RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 8 15 MARCH 1989-I

Phonon sideband of photoluminescence as a probe of exciton states in a quantum well

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(Received 6 December 1988)

We report a novel technique to probe the length scale of exciton localization, by disorder, in semiconductor quantum wells (QW's). The method is based on the study of longitudinal-optic (LO) phonon satellites of exciton photoluminescence. It is applied to the (In,Ga)As/InP QW system, in which we observe coupling to LO modes of both (In,Ga)As and InP. For a QW with weak disorder, in a magnetic field, the method probes the most localized states of the quantum Hall system.

We present a new method to characterize luminescent excitons in direct-gap quantum wells (QW's) using measurements of both the longitudinal-optic (LO) phonon satellites[1,2] of exciton photoluminescence (PL) and the exciton energy, as a function of magnetic field B normal to the QW. We propose a theory which relates the satellite strengths to the length scale of exciton localization, by disorder, in the plane of the QW. When the disorder is weak, the method probes the most localized states of the quantum Hall (QH) system. Phonon satellites of exciton PL[1,2] arise from the electron-phonon interaction, which is manifested in many other properties of semiconductor heterostructures, including the polaron mass enhancement,[3,4] magnetophonon resonance (MPR),[5,6] Raman scattering,[7] hot carrier relaxation,[8] optical absorption,[9] and resonant tunneling.[10]

The experiments were performed on a sample containing five nominally lattice matched (In,Ga)As QW's with thicknesses $d=110$, 50, 28, 20, and 10 Å, grown in that order on the same InP substrate, and separated by 1000-Å layers of InP. The sample was grown by solid-source molecular-beam epitaxy (SSMBE)[11] using a cooled shutter assembly on each group-V cracker cell, and special pumping techniques to control the phosphorous vapor pressure.[11] PL was excited by ~ 50 mW cm^{-2} of 5145-Å Ar^+ laser light and measured at 4.2 K for $B \leq 9.6$ T. The PL spectrum for each QW consists of a single strong peak X due to exciton recombination,[11] and weak LO phonon satellites X_m at energies $\hbar\omega_m$ below X (Fig. 1). Figure 1 shows a strong trend from coupling to barrier modes for the narrow QW's to coupling to well modes for the wide QW's. A similar variation has been found in MPR experiments.[5] Coupling to LO modes of both the well and the barrier has also been observed in Raman scattering.[7]

The Stokes shifts[12] for the 110- and 50-Å QW's[13] show that the luminescent excitons are extrinsic and are bound to defects in the structure. The theory[14] of the phonon satellites of the allowed recombination of a bound state near the band edge of a direct-gap polar semiconductor is a special case of the "accepting mode" mechanism,[15] and for a loosely bound exciton involves coupling only to the polar LO phonons. LO phonon satellites arise from the polarization of the lattice by the localized exciton, i.e., from the relaxation of the LO modes due to the interaction of the electron and hole charges with the crystal ions. For the LO phonon satellite of a bound exciton (BE) in

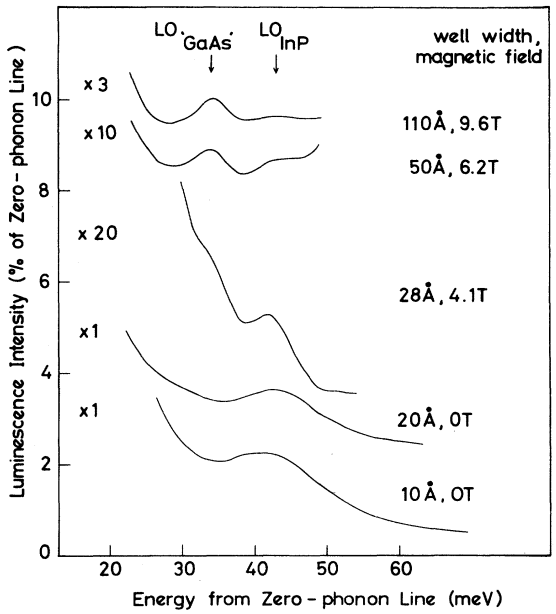

FIG. 1. PL spectra of (In,Ga)As/InP QW's, for photon energies below the exciton zero-phonon line X. Phonon satellites X_m are observed at the known Raman energies of GaAs-like LO modes in $In_{0.53}Ga_{0.47}As$ and of LO modes in InP, marked by vertical arrows. The sloping background spectrum is the disorder-induced low-energy tail of X. For clarity, the different spectra are vertically offset. Phonon satellites are not observed at $B=0$ for the 50- and 110-Å QW's and, though present at $B=0$ for the 28-Å QW, are clearer at $B=4.1$ T. The overall strength of the phonon sideband is approximately proportional to B in the 50- and 110-Å QW's, but the intensity ratio of the two satellites in any QW is comparatively insensitive to B.

