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Exciton delocalization in thin double-barrier GaAs/AlAs/(Al,Ga)As quantum-well structures

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Nonconventional GaAs/$Al_{1-x}Ga_xAs$ quantum-well structures, with one or two monolayers of AlAs inserted between the GaAs layers and the $Al_{1-x}Ga_xAs$ barriers (double-barrier quantum wells), have been investigated to observe the quasi-three-dimensional behavior of excitons in thin quantum wells. These samples provide higher confinement energies than single quantum wells of the same thickness, in such a way that relatively thick wells produce shallow carrier subbands. An increase of the photoluminescence lifetime of excitons has been found when narrowing the well thickness. The analysis of intensity and shape of the photoluminescence spectra made us confident in interpreting this increase as an effect of the exciton delocalization, and a qualitative agreement with a simple model for the exciton radiative lifetime is obtained.

Carrier confinement in quasi-two-dimensional semiconductor heterostructures strongly modifies the physics of excitons with respect to bulk material. The most evident and discussed effect is the increase of the exciton binding energy, which, together with the unchanged electron-phonon coupling, determines the well-known influence of the excitonic features on the linear- and nonlinear-optical properties of semiconductor quantum wells (QW's). The increase of the exciton binding energy with carrier confinement is related to an increase of the oscillator strength and, therefore, a decrease of the radiative lifetime. A dependence of the exciton lifetime as a function of the well width L_w has been theoretically predicted[1,2] and experimentally established[1,3,4] even if a non-negligible spread of the experimental data suggests sample-dependent contributions.[5]

An even more interesting property is the reduction of the carrier confinement when narrowing the well width below a certain value (<10 Å for GaAs/$Al_{0.3}Ga_{0.7}As$) due to the finite height of the barrier potential and the subsequent spread of the exciton wave function into the barrier region. Therefore, in the limit $L_w \rightarrow 0$, the exciton in the QW, instead of reaching the two-dimensional (2D) limit, becomes a bulk exciton of the alloy. This delocalization is expected to produce both a reduction of the exciton binding energy[2] and an increase of the radiative time constant, but very few experimental results confirming this effect have been reported, mainly due to the difficulty of growing ultrathin QW structures of good quality. The increase of the exciton lifetime has been observed by Cebulla *et al.*[6,7] in $In_{1-x}Ga_xAs$/InP QW's with thicknesses below 40 Å, even if a controversy regarding these results can be found in the literature.[8] Other results have claimed to show, although in an indirect way based on the spectral analysis of the continuous-wave (cw) photoluminescence (PL), the increase of the excitonic lifetime for GaAs/$Al_{1-x}Ga_xAs$ QW's with thickness smaller than 15 Å.[9]

In this work we study the exciton radiative lifetime at low temperature in a set of nonconventional GaAs/$Al_{1-x}Ga_xAs$ QW heterostructures, characterized by extremely high confinement energies (sum of the energies of the first electron and heavy-hole subbands) for relatively thick QW's. This effect can be obtained by growing one or two monolayers (1–2 ML) of AlAs at each interface between GaAs and the $Al_{1-x}Ga_xAs$ barriers; these hetrostructures are thus named double-barrier quantum wells (DBWQ's).[10,11] The resulting shallow subbands (very close to the $Al_{1-x}Ga_xAs$ band edges) allow us to investigate the effects of the reduction of exciton localization in relatively thick QW's. In fact, the confinement energy in a 20-Å DBQW with 2 ML of AlAs coincides with that of a conventional single QW (SQW) of about 8 Å.

The exciton radiative lifetime has been studied by means of time-resolved photoluminescence (TRPL). We find an increase of the PL decay time greater than a factor 2 from a 20-Å SQW to a 20-Å 2 ML DBQW. An analysis of the nonradiative-decay mechanisms allows us to attribute the observed increase to a radiative property of the recombination. This effect turns out to be in qualitative agreement with the resulting high decrease of the exciton oscillator strength.

