Raman spectroscopy of long-range order in epitaxial $Si_{0.5}Ge_{0.5}$ alloys

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The Raman spectrum of compositionally ordered $Si_{0.5}Ge_{0.5}$ grown at low temperatures by molecular-beam epitaxy has been measured and compared to the spectrum of the corresponding random alloy. We observe changes in the relative intensities of the different optical phonons which are consistent with the proposed structure of a microscopically strained, ordered phase where the majority of the bonds are homopolar and the minority are heteropolar. Within this model, the ordering appears to be incomplete. Resonant Raman scattering suggests that the E_1 gaps of the ordered layers can become identifiable at the bilayer thickness level.

INTRODUCTION

Raman spectroscopy has been widely used to study ordering phenomena in semiconductor superlattices.[1-4] In this paper, we show how very short period ordering in thick, unstrained layers of $Si_{0.5}Ge_{0.5}$ can produce observable changes in the Raman scattering from the Si- and Ge-layer optical phonons. These changes provide external confirmation for the structural model of LeGoues, Kesan, and Iyer[5] of a microscopically strained phase. We use resonant Raman scattering to provide information about the electronic structure of these layers and the local character of the E_1 gaps that dominate the dielectric response of these materials below 4 eV.

LeGoues, Kesan, and Iyer[5] recently found that low-temperature growth by molecular-beam epitaxy (MBE) of $Si_{1-x}Ge_x$ on Si(100) results in an ordered phase where the diamond-structure unit cell is doubled along a (111) axis. This ordered phase can be destroyed by annealing at temperatures above 800 °C and has not been observed for MBE growth at temperatures above 600 °C or when the (2×1) Si reconstructed surface is modified.[6] LeGoues, Kesan, and Iyer proposed that the ordered phase consists of Ge and Si (111) planes in an $AABBAABB \ldots$ sequence. When the ordering is complete, three-fourths of the bonds are homopolar and one-fourth are heteropolar. This structure is very different from the structure previously derived for the metastable ordered phase of thin, strained layers of these alloys.[7-9] In the older alternate structure, three-fourths of the bonds were heteropolar and the remainder homopolar. Raman scattering excited over a wide range of photon energies between 2 and 3.5 eV from the ordered phase of these thick, macroscopically unstrained layers show increases in the relative intensities of the homopolar Ge-Ge and Si-Si vibrational bands with respect to the intensity of the heteropolar Ge-Si vibrational bands when compared to the relative intensities for the same lines in the unordered layers. These intensity changes support the structure for the ordered phase proposed by LeGoues, Kesan, and Iyer. The Raman spectra also show that the ordering is incomplete in these samples.

Alonso and Winer[10] calculated the Raman spectra of $Si_{1-x}Ge_x$ random alloys and the originally proposed ordered phase of the thin, strained alloy layers where three-fourths of the bonds are heteropolar and one-fourth homopolar.[7,8] The phonon eigenfunctions and eigenvalues were obtained using a supercell approximation and the Raman spectra calculated with the bond polarizability model of Alben et al.[11] The calculations showed that ordering of the random alloy produced changes in the relative intensities of the different Ge-Ge, Ge-Si, and Si-Si-like phonons.[12-14] In the random alloy, Renucci, Renucci, and Cardona[12] showed explicitly for the first-order Raman scattering and published results of Lannin[13] for the overtone scattering suggested that the intensities of these bands are roughly proportional to $(1-x)^2:2x(1-x):x^2$, which describe the ratio of bonds of each type. The derived Raman spectrum of AW for the random alloy $Ge_{0.53}Si_{0.47}$ was consistent with these ratios. Their calculated Raman spectrum in the ordered phase where three-fourths of the tetrahedral bonds were heteropolar showed that the Si-Ge scattering was 3–5 times stronger than the Ge-Ge and Si-Si scattering, in rough agreement with a simple bond-counting model. Bond counting for the structure proposed by LeGoues, Kesan, and Iyer produces a different set of ratios for the numbers of bonds of each type and consequently, the expectation of a different set of relative intensities for the Raman bands. For a fully ordered $Si_{0.5}Ge_{0.5}$ structure where only one-fourth of the bonds are heteropolar, the ratio of the numbers of Ge-Ge to Ge-Si to Si-Si bonds will be 0.375:0.25:0.375. If the ordering is not complete, the magnitudes of these intensity changes decrease. However, as compared to the disordered, random phase, the relative numbers of homopolar as compared to heteropolar bonds will still increase and we show here that this is the case. Finally, AW found that their ordered phase produced small shifts in the energies of the Raman-active phonons as compared to the phonon energies in the random phase. Similar shifts in phonon energies from their random-phase values are observed in the ordered phase of LeGoues, Kesan, and Iyer.

