Resonant Raman Line Shape of Optic Phonons in GaAs/AlAs Multiple Quantum Wells

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We study the dependence of the optic phonon Raman line shape of GaAs/AlAs multiple quantum wells on photon energy and AlAs layer thickness. Broad features due to the forbidden interface modes, observed more strongly for outgoing than for incoming resonance, are induced by elastic scattering of the photoexcited exciton. The interface feature in the GaAs-like phonon region has several minima due to anticrossings of its dispersion with the odd-order confined modes. This corrects previous interpretations of these structures as due to higher even-order confined modes.

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In polar semiconductor heterostructures the phonon modes influenced by the long-range electrostatic field are highly dispersive for propagation away from the layer normal, forming the so-called *interface* (IF) bands [1–3]. These produce broad features in the Raman spectra between the bulk LO and TO frequencies. For GaAs/AlAs systems the IF bands dominate the AlAs optical phonon region of the spectra under resonant photoexcitation conditions [1]. In the GaAs region, however, a complex structure consisting of sharp peaks superimposed on a broad background is observed [4–10]. Those peaks have so far been assigned to even-order confined modes [4]. Here we demonstrate that in fact they are not peaks, but result from minima in the IF feature produced by anticrossings of the IF bands with the *odd* confined modes. We report also that the IF features are more prominent for outgoing than for incoming resonance. This is explained by the photoexcited exciton for outgoing resonance being an extended continuum state and therefore more susceptible to the elastic scattering required to couple to the IF mode.

The dissimilarity of the vibrational frequencies of GaAs and AlAs results in the optic modes of their multiple quantum wells (MQW's) being confined to individual layers, with quantized k vector along the MQW axis, labeled by an integer (m) called the mode order [5]. This leads to a number of so-called *confined* phonon peaks being seen in the Raman spectra, whose frequencies, plotted against their effective k vectors due to confinement, map the bulk dispersion. Models [2,3] which incorporate the quantization of the phonon k vector along the MQW axis reveal that the IF modes evolve out of the m=1 LO and TO confined modes as the in-plane k vector increases and anticross with the other odd-order confined modes, as demonstrated in Fig. 1(a) calculated using Ref. [3].

To investigate the influence of the IF band on the GaAs region of the Raman spectra, we measured MQW's with a systematic variation in the AlAs layer thickness, since such structures have similar GaAs confined phonon but differing IF bands [1]. We chose the GaAs layers to be sufficiently wide to produce narrow spectral features, allowing resolution of incoming and outgoing resonances, while also being narrow enough to observe confined optical modes of different order in the Raman spectra. The layer dimensions determined by x-ray diffraction were 45/22, 46/46, 51/46, and 43/85 Å. Each MQW consisted

