X-Ray-Photoelectron-Diffraction Investigation of Strain at the Si/Ge(001) Interface

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We describe a structural determination of pseudomorphic Si on Ge(001) by means of x-ray-photoelectron diffraction. By comparing the measured angular coordinates of the forward-scattering-induced [001] peak with those calculated by means of single-scattering theory, we find that the lattice constant perpendicular to the interface is 5.34 ± 0.04 Å. This value exceeds that predicted by elastic theory by 0.08 Å.

The effects of strain on the band offset at a semiconductor heterojunction are significant, yet they are not completely understood and are often ignored.[1] Experimental determination of tetragonal distortion in strained semiconductor overlayers has proven to be an exceedingly difficult task, largely because the layer of interest is often only a few atomic spacings in thickness. Thus, theoretical rather than experimental means have often been used to determine the strain. Both classical elastic theory and full quantum-mechanical calculations have been employed. However, there are very few experimental values of the lattice constant normal to the interface, $a_\perp$, with which to compare theoretical results.

In this Letter, we describe the use of x-ray photoelectron diffraction (XPD) in conjunction with low-energy electron diffraction (LEED) and high-energy-resolution x-ray photoelectron spectroscopy (XPS) to characterize a lattice-mismatched heterojunction, Si/Ge(001), prepared with different amounts of strain and intermixing. We have determined $a_\perp$ by comparison of experimental XPD angular distributions with those calculated via single-scattering theory[2] for various amounts of strain, and have assessed the effects of strain and intermixing on core-level binding energies.

All experiments were performed in a system of three interconnecting ultrahigh vacuum chambers equipped for sample preparation, molecular-beam epitaxial (MBE) growth, and interface characterization by means of XPS, XPD, and LEED.[3] Scanned-angle XPD measurements were carried out with a full angle of acceptance of 5°, and with a precision and accuracy of $\pm 0.2°$. High-energy-resolution XPS measurements were made using a monochromatic Al $K\alpha$ x-ray source, yielding a total energy resolution of 0.74 eV, as judged by the full width at half maximum of the Au $4f_{7/2}$ peak from a clean Au surface. The binding energy of the Au $4f_{7/2}$ peak was monitored frequently during the course of the investigation to insure that the spectrometer electronics were sufficiently stable to insure highly accurate core-level binding energies. These measurements yielded a constant value of 84.00 ± 0.01 eV. Ge(001) surfaces were prepared by

growing 150–200 Å of epitaxial Ge at a temperature of 350 °C on clean, semi-insulating GaAs substrates cut to within $\pm 0.5°$ of (001). Thin epilayers of Si were then grown at temperatures of 335 °C, which is near the minimum temperature required for good epitaxy and laminar growth of up to four monolayers (ML) of Ge on Si(001),[4] and 450 °C, which is ~50 °C above the onset temperature for intermixing.[5] Thicknesses were determined by means of calibrated quartz-crystal monitors in the MBE chamber.