AW showed that the Raman bands seen between 52 and 60 meV in the random alloy[15,16] can be due to disorder-induced Raman scattering. In the completely

ordered phase, their calculations showed that this scattering disappears. We find that while our ordered phases demonstrate increases in the number of homopolar bonds at the expense of the heteropolar bonds, the Raman bands between 52 and 60 meV do not disappear. This shows that the ordering in these layers is incomplete. This is consistent with the x-ray diffraction studies of these samples which show an ordering parameter of 0.64 with respect to the average composition.[17] Therefore, Raman scattering provides two different ways of measuring bond ordering in this alloy system.

Bond polarizability models of Raman spectra in covalent semiconductors such as that used by AW should be accurate for spectra excited at photon energies away from strong resonances such as the E_1 gaps. However, resonance Raman studies of random alloys of $Si_{1-x}Ge_x$ show that the relative intensities of the Si-Si, Si-Ge, and Ge-Ge lines depend only weakly on the excitation energies[18,19], so that theoretical results obtained from bond-polarizability models for the relative intensities of the Raman lines in alloys appear to be applicable even under resonant excitation. The applicability of bond-polarizability models of Raman spectra in the ordered phases where the electronic states can be localized to the individual layers is also open to question when the exciting radiation is resonant with the localized states. However, under these circumstances, the discussion of Raman intensities is usually carried out in terms of the band structure and the dielectric response of the system.

The dielectric response of the $Si_{0.5}Ge_{0.5}$ alloy shows resonances due to the E_1 and E_2 gaps.[20] The effects of the former, which dominate the optical properties of the Si-Ge system in the visible, on Raman scattering have been reviewed by Cardona.[21] Both the first- and second-order Raman scattering can be described in terms of the modulation of the electronic susceptibility, $\chi(E)$, by optical phonons. For excitation energies near E_1 and $E_1+\Delta_1$, there are two mechanisms involving these gaps. The first is the three-band contribution due to the phonon-induced mixing of the spin-orbit split valence bands which is described by terms of the form $(\chi_{E_1+\Delta_1}-\chi_{E_1})/\Delta_1$. The two-band contributions are due to the modulation of the energy gaps by phonons and are described by $d\chi(E)/dE$. The resonant first-order spectrum shows strong contributions from the former processes, while the overtone scattering is dominated by the latter. Ordering of the Si and Ge atoms also produces changes in the E_1 gaps since the alloylike behavior eventually yields to Ge and Si-like E_1 gaps when the pure layers are more than 6 Å thick.[22] In addition, the (111) oriented structure of the ordered phase will produce a splitting of the eight degenerate (111) transitions into a singlet and a triplet transition which will modify the resonant Raman spectra of materials like Ge through the two-band contributions to the Raman tensor.[23] The simple dependence of the relative Raman intensities on the ratios of the number of bonds of each type will therefore be complemented by the order-induced changes in the dielectric response, the electron-phonon coupling, and the phonon wave functions. Much of this paper will be concerned with placing upper

bounds on the magnitudes of these effects to obtain a quantitative estimate of the magnitude of the bond ordering.

EXPERIMENT

Our experimental results were obtained on alloy samples grown by MBE on Si(100) at a temperature of about 390 °C. Details of the growth conditions and the properties of these samples have been presented elsewhere.[5,17] X-ray diffraction has been used to measure the relative intensities of the allowed $\frac{1}{2}(7,7,7)$ reflections from the zinc-blende lattice as compared to the superlattice-induced $\frac{1}{2}(8,8,8)$ reflections of these samples to measure the magnitude of the ordering in the layers. The measured intensity ratio of the $\frac{1}{2}(7,7,7)$ and $\frac{1}{2}(8,8,8)$ spots was 0.114. When combined with the model structure described in the Introduction, including (1) the effects of ordering of the atoms, (2) the change in lattice parameters due to the microscopically strained structure, and (3) various geometric corrections, this produces an order parameter of 0.64 for the Ge and Si layers.[17] The ordered $Si_{0.5}Ge_{0.5}$ sample in the (111) direction consists of $Ge_{0.82}Si_{0.18}$-$Ge_{0.82}Si_{0.18}$ pairs of planes alternating with $Ge_{0.18}Si_{0.82}$-$Ge_{0.18}Si_{0.82}$ pairs of planes. Annealing of the ordered sample at 800 °C for 2 h in forming gas or vacuum results in the irreversible annihilation of ordering as seen by electron and x-ray diffraction.[17]

