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Unambiguous observation of the 2s state of the light- and heavy-hole excitons in GaAs-(AlGa)As multiple-quantum-well structures

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Discrete peaks are seen in the photoluminescence excitation spectra of GaAs-(AlGa)As multiple-quantum-well samples which we identify as the excited 2s state of the $n=1$ heavy- and light-hole excitons. The 1s-2s splitting of the excitons is accurately determined and combined with calculations of the 2s heavy-hole exciton binding energy to give an accurate determination of the binding energy of the ground state.

Previous low-temperature ($\sim$4 K) photoluminescence excitation spectroscopy (PLE) on GaAs-(AlGa)As quantum wells (QW's) from a number of groups[1,2] has revealed shoulders on the high-energy side of each of the fundamental exciton creation peaks. Without exception these shoulders have been interpreted as representing the onset of the excited states of the heavy- (HH) and light-hole (LH) excitons which are not resolved from the continuum. In this Communication we report the observation of a clearly resolved peak on the high-energy side of both the heavy- and light-hole excitons before the onset of the continuum which we interpret as the excited 2s state of the heavy- and light-hole excitons. The appearance of the 2s peaks in the spectra allows what we believe to be the first precise determination of the difference in binding energy between the 1s and 2s states. The combination of this measured splitting with our calculation of the 2s exciton binding energy allows us to obtain the binding energy of the 1s state accurately.

The multiple-quantum-well (MQW) samples studied here were all grown in a Varian Gen-II molecular-beam-epitaxy system. More than 100 μm of GaAs and (AlGa)As had been deposited previously in this system, and at this stage the level of unintentional dopant in the GaAs has been established as below 2×10^{14} cm^{-3} with the mobility of electrons in a two-dimensional electron gas in excess of 2×10^6 cm^{2}V^{-1}s^{-1} at 4.2 K.[3] All the layers were deposited on (001)-oriented semi-insulating GaAs substrates held at a nominal substrate temperature of 630 °C. The growth sequence was as follows: (a) a 1-μm GaAs buffer, (b) 0.13 μm of (AlGa)As, (c) 60 periods of GaAs wells and (AlGa)As barriers, and (d) 0.13 μm of (AlGa)As. None of the layers were deliberately doped. In all samples the (AlGa)As barrier thickness was chosen so as to ensure that the wells were effectively decoupled electronically. Details of the well dimensions, together with the Al molar fraction in the barriers, are given in Table I.

Low-intensity ($\sim$5 W cm^{-2}) PLE spectra at $\sim$8 K were recorded using a Ar$^+$-pumped tunable dye laser. Figure 1(a) shows the excitation spectrum of an 82-Å GaAs MQW sample whose barriers were the binary compound AlAs. The PL from this sample was detected at an energy of 1.574 eV. The two most prominent peaks are evidently the 1s state of the $n=1$ heavy- and light-hole excitons. Clearly resolved on the high-energy side of each of these excitons are additional, previously unreported, discrete peaks. We assign these to the excited 2s state of the heavy- and light-hole excitons. The 2s states of the heavy- and light-hole excitons are split from the ground state by 10.9 and 12.5 meV, respectively. A similar, high quality spectrum is shown in Fig. 1(b). The detection energy for this sample was set at 1.569 eV. Here the GaAs wells are 75 Å wide and the barriers are now of (AlGa)As whose Al mole fraction is close to 0.4. Again the 2s states of both excitons are well resolved in the spectrum and the splitting of these states from the 1s states is 9.5 and 10.3 meV for the heavy- and light-hole excitons, respectively. These values are slightly smaller than the values for the 82-Å sample and reflect the reduction in exciton binding energy due to the decrease in the confining potential for both the electrons and holes. The difference in 1s and 2s binding energies for both heavy- and light-hole excitons for all the samples measured are listed in Table I. For the 92-Å sample the 2s state of the heavy-hole exciton could

TABLE I. Sample details and experimentally determined and theoretically calculated splitting between the 1s and 2s exciton states.

Well width L_z (Å)	Al fraction x	1s-2s exciton splitting (meV) HH1 expt.	Calc.	LH1 expt.	Predicted HH1 1s binding energy (meV)
75	0.40	9.5	9.5	10.3	11.2
82	1.00	10.9	10.6	12.5	13.0
92	0.35	8.5	8.6	10.2	10.1
112	0.35	...	...	9.1	...

