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Observations and calculations of the exciton binding energy in (In,Ga)As/GaAs strained-quantum-well heterostructures

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We present the first direct measurements of the heavy-hole exciton binding energy in a III-V-compound quantum-well system where the well widths are 25 Å or smaller. The 4-K photoluminescence excitation (PLE) spectrum from $In_{0.15}Ga_{0.85}As/GaAs$ multiple-well samples with 48-, 25-, and 14-Å wells displays a sharp heavy-hole exciton feature well resolved from the continuum edge; the separation between these features yields exciton binding energies of 9.2, 8.7, and 6.5 meV, respectively. The decrease in binding energy with decreasing well width confirms the predicted trend from our calculations. Quantitative agreement between the model calculations and the observations is good. In addition, we have seen fine structure in the PLE spectrum of the 14-Å sample in both the heavy- and light-hole excitonic peaks. The energy splitting in the fine structure equates with changes in In fraction of less than 0.5% in 15% or changes in *average* well width of < 1 Å.

I. INTRODUCTION

In this paper we report both measurements and calculations of the fundamental electron–heavy-hole exciton binding energies in isolated (In,Ga)As/GaAs quantum wells. Measurements have been made on samples where the (In,Ga)As wells are only 14 Å thick which has allowed the observation of the theoretically predicted decrease in the exciton binding energy at very narrow well widths. Before proceeding to the experimental results and description of the calculations, we begin by comparing and contrasting the (In,Ga)As/GaAs system with the more familiar and well-studied GaAs/(Al,Ga)As system. We point to those particular features of the strained system which have allowed us to observe this decrease in exciton binding energy as the well width decreases—an observation not yet made directly in the GaAs/(Al,Ga)As system.

The replacement of one group-III element, Al, in the GaAs/(Al,Ga)As system by In, to make the heterostructure combination of (In,Ga)As/GaAs has a number of interesting physical consequences. Most obviously, this substitution now means that the system is one which has a non-negligible lattice mismatch. Additionally the GaAs layers have undergone a role reversal; becoming the barriers (for electrons and heavy holes), rather than the wells, in the strained configuration. For modest amounts of In in the alloy the barrier heights are relatively low (electron barrier heights of ~ 80 meV for 12% In concentrations, for example), making superlattice effects far more pronounced for quite wide barriers. As an example we find that for 14-Å $In_{0.15}Ga_{0.85}As$ quantum wells separated by 200-Å barriers the electron miniband width is a few meV and that, even with barriers that are 400 Å wide, the miniband width is still ~ 0.5 meV.

A general observation in the GaAs/(Al,Ga)As system is that the width of the lowest electron–heavy-hole excitonic resonance seen in photoluminescence excitation (PLE) at low temperatures increases as the well width L_z decreases. There are two contributory factors which explain this observation: the first being that fluctuations in the well width (as $L_z \rightarrow 0$) lead to increasing splitting of the eigenvalues between each part of the "imperfect" well. If the lateral extent of these regions is comparable to the diameter of an exciton the PLE excitonic creation lines will broaden and overlap. Secondly, as the well width decreases the exciton wave function samples the barrier layers to an increasing extent; since these are generally alloys a broadening of the excitonic resonance occurs due to increased scattering from the random-alloy potential. As the well width L_z tends toward zero the first of these broadening mechanisms is suppressed; the reason being that the $n = 1$ eigenvalues of the individual wells will all reside extremely close to the top of the quantum well, so changes in this quantity due to monolayer fluctuations in the well width will be minimized. Broadening due to the second mechanism is still present and indeed increases as the well width diminishes. These phenomena have thus far not allowed direct observation of a heavy-hole excitonic resonance clearly resolved from either its excited states or the continuum edge in GaAs/(Al,Ga)As samples where the well width is smaller than ~ 31 Å (Ref. 1). The situation is interestingly different in the (In,Ga)As/GaAs case. At wide well widths (greater than the exciton diameter) the behavior is quantitatively similar to that of the GaAs/(Al,Ga)As case, however as $L_z \rightarrow 0$ an important difference occurs which is a consequence of the barrier being a binary compound. As $L_z \rightarrow 0$, not only are the effects of well width fluctuations reduced for the reason given above but also the exciton wave function samples a larger volume of the binary GaAs barriers, so diminishing the effects of alloy broadening and leading to *sharper* photoluminescence (PL) and PLE linewidths.[2]

