Relation of resonant Raman line shape to electronic structure in quantum wells

J. E. Zucker
AT&T Bell Laboratories, Holmdel, New Jersey 07733

A. Pinczuk
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

D. S. Chemla
AT&T Bell Laboratories, Holmdel, New Jersey 07733

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We demonstrate the importance of energy-level structure and intersubband exciton-phonon scattering processes in GaAs/$Al_xGa_{1-x}As$ quantum wells through analysis of the resonant Raman profile. In high-quality samples, the intersubband exciton–longitudinal-optical-phonon mechanism appears to dominate over impurity-mediated intrasubband processes.

Resonant Raman scattering has become a widely used method for the study of excitons and phonons in quantum-well heterostructures.[1] The strong dependence of the Raman efficiency on the incident photon energy can be used to provide a detailed spectrum of quantum-well exciton states. In addition to exciton transition energies and widths, the shape of the resonant Raman profile contains information on exciton-phonon scattering. The characteristic profile shows two resonances for each exciton transition: the incoming, when the incident photon energy corresponds to the transition, and the outgoing, when the scattered photon is in resonance. Analysis of the resonant line shape[2] has been used to identify the intermediate electronic states involved in exciton–longitudinal-optic-phonon scattering. Interpretation of the asymmetry of the resonant profile indicated the presence of an exciton transition that is specific to quantum-well heterostructures, i.e., one in which the phonon couples excitons formed from *different* quantum-well subbands. Definitive evidence for intersubband terms in which there is coupling of different subbands via the exciton–longitudinal-optical-phonon interaction appeared in the experiments of Miller *et al.*[3,4] Recently Kauschke *et al.*[5] have proposed an analysis of the asymmetry of the resonant Raman profile which is based on impurity-induced scattering. In this model, no changes in exciton subband occur and both the scattering intensity and the asymmetry of the resonant profile depend strongly on the number of ionized impurities per unit volume n_I. Such an analysis in terms of impurity-induced intrasubband scattering also makes a prediction which is easily tested by experiment: namely, that the outgoing resonance will always be stronger than the incoming one in both two- and three-dimensional systems.[5] Our own data[6] clearly shows that this is not the case.

In this Brief Report we present new resonant Raman data from high-quality multiple-quantum-well samples which cannot be interpreted in terms of the theory of Kauschke *et al.*[5] We show instead that our data can be understood in terms of relatively simple and general considerations of resonant Raman scattering mediated by exciton–longitudinal-optic-phonon processes in semiconductor quantum wells.

Figure 1 shows the resonant Raman profile for the $n=2$ exciton in a modulation doped p-type GaAs/$Al_{0.51}Ga_{0.49}As$ multiple-quantum-well heterostructure with 112 Å quantum wells. The asymmetry between the incoming resonance (at 1.624 eV) and the outgoing resonance (at 1.660 eV) is strikingly similar to that observed for the $n=2$ exciton in undoped samples.[2,5] The measured mobility in this sample is $\mu=5.4\times10^4$ cm^2/V sec. In order to have such a high hole mobility, the background impurity concentration in the quantum well n_I must be less than 5×10^{15} cm^{-3}.[7] However, for this concentration the theory of Ref. 5 predicts a nearly symmetric resonance. In order to explain the asymmetry shown in Fig. 1, the model of Kauschke *et al.*[5] would

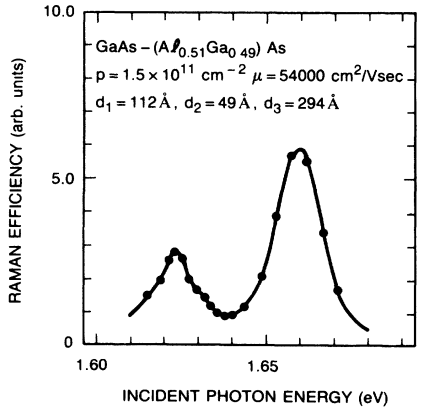

FIG. 1. Resonant Raman profile for the $n=2$ exciton in a Be-doped GaAs/$Al_xGa_{1-x}As$ heterostructure. The undoped quantum wells of thickness d_1 are separated from the doped layers of thickness d_2 by spacers of thickness d_3.

