RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 34, NUMBER 2 15 JULY 1986

Thermally modulated photoluminescence in $Ga_xIn_{1-x}As$-InP quantum wells

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(Received 6 December 1985; revised manuscript received 28 April 1986)

The utility of the thermally modulated photoluminescence technique is demonstrated for $Ga_xIn_{1-x}As$-InP quantum wells. Using different well widths, we have measured the binding energy of excitons (either free or impurity bound) in these structures. The binding energy increases monotonically with decreasing well thicknesses, in good agreement with the available theoretical predictions for free excitons.

It is well known that confining the electrons and holes in a semiconductor quantum well (QW) leads to quantization of the particle motion normal to the plane of the film, and inherently, to bound states for the electrons as well as for the holes (quantum size effect).[1] These bound states have been identified in the optical spectra of many different types of QW's, such as GaAs-$Ga_{1-x}Al_xAs$, $Ga_xIn_{1-x}As$-InP, $Ga_xIn_{1-x}As$-$Al_xIn_{1-x}As$, etc.[2,3]

In addition to the effect on the single-particle states (electrons, holes), the spatial confinement will also affect the two-particle states, such as excitons.[4] In analogy with the hydrogen atom, where the binding energy for confinement in two dimensions is four times that in three dimensions, the binding energy of the exciton is expected to increase in a QW as the two-dimensional confinement begins to dominate. Although some controversy still exists,[5] there are experimental data[6] and theoretical calculations for GaAs-$Ga_{1-x}Al_xAs$ QW's[7,8] which support this increase in the binding energy. In the case of the $Ga_xIn_{1-x}As$ QW's, where the excitonic Bohr radii are larger than in GaAs, the two-dimensional character of the excitons should be apparent for larger QW widths. At present, no data are available for $Ga_xIn_{1-x}As$ QW's, other than the observation that excitons seem to exist up to room temperature.[9]

In this Communication we describe an optical modulation technique that permits the measurement of resolved structures in a photoluminescence (PL) spectrum when the spectrum itself is featureless. This technique should be particularly important in QW's because the PL spectra are usually observed to broaden considerably with decreasing well width in most systems. We show that this modulation technique permits the measurement of the binding energy for excitons. Our results for $Ga_xIn_{1-x}As$-InP QW's indicate a large increase in the excitonic binding energy with decreasing QW width, as predicted theoretically.

In a QW under low-intensity, cw optical excitation the excited free electrons and holes will be in thermal equilibrium with the exciton population.[10] Whether or not the excitons are free or bound to an impurity is difficult to determine with certainty because of the very small differences in binding energy in these two cases. For reasons to be mentioned below we conclude that the excitonic recombination in our samples is due to free excitons or to excitons bound to impurities. However, the method which we shall describe applies to any situation where there is recombination from two different states which are closely spaced in energy. The ratio of the concentrations of excitons to free carriers can be described, to a good approximation, by the Boltzmann factor

$$\frac{N_F}{N_x} \sim e^{-E_B/kT} ,$$

where N_F is the number of photoexcited free carriers and N_x is the number of excitons. E_B represents the exciton binding energy. Under these conditions, the photoluminescence (PL) emission from the QW is the sum of the emission from the free-exciton gas and the emission originating from the free-carrier recombination

$$\begin{aligned} I^{\mathrm{PL}}(\omega) &= I_x(\omega)+I_F(\omega) \\ &= N_x f_x G(\hbar\omega,\Gamma_x)+N_F f_F G(\hbar\omega+E_B,\Gamma_F) , \end{aligned} \tag{1}$$

where f_x (f_F) is the radiative probability for the excitons (free electron to free hole) and $G(\hbar\omega,\Gamma_{x,F})$ is the Gaussian line-shape function which accounts for the fact that the PL is known to be inhomogeneously broadened by fluctuations in the width of the well.[11] Γ_x and Γ_F are the full widths at half maximum (FWHM's) of the respective emission spectra. The difference between the peak positions of the two emissions is, in well-resolvable cases, a measure of the exciton binding energy, E_B. Due to the large linewidth and, at low temperature, the weak free-carrier recombination, conventional PL spectroscopy cannot resolve the two individual emission bands. Thus, the exciton binding energy cannot be determined by directly measuring the PL spectrum.