The decrease in PLE linewidth with decreasing well width offers the possibility of being able to resolve the fundamental heavy-hole excitonic resonance from any excited states and/or continuum edge and so measure *directly* the exciton binding energy in *narrow* quantum wells—something yet to be achieved (to our knowledge) in any quantum-well system. The observed binding energies should test the prediction of a "turnover" in exciton binding energy with decreasing well widths. In this paper we present calculations of the heavy-hole exciton binding energy for strained, isolated (In,Ga)As/GaAs quantum wells where we presume that only the (In,Ga)As layers are strained. The calculations have been made in the spirit of an "effective-potential" approximation that includes the effects of the finite potential barriers. For In fractions of around 0.12 to 0.15 the binding energy is predicted to go through a maximum at around $L_z = 50$ Å. We have measured the heavy-hole exciton binding energy from PLE measurements at ~4 K in wells of 48, 25, and 14 Å. The predicted trend in the binding energy is confirmed by the experimental observations.

Not only do our results show the expected decrease in PL linewidth with decreasing well width but also that under certain growth conditions it is possible to resolve two intrinsic peaks in PL in a "total" full width at half maximum of only 1.4 meV in a 14-Å $In_{0.15}Ga_{0.85}As$ quantum well. The fluctuations in the potential that causes these splittings cannot be tied down unambiguously by our observations. However, they are much smaller than would be predicted by discrete monolayer changes in well width and would correspond to fluctuations in In fractions of only 0.5% in 15%.

II. GROWTH DETAILS

The layers were all deposited by molecular-beam epitaxy in a Varian modular Gen II growth system. The samples were deposited on undoped (001) GaAs substrates mounted in In free holders and rotated at ~20 revolutions per minute during growth to ensure lateral uniformity of the alloy layers. The substrate temperature during growth was nominally 580 °C which is in the temperature range where significant reevaporation of In occurs. To compensate for the loss, an increased In flux has to be used. Growth rates for both GaAs and (In,Ga)As were measured using the reflection high-energy electron diffraction oscillation on a GaAs monitor slice prior to growth of the quantum-well samples. The growth rate for GaAs was 1 μm/h and the As_4 flux supplied to the surface was just sufficient to maintain an arsenic stabilized surface for both GaAs and (In,Ga)As.

We have grown a wide range of samples with differing well and barrier thicknesses but concentrate on a few specific examples here. The growth sequence for each of the samples was as follows: (i) a 1-μm GaAs buffer, (ii) 5 or 20 periods of (In,Ga)As wells and GaAs barriers, and (iii) a GaAs capping layer. None of the samples was intentionally doped. We have no evidence that suggests that any sample exceeds the critical thickness limit for the relaxation of the compressive strain via dislocation generation and preliminary x-ray analysis of these samples supports this assertion.[3]

As noted above, the substrate temperature for the growth of these samples is one at which significant reevaporation of In is occurring. Great care was taken to calibrate the growth so that the In fraction can be specified with some confidence. We have checked this calibration by comparing the measured exciton positions seen in the PLE with calculations of their energies made using the In fraction as an adjustable parameter. Our calculations do indeed show that for wide well widths the most sensitive parameter in determining the transition energy is indeed the In fraction; the band-offset fraction and well width being of secondary importance. A comparison of the In fraction determined in this way with the nominal value specified from the growth conditions showed good agreement.

