Delocalized excitons in semiconductor heterostructures

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A delocalized exciton state is revealed by resonant Raman scattering in GaAs-AlGaAs multiple-quantum-well heterostructures where only lower energy, confined quasi-two-dimensional excitons had previously been observed. In spite of its extension across the abrupt GaAs-AlGaAs interface, the delocalized exciton remains a well-defined state inhomogeneously broadened to widths between 6 and 14 meV. We estimate an exciton binding energy greater than 2 meV. Scattering of the delocalized state by the exciton-optical phonon interaction results in transitions to both delocalized and quasi-two-dimensional localized excitons.

GaAs-$Al_xGa_{1-x}As$ quantum-well heterostructures are currently attracting much interest as systems which display quasi-two-dimensional (quasi-2D) electronic properties. Confinement of electron and hole wave functions to the GaAs quantum well results in a quasi-2D exciton behavior which is fundamentally different from that of bulk GaAs. The effects of confinement include the quantization of energy levels,[1] the enhancement of intrinsic over extrinsic recombination,[2] and a substantial increase in exciton binding energy.[3] Other related quasi-2D phenomena are the persistence of exciton behavior at room temperature,[4] the tunability of exciton properties with electric field,[5,6] the decrease of carrier lifetime in quantum wells,[7] and the existence of virtual bound states.[8]

In this paper we present the first evidence which shows that the same GaAs-(AlGa)As multiple-quantum-well heterostructures which exhibit quasi-2D exciton behavior also support extended, or delocalized, exciton states. Unlike the confined excitons, which are formed from the bound states of the GaAs potential well, the extended excitons are composed of higher-energy electron and hole continuum states which range throughout the whole multilayer heterostructure. We show that these higher-energy states can be interpreted in terms of the Kronig-Penney model as the unbound states of the well. While in the quasi-2D case the exciton envelope function nearly vanishes at the interface, the envelope function for the extended exciton continues undiminished in amplitude across the boundary between GaAs wells and AlGaAs barriers. Thus, delocalized exciton formation requires that correlation of electron and hole is not destroyed by the abrupt interface between two semiconductors of different composition and band gap. It is therefore most surprising that this excitation remains a narrow well-defined state.

The extended exciton transitions occur in the neighborhood of the AlGaAs band gap. In this energy range there is already large absorption due to lower-lying excitons associated with confined states of the GaAs quantum wells. Thus, detection of the delocalized excitations by either luminescence or absorption spectroscopy is difficult. Clear observation of the delocalized exciton was made possible by the use of resonant Raman scattering, a method which exploits the modulation of optical properties by lattice vibrations in order to reveal exciton behavior. When the exciton envelope function extends across the interface the observation of both GaAs and AlGaAs phonons in the Raman spectrum provides direct evidence of the degree of exciton confinement. In addition, Raman scattering brings out the significant differences between quasi-2D and delocalized exciton-optical phonon interactions.

The height and width of the $Al_xGa_{1-x}As$ barrier strongly determine both the confinement of the well-bound quasi-2D excitons and the energy dispersion of the delocalized exciton. We studied several samples grown by molecular-beam epitaxy, all having GaAs quantum-well widths $d_1 \sim 100$ Å but differing in $Al_1Ga_{1-x}As$ barrier thickness (50 Å $< d_2 <$ 200 Å) and in Al content ($0.15 < x < 0.3$). The total thickness of multiple-quantum-well structure ranged from 1.5 to 2.7 μm. Raman measurements were made on samples at $T \lesssim 2$ K in the $z(x',x')\bar{z}$ backscattering configuration, with $z \parallel (001)$ perpendicular to the layers and x' along one of the (011) directions. It was checked that the spectra in this configuration were essentially the same as those taken in the $z(x,x)\bar{z}$ geometry [x along (100) or (010)], where only forbidden LO scattering due to the Fröhlich interaction is present. This suggests that forbidden scattering is dominant and that interference effects with allowed deformation-potential scattering as described by Menendez and Cardona[9] are small.