Four samples have been used in this work: two DBQW heterostructures with one and two AlAs monolayers at each side of the QW (named 1 ML and 2 ML, respectively), and two SQW samples, all of them grown by molecular-beam epitaxy (MBE) under similar conditions. Each structure contains three QW's with nominal thicknesses of 20, 40, and 80 Å; the Al content in the alloy is always around 0.3.

Continuous-wave photoluminescence and luminescence excitation (PLE) measurements have been performed at 4 K, using, for excitation, the 5145-Å line of an Ar^+ laser or an Ar^{+}-pumped dye laser (6200–6700 Å), respectively. The PL signal was dispersed by a double-grating monochromator and analyzed by usual photon-counting detection. The excitation source for TRPL was a Nd:YAG (yttrium aluminum garnet) synchronously pumped dye laser, operating at about 620 nm; the time duration of the pulses was 3 ps and the repetition rate 76 MHz. A synchroscan streak camera with a temporal resolution of the order of 20 ps was used to measure the PL decay times at 4 K.

Figure 1 shows the comparison of the PL spectra from a SQW sample (0 ML) and the two DBQW samples (1 and 2 ML). The most striking feature in these spectra is the shift of the excitonic transitions towards higher energies by adding the AlAs ML's; in the case of 20-Å wells, we find an increase of more than 100 meV from the 0-ML to the 2-ML DBQW. This directly shows the strong increase of the carrier confinement energy in the DBQW structures. It is worth noting that the PL integrated intensity of all the QW's investigated turns out to be of the same order of magnitude, even for the 20-Å DBQW's, while a strong reduction of the PL efficiency has been reported for thin SQW's of $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As/GaAs}$ (Ref. 12) having subbands of similar shallowness as in our case.

Useful information about the quality of the samples can be inferred from the analysis of the PL spectra. We find that the full width at half maximum (FWHM) ΔE of the excitonic lines depends on the confinement energy and is lower for the SQW's than for the DBQW's. In particular, in the case of the 20-Å QW's, ΔE varies from 9 meV for the SQW up to 18 and 20 meV for the 1- and 2-ML DBQW's, respectively, while very similar values of ΔE are found for the 80-Å ($\Delta E \approx 3$ meV) and 40-Å ($\Delta E \approx 6-10$ meV) QW's. The higher values of ΔE in the thinnest DBQW's can be accounted for by the increase of the carrier confinement energy. In fact the inhomogeneous linewidth can be estimated from the relation

$$\Delta E = \Delta E_H + \frac{d(E_e + E_{\mathrm{hh}})}{dL_w}\Delta L_w , \qquad (1)$$

where E_e and E_{hh} are the energies of the electron and heavy-hole subbands, respectively, and ΔE_H is the homogeneous linewidth. This expression yields a fluctuation of the well thickness ΔL_w very close in all the samples investigated ($\Delta L_w \approx \frac{1}{4}$ ML for SQW's and $\Delta L_w \approx \frac{1}{2}$ ML for DBQW's), thus showing a similar interface roughness. We would like to point out, as an additional indication of the quality of our samples, that we do not detect in the spectra of Fig. 1 relevant luminescence signals associated to shallow acceptor impurities at the low-energy side of the excitonic PL lines.

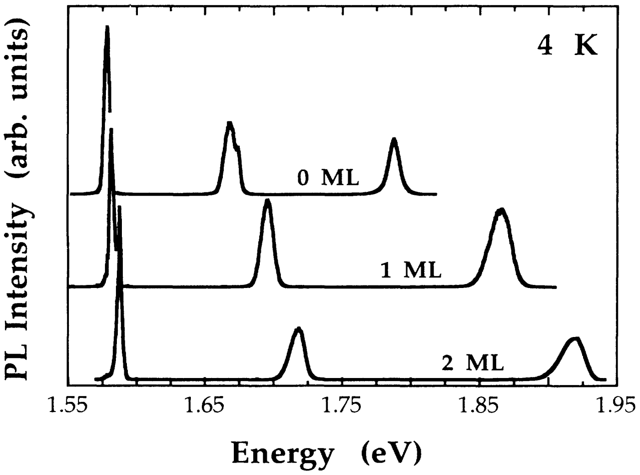

FIG. 1. Experimental PL spectra for 0-, 1-, and 2-ML samples at 4K.

