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Localized electronic states and resonant Raman scattering from localized and quasiresonant phonons in Si-Ge layers

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Resonant Raman scattering from localized Si and quasiresonant Ge and Ge-Si optical phonons has been used to study the characteristics of optical transitions at energies near the E_1 gap of Ge for structures of ultrathin Ge layers in bulk Si(100) and ultrathin Si layers in bulk Ge(100). Strong enhancements of the Ge-derived Raman scattering at excitation energies near 2.3 eV have been observed for Ge layers as thin as 7 Å. Si layer scattering shows no enhancement at the Ge host resonance. These results show localized electronic states exist in these materials well above the fundamental band edges.

The electronic and vibrational states of a thin layer in a host can be described as either confined or free.[1] An electronic resonance arising from states confined in one material can produce an enhancement of the Raman scattering intensity for phonons in that material. Such a resonance cannot produce a significant enhancement of the Raman scattering from phonons that have little or no amplitude at the confined electronic states. The optical phonons in structures composed of layers of Si and Ge show local or quasilocal behavior,[2,3] so that resonant Raman scattering from these phonons provides information about the spatial characteristics of the electronic states in Si-Ge layers. We have used resonant Raman scattering from the Ge-Ge, Ge-Si, and Si-Si phonons in Si-Ge layered quantum wells to study the electronic structure of thin Ge and Si layers for photon energies between 1.8 and 2.8 eV.[4-6] Large enhancements of the Ge phonon Raman scattering at excitation energies near 2.3 eV have been observed for Ge layers as thin as 7 Å in bulk Si. There is no comparable large enhancement of the Si-Ge interface derived scattering in these samples or of the Si Raman scattering from 6-15-Å Si layers in bulk Ge when the host $E_1-E_1+\Delta$ resonances of the unstrained Ge surrounding the Si are excited. The strong E_1 enhancement of the Raman scattering from the phonons in our Ge layers as compared to the Ge-Si phonons from the interfaces between the Ge and Si layers and the Si layer phonons suggests that the electronic transitions involving the conduction band and heavy-hole valence band in the Λ direction retain considerable Ge and Si character in our structures.

All of our samples were grown by molecular-beam epitaxy on Si(100) substrates.[7,8] The growth temperatures were held below 350 °C to produce atomically abrupt interfaces.[8] The Ge layers were grown on Si buffer layers and capped by 30-50 Å of Si. The thin crystalline Si layers were grown on 2000-Å-thick, relaxed Ge films and covered by a Ge cap with a thin layer of amorphous Si for oxidation protection. The Raman measurements were made in air, under flowing He using a multistage spectrograph with a multichannel optical detector.[7] The spectra were excited using lines from Ar^+, Kr^+, and dye layers.

The Raman-active modes of Si and Ge layers provide spectroscopically distinct, local probes of these layers. There are three Γ'_{25} symmetry Raman-active modes which are derived from the nearest-neighbor vibrations of Si pairs, Si-Ge pairs, and Ge pairs.[9] The Si pair derived modes are localized on the Si sites by energetic considerations. The Si-Ge and Ge-Ge pairs are resonances of the Si host. However, calculations for both the alloy[10] and thin-layer superlattices[11] suggest that the Ge phonon wave functions are largely localized. Recent one-dimensional, interplanar force-constant calculations[11] suggest that the Raman-inactive TO modes of the perfect Si-Ge interface are localized while the LO modes are delocalized. Disorder at the interface would result in Raman-active Si-Ge interface modes.

The resonant Raman spectra of Ge, Si, and Ge_xSi_{1-x} are proportional to terms such as $d_a[d\chi(\omega)/d\omega]$, and $d_a^b\chi^{(i)}(\omega)$ where d_a^b, are the different deformation potentials and the $\chi^{(i)}(\omega)$ the susceptibility or the contributions of particular gaps, i, to the susceptibility.[5,6,9] The deformation potentials depend on the electronic wave functions and the phonons. For our Ge and Si layers, Ge-like $E_1-E_1+\Delta$ transitions will produce a resonance in the intensity of the Ge Raman scattering, I_{Ge}. The intensities of the Ge-Si and Si phonons, $I_{Ge\text{-}Si}$ and I_{Si} at the Ge $E_1-E_1+\Delta$ gaps will depend on how the wave functions of the Ge electronic states behave near and in the Si.[12-15] If they have no amplitude, then the deformation potential for the Si vibrations will be small and I_{Si} will show no resonant enhancement. If the electronic states are delocalized, resembling those found in random alloys, all the Raman modes will be simultaneously enhanced since the deformation potentials for Si and Ge are comparable. There would also be an alloylike shift of $E_1-E_1+\Delta$.[15] Small values of the deformation potential connecting the Si vibrations and the Ge electronic states could occur even if the mixing of the Si and Ge electronic states were large.

