

## Nonlocal resonant optical phonons and the local properties of ultrathin Ge layers on Si(100)

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The effect of the degeneracy of the Ge optical modes with the phonons of Si in an epitaxial Ge(100) layer less than 10 Å thick in Si(100) has been studied by Raman scattering. The interaction of the Ge modes with the Si acoustic phonons produces changes in frequency that are small compared to the shifts due to strain. While the Ge-derived modes are resonances of the Ge-Si system, the weak mixing of the Ge and Si modes means the Raman spectra can still be used to characterize the Ge layers.

In this paper, we describe the first- and second-order Raman active optical phonons of ultrathin ( $< 10$  Å thick) films of epitaxially grown Ge in Si(100). Our ability to make well-defined Ge layers in Si(100) with abrupt Si-Ge interfaces provides us with the opportunity to look at one of the venerable models in physics: the one-dimensional linear chain with a resonant mode. The Ge-derived modes are degenerate with the vibrational modes of the Si host and can mix with the host phonons. A different situation occurs in the AlAs-GaAs system where the optical modes are localized, producing new Raman-active modes and the effects of the localization can be largely parametrized by the layer thickness.<sup>1</sup> In the case of Ge in Si, the Ge optical phonons are resonances of the system and need not be localized.<sup>2,3</sup> The quantitative characterization of interacting Si and Ge layers by their Raman active phonons requires a detailed description of (1) the layer composition since Si and Ge readily mix, (2) strain, since the lattice mismatches are large, and (3) the strength of the

layer-host interaction. These three parameters raise a challenge to the usefulness of Raman scattering for the quantitative characterization of such systems since there are only two Raman active lines in addition to the host mode. We show that the frequency shift due to the host-layer interaction is small compared to the shifts from strain and alloying so that the resonance effects are not important. This is in contrast to systems such as molecules on surfaces where the degeneracy of the molecular vibrational modes and the host results in large changes of the molecular vibrational spectrum.<sup>2</sup>

We have measured the symmetry-allowed first- and second-order Ge-derived modes in thin, unalloyed, Ge films for several values of Ge layer thickness,  $t_{\text{Ge}}$ . We present results in Figs. 1 and 2 to show that our Ge layers can have negligible intermixing with the Si host so that the dominant effect of the host on the Ge-derived optical modes is the shift in energy due to the strain in the pseu-

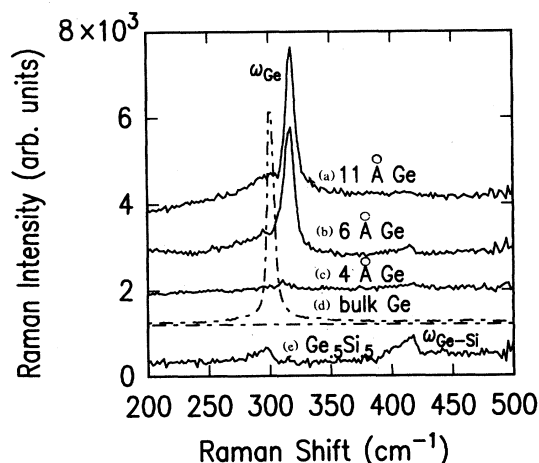


FIG. 1. The Raman spectra of thin layers of Ge grown by MBE on an Si(100) buffer layer and covered by a thin layer of Si(100). (a) 11 Å of Ge. (b) 6 Å of Ge. (c) 4 Å of Ge. Ge thicknesses measured by Rutherford backscattering. Spectra are normalized against the Si substrate and cap intensity. Included for reference are the Raman spectra of bulk Ge and pseudomorphic  $\text{Si}_{0.5}\text{Ge}_{0.5}$ .