three dimensions, Hopfield[14] has calculated the intensity ratio S of the one-phonon line to the zero-phonon line. His results may be manipulated[16] to show that $S=r_sQ$, where the "coupling radius" $r_s=\pi^{-1/2}\alpha r_p$,

$$Q=\frac{4\pi^{3/2}}{e^2}\int d^3r\,|\mathbf{D}(\mathbf{r})|^2, \tag{1}$$

and $\mathbf{D}(\mathbf{r})$ is the electric displacement due to the exciton charge $-en(\mathbf{r})$. α is the Fröhlich parameter and r_p is the polaron radius. The length r_s is a measure of the polarizability of the lattice. Q is an inverse length which characterizes $n(\mathbf{r})$; Q is large if $n(\mathbf{r})$ includes a compact charge. Thus S is related to the length scale of binding.[14] In two-mode alloys, S for each LO branch is the product of r_s for that branch[2] and Q. r_s is 1.50 Å for the GaAs-like LO modes of $In_{0.53}Ga_{0.47}As$, and 2.17 Å for InP.[2]

We calculate S in the adiabatic approximation using a result[15] that applies for any form of linear electron-phonon coupling to harmonic accepting modes of frequency ω_m: $\hbar\omega_m S$ for these modes is equal to $|\Delta E_m|$, the difference, between the initial and final electronic states, of the relaxation energy of these modes. Hopfield's calculation[14] uses the Fröhlich Hamiltonian H_F, which expresses the electrostatic interaction of an electron with the lattice. In contrast, we use electrostatics directly to evaluate ΔE_m without using H_F as an intermediate step. The form of Eq. (1) can now be understood. The lattice relaxation energy per unit volume is proportional to the square of the distortion, and hence to D^2, the integrand in Eq. (1).

The polar LO modes of a QW (Ref. 17) form a band close to each bulk LO (Γ) frequency $\omega_{m\lambda}$ of each material m [$m=w$ for well material, b for barrier; for (In,Ga)As λ = InAs-like, GaAs-like]. Every band produces a phonon satellite, whose strength $S_{m\lambda}$ is the sum of unresolved contributions from each mode within the band. The InAs-like satellite[2] is not resolved in the present work because of its small r_s and proximity to the GaAs-like satellite, so the subscript λ will be dropped.

The distortion of the lattice by $n(\mathbf{r})$ is approximated with a continuum model. We find $\mathbf{D}(\mathbf{r})$ from $n(\mathbf{r})$ using the Coulomb law, neglecting the $\sim$10% difference in dielectric constant between (In,Ga)As and InP. In each material, the lattice distortion is proportional to $\mathbf{D}(\mathbf{r})$, these quantities having the same ratio as in the bulk.[17] Hence the distortion energy of material m is $\bar{S}_m\hbar\omega_m$, where $\bar{S}_m=r_{sm}Q_m$, r_{sm} is the coupling radius for m, and

$$Q_m=\frac{4\pi^{3/2}}{e^2}\int_m d^3r\,|\mathbf{D}(\mathbf{r})|^2. \tag{2}$$

$\bar{S}_m$ is equal to S_m, the strength of the phonon satellite for the polar LO band close to ω_m, only if every mode in the band has frequency ω_m, and is confined to m. This is a good approximation: In microscopic theories,[18] the modes in the band close to ω_m are either confined to m or, like interface modes,[17] have fields in all materials but have the largest distortions in m. Thus we assume $S_m=\bar{S}_m$. S_m has a simple dependence on $\mathbf{D}$, so we can use elementary electrostatics to interpret the dependence of S_m on $n(\mathbf{r})$.

We calculated Q_m from Eq. (2) using effective-mass theory for the BE. $n(\mathbf{r})$ is the sum of electron and hole terms $n_e(\mathbf{r}),n_h(\mathbf{r})$. We assume that the electron and hole are each restricted to a single subband. Thus $n_a(x,y,z)=n_{1a}(x,y)n_{0a}(z)$ $(a=e,h)$, where the z axis is normal to the QW. The n_{0a} are calculated in the envelope-function approximation with a single parabolic valence band, and the n_{1a} are modeled as normalized Gaussians with variances $\langle x_a^2\rangle=\langle y_a^2\rangle=\sigma_a^2$. σ_e,σ_h are the radii of localization about the exciton binding center of the electron and hole charges, respectively. Our models for $n(\mathbf{r})$ and the electron-phonon interaction suffice to describe the important physical effect, i.e., the polarization of the lattice by the localized exciton charge. The theory makes the adiabatic approximation for the vibronic wave functions, which is not always appropriate for a shallow BE. However, the weak phonon sideband calculated[16] perturbatively without the adiabatic approximation is qualitatively unchanged from the adiabatic theory.