All of the Raman measurements were obtained in air at 300 K using a multichannel Raman-scattering system.[24] The spectra were excited with laser lines between 2.0 and 3.5 eV generated by either an Ar^+ laser or a dye laser. The experimental Raman difference spectra in this paper were obtained by the subtraction of the spectra obtained on samples which were microscopically ordered on growth and pieces of these samples which were annealed in a nonreactive environment to destroy the ordered phases but not remove any of the material making up the layer. This meant that it was not necessary to compensate for differences in Ge-Si layer thickness or composition. Spectroscopic ellipsometry measurements of the dielectric response of the same samples were performed using a rotating polarizer ellipsometer for energies between 1.34 and 5.4 eV.[25] The submicrometer thicknesses of the Si-Ge layers meant that usable results for the layer dielectric functions were obtainable only for energies above 2.4 eV. The experimentally obtained values for the ellipsometric parameters were reduced to the layer dielectric functions using procedures described previously.[22]

EXPERIMENTAL RESULTS

Figure 1 shows the first-order Raman spectrum of an ordered, 8000-Å $Si_{0.5}Ge_{0.5}$ layer (b) and of an ordered layer that was annealed at 800 °C to destroy the ordered phase (a). Both spectra were excited at 2.71 eV. The shoulder near 64 meV is due to the Si substrate. The ordered phase produces small changes in the relative intensities of the homopolar and heteropolar phonon Raman scattering from the random alloy values. This is shown unambiguously in the upper line of Fig. 1(c), the
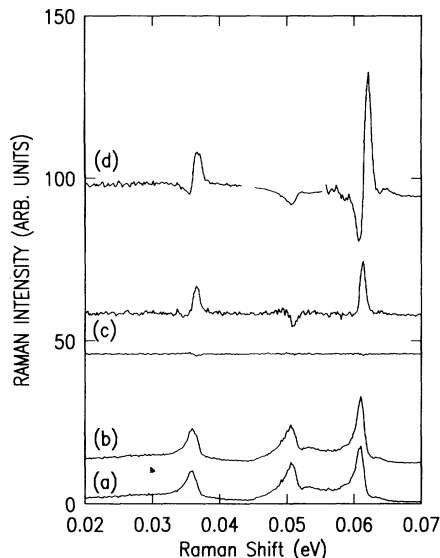
FIG. 1. The first-order Raman spectra for energy shifts between 20 and 70 meV of random (a) and ordered (b) $Si_{0.5}Ge_{0.5}$ alloys excited by 2.71-eV laser light. (c) The difference between the ordered- and random-alloy spectra shown in (a) and (b) (multiplied by 4). The flat line under this curve is the result of summing the spectra used to obtain (c) in quadrature and shows the accuracy of the subtraction process. (d) A constructed difference spectrum in the case where the only intensity changes arise from bond-counting changes due to ordering. The ordered-state Ge-Ge and Si-Si modes are shifted in energy to reflect the random-alloy values for these modes for the compositions of the ordered layers ($Ge_{0.75}Si_{0.25}$ and $Ge_{0.25}Si_{0.75}$).

difference spectrum obtained from subtracting curve (a) from curve (b). The amplitude of this difference spectrum has been multiplied by 4 so that the peak intensities of the Ge-Ge and Si-Si difference peaks are comparable to the lines in Figs. 1(a) and 1(b). If the ordering parameter within the individual (111) Ge and Si planes was 75%, then the number of Ge-Ge and Si-Si bonds would increase by 25% each while the number of Ge-Si bonds would decrease by 25% with respect to the values for the random alloy. The factor-of-4 normalization used in Fig. 1(c) means that 75% ordering of the Si and Ge atoms in the (111) planes would produce a difference spectrum whose peaks would be equal in amplitude to the peaks in the random alloy spectrum. Figure 1(c) shows that the Raman spectrum of the ordered phase has increased scattering from the Ge-Ge (36 meV) and Si-Si (61 meV) and decreased scattering from the Ge-Si (51 meV) vibrations. The changes in the scattering intensities are at the 10–20 % level. This is smaller than the 25–30 % expected from a simple model where the relative intensities of the Raman lines only reflect the numbers of bonds of each type in the partially ordered structure of Kesan, LeGoues, and Iyer.[17] The pattern shown in Fig. 1(c), where the Ge-Ge and Si-Si scattering intensities increase and the Ge-Si intensity decreases, can only occur on ordering since changes in composition, for example, would result in an increase in the scattering intensity at one end of the spectrum and a decrease at the other end.

