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Conservation of bond lengths in strained Ge-Si layers

J. C. Woicik, C. E. Bouldin, and M. I. Bell
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. O. Cross, D. J. Tweet, B. D. Swanson, T. M. Zhang, and L. B. Sorensen
Department of Physics (FM-15), University of Washington, Seattle, Washington 98195

C. A. King,* J. L. Hoyt, P. Pianetta, and J. F. Gibbons
Stanford Electronics Laboratory, Stanford, California 94305-4055

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The combined techniques of x-ray-absorption fine structure and x-ray diffraction have been used to study the strain and bond distortions in epitaxial Ge-Si on Si(001). In a 31% Ge, 340-Å pseudomorphic Ge-Si film, the Ge-Ge and Ge-Si first-neighbor bond lengths have been found to be 2.44±0.02 and 2.38±0.02 Å, respectively. The lattice parameter perpendicular to the Ge-Si/Si(001) interface has been found to be $a_\perp = 5.552 \pm 0.002$ Å, in agreement with the predictions of macroscopic elastic theory. These results show that the bond-length strain in the epitaxial layer appears in the second and higher coordination shells, rather than in the nearest-neighbor bond lengths, which remain the same as in unstrained Ge-Si. A microscopic model is presented that accounts for these findings.

The interest in semiconductor heterojunctions and superlattices has grown rapidly over the past few years. Most of the early work on superlattices and heterojunctions involved materials that were nearly lattice matched, such as the GaAs/$\mathrm{Al}_x\mathrm{Ga}_{1-x}$As system. More recent work, however, has shown that lattice-mismatched layers may be grown epitaxially, i.e., without misfit dislocations, provided that the layers are thin enough (below the critical thickness) and that the lattice mismatch is not too great.[1] In this strained-layer epitaxial growth, the lattice parameter parallel to the interface, $a_\parallel$, of the strained layer is equal to that of the substrate, and the lattice parameter perpendicular to the interface, $a_\perp$, is that determined by the strain tensor.[2] Because of recent applications in heterojunctions and high-performance transistors, there is presently intense interest in strained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ heterostructures. In addition to the device applications, strained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ is an interesting system to compare with III-V strained-layer materials, such as $\mathrm{In}_x\mathrm{Ga}_{1-x}$As, since the underlying structures are quite similar.

Considerable theoretical and experimental efforts have been made to understand the electronic properties of strained and unstrained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layers.[3] However, to fully understand the electronic properties, it is essential to have detailed information about the atomic structure. In this work, we have combined two atomic-scale probes, extended x-ray-absorption fine structure (EXAFS) and x-ray diffraction, to study the geometric structure of strained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layers on Si(001). The advantages of combining these techniques arises from their complementary sensitivities to atomic structure. Diffraction can easily determine the unit-cell dimensions parallel and perpendicular to the interface very accurately and measure epitaxy, composition, and thickness. EXAFS, on the other hand, is a short-range probe that can easily determine bond lengths for different types of neighbors and corresponding fractional occupancy of each type of neighbor. By combining both techniques to the study of the same system, we can determine both the long- and short-range order much more easily than with either method separately. We show that, by combining these techniques, the bond angles, bond lengths, and lattice constants can be determined accurately enough to locate the atomic positions inside the unit cell without a full crystallographic analysis.

The pseudomorphic $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layer studied was from a group of $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ heterojunction bipolar transistors grown on Si(001).[4] The strained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ epitaxial layer, which serves as the base of the transistor, was grown by limited reaction processing, a chemical vapor deposition technique. The transistor was fabricated using standard Si processing. Layer thicknesses and concentrations were determined by Rutherford backscattering (RBS). Extensive details of the growth process and the sample characterization have been given previously.[4] The sample selected had a Ge fraction of 0.313±0.003 and a $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layer thickness of 340±25 Å, as determined by RBS. This sample was chosen because it provided a strained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layer with sufficient Ge concentration to allow a reliable determination of the Ge-Ge first-neighbor bond length. Results for the other samples will be reported elsewhere.

The EXAFS data were collected on beamline X23-A2 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (Upton, NY), using a fixed-exit double-crystal monochromator with Si(220) crystals. The sample photocurrent (which is proportional to the x-ray absorption[5]) was measured as a function of incident photon energy and flux across the Ge K absorption edge ($h\nu = 11\,104$ eV). In this detection method, the sampling depth of the electrons is ~ 1000 Å, and so the EXAFS measurement samples the entire Ge_xSi_{1-x} film.[5,6] To avoid contamination of the EXAFS spectra by Bragg diffraction peaks from the single-crystal substrate and the epitaxial layer, the sample was rocked about the vertical axis by approximately 4° during data acquisition, as described previously.[6] The sample was oriented so that the polarization vector of the x rays was parallel to the (001) surface, and the incident wave vector was 75° from the [001] direction. The EXAFS data for the standards, crystalline Ge and GaP, were recorded in transmission.