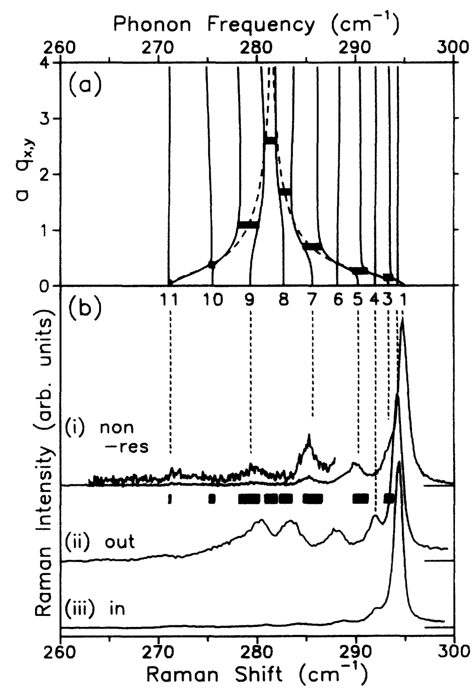

FIG. 1. (a) Calculated dispersion with in-plane k vector ($q_{x,y}$) of GaAs-like optical phonons in a 46/46 Å GaAs/AlAs MQW. The MQW Bloch wave vector is taken as q_z=0.5/(a + b). a and b are the GaAs and AlAs layer widths. The mode order is indicated at $q_{x,y}$=0. Dashed lines plot the IF bands in the absence of mixing with the confined modes. (b) Raman spectra taken on a 46/46 Å GaAs/AlAs MQW with laser energies corresponding to (i) an energy away from any electronic transition, (ii) outgoing resonance with e1-lh1(1s), and (iii) incoming resonance with e1-hh1(1s). (ii) and (iii) were recorded for $z(x,x)\bar{z}$ at 10 K, while (i) was measured for $z(x,y)\bar{z}$ at 80 K. The horizontal bars indicate gaps opened in the IF dispersion [dashed line in (a)] by anticrossings with odd-order confined modes, which produce minima in the resonant Raman spectra.

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of 70 periods and was grown by molecular beam epitaxy on a (001)-oriented GaAs substrate. Raman measurements were performed with the incident and backscattered light propagating normal to the sample surface (z direction) and linearly polarized parallel to the crystal axes (x and y).

Figure 1(b) displays three Raman spectra recorded on the 46/46 Å GaAs/AlAs MQW with different laser energies, corresponding to (i) a photon energy far from any electronic transition, (ii) outgoing resonance with the first electron–light-hole excitonic transition [e1-lh1(1s)] [11], and (iii) incoming resonance with the first electron–heavy-hole exciton [e1-hh1(1s)]. Under nonresonant photoexcitation conditions [Fig. 1(b), spectrum (i)] we, like others [4,5], observe odd-order confined modes in crossed polarization geometry, $z(x,y)\bar{z}$, consistent with the symmetry of the deformation potential interaction Hamiltonians [4,5]. In $z(x,x)\bar{z}$ we observe weak peaks due to LO_2 and LO_4 induced by the Fröhlich interaction (FI). The frequency of these confined mode peaks plotted against their confinement k vector maps the bulk dispersion [5]. The spectrum taken for outgoing resonance is also similar to those reported previously [4–10]. All peaks in Fig. 1(b), spectrum (ii) have been previously assigned to even-order modes, consistent with the symmetry of the FI potentials [4,5]. (The peak at 280.4 cm^{-1} in this MQW has been ascribed to either the IF [1,6,8] or another even-order [9] mode.) We demonstrate later that only the peak near 294.2, and possibly that at 291.9 cm^{-1}, originate from even-order modes (LO_2 and LO_4, respectively). The rest of the structure is due to the IF mode, with the *minima* arising from anticrossings of the IF dispersion with the *odd*-order modes. Selection rules for the FI [4,5] predict the scattering to be parallel polarized; however, we, like others [4,6–8,10,12,13], find a weaker spectrum with similar line shape for crossed polarizations. It is most striking that the structure to lower frequency than LO_2 is much less prominent for incoming [Fig. 1(b), spectrum (iii)] than for outgoing resonance. The incoming resonant scattering is also partially depolarized.

The Raman line shape of the GaAs-like modes for outgoing resonance displays a curious and unexpected dependence on the AlAs layer thickness. Figure 2 shows Raman spectra measured on three GaAs/AlAs MQW's with differing AlAs thicknesses, each recorded for outgoing resonance with e1-lh1. Since these MQW's have similar GaAs layer widths and were grown under identical conditions, their GaAs-like confined modes lie at roughly the same frequencies and have similar linewidths. However, the 45/22 Å MQW does not show the peak near 282 cm^{-1} observed for the other MQW's. We found qualitatively similar behavior for outgoing resonance spectra taken on 28/28 and 28/14 Å GaAs/AlAs structures. The 28/28 Å sample showed three peaks apart from LO_2, while only two were observed for 28/14 Å. The dependence of the GaAs-like line shape on the AlAs-layer thickness suggests it is influenced by the IF mode dispersion, which differs for these MQW's [1].