The physical basis of the following analysis centers around the well-known fact that a high-energy Auger or x-ray photoelectron wave emitted from an atom in a single crystal elastically scatters most strongly along the close-packed, low-index directions in the vicinity of the emitter.[2,3,6-9] In addition, the phase shifts associated with such forward scattering are small, leading to strong constructive interference along low-index directions. Thus, any change in the orientation of such a low-index direction with respect to the rest of the crystal is readily monitored by following changes in the solid angle at which the associated diffraction-induced peak occurs.[6] We show in Fig. 1 polar-angle distributions of Ge $3d$ and Si $2p$ integrated intensities in the vicinity of the forward-scattering-induced peak along [001] for 5 ML Ge on GaAs(001) grown at 335 °C, 4 ML Si on Ge(001) grown at 450 °C and 335 °C, and 16 ML Si on Ge(001) grown at 335 °C. The substrate peak along [001] (normal emission) was used as an internal calibration of the goniometer-analyzer geometry for each specimen. All surfaces exhibited clear, sharp, orthogonal $p(2 \times 1)$ LEED patterns, with the exception of the 16-ML overlayer, which exhibited a very faint, fuzzy 1×1 pattern. As discussed below, the later coverage is above the critical thickness, causing the overlayer to be partially relaxed and ridden with misfit dislocations. Such a film is not expected to possess a high degree of structural order until such coverage as the lattice is more fully relaxed and the interfacial region containing the dislocations is buried.[4] For unstrained Ge on GaAs(001) (top peak), the diffraction-induced peak along [011] falls precisely
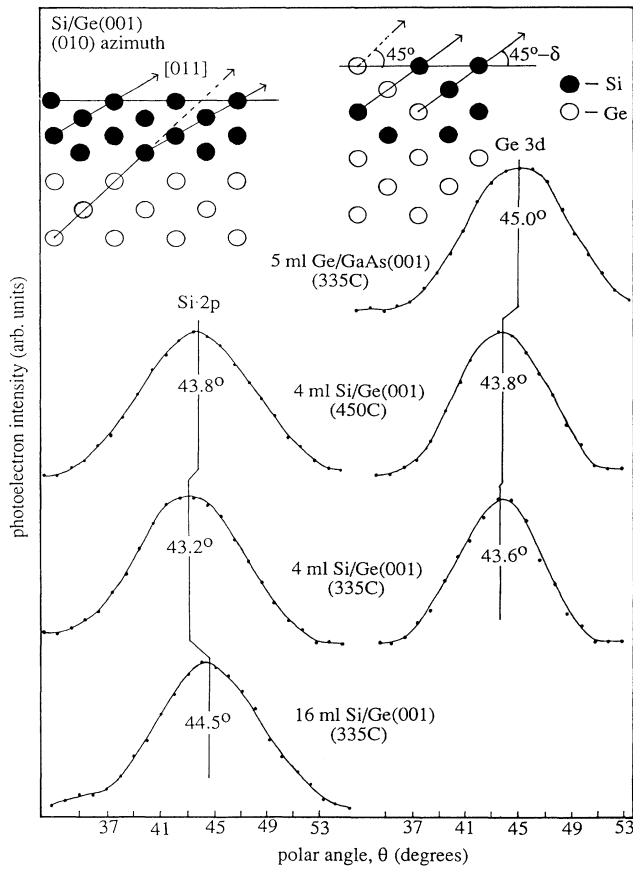
FIG. 1. Ge $3d$ and Si $2p$ XPD scans along [011] for various Si/Ge(001) interfaces after a linear background subtraction. The shift in the peak position to lower polar angle indicates tetragonal contraction association with pseudomorphic growth and/or alloy formation.
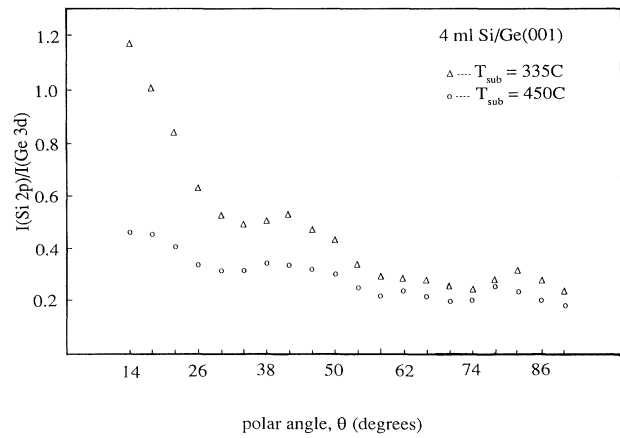

FIG. 2. The ratio of Si $2p$ to Ge $3d$ intensity as a function of polar angle for two different Si/Ge(001) interfaces. This ratio is expected to rise sharply for low θ (grazing emission) in the absence of extensive intermixing, but remain near the value observed at high θ when extensive intermixing occurs.

at 45.0°. This result suggests that averaging effects are sufficient to cause the [011] peak to fall at the value expected on the basis of the bulk crystal structure. These averaging effects are caused by the presence of orthogonal 2×1 domains as well as the probable presence of both buckled and nonbuckled dimers as found on closely related Si(001)-2×1.[10] When 4 ML of Si are grown at 450 °C, both the Ge $3d$ and Si $2p$ peaks along [011] ex-

hibit a shift, δ, to lower polar angle by an amount equal to $1.2° \pm 0.2°$. This uniform shift results from the formation of a SiGe alloy of smaller lattice constant than the Ge substrate.[5] Expansion in the plane of the interface to accommodate the substrate causes contraction normal to the interface. This situation is depicted schematically at the top of Fig. 1. Assuming the in-plane lattice constant to be equal to that of the substrate (5.65 Å), as previous work for $Ge_{0.5}Si_{0.5}$ on Si(001)[11] and Si(111)[12] suggests, a shift of this magnitude corresponds to $a_\perp = 5.42 \pm 0.04$ Å on the basis of simple geometric considerations.[13]