The diffraction measurements were made using beamline X22B, also at NSLS. The beamline optics consisted of a nickel-coated quartz focusing mirror followed by a flat, horizontal diffracting Ge(111) monochromator. To minimize the energy spread of the incident beam, the vertical divergence of the beam was reduced by closing the vertical slits in front of the mirror to 0.1 mm. The scattering measurements were made with an x-ray energy of 7890 eV in the standard double-crystal geometry (i.e., without an analyzer), using a Huber 5020 six-circle goniometer operated with a vertical scattering plane.

Figure 1(a) shows the k^2-weighted Ge K-edge EXAFS from the Ge_xSi_{1-x} layer and its Fourier-filtered first-shell contribution. Figure 1(b) shows the best fit to the Fourier-filtered signal assuming Ge and Si first-shell backscattering. These components are closely represented by the experimentally determined EXAFS from the crystalline Ge and GaP, which have known structures. The parameters determined by the fit are a Ge-Ge distance of 2.44±0.02 Å, a Ge-Si distance of 2.38±0.02 Å, a Ge-Ge fraction of 0.31±0.05, and a Ge-Si fraction of 0.70±0.05. The EXAFS determination of the alloy's concentration closely agrees with the RBS determination (Ge fraction 0.313±0.003). Therefore, we may conclude that we have not observed the alloy ordering effect in our sample, which was first found in Ge-Si/Si superlattices by Ourmazd and Bean.[7] As pointed out by Incoccia *et al.*,[8] ordering of the alloy would distort the EXAFS determination of the coordination numbers. These bond-length determinations are similar to those determined by EXAFS for a wide range of amorphous Ge_xSi_{1-x} alloys studied at both the Si (Ref. 9) and Ge (Ref. 8) K edges and to those of amorphous Ge_xSi_{1-x} superlattices studied at the Si K edge.[10] In these studies, the measured Ge—Ge bond length was equivalent (i.e., within the EXAFS experimental uncertainty of 0.02 Å) to its crystalline value of 2.45 Å, the measured Si—Si bond length equivalent to its crystalline value of 2.35 Å, and the Ge—Si bond length close to the average of the two.

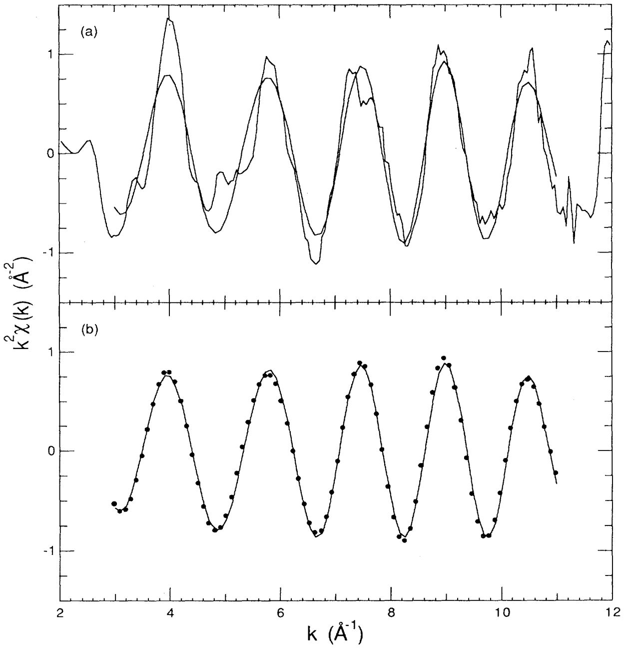

FIG. 1. (a) The k^2-weighted Ge K-edge EXAFS, $\chi(k)$, from the 31 at. % Ge, 340-Å pseudomorphic Ge_xSi_{1-x} layer on Si(001). Superimposed on the data is the Fourier-filtered first-shell contribution; (b) the fit to the first-shell signal assuming Ge-Ge and Ge-Si backscattering. The solid line is the fit, and the dots are the data points of the backtransform. The values returned from the fit are a Ge-Ge first-neighbor bond length of 2.44±0.02 Å, a Ge-Si first-neighbor bond length of 2.38±0.02 Å, a Ge-Ge atomic fraction of 0.31±0.05, and a Ge-Si atomic fraction of 0.70±0.05.