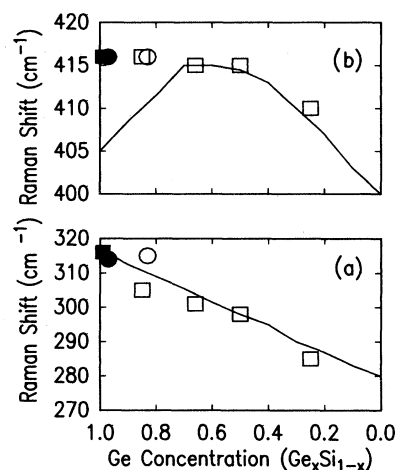


FIG. 2. The variation of (a)  $\omega_{\text{Ge}}$  and (b)  $\omega_{\text{Ge-Si}}$  in thick, strain layer  $\text{Ge}_x\text{Si}_{1-x}$  with alloy composition (Refs. 4 and 9) (solid lines). The points are the experimentally obtained values of these mode energies and the intensity ratio derived alloy compositions for a number of different samples. Solid square, Fig. 1(a) spectrum. Solid circle, Fig. 1(b) spectrum. Open circle, 12-Å sample grown at 350°C. Open squares are for 6-Å Ge layers grown or annealed at temperatures above 350°C.

domorphic Ge layer in Si and not alloying. Comparison of the first- and second-order Raman scattering from the Ge layers in Fig. 3 shows that the optical phonons of our Ge layers still have well-defined dispersion with the Raman active  $k=0$  mode remaining at the top of the optical-phonon band. This shows that the Ge optical-phonon band is strongly affected only by strain and that localization shifts are small.

The Ge-Ge vibration,  $\omega_{\text{Ge}}$  in bulk  $\text{Ge}_x\text{Si}_{1-x}$  shifts  $20 \text{ cm}^{-1}$  for  $1 > x > 0$ .<sup>4</sup> Contributing to this shift in the alloy are the 4% change of the lattice constant from that of Ge to Si and the interaction between the different modes in this three-mode system.<sup>5</sup> If the lattice constants of the alloy were held at a fixed value,<sup>6</sup> as  $x$  varied,  $\omega_{\text{Ge}}$  would shift about  $65 \text{ cm}^{-1}$  for  $1 > x > 0$ . In this paper, we show the shift, at a fixed lattice constant, of  $\omega_{\text{Ge}}$  due to the interaction with the Si host, for a 6 Å thick epitaxial Ge layer in Si(100), is  $< 6 \text{ cm}^{-1}$ . This is less than half of the shift in phonon frequency arising from strain in this system and considerably smaller than the shifts arising from alloying. As a result, we conclude that the Ge-Ge and Ge-Si Raman modes can provide useful information about thin Ge layers in Si(100).

Our samples were grown by molecular-beam epitaxy (MBE) (Refs. 7 and 8) at temperatures and rates which can produce uniform layers and abrupt Si-Ge interfaces. The Ge content was measured by Rutherford backscattering. The effective layer thicknesses,  $t_{\text{Ge}}$  were between 4–13 Å. The films were nonpseudomorphic for  $t_{\text{Ge}} > 10$  Å. Reflection high-energy electron diffraction (RHEED) showed that for growth temperatures near  $250^\circ\text{C}$ , there were at least 3 atomic layers ( $\approx 4.5$  Å) of layer by layer growth before Stanski-Krastanov type island growth.<sup>9,10</sup> Ge layers were grown on Si buffer layers and capped by 30–50 Å of Si. For contrast, measurements were also

made on crystalline Si layers grown on thick, relaxed Ge layers deposited on Si and capped by Ge and amorphous Si. The Raman spectra were excited at 300 K by ion lasers, filtered and dispersed by a multistage monochromator and detected by a microchannel plate photomultiplier with a position-sensitive resistive anode<sup>6</sup> or a silicon charge couple device (CCD).