There is very strong corroborating evidence which supports our assignment of the dominant PL process in our $Ga_xIn_{1-x}As$ quantum-well structures to excitonic recombination. Weisbuch *et al.*[12] have measured both PL and optical absorption in $Al_xGa_{1-x}As$-GaAs quantum wells, and they find by comparison of these two measurements that the PL is due to recombination of free excitons. In the $Ga_xIn_{1-x}As$ system both Temkin *et al.*[13] and Kawamura, Wakita, and Asahi[14] have performed PL and optical-absorption measurements on single and multiple quantum-well structures. These authors also find that the PL is due to an intrinsic mechanism (excitons) and not to impurities. From PL measurements alone Welch, Wicks, and Eastman[15] have ascribed the emission in $Ga_xIn_{1-x}As-Al_xIn_{1-x}As$ multiple quantum wells to intrinsic processes.

In earlier measurements on the samples used in the present study, Kuo, Fry, and Stringfellow[16] found that in these wells the PL intensity increased by over an order of magnitude from its value in thicker layers. This observation is consistent with that which is commonly observed in GaAs quantum wells[17] where the effect has been ascribed to the suppression, in thin wells, of the capture of free carriers by impurities. In addition, in our samples the observed shift of the peak energy of the PL as a function of well thickness[16] is consistent with theoretical calculations based on excitonic recombination, and inconsistent with the participation of impurities in the recombination.[18] We therefore conclude that there is strong evidence that the PL in our $Ga_xIn_{1-x}As$-InP quantum wells is due to an excitonic mechanism, although it is difficult to say whether the excitons are free or bound to shallow impurities.

To determine the exciton binding energy, we have measured the *temperature derivative* of the photoluminescence, instead of the conventional PL spectrum itself. The temperature derivatives of the intensities of the two emission bands have opposite signs (see below). This fact allows us to separate the two bands and determine the binding energy.

The temperature derivative of the photoluminescence can be measured by measuring the temperature-modulated photoluminescence (TMP) spectra. The TMP technique has been described in detail elsewhere,[19,20] and therefore we shall only summarize the main features of the method. In this method the temperature of the sample is modulated between T and $T+\Delta T$ and the temperature-induced changes in the PL emission ΔL are measured. The measured signal is proportional to the temperature derivative of the photoluminescence, $\partial I^{\mathrm{PL}}/\partial T$,

$$\Delta L = I^{\mathrm{PL}}(T+\Delta T) - I^{\mathrm{PL}}(T) \sim (\partial I^{\mathrm{PL}}/\partial T)\Delta T \ . \qquad (2)$$

The major contribution to ΔL can be shown to be due to changes in the exciton and free-carrier concentrations.[20] Raising the temperature by ΔT will increase the free-carrier population ($\partial N_F/\partial T > 0$) at the expense of the exciton population ($\partial N_x/\partial T < 0$). If we neglect impurity effects in the QW, it is easy to show that $\partial N_x/\partial T = -\partial N_F/\partial T$. Since at low temperatures ($T \ll 20$ K) $\partial E_G/\partial T$ and $\partial \Gamma/\partial T$ can be neglected,[21] one obtains

$$\Delta L = \frac{\partial N_x}{\partial T}[f_x G(\hbar\omega,\Gamma_x) - f_F G(\hbar\omega+E_B,\Gamma_F)]\Delta T \ . \qquad (3)$$

Thus, the contributions to the TMP spectrum by the two bands are opposite in sign.

If $E_B \gg \Gamma_x,\Gamma_F$, the two bands are separated in the TMP spectrum, and the exciton binding energy can be determined from the separation of the two bands. If, however, $E_B \ll \Gamma_x,\Gamma_F$, the bands overlap even in the TMP spectrum (although they have opposite signs). In this case a curve-fitting procedure is necessary to determine the binding energy. However, unlike in the case of the PL spectrum, in the TMP spectrum the amplitude of the two bands is of the same order of magnitude, since they are proportional to $\partial N/\partial T$ and not to N. Thus, at low temperture even the weak free-to-free emissions will be observed in the derivative spectra.