III. RESULTS AND DISCUSSION

A. Exciton binding-energy calculations

We proceed with the calculation of the exciton binding energy in a spirit similar to that used by us previously to successfully describe the binding energy of both the ground and excited states of heavy-hole excitons (and magnetoexcitons) in the GaAs/(Al,Ga)As multiple–quantum-well (MQW) system.[4,5] The equation describing the electron-hole relative motion is

$$\left[-\frac{\hbar^2}{2\mu}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}\right]+V(\rho)-E\right]F(\rho)=0\;, \qquad (1)$$

where the "effective" potential for the in-plane, relative motion is given by

$$V(\rho)=-\frac{e^2}{4\pi\epsilon_0\epsilon_r}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{|f_e(z_e)|^2\,|f_h(z_h)|^2}{[\rho^2+(z_e-z_h)^2]^{1/2}}dz_e\,dz_h\;. \qquad (2)$$

The exciton binding energy is determined directly by numerical integration of Eq. (1). f_e and f_h are the eigenfunctions of a particle in a finite box. The eigenvalues of the electron and heavy-hole subbands have been calculated in the envelope-function approximation; matching conditions were used that ensured continuity in the particle wave function and "current" at each heterointerface. The effect of uniaxial and hydrostatic components of strain on the band gap of the well material are of course included in the calculation (see Refs. 6 and 7 for details). Our chosen offset ratio makes the system a mixed one; being type-I for the electron–to–heavy-hole transitions and type-II for the electron–to–light-hole transitions. It should be said that we have no *a priori* reason to believe that this is the "correct" band-offset ratio for this sytem. Suffice to say that up to the present time, and given our knowledge about sample dimensions etc., we are able to adequately assign and understand all the features (including those associated with light-hole transitions) in our PLE spectra using this value of the offset ratio. The parameters pertinent to the subband calculations are gathered in Tables I and II.

TABLE I. Deformation potentials and elastic stiffness constants used in the calculation of the strained- (In,Ga)As band gap. Values for the ternary alloy are found by linear interpolation.

Material	a (eV)	b (eV)	C_{11} (10^{11} dyn/cm^2)	C_{12} (10^{11} dyn/cm^2)
GaAs	-9.8	-1.7	11.88	5.38
InAs	-5.9	-1.8	8.33	4.53

In Fig. 1 we show the calculated dependence of the 1s binding energy of the heavy-hole exciton for isolated $In_{0.15}Ga_{0.85}As$ quantum wells and GaAs barriers. Nonparabolicity of the electron band is not included in our calculation. Two curves are shown in Fig. 1; the lower corresponds to an in-plane heavy-hole mass of $0.16m_0$ while the upper one is appropriate to an in-plane mass of $0.21m_0$. Both these values are in excess of that value obtained by using the published Luttinger parameters for the binary end members and making the appropriate linear interpolation.[8] However the calculated[9] and measured[10] in-plane heavy-hole mass in GaAs/(Al,Ga)As quantum wells is invariably larger than that calculated in the fully decoupled limit using the published Luttinger parameters. Furthermore, magneto-optical measurements on samples similar to those studied here show a variation of the in-plane heavy-hole mass between $0.17m_0$ and $0.22m_0$ as the $In_{0.12}Ga_{0.88}As$ well width varies between 200 and 50 Å.[11] Both curves in Fig. 1 were calculated using ϵ_0 of 12.9; again a value interpolated between the values for the binary end members.[8] As expected, qualitatively the trend in the calculation follows that for the familiar GaAs/(Al,Ga)As system. The effect of quantum-mechanical confinement being to increase the binding energy of the well material from its bulk value as the well width is reduced, reaching a maximum at a well width of about 50 Å until leakage of the wave function into the barrier regions eventually causes the exciton to look more three dimensional (3D) with an attendant fall in its binding energy to that of the barrier material. Further calculations for varying In fractions have shown the principal effect is simply to shift the point at which the maximum occurs (to smaller or larger well width depending on whether the In fraction increases or decreases).

TABLE II. Variation of material parameters as a function of the In fraction, x. All masses are in units of m_0 and all energies in eV.