Both specular $(00L)$ and nonspecular $(11L)$ x-ray-scattering measurements were made. The specular data are shown in Fig. 2(a); the scattered-beam intensity is plotted versus the perpendicular momentum transfer Q_z measured in units of $L = 2\pi/a$, where a is the Si bulk lattice constant. Note the logarithmic intensity scale. The very sharp, intense peak near $L=4$ is due to the (004) Bragg reflection from the Si substrate. The characteristic $\sim Q^{-2}$ falloff of the substrate peak is clearly visible above $L=4$. The scattering from the strained pseudomorphic Ge_xSi_{1-x} layer consists of a central primary maximum, centered at approximately $L=3.9$, surrounded by subsidiary maxima that decrease in intensity away from the central maximum. The nonspecular data are shown in Fig. 2(b). In this case, the sharp intense peak near $L=3$ is due to the (113) Bragg reflection from the Si substrate, and the central primary maximum from the pseudomorphic Ge_xSi_{1-x} layer is near $L=2.94$.

From the positions of the specular and nonspecular primary maxima relative to their corresponding Bragg peaks from the Si substrate, the perpendicular lattice constant of the Ge_xSi_{1-x} layer, $a_\perp$, can be determined quite precisely. For the specular scan, $a_\perp = 5.553 \pm 0.002$ Å, and for the nonspecular scan, $a_\perp = 5.551 \pm 0.002$ Å, so together we find an average perpendicular lattice constant, $a_\perp = 5.552 \pm 0.002$ Å. This corresponds to a strain of 1.02% relative to unstrained Ge_xSi_{1-x} of the same composition, which has a lattice constant of 5.496 Å.[11] Since the primary maximum and the subsidary maxima are direct consequences of the finite thickness of the Ge_xSi_{1-x} layer, the thickness t of the layer can be calculated from the observed periodicity ΔQ of the minima $t = 2\pi/\Delta Q$. The calculated thickness for the specular scans is $t = 346 \pm 6$ Å, while for the nonspecular scans $t = 345 \pm 7$ Å. Together, the data produce an average

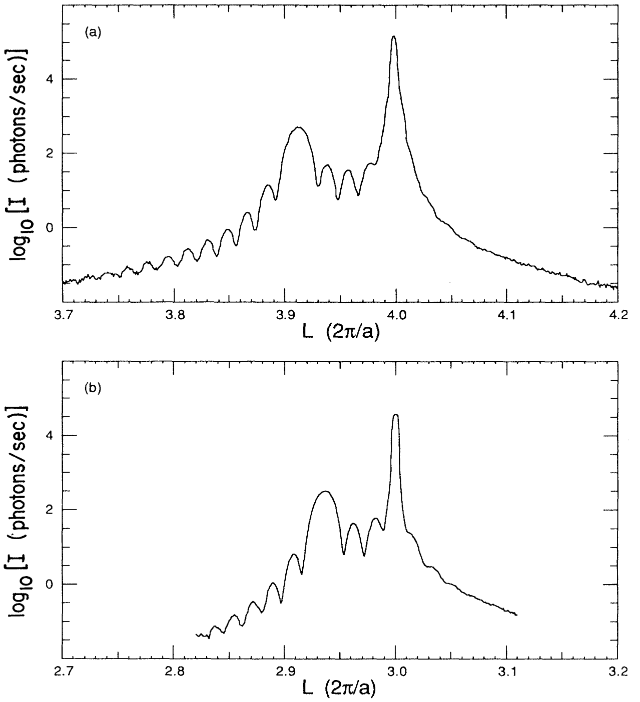

FIG. 2. Scattered intensity vs L in units of $2\pi/a$. Note the $\log_{10}$ intensity scale. (a) Scattered intensity near the Si(004) reflection. The peak at $L=4$ is from the Si substrate. The primary maximum near $L=3.91$ is from the Ge_xSi_{1-x} layer. The spacing of the subsidiary maxima on both sides of the primary maximum is determined by the layer thickness; (b) scattered intensity near the Si(113) reflection. The peak at $L=3$ is from the Si substrate. The primary maximum near $L=2.93$ is from the Ge_xSi_{1-x} layer.

thickness $t=346\pm6$ Å, in agreement with the thickness determined by RBS, 340 ± 25 Å. We also measured the in-plane momentum transfer for the nonspecular scattering from the epitaxial layer relative to the in-plane momentum transfer for the scattering from the Si substrate to determine whether the Ge_xSi_{1-x} layer is, in fact, epitaxial with the Si substrate. We found it to be epitaxial within our experimental accuracy, $(a_{\parallel}-a_{\mathrm{Si}})/a_{\mathrm{Si}}=(5\pm6)\times10^{-4}$.