In Fig. 1, we show the first-order Raman spectra obtained from an 11-Å Ge layer in Si(100) excited at several different energies between 1.92 and 2.7 eV. In all of these spectra, the contributions to the light scattering from the Si host have been subtracted. The scattering, ω_{Ge}, between 300 and 320 cm^{-1} is analogous to the Raman-active phonon of bulk Ge.[9] The scattering, $\omega_{Ge\text{-}Si}$, near 415 cm^{-1} comes from the Si–Ge bonds at the interfaces

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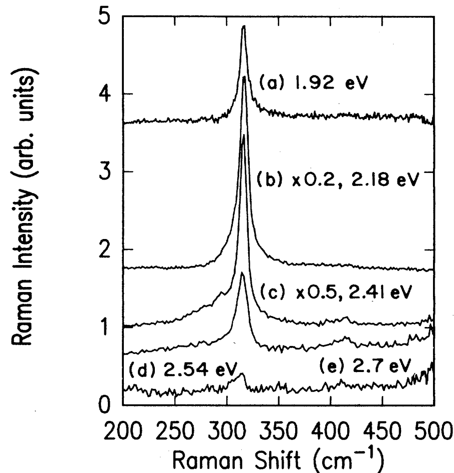

FIG. 1. The Raman spectra of a 11-Å layer of Ge grown in Si(100) excited at a variety of energies between 1.92 and 2.7 eV. The spectra are normalized against the Si substrate scattering.

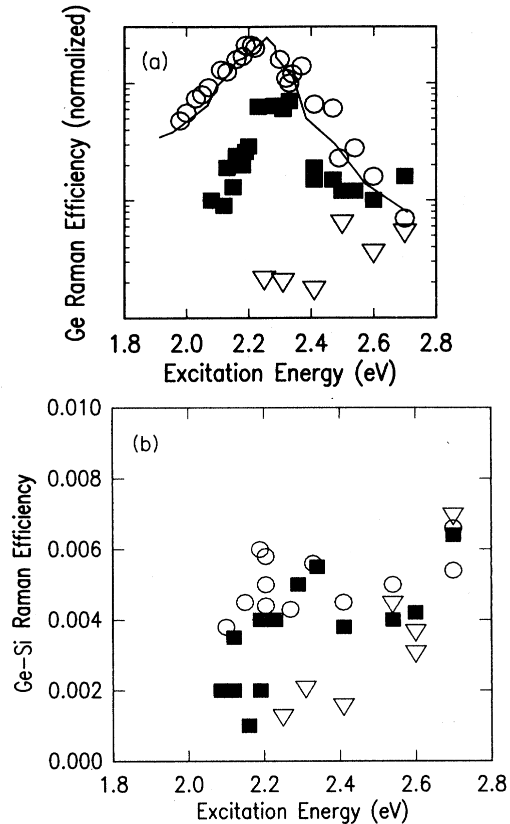

FIG. 2. (a) The excitation energy dependence of $I_{Ge}(\omega)$ for three different thickness Ge layers in Si(100). Open circle, 11 Å; solid squares, 7 Å; open inverted triangles, 4 Å. The resonant Raman profile of bulk Ge is shown as a solid line. (b) The excitation energy dependence of $I_{Ge\text{-}Si}(\omega)$ for three different thickness Ge layers in Si(100). Same symbols as in (a).

between the Ge layer and the Si host.[7,10] Although the Si substrate contribution to the Raman spectra in Fig. 1 has been subtracted, the curves in Fig. 1 are still normalized against I_{Si} from the Si host which shows only a small increase between 1.92 and 2.7 eV.[6] The large enhancement of I_{Ge} near 2.2 eV is clearly seen in Fig. 1.

