of equilibrium segregation at GeSi surfaces

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Photoemission spectroscopy is used to demonstrate that Ge segregates to the first atomic layer of $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ and that the second layer is predominantly Si. Comparison of the resolved signals from the dimer atoms of the reconstructed $(100)2\times 1$ surfaces of Ge, Si, and equiatomic Ge-Si alloy shows that the surface layer of the alloy is extremely Ge rich and the second layer is occupied mainly by Si atoms. This result is in good agreement with theoretical predictions.

Atomic layer abruptness is highly desirable for quantum-well heterojunction electronic devices. In GeSi heterostructures interface width is seriously affected by segregation of Ge during growth.¹⁻⁶ This effect has been previously studied mainly by secondary ion mass spectrometry (SIMS) which is very useful for buried interfaces but lacks atomic layer resolution in this case. In addition one must consider matrix effects and preferential sputtering in order to quantitatively interpret SIMS measurements. Here we report on an experimental investigation of the surface segregation properties of GeSi epitaxial films using core-level photoemission. In excellent agreement with theoretical simulations,⁷ the first layer is shown to be composed nearly entirely of Ge atoms. Kelires and Tersoff have used theoretical simulations to investigate the equilibrium composition profile at the (100) surface of the equiatomic Ge-Si alloy.⁷ They predict that the surface layer is entirely occupied by Ge atoms, but that the second layer contains more than 80% Si atoms. Deeper layers are close to the bulk composition. In addition to the agreement with the simulation for the first layer, we find that our data are consistent with a second layer composed largely of Si atoms also in agreement with theory.

The data were taken on the AT&T Bell Labs' 6 m toroidal grating monochromator (TGM) beamline on the vacuum ultraviolet ring of the National Synchrotron Light Source at Brookhaven National Laboratory. The samples were grown by molecular beam epitaxy (MBE) on $\text{Si}(100)$ substrates with several thicknesses (300, 400, 700, 1250 Å) and capped with a thin (50–70 Å) amorphous Si layer to prevent oxidation of the MBE Ge-Si alloy during transfer to the photoemission apparatus. The samples were cleaned *in situ* by sputtering with 1 keV Ne ions and subsequent annealing to ~350–700 °C. Low-energy electron diffraction was used to confirm that the resulting (100) surfaces of both alloy and elemental materials had the 2×1 reconstruction. The photoemission data were taken with the samples at room temperature, using a Vacuum Science Workshop 100 mm hemispherical analyzer operated with a resolution of 40 meV. The combined instrumental resolution of the TGM and electron analyzer was typically in the range from 90 to 120 meV. This is less than the phonon broadening (~160–200 meV) associated with the respective core levels, so that the data are little affected by instrumental broadening.

It is well known that the core-electron binding energies of atoms in the dimerized outer layer of the reconstructed 2×1 surfaces of Ge and Si exhibit sizable shifts.⁸⁻¹² Since the isostructural, equiatomic alloy $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ undergoes the same 2×1 reconstruction, it is no surprise that we resolve the surface-atom signal for this material as well. This provides a means of monitoring the predicted surface segregation studied theoretically by Kelires and Tersoff.⁷ Essentially identical core-level line shapes were observed over a wide range of annealing temperatures, a result which we interpret as evidence that the surface composition is in equilibrium.

We obtained $\text{Si}(2p)$ and $\text{Ge}(3d)$ core level spectra of $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ taken with a wide range of photon energies from 38 to 140 eV. At the smallest energies, typically 8 eV above threshold, the escape depth is relatively large, making the bulk components dominate. At the largest photon energies (typically 31 or 41 eV above threshold) the escape depth is near its minimum, yielding the most surface-sensitive spectra shown in Figs. 1 and 2. The $\text{Si}(2p)$ spectra of the GeSi sample show very little change with photon energy and give no indication of a surface signal. The $\text{Ge}(3d)$ spectra, in contrast, exhibit a pronounced surface signal at a binding energy of 28.7 eV, which is significantly attenuated closer to threshold and indicates that the surface layer of $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ contains mainly Ge atoms.