Finally, we have performed PLE measurements of the different QW's with photon energies around the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ absorption edge, in order to obtain the height of the potential barriers in each sample (e.g., the Al content, x). At the same time, the confinement energies [experimental points in Fig. 2(a)] have been estimated from the energy position of the PL peaks, after taking into account the calculated exciton binding energy.[11]

The energies of the subbands in the DBQW structures have been determined by using an effective-mass model, which gives the following equation[10]:

$$\left[\frac{\bar{K}_i}{\bar{m}_{ib}^*}\right] + \left[\frac{K_i}{m_{ib}^*}\right]\tanh(K_i d) - \left[\frac{k_i}{m_{iw}^*}\right]\tan\left[k_i\frac{L_w}{2}\right] - \left[\frac{k_i\bar{K}_i m_{ib}^*}{K_i m_{iw}^* \bar{m}_{ib}^*}\right]\tanh(K_i d)\tan\left[k_i\frac{L_w}{2}\right] = 0 , \qquad (2)$$

where

$$\begin{aligned} k_i &= k_i(E_i) = (2m_{iw}^* E_i/\hbar^2)^{1/2} , \\ K_i &= K_i(E_i) = [2m_{ib}^*(V_i - E_i)/\hbar^2]^{1/2} , \\ \bar{K}_i &= \bar{K}_i(E_i) = [2\bar{m}_{ib}^*(\bar{V}_i - E_i)/\hbar^2]^{1/2} , \end{aligned} \qquad (3)$$

and i stands for electrons, heavy holes, and light holes; V_i and $\bar{V}_i$ are the confinement potentials of the AlAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ barriers, and d is the thickness of the AlAs layer. The effective masses along the growth direction (z) in GaAs, AlAs, and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ regions are m_{iw}^*, m_{ib}^*, and $\bar{m}_{ib}^*$, respectively. They have been corrected for nonparabolicity according to an empirical two-band model.[13]

The results of this calculation, with the usual values for the parameters involved (namely band-gap offset $\Delta E_c{:}\Delta E_v = 65{:}35$ and the standard effective masses) are shown in Fig. 2(a) and provide an estimate, by comparison with the experimental confinement energies, of the thicknesses of the different QW's [Fig. 2(a)]. Equation (2) gives a good concordance with the experimental data, in agreement with similar findings in the case of SQW's, if one reduces by nearly 2 ML and 1 ML the nominal thickness of the 80- and 40-Å DBQW's, respectively, while, for the thinnest DBQW's, the nominal thickness is obtained within the error due to the well width fluctuation ΔL_w.

As already mentioned, it turns out from Fig. 2(a) that in the DBQW systems the carrier subbands can be located very close to the barrier band edges, still for relatively large well widths. In fact, we found that no bound states are allowed below a minimum width of the DBQW. This can be deduced from Eq. (1) by substituting the energy E_i of the bound state by its maximum value $\bar{V}_i$, i.e., the continuum threshold for electrons or holes,

$$L_i^{\min}=\frac{2}{k_i(\bar{V}_i)}\arctan\left[\frac{m_{iw}^{*}K_i(\bar{V}_i)}{m_{ib}^{*}k_i(\bar{V}_i)}\tanh\{K_i(\bar{V}_i)d\}\right] . \quad (4)$$

The resulting widths for electrons (heavy holes) are 11.6 (10.1) and 18.3 Å (13.8) for 1 and 2 ML, respectively. A similar effect does not exist in a SQW structure, which always admits at least one bound state, and it evidences the relevance of DBQW's for investigating the 2D→3D transition of the carrier properties when decreasing the well width.