In Fig. 2(a), we show the excitation wavelength dependence of $I_{Ge}(\omega)$ for Ge layers of three different thicknesses. Also given in this figure is the resonant Raman profile of bulk Ge which is dominated by the three-band term involving the $E_1-E_1+\Delta$ gaps in Ge.[6] Figure 2(a) shows that $I_{Ge}(\omega)$ for 7- and 11-Å-thick Ge samples grown at low temperatures is strongly enhanced for excitation energies between 2.2 and 2.3 eV with a full width at half maximum of about 150 meV. This linewidth is similar to that observed in the bulk. The Raman spectrum of the 11-Å sample is shown in Fig. 1 and the spectrum of the 7-Å sample similarly shows $I_{Ge} \gg I_{Ge\text{-}Si}$ for these excitation energies. $I_{Ge} \gg I_{Ge\text{-}Si}$ is required for well-defined Ge layers with abrupt Ge-Si interfaces.[7,8] The excitation wavelength dependence of the Raman spectra and the Raman spectra themselves in both the 7- and 11-Å samples strongly resembles that of bulk Ge. The resonance Raman profile of the 4-Å-thick sample does not show evidence of a significant resonant enhancement of I_{Ge} near 2.2 eV. The Raman spectrum of this sample is similar to that obtained from $Ge_{0.5}Si_{0.5}$.[9] The resonance Raman profile of the 4-Å Ge layer resembles that measured by Cerdeira, Pinczuk, and Bean for Si/Ge_xSi_{1-x} superlattices where $x \simeq 0.5$,[16] which is consistent with the alloy-like Raman spectrum of this sample.

Figure 2(b) shows the excitation wavelength dependence of $I_{Ge\text{-}Si}(\omega)$ for the above samples. The excitation wavelength dependence $I_{Ge\text{-}Si}(\omega)$ depends on the existence of a well-defined Ge layer. Samples which show a strong enhancement of $I_{Ge}(\omega)$ for excitation energies near 2.2 eV and Raman spectra where $I_{Ge} > I_{Ge\text{-}Si}$ in the visible region, show no similar strong structure in $I_{Ge\text{-}Si}(\omega)$ between 2.2 and 2.7 eV. The 4-Å layer also does not show bulk Ge-like behavior but rather a modest increase in intensity with increasing excitation energies near $E_1-E_1+\Delta$ for a Ge_xSi_{1-x} alloy. This is similar to the behavior observed in Si-Ge alloys. In all cases, we do not observe a strong enhancement of $I_{Ge\text{-}Si}(\omega)$ for excitation energies near 2.25 eV.

Figure 3 shows $I_{Si}(\omega)$ for a $\simeq$10-Å layer of Si in Ge(100) for $2.0 < \hbar\omega < 2.8$ eV. The Raman spectrum of the Ge host is strongly enhanced near 2.25 eV. The Si layer scattering intensity shows a gradual increase with increasing photon energy with no peak near the Ge $E_1-E_1+\Delta$ transition. The corresponding transitions in bulk Si are near 3.4 eV.

Resonant Raman scattering from Si-Ge alloys shows that the ω_{Ge}, ω_{Si}, and $\omega_{Ge\text{-}Si}$ modes are generally enhanced together even though they retain their "localized" identities. This is because the electronic states are delocalized. The failure to observe an enhancement of I_{Si} at the Ge host resonance in Fig. 3 shows that the deformation potentials coupling the Si vibrations to the conduction and valence-band states responsible for $E_1-E_1+\Delta$ in Ge are small. This will occur if the relevant Ge electronic wave functions are excluded from the Si layers. The increase in I_{Si} and $I_{Ge\text{-}Si}$ for energies above 2.6 eV suggests

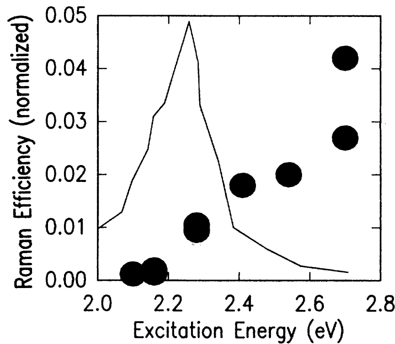

FIG. 3. The excitation energy dependence of I_{Si} for a crystalline Si layer in Ge(100). The solid curve is the resonant behavior of bulk Ge.

that there may be localized Si-Ge–like electronic states introduced by the Si layer.