In Fig. 1, we show Raman spectra obtained for  $\hbar\omega_1 = 2.41 \text{ eV}$  from three different Ge layers in Si(100). Figure 1(d) is the Raman spectrum of an 850-Å relaxed Ge layer grown on Si(100) and Fig. 1(e) the spectrum of a 100-Å pseudomorphic  $\text{Ge}_{0.5}\text{Si}_{0.5}$  layer. The Raman scattering due to the Si substrate and overlayer has been subtracted from the curves in Fig. 1. The Raman lines near  $315 \text{ cm}^{-1}$  ( $\omega_{\text{Ge}}$ ) are due to Ge-Ge bonds in the pseudomorphic Ge layer. The  $415\text{-cm}^{-1}$  scattering is due to the presence of Ge-Si bonds ( $\omega_{\text{Ge-Si}}$ ).<sup>5</sup> The intensity of the Raman scattering near  $300 \text{ cm}^{-1}$  as compared to the weak scattering near  $415 \text{ cm}^{-1}$  is evidence for the abruptness of the Si-Ge interfaces.<sup>8</sup> Figure 1 shows that for decreasing  $t_{\text{Ge}}$ ,  $\omega_{\text{Ge}}$  shifts to lower energies and its intensity,  $I_{\text{Ge}}$ , decreases. Since the interlayer spacing between Ge and Si atoms in the (100) direction is about 1.5 Å, mixing of interfacial Ge and Si atoms at the monolayer level will turn the three-layer Ge sample into a Ge-Si alloy. This can shift  $\omega_{\text{Ge}}$  to lower energies.<sup>5</sup> The ratio  $I_{\text{Ge}}/I_{\text{Ge-Si}}$  (where  $I_{\text{Ge-Si}}$  is the intensity of  $\omega_{\text{Ge-Si}}$ ) shows a roughly linear variation with  $t_{\text{Ge}}$  for  $t_{\text{Ge}} > 6$  Å. The full width at half maximum of  $\omega_{\text{Ge}}$ ,  $\Delta_{\text{Ge}} \approx 8 \text{ cm}^{-1}$  for the 11-Å Ge film and  $\approx 7 \text{ cm}^{-1}$  for the 6-Å sample as measured under higher resolution than the curves in Fig. 1. Still thicker Ge layers show values of  $\Delta_{\text{Ge}} > 20 \text{ cm}^{-1}$  reflecting departures from pseudomorphic growth. The Ge-Ge lines have a slight asymmetry to lower energies with a shoulder near  $300 \text{ cm}^{-1}$ . For bulk Ge, this line is symmetric and  $\Delta_{\text{Ge}} \approx 4 \text{ cm}^{-1}$  at 300 K.

In Fig. 2, we consider how (a)  $\hbar\omega_{\text{Ge}}$  and (b)  $\hbar\omega_{\text{Ge-Si}}$  for the spectra in Fig. 1 and a number of other samples produced using different temperatures and Ge thicknesses can depend on the composition of the layers. The fact that a sample is grown to be a 10-Å pure Ge layer does not mean that it is such a layer. In this figure we demonstrate that we have well-defined, ultrathin, pure Ge layers by showing we can use our Raman spectra to identify deviations from this behavior in the form of the alloying of the Ge layer with the Si host. The lines in this figure show the dependence of  $\omega_{\text{Ge}}$  and  $\omega_{\text{Ge-Si}}$  on  $x$  for thick, pseudomorphic  $\text{Ge}_x\text{Si}_{1-x}$  on Si(100). The curves are based on alloy data of Byra,<sup>4</sup> and Cerdeira *et al.*<sup>11</sup> The distribution of our experimental points along the composition axis in Fig. 2 was obtained from  $I_{\text{Ge}}/I_{\text{Ge-Si}}$ . Assuming (1) that there is a uniform region containing Ge in the samples, (2) any Si atoms in the Ge layer are randomly distributed, and (3) the Raman intensities are proportional to the number of bonds of each type in the layer, then<sup>12</sup> from simple bond counting,  $I_{\text{Ge}}/I_{\text{Ge-Si}} = x/2(1-x)$ . This relationship should correctly order the samples with respect to  $x$ . The results of Renucci, Renucci, and Cardona<sup>12</sup> suggest that errors in the absolute values of  $x$  are  $\approx 0.1$ . When  $I_{\text{Ge}} \gg I_{\text{Ge-Si}}$  ( $x \approx 1$ ),  $\omega_{\text{Ge}}$  is at the value expected for a strained Ge layer grown on Si(100) without any need of