Figure 1 shows the typical Raman scattering efficiency from a quantum-well heterostructure as a function of incident laser energy. The three phonons observed are the LO mode of bulk GaAs and the GaAs-like and AlAs-like LO modes of bulk $Al_xGa_{1-x}As$.[10] The large resonances below 1.8 eV are present only in the resonant profile of the GaAs phonon and are associated with excitons formed from the lower bound states of the GaAs quantum well.[11] In this sample such states do not significantly penetrate the $Al_xGa_{1-x}As$ barriers and are not expected to interact with $Al_xGa_{1-x}As$ phonons. However, the features above 1.8 eV appear in the resonant profiles of both $Al_xGa_{1-x}As$ and GaAs phonons with comparable scattering efficiency. The

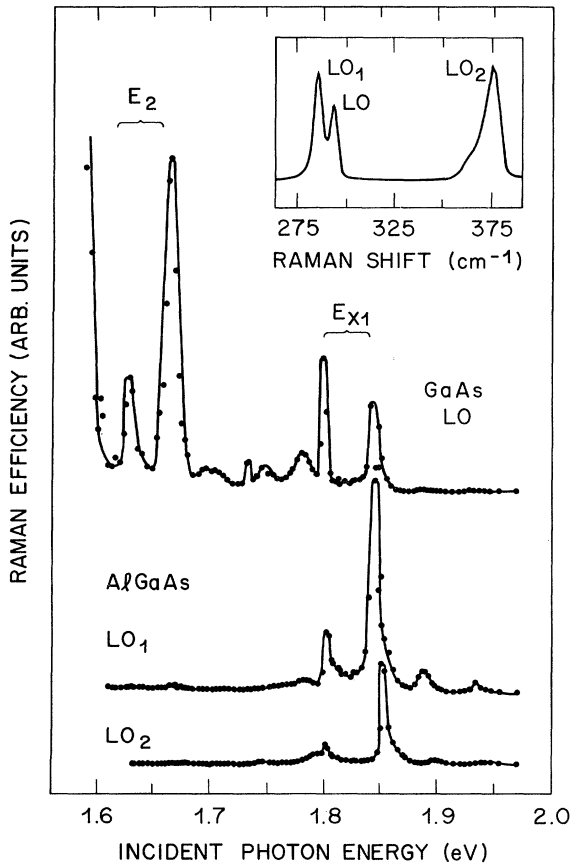

FIG. 1. Resonant Raman profiles from the LO phonons of a GaAs-$Al_{0.2}Ga_{0.8}As$ heterostructure ($d_1 = 106$ Å, $d_2 = 219$ Å). The insert is the Raman spectrum at 1.85 eV, showing the GaAs (LO) and AlGaAs (LO_1, LO_2) lines. The incoming and outgoing resonances for the confined $n = 2$ exciton (E_2) and the first extended exciton (E_{x1}) are indicated.

sudden onset of scattering by the vibrations of both layers implies that these resonances represent extended states which are not confined to the GaAs quantum wells. Excitonic intermediate states, rather than band-to-band transitions, are indicated by the presence of characteristically narrow resonant doublets. In each doublet the incoming resonance, which reflects the exciton transition energy, is accompanied by an outgoing resonance one LO phonon energy above. This sharp excitonic structure appears to be in contrast to previous investigations of GaAs-AlGaAs quantum-well heterostructures where resonances in this energy range were single broad features and attributed to the GaAs $E_0 + \Delta_0$ band gap.[12,13]

Structure at E_{x1} is also found in the absorption spectra of samples where the substrate had been removed with minimal stress.[14] In contrast to the sharp peaks of the confined quasi-2D excitons,[1,15] the delocalized exciton peak is barely resolved from the rising absorption continuum. Although the structure is much less pronounced than the corresponding Raman resonance, the energies are in excellent agreement. From the absorption line shape we estimate[16,17] an exciton binding energy larger than 2 meV. From the widths of the Raman resonances we obtain the broadening of the transitions. These widths are in the range $6\ \text{meV} < \Gamma_{x1} < 14$ meV, several times larger than that of the lowest $n = 1$ quasi-2D exciton, but comparable to the widths of the $n = 2$ and $n = 3$ excitons.[11]

Figure 2 displays additional evidence that the excitation we observe is unrelated to the $E_0 + \Delta_0$ gap. Here, the energy of the incoming resonance for the first extended state E_{x1} is plotted as a function of Al content for six samples. In the extrapolated limit of $x \rightarrow 0$ this energy clearly approaches that of the GaAs band gap, 1.519 eV, indicating that the transition is closely tied to the $Al_xGa_{1-x}As$ band gap. The characteristics of the E_{x1} transition—the narrowness of the state, its dependence on the barrier height, and its delocalized behavior—indicate that this resonance represents an exciton formed from the first continuum levels above electron and hole potential wells.