Our observation of a strong enhancement of I_{Ge} at excitation energies near 2.3 eV in our ultrathin Ge layers can be compared to similar work by Cerdeira and coworkers[16,17] on thicker Ge_xSi_{1-x} layers in Ge_xSi_{1-x}/Si superlattices and ultrathin Ge layers in short-period Ge_n/Si_m superlattices where $4 < (m,n) < 12$. They concluded that their resonant Raman profiles in the thick alloys were dominated by confined E_0 transitions. Comparison of their Ge_n/Si_m superlattice results with theoretical treatments of the electronic band structure of these superlattices suggested to Cerdeira *et al.*[17] in their most recent work that their resonant transitions are like E_1.

Our results from ultrathin Ge quantum wells cannot arise from E_0 transitions of the Ge-Si system. Confinement shifts of the energies of the zone-center states contributing to E_0 move this transition to energies near our observed resonant Raman maximum.[16] Theoretical treatments of ultrathin, short-period Ge-Si superlattices grown on Si(100) show that there can be a Ge-derived E_0 gap near 2.1 eV.[12,14] However, the theoretical treatments show that both the top of the valence band and the Γ_4 and Γ_1 conduction-band states responsible for this transition are delocalized. While our quantum wells must support a single bound hole and single bound electron state near Γ, their small widths (7 Å) and the small masses of the carriers place the bound states at the top of the wells, close to the Si continuum, and well above 2.3 eV. The bound states would have significant tunneling into the host and we would expect to see the simultaneous resonant enhancement of both I_{Ge} and $I_{Ge\text{-}Si}$ in our Ge layers. This is not observed at 2.3 eV.

The electroreflectance results of Chandresekhar and Pollak[18] provide a basis for the identification of the electronic resonance seen in Fig. 2 at 2.3 eV in terms of the Ge-derived E_1 transitions. The [100]-direction uniaxial and hydrostatic contributions to the E_1 gap of Ge have different signs so that the shift of this gap with applied uniaxial stress was small. Extrapolating the results of Ref. 18 to the 4% lattice mismatch of the pseudomorphic growth of Ge on Si predicts that the E_1 gap will be below 1.8 eV and $E_1+\Delta$ gap above 3.0 eV. Since our Ge layers can be as thin as 7 Å there are shifts in E_1 due to confinement effects. The magnitude of the electron and hole potential wells can be estimated from the band alignments of van de Walle and Martin.[19] The Ge conduction-band minimum at L is 1.45 eV above the top of the Si valence band and about 0.20 eV below the Si conduction band at L using the 1.65-eV value of Foreman and Aspnes[20] for the L to Γ conduction-band difference of Si. If $E_1 = 1.8$ eV for epitaxial Ge on Si, the Ge heavy-hole valence band at L will be about 1.3 eV above the Si valence band. In the case of the 200-meV binding energy of the Ge conduction band with respect to the Si states, the $0.11m_0$ [100] mass of the L point conduction-band minimum will result in a single bound state near the top of the well with significant tails in the Si barriers.[12,13] Similarly, the small widths of our Ge layers when combined with the relatively small [100]-direction valence-band masses at the L point will result in large confinement shifts which move the Ge level close to the Si continuum. If E_1 arose from the L point, confinement effects would shift E_1 well above 2.3 eV.