Our determination of the Ge—Ge first-shell bond length (2.44±0.02 Å) in the strained Ge_xSi_{1-x} layer is equivalent to that of pure crystalline Ge (2.45 Å). In addition, our measured Ge—Si bond length (2.38±0.02 Å) is equivalent to that found in amorphous Ge_xSi_{1-x} alloys (2.38 Å).[8] It is most significant that the measured Ge—Ge bond length is equivalent to that of crystalline Ge and is larger than that of Si (2.35 Å) by a full 0.1 Å. Since the lattice constant of Si is about 4% smaller than the lattice constant of Ge, pseudomorphic epitaxial growth of a Ge_xSi_{1-x} layer on Si(001) results in a biaxial compression in the (001) plane of the substrate and a uniaxial expansion along the [001] surface normal. Figure 3 shows a tetrahedron under such strain. The bold arrows indicate the compressive strain in the xy plane imposed by the substrate. Our diffraction measurements have shown that the epitaxial Ge_xSi_{1-x} layer is in lateral registry with the Si lattice; therefore, the second-neighbor distances of the tetrahedrally bonded epilayer must compress along the x and y directions, as indicated in the figure. If the strain imposed on the Ge_xSi_{1-x} layer by the Si substrate produced only changes in the first-neighbor bond lengths, then all the first-neighbor distances in the strained layer would be equal to the bond length of the crystalline Si substrate. Our measurements clearly show that the strain in the Ge_xSi_{1-x} layer does not produce measurable changes in the first-shell bond lengths; therefore, the bond angles must bend to accommodate the strain.

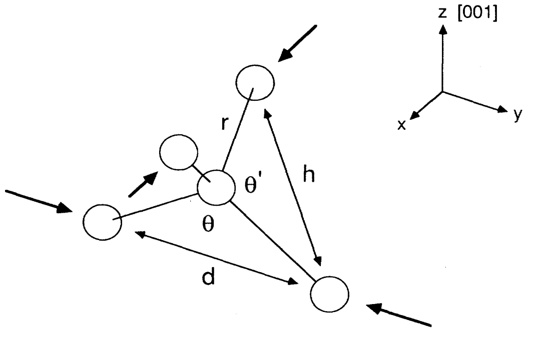

FIG. 3. A tetrahedron compressed in the xy plane with equivalent near-neighbor bond lengths r. Here $\mathbf{z}$ is the [001] direction. The second-neighbor distances are $d=2r\sin(\theta/2)$ and $h=2r\sin(\theta'/2)$.

In order to evaluate the relative contributions of bond stretching versus bond bending, the energy costs of the two distortions must be compared. For example, if we consider a central Ge atom surrounded by four Si atoms, the leading terms in the expansion of the total energy under this strain-induced distortion[12] are

$$E(\Delta r/r,\Delta\theta)=-E_0+4[\tfrac{1}{2}k_r(\Delta r/r)^2]+3[\tfrac{1}{2}k_\theta(\Delta\theta)^2] .$$

Here k_r is the bond-stretching force constant and k_θ is the bond-bending force constant. Δr and $\Delta\theta$ are the bond stretch and bond bend, respectively. The second-neighbor distance d in the two in-plane directions is given in terms of the first-neighbor distance r and the bond angle θ by $d=2r\sin(\theta/2)$. So, to first order in the distortions,

$$(\Delta d/r)=2(\Delta r/r)\sin(\theta/2)+(\Delta\theta)\cos(\theta/2) .$$

Minimization of the above energy subject to this geometric constraint yields the ratio of the radial to angular distortions in terms of the force constants,

$$(\Delta r/r)/(\Delta\theta)=(3\sqrt{2}/2)k_\theta/k_r .$$

From the radial and angular force constants for Ge and Si tabulated by Harrison,[13] this ratio is estimated to be ~0.12 for our alloy concentration. Since the strained layer is laterally epitaxial, Δd is known and the distortions can be calculated. The corresponding compression in the first-neighbor bond length is $\Delta r\sim-0.0073$ Å, and the bond angles are shifted anisotropically with respect to the interface $\Delta\theta\sim-1.4°$ and $\Delta\theta'\sim+0.7°$. These calculated changes are consistent with our measured nearly invariant first-shell bond lengths in the strained layer, and they are clearly the direct consequence of the much lower energy cost of bond bending relative to bond stretching. This strain-induced bond bending also produces an expansion in the out-of-plane second-neighbor distance, h. For the calculated change in the tetrahedral angle, $\Delta\theta' \sim +0.7°$, the corresponding expansion of the lattice constant along the [001] direction is ~ 0.08 Å. This estimate is close to the actual $a_\perp$ expansion, ~ 0.06 Å, measured by diffraction, but it is overestimated slightly since second- and higher-neighbor interactions have been neglected. Thus this microscopic model adequately accounts for both the nearly invariant first-shell bond lengths and the expansion of the lattice parameter perpendicular to the Ge-Si/Si interface.