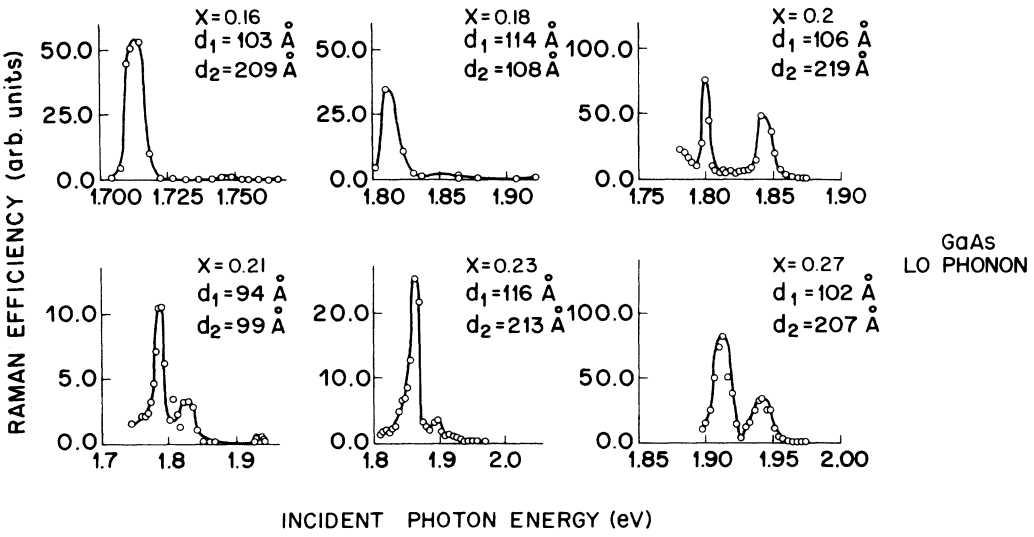

FIG. 2. Resonant Raman profiles for scattering of the E_{X1} exciton by the GaAs LO phonon in six GaAs/$Al_xGa_{1-x}As$ multiple quantum well samples with well thickness d_1 and barrier thickness d_2.

necessitate a density of at least $n_I = 5\times10^{16}$ cm^{-3}, which is clearly incompatible with this sample.

We now consider Raman data resonant with higher-lying quantum-well exciton states which suggests an alternative interpretation for the results shown in Fig. 1. Figure 2 shows Raman profiles for six high-quality undoped multiple-quantum-well samples which represent a wide range of $Al_xGa_{1-x}As$ barrier heights and widths. In each case, the incident photon energy $h\nu_L$ is near resonance with the first delocalized exciton transition E_{X1}, an exciton state which is formed from the first continuum electron and hole energy levels and which spatially extends into the $Al_xGa_{1-x}As$ barriers.[6] Thus Raman scattering resonant with this exciton yields resonant profiles for the GaAs longitudinal-optical (LO) phonon (Fig. 2) and for the GaAs-like $Al_xGa_{1-x}As$ phonon LO_1 (Fig. 3).

Figure 2 shows that for scattering by the GaAs LO phonon, the incoming resonance is larger than the outgoing in all six samples. This is notable for two reasons. First, the asymmetry is opposite to that observed for the $n=2$ exciton, as can be seen from Fig. 1 of this paper and the figures of Refs. 1, 5, and 8. This dominance of the incoming resonance cannot be accounted for at all in the model of Kauschke *et al.*[5] Second, comparison with Fig. 3 shows that in the same sample for the same exciton the asymmetry in the $Al_xGa_{1-x}As$ LO_1 resonant profile can be reversed from that of the GaAs LO. In fact, we find