This TMP technique has been used to study the dependence of the exciton binding energy on the well width L_z in $Ga_xIn_{1-x}As$-InP QW's. The temperature modulation was achieved by indirect heating.[22] The sample was mounted on a miniature heater, which in turn was fastened to the cold finger of a variable-temperature cryostat. The temperature of the sample was modulated by the heater between T and $T+\Delta T$, where T was 8 K and $\Delta T = 1$ K. The frequency of the temperature modulation was 8 Hz. The optical arrangement was similar to that employed for conventional PL. The PL was excited by the 514-nm line of an argon-ion laser and collected from the excited face of the sample. The measurements used a Jobin-Yvon model No. 320 grating monochromator, a lock-in amplifier, and a nitrogen-cooled Ge p-i-n diode detector. The reference signal for the lock-in amplifier was provided by the current source which generated the temperature modulation.

The samples used in this study were $Ga_{0.47}In_{0.53}As$-InP quantum wells grown by the atmospheric-pressure organometallic vapor-phase epitaxial technique (OMVPE). The growth procedure employed trimethylindium, trimethygallium, and AsH_3 as reactants, and the films were deposited on (100)-oriented InP substrates.[16] The well thicknesses were estimated from the growth rate to be 62, 125, and 500 Å. The thicknesses of the confining layers were typically 2000–3000 Å. The low-temperature PL spectrum for the 125-Å well is reproduced in Fig. 1(a). (The observed energy shifts of the PL peaks for the different well widths were published earlier[16] and they are consistent with those calculated.)

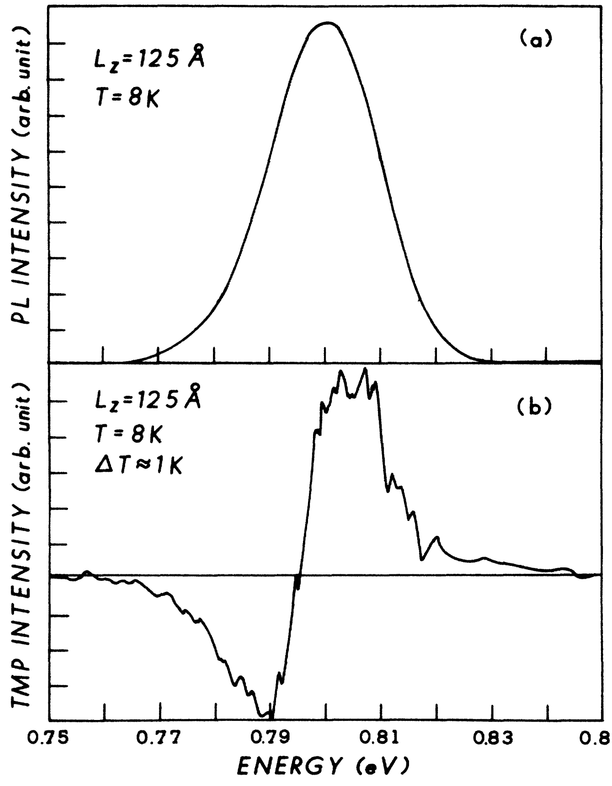

FIG. 1. (a) Photoluminescence (PL) spectrum of an InP-$Ga_xIn_{1-x}As$-InP quantum well ($L_z = 125$ Å). The temperature-modulated PL (TMP) spectrum for the same sample is shown in (b).

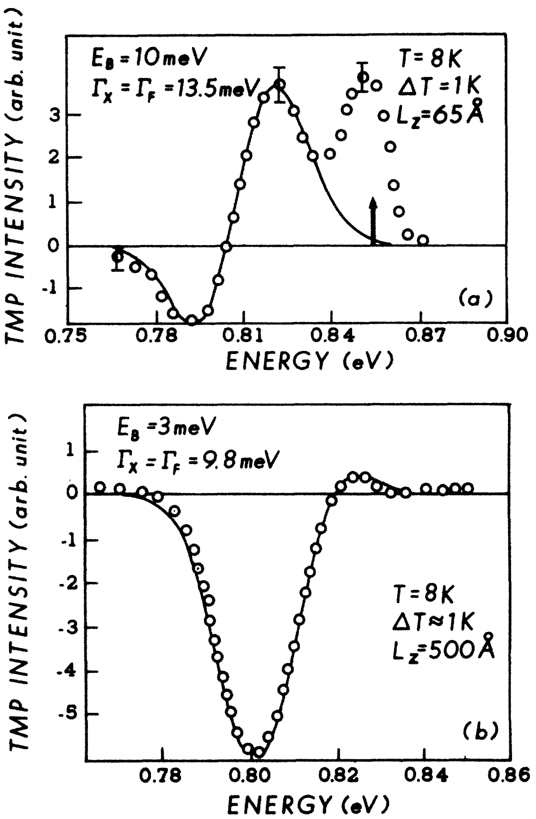

FIG. 2. TMP spectra of two $Ga_xIn_{1-x}As$-InP QW's having well thicknesses of (a) 65 Å and (b) 500 Å. The circles are the measured points and full lines are the result of the curve fitting. Fitting parameters are given in the figure. The arrow in (a) indicates the calculated position of the electron–light-hole transition.