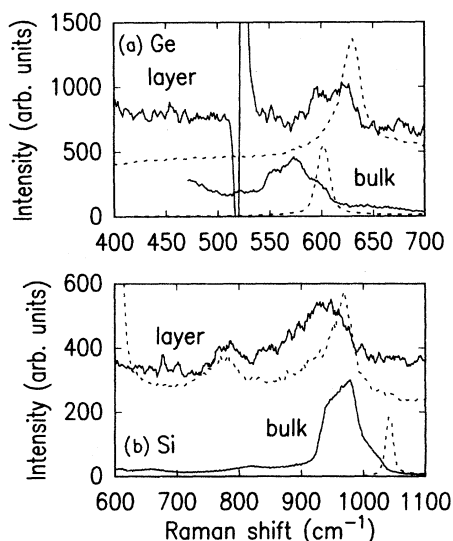


FIG. 3. The first- and second-order Raman spectra of thin layers of (a) Ge in Si(100) and (b) Si in Ge(100). Shown in both figures are the second-order Raman spectra of bulk Ge and Si. The dotted lines show the first-order Raman spectra of the samples where the energy axis has been doubled.

corrections for the presence of the Si host. However,  $\omega_{\text{Ge-Si}}$  is too large by  $10 \text{ cm}^{-1}$  for it to come from a homogeneous Ge-rich layer consistent with the value of  $\omega_{\text{Ge}}$  measured for this sample.  $\omega_{\text{Ge-Si}} = 415 \text{ cm}^{-1}$  can come from Si bonded to Ge at the surface of the Ge layer assuming there is an interface with an average composition of  $\text{Ge}_{0.5}\text{Si}_{0.5}$  and there are no shifts arising from the Si and Ge bounding layers. We have shown that growth at temperatures above  $350^\circ\text{C}$  of our Ge films produces intermixing of the Si and Ge.<sup>8</sup> This is clearly demonstrated in Fig. 2(a) for  $x < 0.8$  where the Raman frequencies and relative intensities of our Ge layers and the known values for a strained alloy are in agreement. The Ge-Si lines are all clustered near  $415 \text{ cm}^{-1}$  except for a sample which was annealed at  $600^\circ\text{C}$  for 8 h and showed significant intermixing of the Ge layer with the Si in medium energy ion scattering.<sup>8</sup> The  $415\text{-cm}^{-1}$  maximum value of  $\omega_{\text{Ge-Si}}$  is close to the value expected for a  $\text{Ge}_x\text{Si}_{1-x}$  alloy for  $0.35 < x < 0.7$ . The  $6\text{-\AA}$  samples grown at higher temperatures which provide the open squares in Fig. 2 all show intermixing of Si and Ge.<sup>8</sup> The solid points in Fig. 2 show that the spectra in Figs. 1(a) and 1(b) are consistent with the presence of pseudomorphic Ge layers with sharp Ge-Si interfaces. The interface will produce a small additional Ge-Ge signal at  $\approx 300 \text{ cm}^{-1}$ . The results in Fig. 2 appear to explain the observed vibrational energies without the need to consider any layer-host interaction, at least on the  $3\text{-}5\text{-cm}^{-1}$  scale of our spectral resolution.

In Fig. 3(a), we show the second-order Raman spectra obtained from a Ge layer in Si(100). Figure 3(b) is the analogous spectra obtained from a  $\approx 15\text{-\AA}$ -thick Si layer grown on  $2000 \text{ \AA}$  of relaxed Ge(100) and capped. Also shown in this figure are the one-phonon spectra from these ultrathin layers where the Raman frequencies have been multiplied by two to facilitate their comparison with the second-order spectra. For reference, the second-order spectra of bulk Ge and Si are given along with the bulk one-phonon scattering where once again, the energy scale for the latter has been doubled. The two-phonon spectrum of the thin Ge layer resembles the two-phonon spectrum of bulk Ge in its full width at half maximum of about  $43 \text{ cm}^{-1}$  and its relationship to the Raman shift doubled, first-order scattering which occurs at the upper edge of the band. While specific features in the thin layer and bulk bands differ, the second-order Raman bands of the Ge layer and bulk are shifted by  $\approx 33 \text{ cm}^{-1}$ , or about twice the  $15\text{-cm}^{-1}$  shift of the first-order Raman peaks. This is consistent with the measured Grüneisen parameters<sup>5</sup> for the critical points of the optical-phonon bands of Ge, and with the dominant perturbation on the optical phonons of the Ge layer being the strain due to the pseudomorphic growth. The behavior of the second-order bands in the Ge layer differs from the behavior of the Si bands in Fig. 3(b). The Si optical phonons are rigorously localized in the Si layer since their energies are well above the top of the Ge phonon bands. The second-order band of the layer is both shifted and broadened with respect to the bulk band. Unlike the Ge case, the  $30\text{-}50\text{-cm}^{-1}$  shift of the second-order band to lower energies is smaller than the  $55\text{-cm}^{-1}$  shift of the one-phonon line. These results are not consistent with just a strain-generated shift of the