Figure 3 plots spectra recorded in the AlAs optic phonon region for outgoing resonance with e1-lh1(1s). Each displays a broad feature due to the IF mode between the bulk AlAs LO and TO frequencies of 404 and 360 cm^{-1}, respectively. The relative intensity of the lower- and upper-frequency AlAs-like IF branches for each MQW is in good agreement with that argued [1] from the symmetry of their FI potentials. For MQW's with thicker GaAs than AlAs layers, the lower frequency IF branch is stronger in the AlAs region, while the upper branch dominates in the GaAs region. In contrast, for

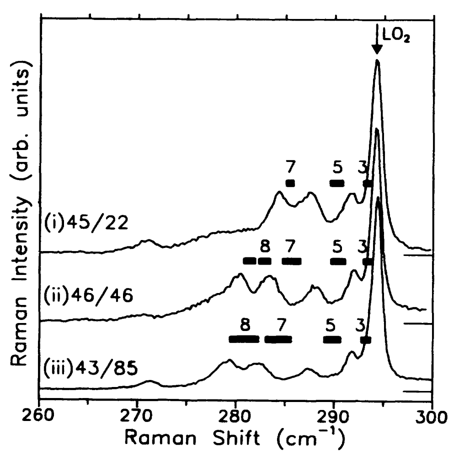

FIG. 2. Raman spectra of GaAs-like optical modes of GaAs/AlAs MQW's with differing layer dimensions, for outgoing resonance with e1-lh1(1s), in $z(x,x)\bar{z}$ geometry and at 10 K. The horizontal bars indicate the calculated gaps in the IF dispersion which produce dips in the Raman spectra.

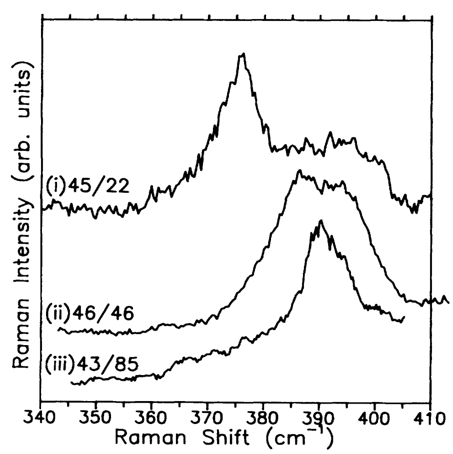

FIG. 3. Raman spectra of the AlAs-like optical modes of the three GaAs/AlAs MQW's, recorded near outgoing resonance with e1-lh1(1s), in $z(x,x)\bar{z}$ polarization and at 10 K. Note the complementary shapes of the spectra to those in Fig. 2 provided one smooths out the peaks and dips seen below 292 cm^{-1}.

MQW's with wider AlAs layers, the GaAs- and AlAs-like phonon regions are dominated by the lower and upper IF branches, respectively. This behavior is apparent in Figs. 2 and 3, where the broad features in the GaAs and AlAs regions have complementary shapes for each MQW. No structure could be resolved in the AlAs-like phonon region for incoming resonance, consistent with the observation for the GaAs region that the IF features are much stronger for outgoing resonance.

We discuss first the observation of IF features in the GaAs and AlAs optic regions. For backscattering normal to the sample surface, the in-plane k vector transferred to the phonon in the simplest three-step Raman process should be zero, forbidding coupling to the IF mode. The fact that we *do* observe the IF mode for outgoing resonance suggests additional elastic scattering in the Raman process, which enables coupling to phonons of finite in-plane k vector ($q_{x,y}$). The origin of this scattering does not alter our conclusions but we suggest it could derive from interface roughness [12], which from the inhomogeneous broadening of the optical transitions [10] is estimated to be about one monolayer. For outgoing resonance, the photocreated state lies in the exciton continuum and has zero in-plane center of mass k vector. We propose that this state dephases rapidly to an excitonic state with finite in-plane center of mass k vector due to elastic scattering, allowing relaxation by the IF mode back to the Brillouin zone center. On the other hand, this coupling is suppressed for incoming resonance where the first intermediate state is the bound $1s$ exciton which dephases more slowly and to states with smaller in-plane center of mass k vectors.