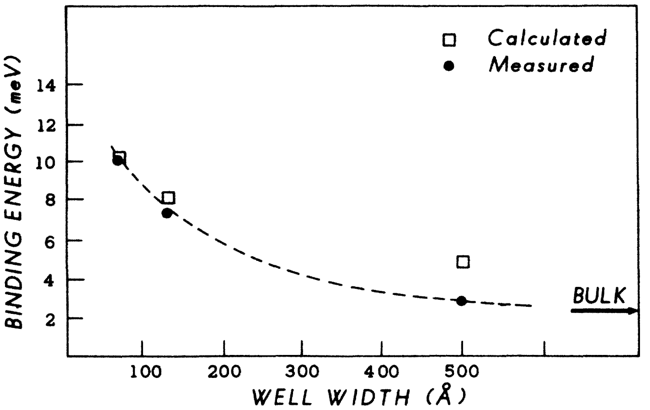

FIG. 3. Exciton binding energy, as a function of quantum-well width, in $Ga_xIn_{1-x}As$ QW's as deduced from the TMP spectra. The theoretical predictions, using the calculations of Bastard *et al.* (Ref. 4), are also shown. (The dotted line is an aid to the eye.)

In Fig. 1(b) we have reproduced the measured TMP spectrum for the 125-Å QW. It can be seen that the sign of the derivative spectrum is negative at low energies and positive at higher energies, as expected from the previous discussion. The TMP signal amplitude is four orders of magnitude smaller than the photoluminescence signal, i.e., $\Delta L/L \sim 10^{-4}$, at $T = 8$ K. [In the case of the 65-Å wide QW, the electron–light-hole transition was also resolved in the TMP spectrum, as can be seen in Fig. 2(a).] The exciton binding energy can be determined from the measured spectra with the help of a curve-fitting procedure which uses two Gaussian functions of opposite sign. In addition to the exciton binding energy, the fitting parameters were the amplitude (transition probabilities) and the linewidths of the two emissions. This method, which was found to be very sensitive to the value of E_B, was used for all three QW's studied (see Fig. 2). The resulting values of E_B are shown on Fig. 3 as a function of well width. Also shown on this figure are theoretical predictions, from the calculations of Bastard *et al.*[4] Although the calculations were made for perfectly confined electrons and holes, they are the only available calculations that can be applied to the $Ga_xIn_{1-x}As$-InP system. Even with the simplifying assumptions, there is good agreement between the measured values and the theoretical predictions. These results are consistent with the observation of excitonic absorption spectra at room temperature in $Ga_xIn_{1-x}As-Al_yIn_{1-y}As$ QW's, which indicated an increase in exciton binding energy with decreasing L_z.[9] From their absorption spectra Weiner *et al.*[9] deduced a binding energy of 6 meV for a well width of 110 Å. This value is very close to our measured 7 meV for a similar QW in the $Ga_xIn_{1-x}As$-InP system.

The fitting procedure was insensitive to the difference between the Γ_x and the Γ_F parameter so we used only a single parameter, Γ. The resulting values for Γ were the following: Γ(65 Å) = 13.5 meV, Γ(125 Å) = 11 meV, and Γ(500 Å) = 9.8 meV. These parameters are difficult to compare with other measured PL data, since the FWHM is known to be sample dependent. However, the observed tendency of increasing PL FWHM with decreasing well width is expected and has been reported previously.[3,16]

In conclusion, we have demonstrated the utility of the temperature-modulated PL technique for resolving PL processes in quantum-well structures. We have measured what we believe to be the ground-state exciton binding energy in $Ga_xIn_{1-x}As$-InP quantum wells, as a function of well width. We find that the binding energy increases monotonically with decreasing well thickness in good agreement with theoretical predictions.

Research in the Department of Physics was supported by the National Science Foundation (M.G., R.R.) and the Office of Naval Research (P.C.T.). The research in the Department of Materials Science and Engineering (C.P.K., G.B.S.) was supported by the Army Research Office.

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