Consider a BE with $\sigma_e=\sigma_h$. If σ_e is much larger than the extent of the charges in the z direction, then $\mathbf{D}(\mathbf{r})$ points in the z direction. This model, which we call the "extended exciton" (EE) charge distribution, demonstrates how S_m can be interpreted physically. $R=S_w/S_b$ depends strongly on QW width d (Fig. 2). For the 10-Å QW the hole is strongly confined to the well, but the wave function for the lower-mass electron spreads far into the barrier. Lines of $\mathbf{D}$ run from net positive charge to net negative charge, and thus through a large thickness of barrier (Fig. 2, inset); so from Eq. (2), $S_b\gg S_w$. For the 110-Å QW the electron and hole and the lines of $\mathbf{D}$ are almost completely confined to the QW (Fig. 2, inset), and $S_b\ll S_w$. For a wide QW with small or unequal σ_e,σ_h, the lines of $\mathbf{D}$ spill out into the barrier, and so R is reduced from its EE value (for a 110-Å QW and $\sigma_e=60$ Å, $\sigma_h=40$ Å, from 64.3 to 2.20). This shows that S_m cannot always be understood by consideration of n_{0a} alone. S_m depends both on wave function penetration into the barrier, and on remote interaction of charge in one layer with

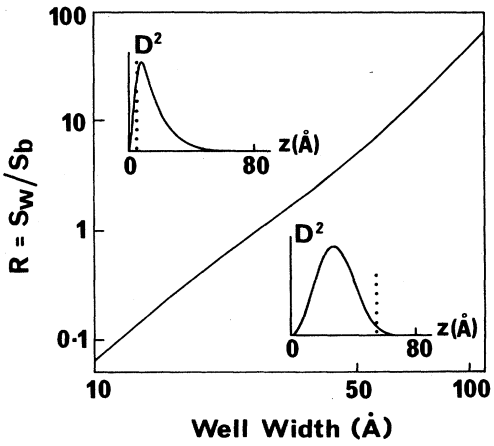

FIG. 2. $R=S_w/S_b$, in the EE model, as a function of QW width d (logarithmic scales). Insets: $D^2(x,y,z)$ in arbitrary units as a function of z (distance from the QW center) for fixed x,y. The interface is marked by a dotted line. In a 10-Å QW (top left) $\mathbf{D}$ extends from the excess hole charge in the well to the excess electron charge far into the barrier. For a 110-Å QW (bottom right), $\mathbf{D}$ is almost completely confined to the well.

vibrations in another.

Varying d for fixed σ_e, σ_h, $R(d)$ always increases rapidly with d, though not as much as in the EE model. In particular, for wide wells R can be a lot smaller than in the EE model, as discussed above. The strong well width dependence of the experimental values of R (Fig. 1) can thus be understood, although the precise values of R depend on σ_e, σ_h.

σ_e and σ_h also govern the exciton diamagnetic shift.[16] When the exciton is bound in a region much larger than the Bohr radius a_x, its motion is dominated by correlation, and the small-B diamagnetic shift E_B tends to the free exciton value. When the electron and hole are both more tightly bound than a_x, the wave function has a product form, and for a binding center with rotational symmetry about the z axis,

$$E_B = \frac{e^2B^2\sigma_e^2}{4m_e} + \frac{e^2B^2\sigma_h^2}{4m_h} .$$

B also shrinks the exciton wave function. For the axially symmetric ground state of a single particle, with a harmonic binding potential,

$$\sigma_a^{-4}(B) = \sigma_a^{-4}(B=0) + l_B^{-4} , \tag{3}$$

where $l_B = (\hbar/eB)^{1/2}$ is the magnetic length ($l_B = 83$ Å at 9.6 T). We use Eq. (3) as a qualitative guide to the shrinkage of the electron and hole charge distributions.