A definitive demonstration of the lack of a surface signal from Si atoms is obtained from comparison of surface-sensitive $\text{Si}(2p)$ core-level spectra of the equiatomic alloy with that of elemental $\text{Si}(100)$ itself, see Fig. 1. In the data for elemental Si in Fig. 1(b), taken with a photon energy of 130 eV (near the minimum escape depth), the signal from the first atomic layer of Si is readily resolved.^{8,9} This layer consists of buckled dimers, and the resulting inequivalent Si surface atoms have been identified with specific features of the photoemission spectrum.^{8,9,12} The signal from the up atoms of the buckled dimers, which is labeled *S*, is seen more clearly in the negative second derivative of the data, shown below. In these room-temperature data, the down-atom contribution manifests itself only as a weak shoulder in the second derivative near 99.2 eV. It has been seen more clearly in data taken at liquid nitrogen temperature,¹² however, compositional fluctuations in the random alloy produce an additional static broadening which is in the range ~100–160 meV. Thus we found no advantage in taking data for the alloy at low temperatures, and room-temperature data are

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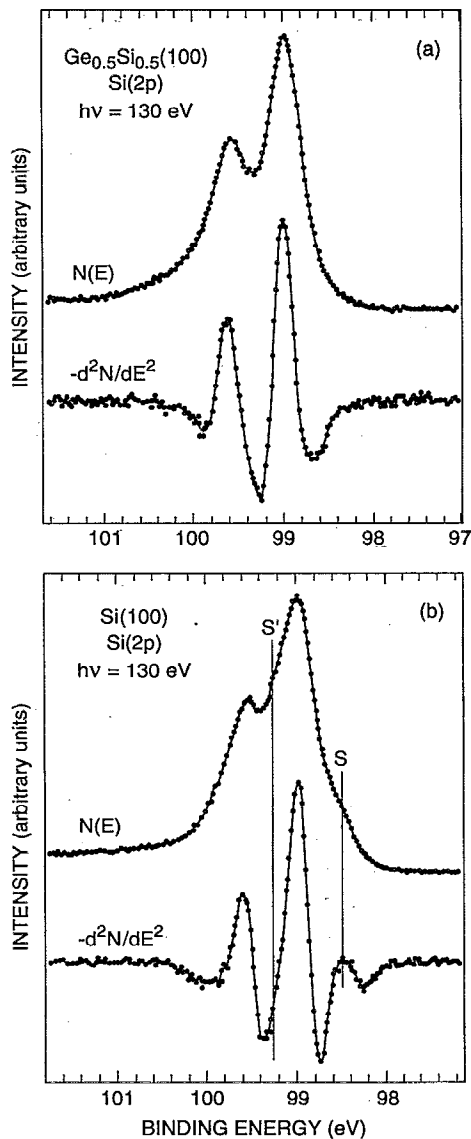


FIG. 1. Comparison of surface-sensitive Si(2p) spectra from (a) $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ and (b) $\text{Si}(100)2\times 1$. The negative second derivative is shown below each spectrum. The vertical lines labeled S and S' indicate resolved features associated, respectively, with first layer up atoms and down atoms of the buckled dimer.

used for consistency in the comparison of elemental and alloy samples. In the corresponding Si(2p) data for the $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ alloy surface, Fig. 1(a), there is no trace of the component S (see also the derivative spectrum). This provides a qualitative confirmation of the theoretical prediction of Kelires and Tersoff,⁷ that the first atomic layer is made up entirely of Ge atoms.

The dimer down-atom signal (the shoulder labeled S') near 99.2 eV in Fig. 1(b) has also disappeared from the derivative spectrum of the alloy, increasing the depth of the valley between the two bulk spin-orbit components of the alloy. This confirms that this feature is also associated with atoms in the first layer rather than with subsurface atoms, as has sometimes been suggested.¹³ Note that in the theory of