The assignment of E_{x1} is also supported by a calculation of transition energies in the Kronig-Penney model. The inputs to the calculation are d_1 and d_2, determined to better than 5% accuracy,[18] and x which can be deduced to within $\sim 5\%$ from the separation of the GaAs and $Al_xGa_{1-x}As$ LO phonon frequencies. Values for the effective masses and energy band discontinuities are taken from Dingle.[15] In Fig. 2 the predicted energy of the lowest delocalized exciton (i.e., that formed from the first electron and hole states above the barrier) is plotted as a function of x for the hypothetical samples $d_1 = d_2 = 100$ Å and $d_1 = 100$ Å, $d_2 = 200$ Å. The difference in energy between delocalized light and heavy holes is typically only a few meV and thus is within our experimental error. The jump in the energy as the barrier height is increased ($x \gtrsim 2$) reflects the capture of the lowest delocalized state by the well. Using the Krönig-Penney model we calculate that local variations in layer thickness as small as one monolayer can result in inhomogeneous widths for the E_{x1} delocalized excitons in our sample between 3 and 22 meV, in good agreement with the observed values.

We now consider the scattering of the delocalized exciton into other exciton states by optical phonons. It has been shown that the asymmetry between incoming and outgoing

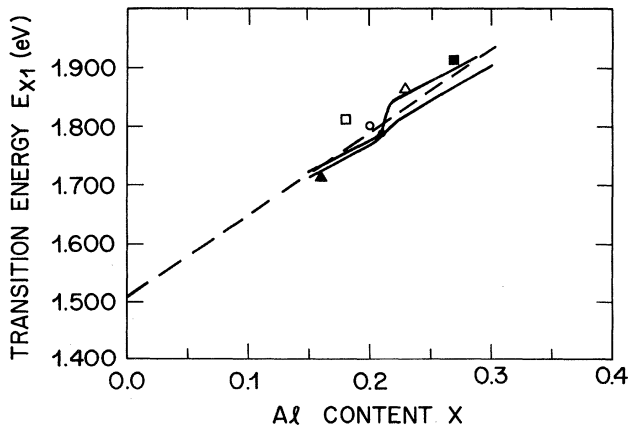

FIG. 2. Delocalized exciton transition energy as a function of Al fraction x. Data points correspond to the following samples: ▲ $d_1 = 103$ Å, $d_2 = 209$ Å; □ $d_1 = 114$ Å, $d_2 = 108$ Å; ○ $d_1 = 106$ Å, $d_2 = 219$ Å; ● $d_1 = 94$ Å, $d_2 = 99$ Å; Δ $d_1 = 116$ Å, $d_2 = 213$ Å; ■ $d_1 = 102$ Å, $d_2 = 207$ Å. Solid lines show the transition energies predicted by the Kronig-Penney model with $d_1 = d_2 = 100$ Å (upper curve) and $d_1 = 100$ Å, $d_2 = 200$ Å (lower curve). The dashed line is a linear fit to the data showing the value extrapolated to $x = 0$.

resonances can be used to determine exciton-phonon scattering channels. Although many states are expected to contribute to the total scattering amplitude, it is possible to fit the resonant profile by including only two exciton levels. The outgoing resonance dominates for transitions to higher-energy states, while the incoming resonance is the strongest when the final state is of lower energy.[11] Let us apply this to the resonant profiles for the delocalized excitons of two different samples shown in Fig. 3.