Quantity	Variation with In fraction, x
Unstrained gap (4 K)	$E_0(x)=1.519-1.5387x+0.475x^2$
Electron mass	$m_e^*=0.0665-0.0435x$
Heavy-hole mass	$m_{\rm hh}^*=0.34$
Light-hole mass	$m_{\rm lh}^*=0.094-0.062x$
Spin-orbit splitting	$\Delta_0=0.341-0.09x+0.14x^2$

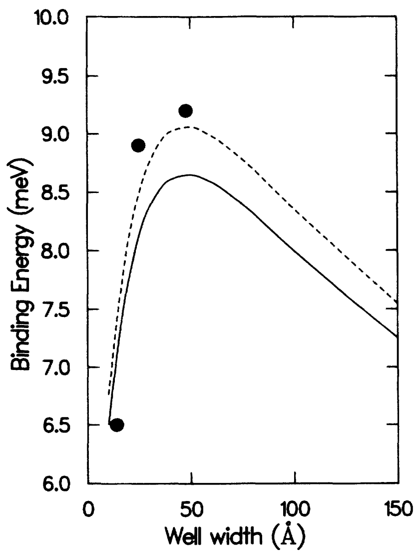

FIG. 1. Comparison of the measured and calculated heavy-hole exciton binding energies. The solid curve was calculated using an in-plane hole mass of $0.16m_0$ while the dashed curve used a value of $0.21m_0$ for this parameter.

B. Exciton binding-energy measurements

PL and PLE measurements were made with samples mounted on the cold finger of a variable temperature, continuous flow cryostat. The excitation source for the 4-K PLE measurements was an Ar^+ pumped dye (styryl-9) laser, which provides a source tunable out to ~9000 Å.

In Fig. 2 we show both the 4-K PL and PLE from a sample of five $In_{0.15}Ga_{0.85}As$ wells each 14 Å thick surrounded by GaAs barriers of 400 Å thickness. With this choice of barrier the lowest-lying confined electron states all lie within a width of 0.5 meV. We have been careful to chose barrier widths that would minimize the "bandwidth" of the electron states as it is well known[12] that when significant coupling is present, i.e., enough to pro-

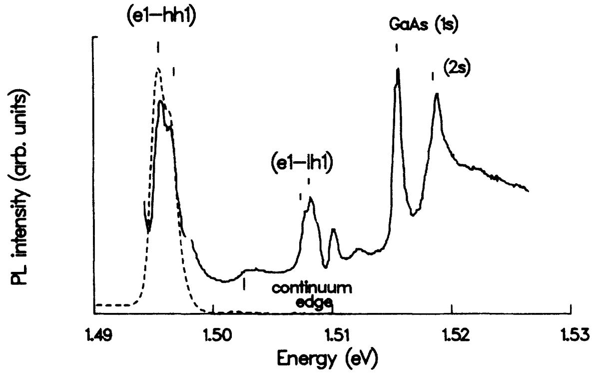

FIG. 2. PL (dotted) and PLE (solid) spectra at 4 K from the 14-Å, $In_{0.15}Ga_{0.85}As$ MQW sample.

duce a bandwidth comparable to the exciton binding energy in an isolated well, a decrease of the exciton binding energy toward that of the bulk occurs. Concentrating first on the PL, we see that there are two peaks resolvable in the spectrum. We believe both these peaks to be intrinsic in nature and are associated with the recombination of electron–to–heavy-hole excitons. Our reasons for this assertion appear in Sec. III D, however, we note at this juncture that even if we are incorrect in one of the assignments it would only alter our measured exciton binding energy by about 1 meV.

We now turn to the excitation spectrum which is rich in detail. At 1.496 and 1.497 eV we can resolve two features that are coincident with the two features seen in the PL spectrum. These peaks we associate with the creation of *e*1-hh1 free excitons. A further prominent feature is seen at about 1.507 eV, this is in the region of the spectrum where we expect to see transitions involving the electron–to–light-hole exciton. Closer examination of this feature suggests that there are, in fact, two contributions to this line split by about 1 meV. These we assign to the creation of *e*1-lh1 excitons; each of which can be paired with the *e*1-hh1 features seen to lower energy. Between the *e*1-hh1 and *e*1-lh1 features we see a steplike feature which we assign to the onset of the continuum. Measuring the energy difference of this feature with respect to the *e*1-hh1 peak at 1.496 eV yields a heavy-hole exciton binding energy for this well width of ~6.5 meV. (The onset of the continuum is taken at the top of the step.)