The present results are quite different from the well-known bond-angle distortions found in amorphous tetrahedral semiconductors, such as amorphous Si, Ge, and GaAs.[5,8] In those systems, the bond-angle distribution remains centered at 109.47° and acquires a rms disorder of ~6–9°. In the present work, the average value of the bond angle shifts while the rms disorder remains virtually unchanged. The coherent anisotropic shifts observed here are, of course, impossible in the amorphous systems, since they must be globally isotropic.

To calculate the perpendicular lattice expansion more accurately, macroscopic elastic theory can be used.[2] In the special symmetrical case of interest here [i.e., an anisotropic cubic pseudomorphic layer grown on a (001) substrate], the lattice strains parallel and perpendicular to the Ge-Si/Si interface are related through the elastic constants c_{11} and c_{12} by

$$\varepsilon_\perp = -2(c_{12}/c_{11})\varepsilon_\parallel \ .$$

In this equation, the parallel and perpendicular strains, $\varepsilon_\parallel$ and $\varepsilon_\perp$, are related to the corresponding parallel- and perpendicular-strained lattice constants, $a_\parallel$ and $a_\perp$, and to the lattice constant a of an unstrained $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ alloy of the same composition by

$$\varepsilon_\perp = (a_\perp - a)/a \quad \text{and} \quad \varepsilon_\parallel = (a_\parallel - a)/a \ .$$

Since the $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layer is epitaxial with the Si substrate, $a_\parallel = a_{\mathrm{Si}}$. The values for c_{11} and c_{12} may be estimated by taking the concentration weighted averages of the elastic constants tabulated by Hornstra and Bartels[2] for Ge and Si. The calculated perpendicular lattice constant is then $a_\perp = 5.546$ Å. This value is within $\sim 0.1\%$ of our diffraction measurement, $a_\perp = 5.552 \pm 0.002$ Å. Because we have measured the lattice parameter $a_\perp$ as discussed by Hornstra and Bartels,[2] we may reverse the formalism above to estimate the concentration of the $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ film from the diffraction measurement and Vegard's law. The result is $x = 0.305 \pm 0.005$. This estimate agrees remarkably well with the concentration as determined by RBS, $x = 0.313 \pm 0.003$.

To summarize, we have measured the Ge-Ge and Ge-Si first-neighbor bond lengths in a strained pseudomorphic $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ layer on Si(001) and have found them to be equivalent to those found in pure crystalline Ge and amorphous $\mathrm{Ge}_x\mathrm{Si}_{1-x}$. The observed invariance of the first-neighbor bond lengths shows that the epilayer strain is accommodated primarily by changes in the second- and higher-coordination-shell bond lengths through coherent, anisotropic shifts in the value of the tetrahedral bond angles. The pseudomorphic epitaxy produces an expansion of the $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ lattice spacing perpendicular to the interface and a contraction of the lattice spacing parallel to the interface. These observed local changes can be understood with a simple microscopic model that compares the relative energy costs of bond stretching versus bond bending. The measured lattice constants are also in excellent agreement with the predictions of macroscopic elastic theory.

This study has demonstrated that x-ray diffraction and EXAFS can determine concentrations and layer thicknesses in pseudomorphic layers with comparable or better precision than RBS. In addition, extremely precise lattice parameters and accurate first-neighbor bond lengths can be measured. Consequently, by combining EXAFS and x-ray diffraction, a rather complete structural determination of strained pseudomorphic layers is possible without a full crystallographic analysis.

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[*] Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974-2070.

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[12] In general, this sum is taken over the four r's and the six θ's of the tetrahedron. However, for the special symmetrical case studied here, Δr is equal for all four bonds, and the in, $\Delta\theta$, and out, $\Delta\theta'$, of plane $\Delta\theta$'s are related by $\Delta\theta' = -\frac{1}{2}\Delta\theta$. Hence the factors of 4 and 3 in the total energy.

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