Shifts in the positions of the Ge-Ge and Si-Si modes to higher energies are also observed in Fig. 1. This is more evident in Fig. 1(c). The observation of this behavior on ordering is consistent with the fact that the Si-Si and Ge-Ge modes both shift to higher energies with increasing Si and Ge concentration, respectively, in the random alloy.[12,14] A simple uniform change in the average composition would produce shifts in the energies of the Si-Si and Ge-Ge bands in opposite directions. For the 8000-Å layers used here, changes in film thickness would have no observable effect on the phonon energies. The lower curve associated with Fig. 1(c) arises from summing the series of ordered and random alloy spectra used to produce the difference spectrum in quadrature and provides a measure of the consistency of the successive runs. A perfect measurement would be a flat line, and comparison of the two traces shows that the spectral subtractions are accurate to better than 5% of the intensities of the peaks in Figs. 1(a) and 1(b). Figure 1(d) shows how partial ordering of the Ge and Si could change the Raman spectrum of the disordered phase. We increase the intensities of the Ge-Ge and Si-Si bands by 12.5% and decrease the intensity of the Ge-Si band by 12.5%, consistent with a model where the Ge and Si layer are $\frac{5}{8}$ ordered. This is about 40% of the value derived by Kesan, LeGoues, and Iyer. In addition, the peak positions of the Ge and Si peaks are shifted to higher energies by about 4 and 9 cm^{-1}, respectively, as though the optical phonons of the ordered layers had the Raman energies of bulk alloys ($Ge_{0.75}Si_{0.25}$ and $Ge_{0.25}Si_{0.75}$) with the layer compositions.[15] The Ge-Si peak is not shifted since this mode shows a relative maximum in energy at a composition of $Ge_{0.5}Si_{0.5}$. Figure 1(d) shows what happens when this derived spectrum is subtracted from the experimentally measured alloy spectrum. The changes in the Ge-Ge and Si-Si lines are similar to those observed experimentally in Fig. 1(c) with respect to their integrated amplitudes. The observed frequency shifts to higher energies are smaller than those generated in Fig. 1(d), and this can be attributed to the fact the optical phonons cannot be simply described by bulk analogs of the individual layers but retain a large measure of their average alloylike behavior.

In Fig. 2, we show the Raman scattering obtained from the samples used for Fig. 1 for energy shifts between 50 and 60 meV where AW observed disorder-induced lines. The ordered phase shows no change in the Raman intensity between 52 and 60 meV and the continued presence of weak structures near 53 and 56 meV. The disorder-induced lines calculated by AW arise from the presence of different cluster environments about the Si (Ge) atoms with distinct lines arising from Si (Ge) atoms with three, two, and one nearest-neighbor Ge (Si) atoms.[10] Complete ordering in the phase derived by LeGoues, Kesan, and Iyer would result in every Si (Ge) atom having the same environment of three Si (Ge) and one Ge (Si) nearest neighbor. There would be no spectral features due to the two and three Ge (Si) nearest-neighbor clusters. This is not the case as seen in the Raman spectrum in Fig. 2(b).

The Raman spectra shown in Figs. 1 and 2 were obtained using 2.71-eV excitation. Figure 3 shows the Raman spectra obtained from the random alloy sample un-
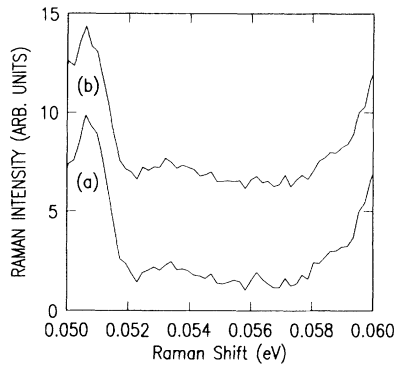
FIG. 2. The first-order Raman spectra for energy shifts between 50 and 60 meV of unordered (a) and ordered (b) 8000-Å unstrained $Ge_{0.5}Si_{0.5}$ alloy layers excited by 2.41-eV light.

der a variety of excitation energies between 2.0 and 3.5 eV [2(a), 2(c), 2(e), 2(g)] with the difference spectra [2(b), 2(d), 2(f), 2(h)] due to the subtraction of the random-alloy Raman spectrum excited at that photon energy from the ordered-alloy spectrum. The measured spectra have been normalized so that the first-order lines have about the same peak intensities. The spectral resolution of the 3.41-eV data is less than that of the other curves. The relative intensity of the order-induced Si-Si scattering increases with increasing photon energy while that of the Ge-Ge scattering decreases. The increase of the Si-Si scattering intensity on ordering over its value for the random alloy can be as large as 35% at 3.5 eV. The small $(3-5 \text{ cm}^{-1})$ shifts to higher energies on ordering of the
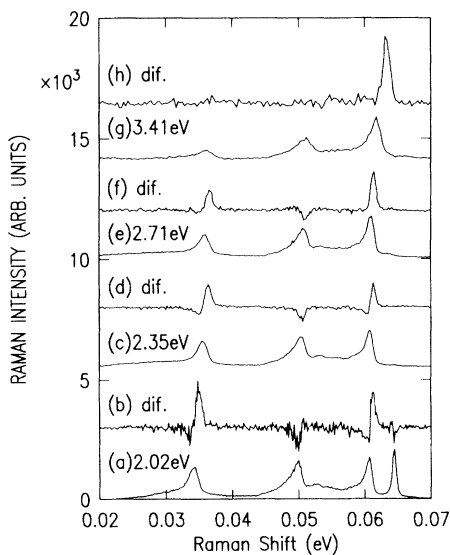
Ge-Ge and Si-Si lines seen in Fig. 1 are independent of the excitation energy. These results are all consistent with the partial ordering of the Ge and Si layers for low-temperature MBE growth. However, it is clear that a quantitative evaluation of the magnitude of the ordered phase requires an understanding of the resonant Raman scattering from these samples.