The dominance of a Raman process with finite in-plane phonon k vector over one where $q_{x,y} = 0$ can be argued from the form of the FI potential

$$\phi(\mathbf{r}_e, \mathbf{r}_h, z_e, z_h) = \frac{c_F}{q}\left[\chi(z_e)e^{i\mathbf{q}_{x,y}\cdot\mathbf{r}_e} - \chi(z_h)e^{i\mathbf{q}_{x,y}\cdot\mathbf{r}_h}\right], \qquad (1)$$

where $\mathbf{r} = (x, y)$, χ denotes the phonon envelope function along z, and c_F is the well-known FI constant. For $q_{x,y}$=0, ϕ is independent of $\mathbf{r}_e$ and $\mathbf{r}_h$, so that the electron and hole contributions to the electron-phonon matrix element almost cancel due to their similar extents along z. Furthermore, if we assume the exciton motion along z and in the x-y plane are separable, which is a good approximation in these narrow layers, there can be no scattering between different excitonic states associated with the x-y motion due to their orthogonality, so that only one state can be resonant in the Raman process. In contrast, the in-plane variation in ϕ for $q_{x,y} \neq 0$, removes the cancellation of the electron and hole terms in the electron-phonon matrix element, thanks to their very different extents in the x-y plane. Secondly, the in-plane variation in ϕ also enables scattering between the various excitonic states of the in-plane motion. Hence a triply resonant process involving bound and continuum exciton states can result for outgoing resonance, where the real part of each energy denominator in the well-known perturbation theory expression [5] for the scattering amplitude vanishes, producing strong scattering.

The elastic-scattering-induced FI process explains several other experimental observations. First, the triple resonance produced in the outgoing case, discussed above, explains why it is much stronger than the incoming one. This is evident [12] in the resonance profile of the 51/46 Å MQW, where the outgoing resonance with $e1$-hh1($1s$) is $\sim$ 30 times stronger than the incoming one. Others have also reported stronger outgoing than incoming resonances for both $e1$-hh1($1s$) [13] and $e2$-hh2($1s$) [14,15]. Secondly, the FI-induced Raman intensity observed for crossed polarization geometry, which contradicts the selection rules of the simplest three-step Raman process [4,5], is explained by dephasing to mixed heavy/light-hole exciton states away from the Brillouin zone center [6,7]. Finally, an elastic-scattering-induced process also explained why odd confined modes did not dominate resonant Raman spectra taken on MQW's under applied electric field [10].

We discuss now the shape of the GaAs-like Raman spectra for outgoing resonance [Fig. 1(b), spectrum (ii)] and its unexpected dependence upon the AlAs layer thickness (Fig. 2). This line shape has been ascribed to peaks due to the even-order confined modes on a background caused by the IF band [4–10]. However, with this assignment it is impossible to explain the relative intensities of the peaks and their dependence on AlAs-layer thickness. The form of the FI potential [Eq. (1)] results in the intensity of the LO confined phonons depending on mode order as [10] $\frac{1}{m^2}|M(m)|^2$, for both the simplest and elastic-scattering-induced processes. The electron-phonon matrix element (M) decreases with m for the first electron or hole subbands. This dependence would result in the intensity of the confined modes dropping off rapidly with increasing mode order, as observed in the nonresonant spectrum of Fig. 1(b), spectrum (i). The intensities of the peaks at 294.2 and 291.9 cm^{-1} may be consistent with scattering due to LO_2 and LO_4, respectively, but the lower frequency peaks are too strong for higher even-order modes. Furthermore, if we assign the lower frequency peaks in Fig. 1(b), spectrum (ii) to LO_6, LO_8, and LO_{10}, why is LO_{12} not observed? Also difficult to explain is the observation of fewer peaks in Fig. 2 for the MQW with narrower AlAs layers.