For this particular sample the range of the excitation spectra is extended to almost 1.53 eV. The rather sharp peak at 1.5153 eV we assign to the creation of GaAs free excitons predominantly in the GaAs buffer and the position of the peak at 1.5185 eV is consistent with the position of the 2*s*, excited state of the GaAs free exciton. Between the *e*1-lh1 exciton resonance and the GaAs free exciton two further peaks are prominent, one at 1.5099 eV and the second slightly broader one at 1.5125 eV. As far as we are aware, this detail has never been seen before in PLE or absorption spectra in this strained-quantum-well system. As to the assignment of these features, allowing for a few meV correction for the exciton binding energy both are consistent with being $\Delta n \neq 0$ transitions. The sharper one at 1.5099 we think most likely to be the *e*1-hh3 transition. This is of interest since the hh3 level is not confined in this structure, it is about 4 meV above the top of the confining barrier if we assume that our value of In fraction is correct. Pan and co-workers[7] have also claimed to see such transitions in 77-K photoreflectance spectra on wider samples of (In,Ga)As with similar In fractions (0.12). The somewhat weaker and broader feature at 1.5121 eV is energetically consistent with this being a transition between two confined states, namely the *e*2-hh1 transition. The apparent reduced strength of this transition in comparison to all those which are parity allowed argues in favor of this assignment.

Figure 3 shows the 4-K PLE spectrum from a sample with five wells of 25-Å $In_{0.15}Ga_{0.85}As$ separated by GaAs barriers 400 Å thick. The PLE signal from this sample was recorded in two parts (i) with the detection energy set in the low-energy tail of the emission spectrum and (ii) with the detection set at the peak of the PL signal at 1.469 eV. With detection set in position (i) the prominent $n=1$ electron–to–heavy-hole resonance is clearly seen, detection at (ii) reveals the further features, the sharpest of these we assign to the creation of electron–to–light-hole excitons. Between the *e*1-hh1 exciton and the *e*1-lh1 exciton we see a further clear feature which we associate with excited states of the exciton and the $n=1$ heavy-hole continuum. Taking the difference between the *e*1-hh1 peak and the onset of the heavy-hole continuum to be a good measure of the exciton binding energy, we find the 1*s* binding energy of the *e*1-hh1 exciton to be 8.9 meV. (The onset of the continuum is assumed at the top of the edge.) Similar structure, although less well resolved is present on the high-energy side of the *e*1-lh1 exciton; we believe this could be related to the onset of the light-hole continuum. If we assume this assignment to be correct we would determine the binding energy of the light-hole exciton to be 3.1 meV; considerably smaller than that for the heavy-hole exciton but a value not inconsistent with the more 3D nature of this exciton, since given our offset ratio the light-hole wave function is extended through both the GaAs and (In,Ga)As layers. Because the light-hole well is so shallow (only 12 meV, with our offset ratio) the possibility cannot be discounted that $\Delta n \neq 0$ transitions might also contribute to this region of the spectrum.

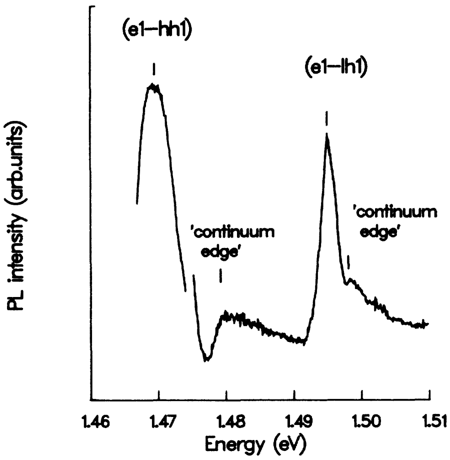

FIG. 3. PLE spectra at 4-K from the 25-Å, $In_{0.15}Ga_{0.85}As$ MQW sample.