optical-phonon bands in the Si layer. Since the effect of localization is to shift the  $k=0$  bulk modes towards the center of the optical-phonon band, the results in Fig. 3(b) are consistent with energy shifts due to both localization of the Si modes and strain. The localization of the vibrational wave functions of a free-standing Si slab has been treated by Campbell and Fauchet<sup>13</sup> and Kanellis, Morhange, and Balkanski.<sup>14</sup> The frequency shifts of the  $k=0$  Si modes we observe are larger than expected from strain and consistent with the theoretical predictions for localization.

Our results for Ge in Si(100) show that the effect of the Si host on the optical phonons of the Ge layer can be explained by shifts in the phonon frequencies due to the strain from epitaxial growth. The degeneracy of the Ge optical modes and the Si phonons means that the Ge modes are not rigorously localized. The high-energy  $k=0$  optical phonon would be more strongly perturbed by localization than the low-energy, zone-edge-derived modes. The observation that the first- and second-order Raman spectra of the Ge layer samples are both related to the bulk spectra by an almost uniform shift in energy is evidence that any localization-induced shift in the Raman-active Ge mode is less than  $6 \text{ cm}^{-1}$ .

Our results are consistent with studies of the phonons in Ge-Si superlattices by Fasolino and Molinari<sup>15</sup> using a simple, interplanar force constant model and Menendez *et al.*<sup>16</sup> using samples with severely disordered interfaces where  $I_{\text{Ge}}/I_{\text{Ge-Si}} \approx 2$ . Fasolino *et al.* found that  $\omega_{\text{Ge}}$  shifted  $10 \text{ cm}^{-1}$  to lower energies in a  $\text{Si}_{10}\text{Ge}_m$  superlattice as  $m$ , the number of Ge layers, changed from 14 to 6. The displacement pattern of the mode had a propagating component in the Si so that the Ge vibrations are not properly confined. The absence of a shift in  $\omega_{\text{Ge}}$  to lower energies as  $t_{\text{Ge}}$  went from 11 to  $6 \text{ \AA}$  in our samples probably reflects this nonlocalized component. Because (1) our samples show less mixing at the Ge-Si interfaces with better definition of the pure Ge region so we can rule out any alloy induced shifts, and (2) we work with only a single Ge layer with no interactions between the Ge layers, our results provide a closer look at the problem of the local properties of the Ge-Ge modes in this system than the results of Menendez *et al.* All results agree on the relatively small size of the confinement shift in this system.

In conclusion, we have studied the effect of a Si host on the Raman scattering from an embedded ultrathin Ge layer. Unlike the GaAs-AlAs system,<sup>1</sup> the vibrational wave functions associated with the Ge layers need not be localized to the Ge layers. While hybridization effects can be large and difficult to evaluate,<sup>2</sup> the three-mode behavior of the  $\text{Ge}_x\text{Si}_{1-x}$  alloy system means the frequency shifts arising from the interaction with the host are small so that the Raman scattering from the Ge layer can be used to quantitatively characterize the strain and composition of the Ge layer. These results are consistent with the recent theoretical work of Fasolino, Molinari, and Maan<sup>17</sup> where they describe the Ge modes as "resonant, quasicontained optical phonons." This suggests that Raman scattering can be used to describe many types of buried layers at the  $10\text{-\AA}$  or smaller level, even when the layer modes are degenerate with the host.

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