Qualitatively similar changes are shown in Fig. 4 for the second order, Γ_1 symmetry, Raman scattering. These spectra were obtained in a scattering geometry where the Γ_{25} symmetry first-order scattering is nominally forbidden. The band near 70 meV is the overtone for the Ge optical branch. The band near 100 meV is the Ge-Si optical branch overtone although it also overlaps the combination band due to the sum of the 37- and 63-meV Ge and Si optical-phonon bands. This overlap reduces the sensitivity of the intensity of the two-phonon band near 100 meV to changes in the relative numbers of homopolar and heteropolar bonds since any increase in the (Ge-Ge) + (Si-Si) scattering will be accompanied by a decrease in the 2(Ge-Si) scattering. The highest-energy band is due to Si optical-phonon overtone scattering. Figure 4(b) shows the ordered-phase overtone Raman spectrum excited at 2.41 eV while Fig. 4(c) is the difference spectrum obtained from subtracting the random-alloy [Fig. 4(a)] spectrum from the ordered-alloy Raman spectrum. As in Fig. 1, the difference spectrum is multiplied by a factor of 4. The Ge overtone scattering shows about a 15% increase in intensity, while the Si-Ge overtone scattering decreases by about 15%. The change in the Si overtone scattering is $< 5\%$. Shown in Fig. 4(d) is the ordered-phase overtone spectrum excited by 2.71-eV light, and in Fig. 4(e) the spectrum obtained by subtracting the second-order random-alloy scattering from the ordered-alloy scattering and multiplying the difference by four. In both cases, the ordered alloy shows
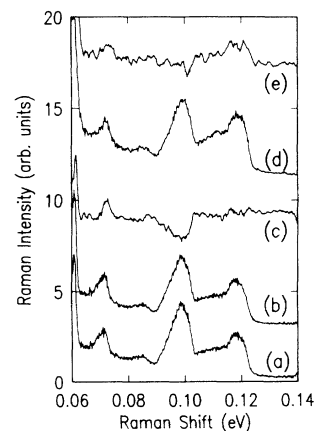

FIG. 3. The first-order Raman spectra of an 8000-Å random-alloy $Ge_{0.5}Si_{0.5}$ layer under (a) 2.02-, (c) 2.35-, (e) 2.71-, and (g) 3.41-eV excitation. Also shown in (b), (d), (f), and (h) are the difference spectra obtained from subtracting the unordered-alloy spectra obtained at these photon energies from the ordered-alloy spectra shown. The intensities of the difference spectra have been multiplied by 4.

FIG. 4. The second-order Raman spectra of ordered and random $Si_{0.5}Ge_{0.5}$ alloys. (a) The random-alloy spectrum excited by 2.41-eV light. (b) The ordered-alloy spectrum under the same excitation conditions. (c) The difference between the ordered- and random-alloy spectra shown in (a) and (b) (multiplied by 4). (d) The ordered-alloy spectrum at 2.71 eV. (e) The difference between the ordered- and random-alloy spectra for 2.7-eV excitation (multiplied by 4).
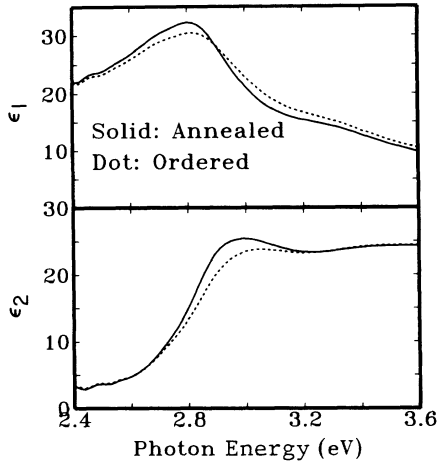
FIG. 5. The experimentally determined dielectric function $\varepsilon_1(\omega)$ (a) and $\varepsilon_2(\omega)$ (b) for both ordered and unordered $Si_{0.5}Ge_{0.5}$.

extra scattering in the Ge-Ge overtone band. Experimentally significant, order-induced scattering is only observed in the Si-Si overtone band for excitation energies in the blue. The magnitude of the order-induced decrease in the Ge-Si overtone scattering also depends on the excitation wavelength.