C. Exciton binding-energy comparison

In Fig. 1 we have plotted the measured binding energies compared to our relatively simple calculation of this quantity. We include on this plot one further point from a sample with 20 wells of $In_{0.15}Ga_{0.85}As$ of width 48 Å separated by GaAs barriers that are 200 Å thick. For these dimensions the wells are coupled very slightly; the bandwidth of the electron states being ~0.5 meV. It is fair to say that given the uncertainties both in the calculation and the measurement that the agreement is good and the fall in the binding energy between the two samples is also in good quantitative agreement. There are, however, discrepancies between the calculation and the experiment even if we take into account the estimated error of ~1 meV in the experimental determination. Reasons exist as to why the calculated energies fall below the measured ones. The principal sources of error in the calculation may be (i) an incorrect value of the dielectric constant, (ii) the neglect of electron nonparabolicity, and (iii) an underestimate of the in-plane hole mass. As the well width is reduced the exciton wave function becomes less confined and spends more time in the barrier material so some weighted average of the dielectric constants of well and barrier material would be more appropriate than the well dielectric constant used here. As the dielectric constant of GaAs is slightly smaller than that of (In,Ga)As such a weighting will increase the binding energy slightly. Similarly both (ii) and (iii) are likely to increase the binding energy as the nonparabolicity always increases the electron mass and the trend in the in-plane mass from magneto-optical measurements suggests that this too will be even larger than the $0.21m_0$ limit we have chosen.

D. Excitonic fine structure

Let us return to the fine structure we see in the PL and PLE spectra in Fig. 2 at the *e*1-hh1 excitonic feature. Given a PL spectrum alone one might be tempted to assign the lower-energy one of these features to a bound exciton, however we also see both these features in the PLE spectrum neither one of which shows any "Stokes shift" from its position in the PL spectrum. We are of the opinion that this argues most strongly in favor of these two features both being intrinsic and from their energy positions we conclude that both must be *e*1-hh1 excitons. The fact that neither shows a Stokes shift also argues that they are both "free," i.e., delocalized excitons. What can give rise to such a splitting? The answer has to be some sample inhomogeneity, either interwell or intrawell potential fluctuations. Detection on the lower energy peak reveals the higher energy feature. For this to happen and be due to interwell fluctuations there has to be either a significant proportion of the wave function in each well, which is the case for this particular sample geometry, or efficient transfer of carriers between the wells. Intrawell fluctuations will lead to the same sort of features.

There are two obvious sources of inhomogeneities that would cause fluctuations in the potential and hence line splittings, these are well width fluctuations and variations in In fraction. An energy splitting corresponding to less than a monolayer is needed to explain the observed energy difference between the peaks. To distinguish between the two, additional information on the nature of the interfaces is needed. For example, if either or both interfaces is rough on a scale small compared to the exciton diameter then it might be possible for there to be predominantly two regions of the sample where the effective well widths were different by less than a monolayer. However, if both interfaces are smooth and the In fraction a constant, the smallest splitting between emission lines would be expected to correspond to a change in the confinement levels equivalent to changing the well width by a monolayer. Similarly the small energy splitting would be reproduced if the In fraction varied slightly between one essentially smooth region of the sample and another. Distinguishing these possibilities is not really possible given the data we have here.

IV. SUMMARY

For the first time results have been presented of direct measurements of the heavy-hole exciton binding energy in (In,Ga)As strained, isolated quantum wells that have a significant In fraction and well widths sufficiently narrow to see a *decrease* in binding energy with decreasing well width. Calculations of this quantity compare very favorably with the observed values.

In addition PLE measurements on isolated 14-Å $In_{0.15}Ga_{0.85}As/GaAs$ quantum wells have revealed a spectrum rich in detail allowing the identification of $\Delta n \neq 0$ transitions involving both confined and unconfined states.

Finally, fine structure has been noted in the proximity of both the *e*1-hh1 and *e*1-lh1 excitonic transitions in this 14-Å sample. Unfortunately, our present knowledge of interfacial details and growth dynamics does not allow us to distinguish whether the interwell or intrawell fluctuations in potential responsible for the splittings are due to inhomogeneity in well dimension or alloy composition.

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