The sample in part (a) has $x = 0.27$ and hence a high barrier while the sample in part (b) has $x = 0.16$; d_1 and d_2 are similar for the two samples. In (a) the incoming resonance with the GaAs phonon is larger than the outgoing resonance. This indicates that GaAs phonons induce scattering from the delocalized exciton to states of lower energy confined in the quantum wells. When the two-level fit is applied to the GaAs profile, the energy of this lower state is found to be that of the $n = 3$ exciton: 1.74 eV. However, we see that the asymmetry is reversed in both AlGaAs profiles, where the larger outgoing resonances imply transitions from the extended state to states of even higher energy. When the two-level fit is applied to the AlGaAs profiles, 2.25 eV is obtained as the energy of the second level. The above pattern, in which the AlGaAs and GaAs asymmetries are reversed, is observed in all samples with high and wide barriers. However, decreasing the barrier height or width causes the asymmetries in the GaAs and AlGaAs resonant profiles to become the same. This is explained by the fact that only when barriers are low or narrow can quantum-well states with the energies below the barrier height penetrate the AlGaAs layer. Then the delocalized exciton can scatter via the AlGaAs phonons to these lower levels. Such behavior is visible in the AlGaAs resonant profiles of (b), and in all samples with $d_2 \lesssim 100$ Å. From the two-level fit for (b) we find that scattering by *both* the GaAs and the AlGaAs phonons results in transitions from the delocalized exciton to the $n = 2$ exciton at 1.63 eV. Thus, asymmetries in the resonant Raman profile are found to consistently reflect the coupling of the delocalized exciton to other excitons by the exciton phonon interaction. In scattering by GaAs phonons, transitions from the extended state to the lower quantum-well states are favored. However, transitions via the AlGaAs phonons may occur either to higher or lower states, depending on the degree of confinement of the lower states.

In summary, we have used resonant Raman scattering to identify a delocalized exciton in multiple quantum-well heterostructures. Unlike the low-lying confined quasi-2D excitons this excitation involves extended, superlattice-type conduction and valence-band states. The delocalized nature of this exciton provides a possible means for the propagation of elementary excitations along the superlattice axis. In the present work we have observed the coupling of the extended state to other excitons by the exciton-optical phonon interaction. We have shown that variation of sample parameters in this system, through their strong influence on the localization of quasi-2D states, can be used to adjust the strength of delocalized-to-localized transitions.

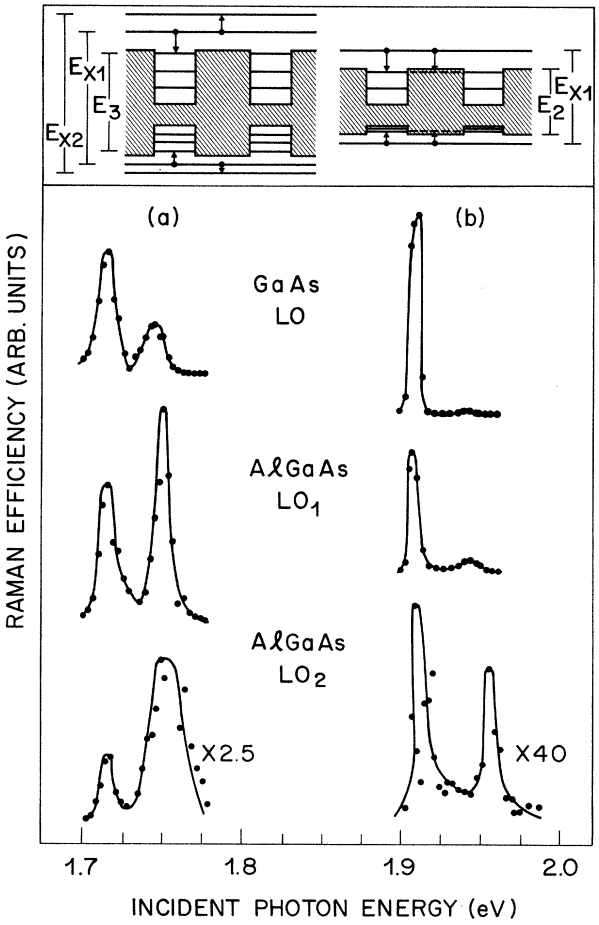

FIG. 3. Resonant profiles of the first extended exciton from quantum wells with (a) $d_1 = 102$ Å, $d_2 = 207$ Å, $x = 0.27$ and (b) $d_1 = 103$ Å, $d_2 = 209$ Å, $x = 0.16$.

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