The Raman spectra in Figs. 3 and 4 show that the order-induced changes in the intensities of the different vibrational lines depend on the excitation energies. Figure 5 shows $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ for the ordered (dots) and disordered (solid line) $Si_{0.5}Ge_{0.5}$ alloys studied in this paper. The dominant structure in the dielectric response is due to transitions across the E_1 and $E_1+\Delta_1$ gaps of the alloy. The results in Fig. 5 for the random alloy are in agreement with other measurements and can be decomposed to produce room-temperature values of about 2.7 eV for E_1 and 130 meV for Δ_1.[20] The weak oscillations in $\varepsilon_1+i\varepsilon_2$ for photon energies below 2.5 eV are due to interference effects from the reflection of light at the alloy-layer substrate and alloy-air interfaces. These oscillations made it impossible to observe the lower-lying gaps in these materials. The ordering of the random alloy has a small effect on the dielectric response of the alloy. The peak in $\varepsilon_1(\omega)$ at 2.7 eV is reduced by about 10% and there is an apparent broadening to higher energies. Any changes for photon energies below 2.5 eV in both the real and imaginary parts of $\varepsilon(\omega)$ are below 2%. The description of the results shown in Fig. 5 in terms of E_1 and $E_1+\Delta_1$ gaps shows that the ordering does not produce large changes in the dielectric response.

DISCUSSION

Although the spatial scale of the ordering phenomena discovered by LeGoues, Kesan, and Iyer on thick unstrained Si-Ge layers is three orders of magnitude smaller than the wavelength of light for most of the measurements shown here, our results in Figs. 1, 3, and 4 clearly show that Raman spectroscopy is sensitive to the order-

ing. In this discussion, we consider the question of how much information on the magnitude of the ordering can be obtained from our Raman data in the absence of a full lattice dynamical calculation of the partially ordered alloy phase. Obtaining meaningful information from absolute changes in Raman scattering intensities is difficult but we show here that the relative changes in scattering intensities due to the kind of partial ordering which exists in our samples can be interpreted using only general physical arguments. We show that order-induced changes in the first-order Raman spectra provide more information about the ordering than the changes in the second-order spectra.

Renucci et al.[26] showed the second-order Raman intensities of materials such as Ge and Si were described by expressions of the form

$$\frac{d^2\sigma}{d\omega_R d\Omega} = A \sum_{e,l,m} F_e(\chi)D_{e,ml}(\xi_1^2)^{1/2}(\xi_m^2)^{1/2} , \qquad (1)$$

where A is a constant, the sum is over all pairs of phonons whose total $k=0$ for second-order scattering, $F_e(\chi)$ is a function of the susceptibility and its first derivatives with respect to photon frequency with terms similar to those described in the Introduction, $D_{e,ml}$ is a deformation potential, and the averages over $(\xi)_{m,n}^2$ describe the $q=0$ projections of the two-phonon amplitudes. Similar expressions differing only in the particular deformation potentials and the order of the amplitudes describe the first-order processes.[21] The effect of ordering on the Raman intensities in both cases will be to modify each of these terms. Since the observed changes in our Raman spectra due to ordering are small, the relative cross-section changes should be expressible as a sum of terms similar to the above that are linear in the order-induced relative changes in the numbers of Raman-active phonons $\delta N_p/N_p$, the deformation potentials $\delta D_{e,ml}/D_{e,ml}$, the dielectric response function $\delta\chi/\chi$, and the spatial extent of the phonon wave functions. The expected effect of the first of these changes was shown in Fig. 1(d). We show in the following discussion how the other parameters make the changes in the second-order scattering difficult to interpret and that the order-induced changes in Fig. 1(c) are close to what is expected for this system.

In Table I, we give the two- and three-band deforma-

TABLE I. Some of the parameters used to describe the effect of the E_1 gaps on resonant Raman scattering from optical phonons in Si, Ge, and alloys of Si and Ge (Refs. 13 and 14). $d_{3,0}^5+(1/(2\sqrt{2})d_{1,0}^5$ is the deformation potential for the three-band, one-phonon scattering process relevant to the results in Figs. 1 and 3, while D_1 is the deformation potential for the two-band, two-phonon processes used to describe the results in Fig. 4. The bracketed numbers are calculated values (Ref. 14).