For each QW, σ_e, σ_h can be found from E_B and the $B=0$ values of S_w, S_b. The B dependence of S_w, S_b is consistent with Eq. (3) in every case, strong experimental support for our theory of the phonon sideband. We shall discuss here the 20- and 50-Å QW's. For the 20-Å QW, the (In,Ga)As LO satellite is too weak to be observed. A fit to the values of S_b (0.0058) and the diamagnetic shift[16] (16 μeV T^{-2}) gives $\sigma_e = 35$ Å, $\sigma_h = 57$ Å. The perturbation of S_b by B is weak, since σ_e and σ_h are small compared to l_B. Only the (larger) hole orbital is significantly reduced by B. This shrinkage implies a *reduction* in S_b: Using values from Eq. (3), S_b is predicted to be 13% smaller at 9.6 T than at $B=0$. Experiment indeed gives a small reduction of 22%.

The PL spectrum of the 50-Å QW has no observable phonon sideband at $B=0$ (i.e., $S_w, S_b < 10^{-4}$). The values $S_w = 10^{-4}$, $R=2$ are consistent with $\sigma_e = 139$ Å, $\sigma_h = 132$ Å, which are thus lower bounds on σ_e, σ_h at $B=0$. σ_e, σ_h are larger than for the 20-Å QW because the influence of imperfections in the interfaces is weaker in the wider QW. Such a diffuse BE will be strongly perturbed by B. Experimentally, S_w is approximately proportional to B, reaching the value 7.3×10^{-4} at 9.6 T. R increases from 2.0 to 3.4 in this range of B. S_w and R are fitted at 9.6 T by $\sigma_e = 58$ Å, $\sigma_h = 52$ Å. This shrinkage of the exciton is in good qualitative agreement[19] with Eq. (3).

The exciton state in the 50-Å QW can be further understood in terms of the wave functions for the QH system.[20] In a weak random potential V_0 the degeneracy of a single-particle Landau level (LL) is lifted. States which have lower energy than any others nearby ("trap states") are the most compact of the localized states in the low-energy tail of the lowest LL. If V_0 is weak, σ_a is large at $B=0$. For $B\neq0$, σ_a is close to l_B, but is reduced by V_0 [Eq. (3)]. For an electron-hole pair, well-width fluctuations (and probably also alloy fluctuations) cause a random potential energy with the *same sign* for electrons and holes. Trap states occur in the same places for electrons and holes, a tendency that is reinforced by the Coulomb attraction. Exciton trap states are localized with approximately the same radius σ_a as for single-particle states, and are the states of the 50-Å QW into which excitons thermalize at 4.2 K. Thus PL studies the spatially most localized states of the lowest electron and hole LL's. The increase of S_w with B is a direct measure of the decreasing length scale of these states.

The 50- and 110-Å QW's appear (from their linewidths,[11,13] Stokes shifts, and phonon satellites) to have disorder of a similar magnitude, their chief difference being the presence in the latter of a two-dimensional electron gas (2D EG). Landau quantization of this 2D EG is directly observed in Shubnikov–de Haas and QH experiments,[21] and as a LL splitting in PL,[11] supporting the idea that the single-particle states of the 50-Å QW in magnetic field are weakly perturbed Landau states.

For direct-gap GaAs/(Al,Ga)As QW's, phonon satellites of exciton PL have not been reported; nor could we observe them in a high-quality SSMBE $d=50$-Å multiple QW for B up to 9.6 T. Hence the disorder in each QW is smaller than in the 50-Å (In,Ga)As/InP QW, at least in part because alloy fluctuations are less important than for alloy QW's. In magnetic field the relatively strongly phonon-coupled trap states must still exist, but presumably are closer in energy to other states than in (In,Ga)As/InP QW's so that the excitons do not thermalize into them at 4.2 K. In $d=100$-Å (In,Ga)As/InP QW's grown by atmospheric pressure metal-organic chemical vapor deposition, strong phonon satellites ($S_w \sim 0.05$) and large E_B show that the luminescent exciton consists of a tightly bound hole (10 Å $< \sigma_h <$ 30 Å) and a loosely bound electron.[1] The most likely[1] binding centers for the holes are alloy fluctuations, which are thus stronger than in (In,Ga)As grown by SSMBE.

In summary, we have observed LO phonon satellites of low-temperature exciton PL in direct-gap (In,Ga)As/InP QW's. We have generalized the theory[14] of these satellites to the case of an exciton bound by disorder in this multimode low-dimensional system. Our theory relates the strengths of the different phonon satellites to the length scales σ_e, σ_h of the electron and hole bound states in the plane of the QW. When combined with experiments that determine the exciton diamagnetic shift and the strengths of the satellites as a function of magnetic field, the theory gives an unambiguous picture of the nature of the exciton localization. For our 50-Å QW, PL has been shown to probe the most localized states of the quantum Hall system.

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