That intermixing occurs at 450 °C is clearly seen by plotting the ratio of Si $2p$ to Ge $3d$ peak intensities, corrected for Scofield cross sections,[14] versus polar angle, and such plots are shown in Fig. 2 for the two 4-ML growths. In the absence of intermixing, this ratio ought to rise sharply as θ approaches zero (grazing emission), and such is the case for growth at 335 °C. However, this ratio approaches a constant low value of 0.46 at shallow polar angles for growth at 450 °C. Modeling the dependence of this ratio on θ, and considering changes in probing depth with polar angle, leads to the equation

$$\frac{I_{Si\,2p}(\theta)}{I_{Ge\,3d}(\theta)} = \frac{(d\sigma_{Si\,2p}/d\,\Omega)p_{Si}\left[1 + \sum_{j=1}^{n}\exp(-jd/\lambda\sin\theta)\right]}{(d\sigma_{Ge\,3d}/d\,\Omega)\left\{p_{Ge}\left[1 + \sum_{j=1}^{n}\exp(-jd/\lambda\sin\theta)\right] + \sum_{j=n+1}^{\infty}\exp(-jd/\lambda\sin\theta)\right\}},$$

which can be used to estimate the stoichiometry of the intermixed phase. Here, $\{d\sigma/d\,\Omega\}$ are the differential photoelectric cross sections for the two core levels, p_{Si} and p_{Ge} are the Si and Ge atom fractions in the intermixed phase, $n+1$ is the number of layers of intermixed phase, d is the interlayer spacing (~ 1.4 Å), and λ is the escape depth (25 Å). Fitting this equation to low-θ intensity ratios with the constraint that $p_{Si} + p_{Ge} = 1$ suggests that the overlayer is nominally $Si_{\sim 0.34}Ge_{\sim 0.66}$.

Returning to Fig. 1, the angular distributions for the 4-ML growth at 335 °C show downward shifts of $1.4° \pm 0.2°$

and $1.8° \pm 0.2°$ in the Ge $3d$ [011] and Si $2p$ [011] diffraction peak positions, respectively. The Si $2p$ peak shift is indicative of strained, pseudomorphic Si and the shift in the Ge $3d$ peak position suggests a bend in the forward-scattering-induced intensity lobe resulting from interaction with the strained overlayer. These two situations are also depicted schematically at the top of Fig. 1. Again assuming an in-plane lattice constant of 5.65 Å, $1.4°$ and $1.8°$ (both $\pm 0.2°$) correspond to $a_\perp = 5.38$ and 5.31 Å (both ± 0.04 Å), respectively.[13] If an additional 12 ML of Si are deposited at 335 °C (bottom trace in Fig. 1), the Si $2p$ diffraction peak along [011] shifts back to 44.5° as the strain energy builds to a point where strain relief by means of misfit dislocation generation occurs. Interestingly, the diffraction peak widths are consistently larger $(9.5°-10.0°)$ for the layers at the vacuum interface than for those buried at the heterojunction interface $(7.5°-8.0°)$, suggesting that surface reconstruction may act to broaden the peak along [011].

In order to verify that the simple geometric considerations described are adequate to determine $a_\perp$, we show in Fig. 3 the results of a detailed comparison of experiment and single-scattering theory in which $a_\perp$ was systematically varied and an R-factor analysis was carried out. We define R as

$$R(n) = \sum_\theta \mathrm{abs}[I_{\mathrm{obs}}(\theta) - nI_{\mathrm{calc}}(\theta)] \Big/ \sum_\theta I_{\mathrm{obs}}(\theta) ,$$

where n is a normalization constant for equating theoretical with experimental intensities. A search for the value of n that minimizes R was carried out for each value of $a_\perp$. The calculations were performed on a slab composed of four pseudomorphic layers of 144 Si atoms constrained to fit on a Ge(001) substrate. We have ignored surface reconstruction because of the averaging effects discussed above. As the top panel of Fig. 3 shows, the R factor is minimized at 5.34 ± 0.04 Å, in good agreement with the number obtained directly from the peak position. An overlay of experiment and theory for $a_\perp = 5.34$ Å is shown in the bottom panel.