Composition	Si	$Si_{0.5}Ge_{0.5}$	Ge
E_1 (eV)	3.39	2.71	2.11
Δ_1 (eV)	0.0	0.13	0.21
$d_{3,0}^5+(1/2\sqrt{2})d_{1,0}^5$	40(39)		34(44.5)
D_1 (eV)	1220		2534

tion potentials relevant to the description of optical-phonon Raman scattering in Si and Ge (Ref. 21) and the published values for the E_1 gaps in Si, Ge, and $Si_{0.5}Ge_{0.5}$.[20] The magnitudes of the two-phonon deformation potentials for Si and Ge in Table I show a factor-of-2 difference. This can produce large changes in the intensities of the two-phonon scattering on ordering of the Si and Ge layers in our samples if the deformation potentials are local properties of the crystals, reflecting the nearest-neighbor bonding around each atom and can change continuously from their Si value to their Ge value. Weinstein and Cardona[27] showed that for bulk crystalline Si or Ge, the two-phonon deformation potential has a simple form[28]

$$D_1 = 2\pi a_0^2 Ze^2 \Phi(0)^2 , \qquad (2)$$

where a_0 is the lattice constant, Z the atomic charge, and $\Phi(0)$ the electronic wave function at the lattice site. Since the wave function at the lattice site depends on the local bonding, the two-phonon deformation potentials will vary continuously in alloys as the composition changes from Ge to Si. The two-phonon deformation potential for the Si-Si vibrations in a random alloy where the average Si atoms has only two Si nearest neighbors will decrease in the partially ordered phase of LeGoues et al.[6] where most of the Si atoms have between two and three nearest-neighbor Si atoms. If the two-phonon deformation potential varied linearly with composition, there would be a 20% decrease in the Si two-phonon deformation potential in going from the random alloy $Si_{0.5}Ge_{0.5}$ to the partially ordered system. This would reduce the intensity of the Raman scattering and compensate for the increase in the number of Si-Si bonds on partial ordering. This provides an explanation for the small increases observed in the Si overtone on ordering in Fig. 4. As mentioned earlier, the order-induced change in the intensity of the two-phonon Raman scattering near 100 meV will be complicated by the overlap of the overtone scattering from the heteropolar bonds and the combination mode of the two different homopolar bonds. Under these circumstances, it would be difficult to obtain any quantitative estimate of the magnitude of the atomic ordering from the second-order scattering in Fig. 4. In contrast, the deformation potentials describing the first-order scattering processes show a much smaller variation ($<10\%$) as one goes from Si to Ge so that the deformation-potential-induced changes on ordering should be less than 2%. This would produce a small effect on the intensity of the first-order Raman scattering as compared to the change in the number of phonons of each type.

The ordering-induced changes in the intensity of the first-order Raman scattering from $Ge_{0.5}Si_{0.5}$ near the E_1 gap due to the changes in the dielectric function can be estimated from the ellipsometry results in Fig. 5. The first-order scattering is dominated by the three-band contributions described earlier. Near 2.7 eV, the change in the dielectric function is a simple decrease in amplitude of about 10% in the ordered phase as compared to its value in the random alloy. For our approximation where the order-induced changes simply add, this would com-

bine with the intensity changes associated with the 30% increases in the number of homopolar bonds of each type and a 30% decrease in the relative number of Ge-Si bonds on partial ordering as observed by Kesan, LeGoues, and Iyer[17] to produce a 20% increase in the intensities of the first-order homopolar scattering and a 40% decrease in the intensity of the first-order heteropolar scattering. This prediction is close to what we observe in Fig. 1 for the Ge-Ge and Si-Si vibrations although it still overestimates the magnitude of the order-induced changes in the Si-Ge modes. This argument is aided by the fact that the Ge-Ge phonons are only quasi-localized and have finite amplitudes on neighboring Si sites.[29,30] These phonon wave functions will not be significantly changed by ordering. Given the small changes in the electronic structure on ordering as seen in Fig. 5, the assumption that the deformation potentials for the Ge-Ge modes depend only weakly on ordering is reasonable.