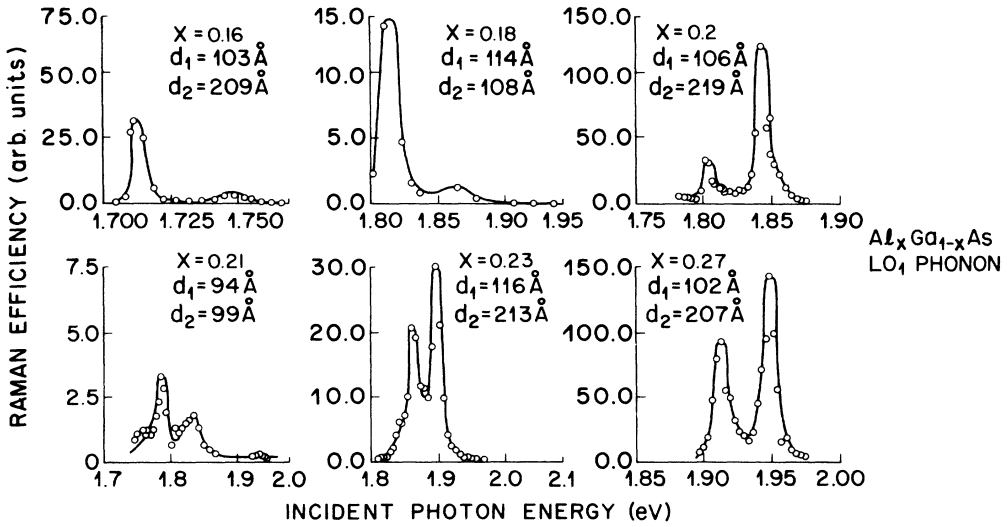

FIG. 3. Resonant Raman profile for scattering of the E_{X1} exciton by the $Al_xGa_{1-x}As$ LO_1 phonon in the same samples as in Fig. 2.

that in the case of the delocalized exciton transition the type of asymmetry is closely correlated with variation of sample parameters.

Among the various types of electron-phonon scattering which can contribute to the resonant Raman intensity, the role of wave-vector-nonconserving processes, both inter- and intrasubband, depends on the defect concentration. Thus it is difficult to make general assumptions about the relative strength of these matrix elements as compared to those describing wave-vector-conserving scattering. Among wave-vector-conserving processes, both intrasubband scattering, treated by Manuel *et al*,[8] and intersubband scattering should be considered. In the following, we adopt a semiempirical approach to the problem of Raman scattering via the intersubband electron-phonon interaction, which is prompted by the two striking features of the resonant Raman spectra of our samples which did not appear in the experiments of Manuel *et al.*:[8] first, the close correlation of sharp structure in the resonant Raman profile to excitonic transitions associated with specific electron and hole subbands, and second, the reversals in asymmetry which are described above.

In the framework of intersubband exciton-phonon scattering,[2] the asymmetry between incoming and outgoing resonances is simply and directly related to the exciton-phonon scattering channels. The outgoing resonance dominates for transitions to higher-energy states, while the incoming resonance dominates for transitions to lower energy states. By making the simplifying assumption that only two excitonic levels are involved in the scattering, we are able to fit the resonant profiles of Figs. 2 and 3 to the expression for the Raman intensity given by third-order perturbation theory,[2]

$$I(h\nu_L)=A\left|\frac{1}{(h\nu_L-E_{X1}-i\Gamma)(h\nu_L-h\nu_{\mathrm{LO}}-E-i\Gamma)}+\frac{1}{(h\nu_L-E-i\Gamma)(h\nu_L-h\nu_{\mathrm{LO}}-E_{X1}-i\Gamma)}\right|^2, \tag{1}$$

where $h\nu_{\mathrm{LO}}$ is the appropriate LO phonon energy (GaAs or $Al_xGa_{1-x}As$), E is the energy of the second exciton state, Γ is the inhomogeneous linewidth of the excitonic transitions, and A is a normalization constant. The only adjustable parameters in the fit are A and E. Although we treat E as an adjustable parameter, this model can only be justified in the case where E corresponds to the energy of an excitonic transition of the quantum well. A typical fit to the data shown in Fig. 4, where Eq. (1) is plotted for $E_{X1}=1.913$ eV and $E=1.8$ eV for the GaAs LO resonant profile and $E=2.25$ eV for the $Al_xGa_{1-x}As$ LO_1 resonant profile. The results of the fits for all six samples are shown in Table I. Breakdown of wave-vector conservation by defects could also be treated in this model by going to higher-order perturbation theory. Anomalous polarization selection rules have shown that wave-vector-nonconserving processes contribute to Raman scattering at the $n=1$ heavy-hole–exciton resonance.[4] These may play a role for higher-lying exciton states. In addition, we have neglected a number of other scattering channels, including transitions to light-hole subbands. We have used the simplified expression (1) to emphasize the role of quantum-well electronic structure and its dependence on sample properties such as layer thicknesses and Al concentration in determining the asymmetry of the resonant profile.