The value we report for $a_\perp$ in pseudomorphic Si on Ge(001) is 0.08 Å larger than that predicted by elastic theory. $a_\perp$ can be computed from the relation $a_\perp = (1 + \epsilon_{33})a_{\mathrm{Si}}$, where ϵ_{33} is the component of the strain tensor normal to the interface. To our knowledge there is no full electronic calculation published for the determination of $a_\perp$ for pseudomorphic Si on Ge(001), although one local-density-functional (LDF) calculation for abrupt Si/Ge superlattices reported that agreement with elastic theory is very good.[15] However, it does not appear that a total-energy minimization was carried out to find the optimal geometry. On the other hand, an ion scattering investigation of Si/Ge/Si(001) showed that the value of $a_\perp$ for the pseudomorphic Ge layer calculated from the elastic theory may be too large by 0.05 Å.[16] Furthermore, an LDF calculation which implicitly included a single intermixed interface layer and deter-
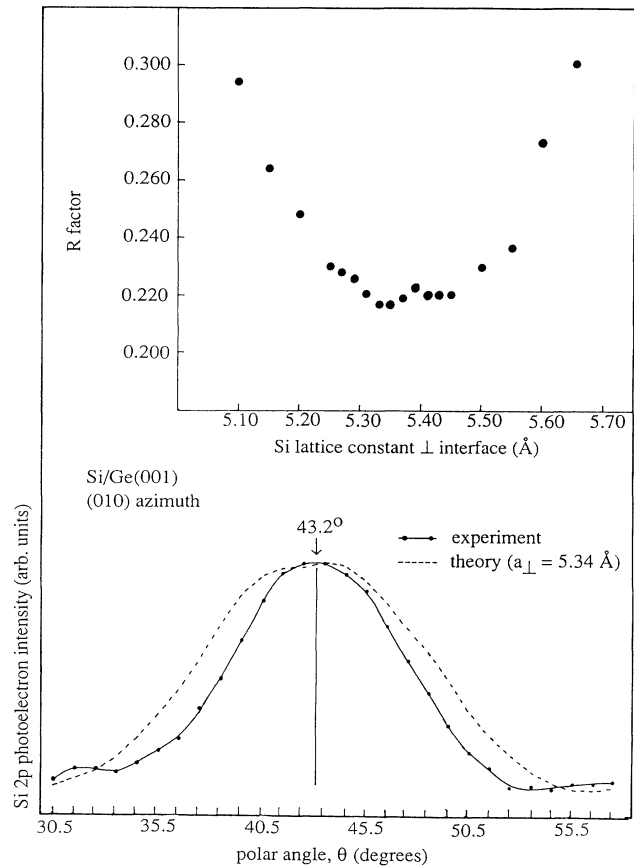

FIG. 3. R-factor analysis for comparison of theory to experiment (both after linear background subtraction) in determining $a_\perp$ for pseudomorphic Si on Ge(001). The in-plane lattice constant has been assumed to be that of Ge, 5.65 Å.

mined $a_\perp$ by total-energy minimization reported a reduction in $a_\perp$ of 0.04 Å relative to that predicted by elastic theory.[17] When combined with the present results, these findings suggest that the tetragonal distortion predicted by elastic theory may be too large by $\sim 0.05-0.1$ Å for either tension or compression. Interestingly, the *average* bond length of any Si atom in the strained overlayer is 2.38 Å which is only 1.3% larger than that found in bulk Si. This result lends further support to the concept of conservation of bond length in strained and reconstructed semiconductor layers.[18]

There are some slight but interesting changes in the core-level photoelectron spectra of these interfaces. The individual Si $2p$ and Ge $3d$ binding energies for the three interfaces are tabulated in Table I. The binding energies for the two growths carried out at 335 °C are well within experimental error, although the peak width on each Si $2p$ spin-orbit component is 0.08 ± 0.03 eV larger for the 16-ML growth, presumably due to the perturbation brought about by the introduction of misfit dislocations. Si $2p$ and Ge $3d$ centroids associated with the growth at

TABLE I. Summary of XPS results for Si/Ge(011) interfaces.

Interface	T_{sub} (°C)	Si $2p$ centroid (eV)	FWHM[a] (eV)	Ge $3d$ centroid (eV)	FWHM[a] (eV)
4 ML Si on Ge(001)	450	99.70(3)	0.62(2)	29.67(3)	0.65(2)
4 ML Si on Ge(001)	335	99.80(3)	0.63(2)	29.74(3)	0.62(2)
16 ML Si on Ge(001)	335	99.78(3)	0.70(2)	29.77(3)	0.60(2)

[a]Full width at half maximum of each spin-orbit component used in fitting the raw spectra. The numbers in parentheses represent the uncertainties in the last digit.

450 °C are *both* lower in energy by ~0.09 eV than those associated with growth at 335 °C, suggesting a change in band bending over the two growth temperatures. However, the *differences* between the two core levels for each interface are within experimental error of each other (±0.04 eV), and are in excellent agreement with other measurements for Ge/Si/Ge(001) heterostructures.[19] These results suggest that the changes in electronic structure brought about by strain are confined to the valence and conduction bands and do not affect the core levels in a major way.

In summary, we have utilized shifts in the forward-scattering-induced XPD peak along [011] to determine the tetragonal distortion associated with strain and intermixing at the Si/Ge(001) interface. Although such shifts represent the most straightforward way of measuring distortion associated with lattice mismatch, additional information about strain and disorder should be available in the XPD fine structure away from low-index directions, as has been observed for the NiO/Ni(001) system.[8] Such measurements are in progress in our laboratory.

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