Another complication in the comparison of the observed intensity changes in the Si-Si and Si-Ge modes with the simple bond-counting model is the experimental fact that the order-induced changes in the difference spectra in Fig. 3 show a significant dependence on the excitation energy. The model used here for the resonant Raman scattering does not explain the observed increase in the relative intensities of the Si-Si and Si-Ge lines compared to the Ge-Ge Raman band in the random alloy as the excitation energy increases.[31] It assumes that the coupling of each vibrational mode to the E_1 gaps can be described by a single excitation-energy-independent parameter. In fact, the electron–optical-phonon deformation potentials must depend on the details of the electronic states and will change as the electronic states change. The changes in the relative Raman intensities in Fig. 3 can be explained if the electronic structure of the alloy changes with increasing energy. For example, if the lower-energy contributions to the E_1 transitions have a large component of Ge-like wave functions while the higher-energy contributions have a large Si-like component of their wave functions, then the Raman spectra obtained at lower excitation energies would be more Ge-like while those obtained at higher energies would be more Si-like. Such effects would be stronger in the ordered alloys where we have already shown that bulk Ge-like behavior can be observed for Ge layers as thin as 7 Å.[30] This would make it difficult to use the relative intensities of the more spatially localized optical phonon modes to estimate the changes in the number of bonds. Some evidence for this behavior can be found in Fig. 5 where both ε_1 and ε_2 show decreases on ordering between 2.6 and 3.0 eV and an increase above about 3 eV. The E_1 maximum for the dielectric function in $Si_{0.5}Ge_{0.5}$ is near 2.8 eV, and about 3.1 eV for $Si_{0.75}Ge_{0.25}$ and 2.4 eV for $Si_{0.25}Ge_{0.75}$. Our results suggest that the dielectric response of a thicker ordered-alloy layer will show an increase on ordering below 2.5 eV due to the initial appearance of a Ge-rich phase. Our choice of 2.7 eV as the excitation energy for the results shown in Fig. 1 was made to avoid these problems by working at photon energies for which the optical response is always dominated by the

alloylike transition, with minimum effects due to the ordering-induced addition of new Ge-like or Si-like electronic states.

We have only considered the effects of alloying on the number of phonons on each type and have not considered how the alloying can change the phonon wave functions. This affects the Raman spectra since only the $k = 0$ components of the dielectric function are measured and changes in the phonon wave functions can change the efficiency of their coupling to light. While this effect should be small for the nonlocalized Ge-Ge modes, it can have a significant effect on the Ge-Si and Si-Si optical phonons that are energetically excluded from the Ge-rich regions of our layers. For the Si-Ge modes, ordering will increase the $k = 0$ component of the amplitude of these modes and therefore also increase the strength of the coupling of these modes to light. This would counter the decrease in the number of Si-Ge bonds on ordering and explain the reduced magnitude of the decrease in the first-order Si-Ge scattering intensity in Fig. 1.

As mentioned earlier, we observed no ordering-induced changes in the weak Raman scattering between 52 and 60 meV which was attributed by AW to the presence of different environments for the Si-Ge bonds. It is difficult to quantify the implications of this result for the degree of ordering present in the ordered phases. However, the failure to observe a significant change in this scattering for any excitation energy between 1.9 and 3.5 eV means that the ordering is not complete, i.e., less than 80% based on the assignment of AW.[10] Lockwood *et al.*[16] argued that the weak additional lines between 52 and 60 meV are due to the existence of an ordered state. Since we observe this scattering in all our samples, the argument of Lockwood *et al.* requires that our random alloys contain ordered regions, in disagreement with our diffraction studies of the random alloys that find no evidence for ordering. The failure to observe any change in the intensities of the weak extra lines on ordering appears to challenge the assignment of AW for these lines. However, the ordering observed by LeGoues, Kesan, and Iyer involves pairs of atoms. The bonding to the Si-Ge pairs invoked by AW to explain the extra lines involve eight atoms and within these eight atom clusters in the ordered phase, there are on the average, four Si and four Ge atoms, the same as in any eight-atom cluster in the random alloy. This will reduce the effects of partial ordering on the distribution of weak lines between 52 and 60 meV.

In any event, the observed changes in the intensities of the dominant first-order Raman scattering provide the strongest evidence for a partial ordering of the Si and Ge atoms in the structure proposed by LeGoues, Kesan, and Iyer. We have argued that the first-order Ge-Ge and Si-Si phonon intensities provide the best measurement of the amplitude of the structural order in these layers with a value of about 70–75 %. Even if we discount the various other contributions to the order-induced changes in the Raman intensities, our results in Figs. 1–4 show that the ordering must be at least at the 60–66 % level.

In conclusion, we have used Raman spectroscopy to help characterize the ordered states observed in MBE-grown layers of SiGe alloys grown on Si(100) surfaces at low temperatures. Both the first- and second-order Raman spectra clearly show that the ordering is associated with an increase in the number of homopolar bonds and a decrease in the number of heteropolar bonds. The observation of disorder-induced spectral features in the first-order scattering shows that the ordering is not complete. On the other hand, the changes in the relative intensities of the first-order Raman bands are quantitatively consistent with recent x-ray diffraction estimates of the ordering in these layers as near 80%.

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