We reinterpret all the intensity, apart from the peak due to LO_2 and part of that due to LO_4, observed in the GaAs-like optic region for outgoing resonance as due to the IF band. This band produces a broad feature between the bulk LO and TO frequencies for outgoing resonance, the intensity of which is modulated by anticrossings of the IF dispersion with the odd-order confined modes. Such anticrossings are illustrated in Fig. 1(a), calculated using a macroscopic model [3,16] for the

46/46 Å GaAs/AlAs MQW. Since the pure odd modes couple only very weakly to electrons, the dominant effect of these anticrossings is to alter the density of states of the IF modes. Gaps opened in the IF mode dispersion produce minima in the broad IF feature. The dips in Fig. 1(b), spectrum (ii) near 292.7, 289.7, and 285.7 cm^{-1} agree well with the calculated gaps (marked by horizontal bars) in the IF dispersion due to anticrossing with LO_3, LO_5, and LO_7, respectively. Notice also the correlation between the size of these gaps and the width of the corresponding minima in the spectra. The lowest frequency dip in Fig. 1(b), spectrum (ii) (near 281.7 cm^{-1}) may be due to the gap between the two IF branches, or, alternatively, to anticrossing with LO_8. (The IF and higher even-order modes also anticross away from zone center [3].) A distinct minimum due to anticrossing with LO_9 is not observed, probably because the IF intensity (in the absence of the mixing) drops sharply in this region. The maxima between the dips in the IF feature coincide with the expected frequencies of the even-order confined modes, explaining why they were previously (and mistakenly) assumed to originate from the even modes. Our interpretation of the line shape observed for outgoing resonance explains why the "peaks" in Fig. 1(b), spectrum (ii) have similar heights. Note that although the IF dispersion in Fig. 1(a) is a function of the MQW Bloch k vector (q_z) as well as $q_{x,y}$, the anticrossings, and hence the dips in the Raman spectra, still occur at the odd-mode frequencies.

Interpretation of this structure as arising from the IF mode also accounts for the dependence on AlAs-layer thickness shown in Fig. 2. For the 45/22 Å MQW the maximum of the IF mode feature is shifted towards the bulk LO frequency in the GaAs-like optic region [1]. This can be inferred from Fig. 3, remembering that the IF features (in the absence of the anticrossing effects) have complementary shapes in the GaAs and AlAs optic phonon region, as discussed earlier. Hence the dip expected near 282 cm^{-1} for the 45/22 Å MQW lies on a falling background and is not discerned. The lack of similar dips in the AlAs region must derive from the fact that the LO branch along [001] is less dispersive for AlAs [8].

In conclusion, we have observed a striking difference between the optic phonon Raman line shapes of GaAs/AlAs MQW's for incoming and outgoing resonance. For outgoing resonance a broad IF feature is induced by elastic scattering of the photoexcited exciton. This dephasing is more significant for outgoing than incoming resonance, since the photoexcited exciton is an extended continuum state. The elastic-scattering-induced process is dominant, because, due to the in-plane variation of the phonon FI potential, (i) the electron and hole contributions no longer cancel so fully and (ii) different excitonic states can be coupled, creating a triply resonant process. The elastic-scattering-induced triple resonance also explains the much stronger outgoing than incoming resonance. Furthermore, the depolarization of the Fröhlich-induced scattering suggests dephasing to mixed light/heavy-hole exciton states away from the Brillouin zone center. We decompose the outgoing-resonant Raman line shape to a peak due to LO_2, possibly another weaker LO_4 peak, and a broad feature caused by the IF mode, which shows several minima due to anticrossings with the odd-order confined modes. This corrects previous interpretations of the latter structure as maxima due to higher even-order modes. Only our assignment explains the relative intensities of the "peaks" and their dependence on the AlAs layer thickness.

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