Other interesting features can be obtained from the analysis of the carrier wave functions and, in particular, of the probability of finding the carriers in the barrier region, reported in Figs. 2(b) and 2(c). In the case of thick QW's, the insertion of one or two monolayers of AlAs increases both the confinement energy and the carrier localization. Due to this peculiar characteristic, DBQW's have been suggested as good systems for obtaining heterostructures with very high optical quality, in particular in the near-infrared region.[10] However, when the confinement energy becomes comparable with the $Al_{1-x}Ga_xAs$ barriers, the penetration of the carrier wave functions into the barrier region strongly increases for DBQW structures, so that the probability of finding the carriers outside the well approaches unity for $L_w \rightarrow L_i^{\min}$. Therefore, in the case of thin wells the insertion of AlAs monolayers produces a delocalization of the carrier wave functions and, as already mentioned, DBQW's seem to be ideal systems for studying the increase of the excitonic lifetime in the limit of high confinement, as well. At the same time, it should be noted that for a given confinement energy, the SQW's exhibit a higher delocalization of carrier wave function than the DBQW's. The key point is that by using DBQW's it is possible to achieve a strong delocalization even for quite thick wells.

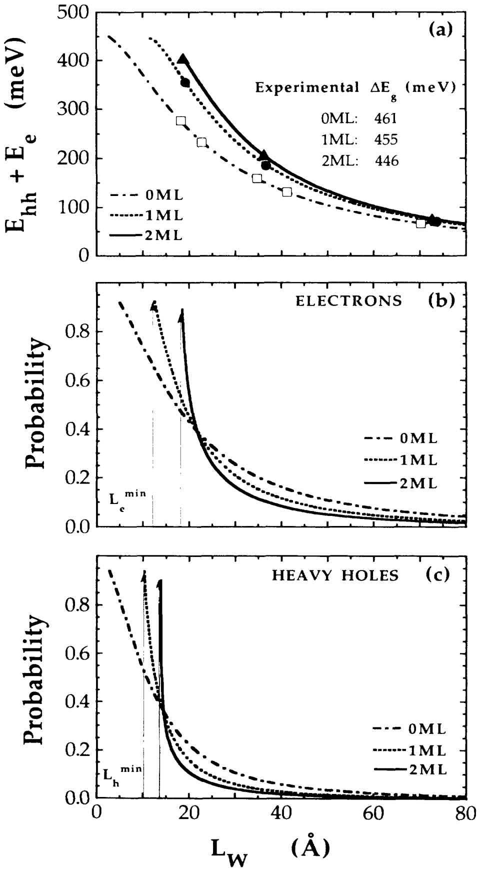

FIG. 2. (a) Calculated confinement energies as a function of the QW thickness for 0, 1, and 2 ML of AlAs, by using the experimental band-gap energy difference between GaAs and (Al,GA)As reported in the plot. The experimental points correspond to 0-ML (□), 1-ML (●), and 2-ML (▲) samples. (b) and (c) Calculated probability of penetration of electrons (b) and heavy holes (c) into the (Al,Ga)As barriers.

We would like also to stress that the insertion of the AlAs monolayers produces an asymmetry in the behavior of electrons and holes. We find a higher delocalization of the electron wave function with respect to the heavy holes when decreasing the well width, the most dramatic evidence being the difference between their corresponding minimum thicknesses. In particular, in the case of a 20-Å well with 2 ML as AlAs, the probability of finding the electron in the barrier region is of the order of 0.6 while the holes are still very well confined (probability ≈0.1). This feature which is not present in SQW's of $GaAs/Al_{1-x}Ga_xAs$, resembles the properties of thin QW's of $In_{1-x}Ga_xAs/InP$, where the band offset $\Delta E_c:\Delta E_v=35:65$ produces a similar effect. However, such asymmetry in DBQW's strongly depends on the choice of the band-gap offset which, in spite of being a key parameter of the $GaAs/Al_{1-x}Ga_xAs$ heterostructures, is still not known with enough accuracy for establishing precise consequences on DBQW's properties. On the other hand, DBQW's seem also to be highly suitable for testing the band-gap offset ratio $\Delta E_c:\Delta E_v$, as has also been stressed elsewhere.[14]