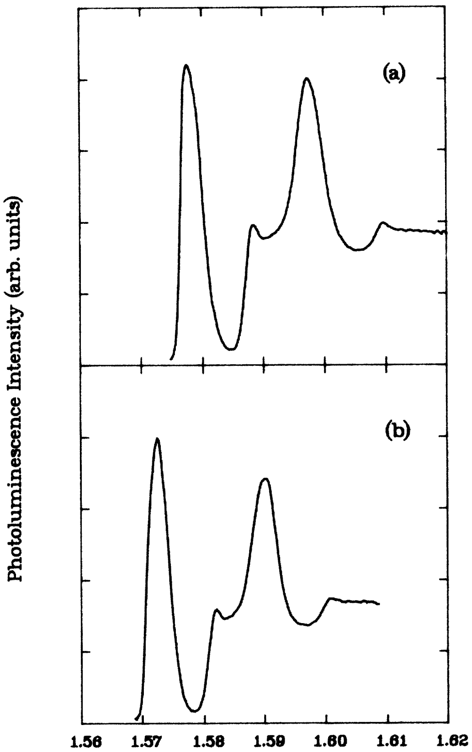

FIG. 1. Low-temperature photoluminescence excitation spectra from multiple-quantum-well samples with (a) 82-Å GaAs wells with AlAs barriers and (b) 75-Å GaAs wells and barriers of $Al_{0.35}Ga_{0.65}As$. (The barriers are wide enough to ensure effective electronic isolation of the wells.)

clearly be seen in the PLE spectrum. However, the energy range accessible with the dye laser meant that simultaneous detection of the 1s state of the heavy-hole exciton could not be achieved. A separate PLE spectrum at the same temperature using a "lamp and monochromator" combination was used to reveal the position of the 1s heavy-hole exciton in this sample.

The 2s exciton peaks are clearly resolved in samples which show spectral features sharper than those seen in other samples grown in a previous growth run. We do not yet know why this is.

In spite of the obvious high quality of these samples further discrete excited states of the heavy- and light-hole excitons are not resolvable in the spectra. (For the 82-Å sample, at least, higher excited states are probably obscured due to the proximity of the $n=1$ light-hole exciton.) This means that the binding energies of the 1s excitons cannot be directly determined from the spectral information at hand. However, what we can do is combine the accurate measurement of the 1s-2s splitting with a calculation of the 2s binding energy of the quasi-2D excitons to predict the 1s binding energy. This is an accurate procedure since the 2s wave function has only a small amplitude near to the origin of the potential describing the Coulomb interaction, where the deviations from the Coulombic form are most marked. In addition the absolute magnitude of the 2s binding energy is small in comparison to the 1s so any error in the calculated absolute value will be proportionally diminished.

The details of our calculation of the exciton binding energy, including the light- and heavy-hole mixing, have already been published[4] so we recapitulate on only the essential aspects. We shall only consider the heavy-hole exciton and assume that confinement of both electron and hole states is ideal, i.e., the potential barriers are impenetrable. We represent the exciton state $|X\rangle$ by the linear combination

$$|X\rangle=\sum_{\mathbf{k}} A(\mathbf{k})|\mathbf{k}\rangle \ , \tag{1}$$

where $|\mathbf{k}\rangle$ is the excited state with an electron in the conduction band and a hole in the valence band, both with inplane wave vector $\mathbf{k}$. The $A(\mathbf{k})$ are coefficients to be determined. We make the approximation that the electron and hole bands are parabolic in the region of $\mathbf{k}$ space which contributes states to the exciton. From the work of Fasolino and Altarelli[5] it is clear that for sufficiently narrow quantum wells (<100 Å) the highest heavy-hole subband becomes well separated from all the others. We thus neglect the Coulomb interaction between the lowest electron and hole bands with the closest other bands. Within these approximations the Fourier transform of (1), $F(r)$, satisfies the equation

$$-\frac{\hbar^2}{2m^*}\nabla^2F(r)+V(r)F(r)=EF(r) \ , \tag{2}$$

where

$$V(r)=-e^2\int dz_e\int dz_h\,|Z_e(z_e)|^2|Z_h(z_h)|^2/\varepsilon\sqrt{(z_e-z_h)^2+r^2} \ ; \tag{3}$$

$Z_e(z_e)$ and $Z_h(z_h)$ are just the sinusoidal solutions to the particle in an impenetrable box problem.[4] m^* is the reduced effective mass of the exciton.

Rather than solve (2) by assuming a trial wave function for $F(r)$ and using a variational procedure we have integrated the equation directly using an appropriate numerical routine.[6] Previous attempts to determine the 2s binding energy have been based on solving Schrödinger's equation variationally.[1,7,8] In Refs. 7 and 8 the authors used 1s and 2s variational functions which were orthogonal to one another. This is computationally convenient as it returns results for the 1s and 2s binding energies simultaneously but as the 1s variational function is not the true ground state wave function of the system the 2s variational function is not orthogonal to the actual ground state and the error in evaluating the 2s binding energy is more uncertain than for the 1s state.

Our calculated values of the 1s and 2s heavy-hole exciton binding energies for GaAs wells and $Al_{0.35}Ga_{0.65}As$ barriers are given in Figs. 2(a) and 2(b), respectively. In both cases we have included nonparabolicity of the electron band in an approximate manner to determine the inplane electron effective mass m_e. Using the Kane $\mathbf{k}\cdot\mathbf{p}$ model[9] for the conduction band of bulk GaAs the energy