We find that in samples with high or wide $Al_xGa_{1-x}As$ barriers, the asymmetry in the $Al_xGa_{1-x}As$ resonant profile is reversed from that of the GaAs, indicating scattering of the delocalized exciton by the LO_1 phonon to states of higher energy. In these cases, the result of the fit E roughly corresponds to the next delocalized exciton transition E_{X2}, as calculated using a Kronig-Penney model of the superlattice potential. However, decreasing the height or width of the barrier causes the asymmetries in the GaAs and $Al_xGa_{1-x}As$ resonant profiles to become the same. This reflects a coupling of the delocalized exciton to the excitons formed from the bound states of the quantum well. Only when barriers are low or narrow can these lower-lying states penetrate the $Al_xGa_{1-x}As$ layers and couple to E_{X1} via the dipole moment of the LO_1 phonon. The electron and hole contributions to the matrix element of the Frohlich exciton-phonon interaction have opposite sign. Therefore the magnitude of the calculated matrix element de-

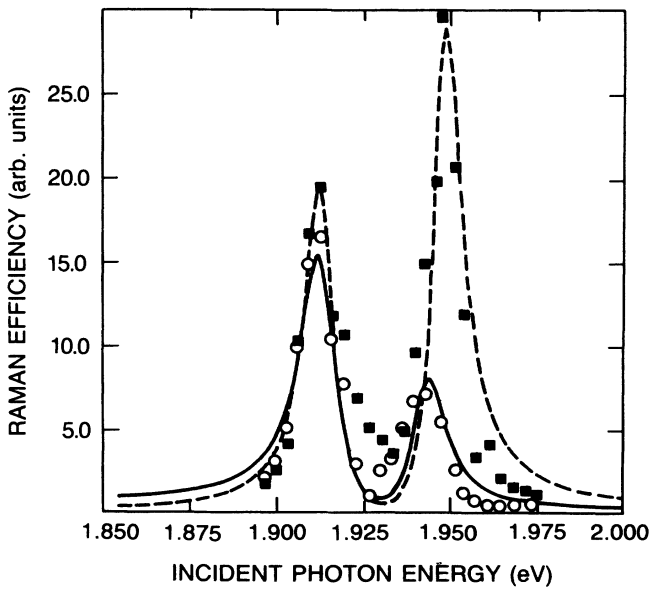

FIG. 4. Reversal of asymmetry in resonant profiles of E_{X1} exciton in the 102 Å quantum-well sample. For the GaAs LO phonon data are shown by open circles and the fit using Eq. (1) is shown by the solid line; for $Al_xGa_{1-x}As$ LO_1 phonon solid squares are data and the dashed line is the fit.

TABLE I. The results for the fits for all six samples. HH represents the heavy-hole exciton resonance.

			E (eV)				
d_1 (Å)	d_2 (Å)	x	$n=1$ HH	$n=2$ HH	$n=3$ HH	E GaAs phonons	E $Al_xGa_{1-x}As$ phonons
102	207	0.27	1.550	1.660	1.80	$n=3$ HH	2.25 eV
94	99	0.21	1.550	1.662	unbound	$n=2$ HH	$n=2$
116	213	0.23	1.540	1.626	1.752	$n=3$ HH	2.21 eV
106	219	0.2	1.550	1.63	1.750	$n=1$ HH	1.91 eV
103	209	0.16	1.540	1.633	unbound	$n=2$ HH	$n=2$
114	108	0.18	1.539	1.622	1.724	$n=3$ HH	$n=3$

pends critically on the accuracy of the electron and hole wave functions. A full calculation of quantum-well intersubband exciton-phonon matrix elements with the inclusion of valence-band mixing[9] remains a theoretical challenge.

In conclusion, we find that the asymmetries in the resonant Raman profile consistently reflect the coupling of the delocalized exciton to other excitons via the exciton–LO-phonon interaction. In scattering by GaAs phonons, transitions from the extended state to the lower quantum-well states are always favored. However, transitions via the $Al_xGa_{1-x}As$ phonons may occur to higher or lower states, depending on the degree of confinement of the lower states. This can naturally result in the dominance of the incoming resonance, a circumstance not easily accounted for in the framework of impurity-assisted scattering.[5] In doped samples, we find much the same resonant Raman profile as in undoped multiple quantum wells for the $n=2$ exciton. However, in these doped samples we are able to obtain through mobility measurements an upper limit on the number of ionized impurities in the quantum well. We have shown here that this number is much too small to account for the observed asymmetry within the model of Kauschke *et al.*[5] On the other hand, we have successfully interpreted the asymmetry of the resonant profile in terms of intersubband exciton-phonon scattering processes.[2]

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