We now discuss the results obtained by TRPL measurements. In Fig. 3(a) the PL decay times τ_L at 4 K are reported for each QW of the samples investigated. We find a pronounced increase of τ_L with increasing the confinement energy when it becomes close to the barrier potential. However, before claiming any consequence on exciton delocalization, let us discuss the influence of nonradiative recombination in our samples. It is well known that τ_L corresponds to the radiative recombination time only when the excitonic energy-loss mechanisms give a negligible contribution. In fact, τ_L can be expressed by $\tau_L=[\tau_r^{-1}\tau_{nr}^{-1}]^{-1}$, where τ_r and τ_{nr} are the radiative and nonradiative lifetimes, respectively. Different mechanisms have been proposed for the excitonic energy losses in QW's at low temperature, but trapping at defects both in the well and in the barriers, seems to play a major role.[8,15,16]

In fact, it has been shown that the presence of nonradiative traps in the QW region is related to shallow-impurity contamination.[15,17] We will assume, from the absence of any notable extrinsic recombination in the PL spectra, that, at most, a small density of nonradiative centers is present in our QW's and, in particular, the 20-Å wells. Furthermore, we have shown in Fig. 2 that the insertion of the AlAs monolayers produces, at a given energy, a higher penetration of the wave function into the barrier regions, which are known to be of lower quality than the QW region. We can therefore infer a higher probability of carrier trapping at crystal defects, and then a lower nonradiative time in the case of 20-Å DBQW's with respect to the SQW's of the same thickness. It follows that the measured increase of τ_L in the 20-Å DBQW's possibly reflects an even higher increase of the corresponding radiative lifetime. A further confirmation of the negligible contribution of nonradiative mechanisms in the thinnest DBQW comes from the value of the integrated PL intensity which, contrary to the reduction of the PL efficiency reported for ultrathin SQW's,[12] is of the same order of magnitude as in thicker QW's.

The radiative lifetime of the exciton is inversely proportional to the oscillator strength of the optical dipole transition. In the simplest approach (two-bands approximation) the exciton wave function is built up from the envelope wave functions of the two lowest subbands of electrons and holes, and a trial function $\phi_{\mathrm{exc}}(\mathbf{r})$ is chosen for a variational calculation. In this model, which so far has been used for establishing the dependence of the excitonic lifetime on the well width,[1,6,7] one obtains

$$\frac{1}{\tau_R} \sim f_{1s} \sim |M_{cv}|^2 |\phi_{\mathrm{exc}}(0)|^2 |\langle \chi_e(z_e)|\chi_h(z_h)\rangle|^2 , \qquad (5)$$

where M_{cv} is the optical transition matrix element between the conduction and valence bands, and the last term is the electron-hole overlap integral.

The factor $|\phi_{\mathrm{exc}}(0)|^2$, which gives the probability of finding the electron-hole pair in the same unit cell, is inversely proportional to the exciton effective area. A rough estimate of the well-width dependence of this quantity can be given by considering the geometrical average of the half width of the squared envelop wave function of electrons and holes, $\langle z\rangle=\sqrt{\langle z_e\rangle\langle z_h\rangle}$. In fact, it has been suggested[6,7] that $\langle z\rangle$ reflects the exciton extension z_{exc} along the growth direction. At the same time, the in-plane radius of the exciton in the QW shows a dependence on the well width very similar to z_{exc}.[2,8]