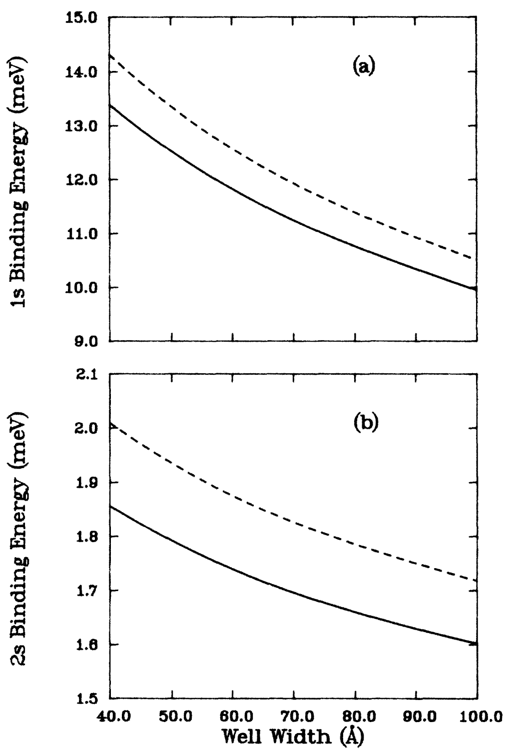

FIG. 2. Calculated dependence of the (a) 1s and (b) 2s heavy-hole exciton binding energy as a function of GaAs quantum-well width. Two different values of the in-plane heavy-hole mass of $0.18m_0$ (full curve) and $0.25m_0$ (dashed curve) have been used. Nonparabolicity is included as indicated in the text for barriers of $Al_{0.35}Ga_{0.65}As$.

dependence of m_e is given by

$$m_e^* = m_{eb}^*(1+2E_c/E_g) \ , \tag{4}$$

where m_{eb}^* is the band-edge effective mass and E_c the confinement energy. E_c was calculated for the appropriate well width L_z using Bastard's implementation of the three-band Kane model[10] for a confining potential equivalent to a band-offset ratio of 65:35.[11] m_{eb}^* was chosen to be $0.0665m_0$ and the dielectric constant fixed at 12.6. We made calculations for two values of the in-plane heavy-hole mass corresponding to $0.18m_0$ (full curves) and $0.25m_0$ (dashed curves). These are larger than the value used previously, by ourselves[4] and the authors in Refs. 1 and 7, of about $0.1m_0$.[4] The value of $0.18m_0$ is close to that calculated by Sanders and Chang[12] for the near $k=0$ value of the in-plane mass derived from a multiband effective-mass model of the hole dispersion in GaAs-$Al_{0.4}Ga_{0.6}As$ quantum wells for L_z of 40 Å. Their approach is similar to that of Fasolino and Altarelli[5] and illustrates that the in-plane dispersion can be quite nonparabolic (particularly for wider wells). The higher hole mass of $0.25m_0$ is the value of $\hbar^2k^2/2E$ for the highest valence subband at an energy about 10 meV below the top.[13] The exciton is constructed out of states some distance away from $k=0$ whose effective mass is somewhat larger than the $k=0$ value; this means that in any equivalent two-parabolic-band model of the exciton a larger value of the in-plane hole mass is appropriate. Just what hole mass to include in the calculation is uncertain, as is its variation with L_z, but within the limits chosen here, for a 75-Å QW, the 1s binding energy changes by 0.6 meV whilst the 2s changes by only 0.13 meV.

Our calculated 2s binding energy is slightly larger than that deduced either by Miller, Kleinman, Tsang, and Gossard[1] or by Greene, Bajaj, and Phelps.[7] This arises in part from our including the conduction-band nonparabolicity in an approximate form and our larger estimate of the in-plane heavy-hole mass.

The experimentally measured 1s-2s splittings of the 75-Å sample are slightly larger than those found by Miller *et al.*[1] on a comparable sample. This difference is almost certainly due to the way in which the authors attempted to locate the 2s exciton position.[1] In Table I we compare the experimentally determined difference between the 1s and 2s heavy-hole binding energies with those calculated above. Note that we used an in-plane heavy-hole mass of $0.18m_0$ in all cases. The agreement between experiment and theory is very good. The effect of changing the in-plane heavy-hole mass can be gauged by comparison of the full and dashed curves in Fig. 2. For the 82-Å sample, which has AlAs barriers, we used the dielectric constant of this material of 11.5. The change in the dielectric constant is necessary to get agreement between experiment and our model calculation. The additional nonparabolicity from having an increased confinement energy due to AlAs barriers is by itself insufficient to explain the larger 1s-2s splitting. This effect causes a calculated increase of less than 0.1 meV from the value deduced from the curves in Fig. 2.

In summary, we have for the first time observed discrete peaks in the low-temperature PLE spectra of GaAs-(AlGa)As MQW samples which correspond to the excited 2s states of the heavy- and light-hole excitons. An accurate determination of the 1s-2s splitting has been made and combined with calculation of the 2s binding energy to yield 1s heavy-hole exciton binding energies given in Table I. Investigation has shown that an in-plane heavy-hole mass of about $0.18m_0$, close to that calculated from a multiband effective-mass approach, produces very good agreement between calculated and measured 1s-2s splittings. Exactly how accurate our calculations of the 2s binding energy are, is not clear. However, variation of the heavy-hole mass between $0.18m_0$ and $0.25m_0$ causes only a small (~0.15-meV) change in the computed 2s binding energy.

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