Vina, Logothetides, and Cardona[21] showed that the dielectric function of Ge at $E_1 - E_1+\Delta$ is described by the nearly parallel behavior of the conduction band and the heavy-hole valence band on the line between Γ and L. Therefore, the effects of confinement on the electronic energies must be considered for all wave vectors on the Λ line. While these states can be treated by the effective-mass theorem, the expansion of $E(k)$ for the valence bands will involve both very large masses because of its saddle-point behavior and linear terms in k. These will produce relatively small confinement shifts for the valence-band wave functions. If we assume that the treatment of the conduction band at L applies to the conduction-band states along Λ, our resonant Raman results require that the confinements shifts in the valence band will be about 500 meV for the 7-Å Ge layer. Such shifts would still result in highly localized valence-band wave functions which would be consistent with the localized behavior we need to explain our resonant Raman spectra with the strong enhancement at 2.3 eV of I_{Ge} as compared to $I_{Ge\text{-}Si}$. It would also explain the absence of an enhancement of the Si scattering when the Ge host resonance was excited in Fig. 3. This model would predict that the E_1 gap in the 11-Å layer should be well below 2.2 eV. However, since the layer thickness is close to the critical thickness, inhomogeneities in the strain on the layer would reduce the shift to lower energies due to strain.

In conclusion, we have used resonant Raman scattering in ultrathin Ge and Si layers in Si(100) and Ge(100) to characterize the electronic structure between 1.9 and 2.8 eV in these systems. As in the recent work of Cerdeira *et al.*,[17] we find evidence for Ge localized E_1 transitions in ultrathin Ge layers. The observation of Ge-derived E_1 gaps in Ge layers only 7 Å thick shows how Raman spectroscopy can provide information about the localized electronic states in ultrathin samples. This can be very useful, especially in conjunction with spectroscopic tools such as ellipsometry, since the Raman data provide independent measurements of the critical point energies of the layers, reducing the number of parameters needed to characterize the ellipsometric response of the layers.

[1]M. V. Klein, IEEE J. Quantum Electron. **22**, 1760 (1986).

[2]J. C. Tsang, S. S. Iyer, P. Pukite, and M. Copel, Phys. Rev. B **39**, 13545 (1989).

[3]A. Fasolino, E. Molinari, and J. C. Mann, Phys. Rev. B **39**, 3923 (1989).

[4]S. Adachi, Phys. Rev. B **38**, 12966 (1988).

[5]F. Cerdeira, W. Dreybrodt, and M. Cardona, Solid State Commun. **10**, 591 (1972).

[6]J. B. Renucci, R. Tyte, and M. Cardona, Phys. Rev. B **11**, 3885 (1975).

[7]J. C. Tsang, S. S. Iyer, and S. L. Delage, Appl. Phys. Lett. **51**, 1732 (1987).

[8]S. S. Iyer, J. C. Tsang, M. Copel, P. Pukite, and R. Tromp, Appl. Phys. Lett. **54**, 219 (1989).

[9]M. A. Renucci, J. B. Renucci, and M. Cardona, in *Proceedings of the Second International Conference on Light Scattering in Solids,* edited by M. Balkanski (Flammarion, Paris, 1971), p. 326.

[10]G. M. Zingher, I. P. Ipatova, and A. V. Subashiev, Fiz. Tekh. Poluprovodn. **11**, 656 (1977) [Sov. Phys. Semicond. **11**, 383 (1977)].

[11]E. Molinari and A. Fasolino, Appl. Phys. Lett. **54**, 1220 (1989).

[12]M. S. Hybertson and M. Schluter, Phys. Rev. B **36**, 9687 (1987).

[13]S. Froyen, D. M. Wood, and A. Zunger, Phys. Rev. B **37**, 6893 (1988).

[14]S. Ciraci and I. P. Batra, Phys. Rev. B **38**, 1835 (1988).

[15]J. S. Kline, F. H. Pollak, and M. Cardona, Helv. Phys. Acta **41**, 968 (1968).

[16]F. Cerdeira, A. Pinczuk, and J. C. Bean, Phys. Rev. B **15**, 2127 (1985).

[17]F. Cerdeira, M. I. Alonso, D. Niles, M. Garriga, M. Cardona, E. Kasper, and H. Kibbel, Phys. Rev. B **40**, 1361 (1989).

[18]M. Chandrasekhar and F. H. Pollak, Phys. Rev. B **15**, 2127 (1976).

[19]C. van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986).

[20]R. A. Foreman and D. E. Aspnes, Solid State Commun. **14**, 100 (1974).

[21]L. Vina, P. Logothetides, and M. Cardona, Phys. Rev. B **30**, 1919 (1984).