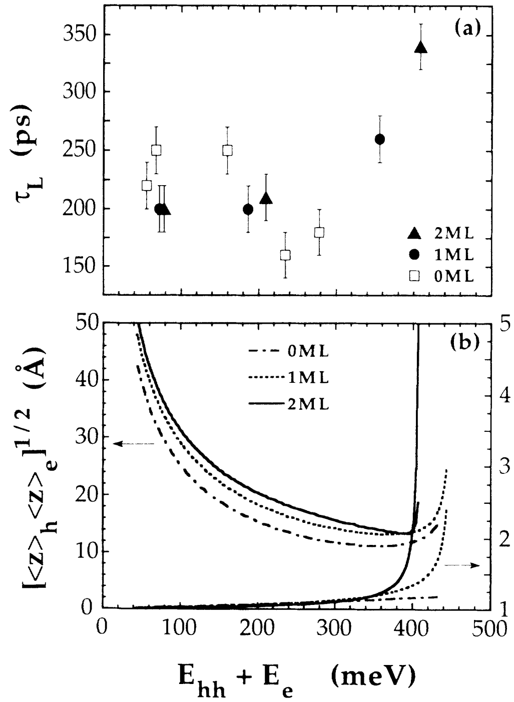

FIG. 3. (a) Experimental recombination lifetimes at 5 K for 0-, 1-, and 2-ML samples. (b) Calculated geometrical average extension and inverse-squared overlap integral of the electron and hole wave functions as a function of the confinement energy for the three cases: 0, 1, and 2 ML.

The electron-hole overlap integral in Eq. (4) is usually neglected in the case of GaAs/Al$_{1-x}$Ga$_x$As QW structures.[2,8] The value of the carrier masses and the band-gap offset ratio determine in the system a symmetry between the electron and hole wave functions producing an overlap integral near to unity even for very thin wells [Fig. 3(b)]. On the other hand, a non-negligible variation of the electron-hole overlap integral with the well thickness has been shown in heterostructures like In$_{1-x}$Ga$_x$As/InP QW's,[6,7] which, as already mentioned, exhibit some analogies with thin GaAs/Al$_{1-x}$Ga$_x$As DBQW's.

We report in Fig. 3(b) the electron-hole extension $\langle z\rangle$ and the inverse of the squared overlap integral as a function of the confinement energy for the heterostructures investigated (0–2 ML). The dependence of these quantities on the well width does not show significant differences for different values of the AlAs ML's as long as the wells are relatively thick; the overlap integral is near unity and the carrier extension decreases linearly with the well thickness. On the other hand, when the confinement energy approaches the continuum threshold the situation changes dramatically. In the case of 1 or 2 ML, both $\langle z\rangle$ and $|\langle\chi_e|\chi_h\rangle|^2$ start increasing very fast with increasing confinement energy, originating an increase of the radiative lifetime. An important contribution to this effect comes from the overlap integral, the more important the nearer is L_w to the minimum thickness for electrons, thus reflecting the asymmetry between electrons and holes. The increase of the exciton lifetime observed experimentally in highly confining DBQW's [Fig. 3(a)] can be therefore inferred by the dependence of the exciton oscillator on the well width, mainly due to the variation of $|\phi_{\mathrm{exc}}(0)|^2$ and $|\langle\chi_e|\chi_h\rangle|^{-2}$ as given in Fig. 3(b).

We would like to stress that even if the dependence of $|\phi_{\mathrm{exc}}(0)|^2$ on the well width has been calculated using the wave functions of the isolated carriers, the result can indeed be assumed as a reasonable estimate of the exciton extension as long as the confinement energies of electrons and holes in our narrowest wells[14] are larger than the exciton binding energy (10 meV as maximum[11]). It should also be noted that the mixing between heavy and light holes and the coupling between the 2D subbands and the 3D continuum are not considered within the two-band approximation, even if they certainly play an important role in DBQW heterostructures. Nevertheless, this type of calculation is not at all trivial and no attempts of this kind have been reported up to now, to our knowledge. We have also pointed out the experimental problems in extracting the value of the radiative lifetime from the measured PL decay times. For both reasons we have only tried a qualitative comparison of our calculations with the experimental results.

In summary, we have shown that the DBQW structures can be used for studying the quasi-3D behavior of excitons in ultrathin wells. We have found an increase of the excitonic PL decay time when increasing the carrier confinement energy. The overall quality of the samples investigated, as shown by the PL spectra, allows us to interpret this increase in terms of a property of the radiative lifetime of excitons. The experimental data turn out to be in agreement with the estimated dependence of the excitonic radiative lifetime on the well thickness.

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