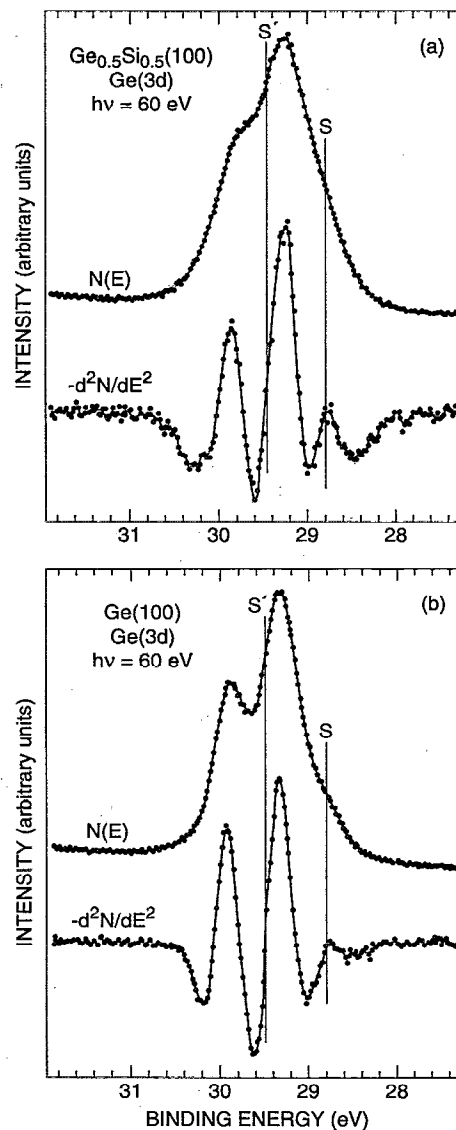


FIG. 2. Comparison of surface-sensitive Ge(3d) spectra from (a) $\text{Ge}_{0.5}\text{Si}_{0.5}(100)2\times 1$ and (b) $\text{Ge}(100)2\times 1$. The negative second derivative is shown below each spectrum. The vertical lines labeled S and S' indicate resolved features associated, respectively, with up atoms and down atoms of the buckled surface dimer.

Kelires and Tersoff the fraction of Si in the second layer is greater than that in the bulk so that subsurface Si features will be enhanced. The absence of enhanced observable features in the alloy spectrum indicates that the core-level shifts of the subsurface layers are not resolved from the bulk line with its inherent width of ~ 270 meV.

A comparison of Ge(3d) spectra of the Ge-Si alloy with that of Ge, see Fig. 2, fully supports the above conclusions. The spectrum of the $\text{Ge}(100)2\times 1$ surface exhibits the familiar component labeled S at smaller binding energy, associated with the dimers in the reconstructed first atomic layer.^{10,11} In the alloy the surface feature is significantly enhanced, but a quantitative measure is difficult to obtain because the alloy spectrum is broadened as mentioned above.

However, the filling in of the valley between the bulk spin-orbit components cannot be entirely due to such broadening, nor is it explained by the $3d_{3/2}$ line of the enhanced surface signal. It is probably due to the signal (labeled S') from the down atoms of the dimers, indicating that they are buckled and ionic.¹²

Although the core-level shift of the atoms in the second layer is not resolved in Ge(100), some information about its occupancy can in principle be obtained from the surface-to-bulk ratio of the Ge($3d$) spectra. If the first layer is entirely occupied by Ge and the second layer has a fraction f of Ge, while the deeper layers have the equiatomic composition, then the enhancement M of the surface to bulk ratio relative to that of Ge itself is given by

$$M = \frac{1}{f + (\frac{1}{2} - f)e^{-d/\lambda}}, \quad (1)$$

where d is the (100) layer spacing, and λ is the escape depth. If the second layer contained equal amounts of Ge and Si ($f=0.5$), then the ratio would be enhanced by a factor of 2. If the second layer contained only Si ($f=0$), then the intensity of this feature would increase by a factor of $2e^{d/\lambda}$ in the alloy. For an escape depth of 3 \AA this yields an enhancement by a factor of ~ 3 . Attempts to determine the surface-to-bulk ratio by least-squares fitting yield enhancement factors near 3, implying that the second layer is mostly Si atoms. However, these results are only modestly reliable because they depend strongly on the linewidth of the bulk and surface features which are quite different for Ge and the Ge-Si alloy.

The present demonstration of the segregation of Ge to the (100) surface of the equiatomic Ge-Si alloy recalls an earlier experiment in which overlayers of Ge were deposited on Si(111) surfaces.¹⁴ It was found there that Ge tends to remain in the surface layer during annealing.¹⁴ It thus seems likely that the surface segregation of Ge is not limited to the (100) surface, but is a more general phenomenon. Our data are also in good agreement with previous core-level photoemission¹⁵ measurements of thin (1–12 monolayer) depositions of Si onto Ge(100) and Ge(111). These experiments showed significant interdiffusion of Si into Ge with a

composition that depended upon deposition thickness and annealing. Thus the equilibrium composition at the surface was not obtained. In summary, we find that the surface dimers of the annealed surface of equiatomic Ge-Si alloys are occupied by Ge in agreement with the theory of Kelires and Tersoff.⁷ Further agreement with the predictions of Ref. 7 comes from the surface enhancement factor of Eq. (1) which implies that the second atomic layer is predominantly occupied by Si. Although the negatively shifted up-atom signal of these dimers is well resolved, the changes in both Si and Ge spectra show that the down atoms have positive shifts, indicating that the dimers are buckled and ionic. Thus our data appear to rule out the suggestion¹³ that the positively shifted surface signal is associated with the second layer.

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