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Exciton binding energy in (Al,Ga)As quantum wells: Effects of crystal orientation and envelope-function symmetry

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We report the first observation of 2*s*-excitonic features in the luminescence of non-(001)-oriented (Al,Ga)As multiple-quantum-well structures and conclude that the heavy-hole excitonic binding energy does not depend significantly on the orientation of the quantum well in the crystalline lattice. This is substantiated by calculations showing only minor changes (~0.3 meV) in the binding energy for the lowest heavy-hole exciton. However, a 10% anisotropy is predicted for the light-hole exciton, which is caused by mixing with the nearby second heavy-hole exciton.

The interpretation of the excitation spectra of (Al,Ga)As quantum wells has long been hampered by the lack of a precise determination of the excitonic binding energy in such structures. It was only recently that samples of a high enough quality could be grown to enable the observation of 2*s*-excitonic features in both luminescence[1] and excitation[2] spectra. Meanwhile, several theories for calculating excitonic binding energies in quantum-well systems have been advanced.[3] Thus far, most of the experiments and theories have focused on the main excitonic transitions in structures oriented along the [001] crystal direction. However, from both a theoretical and a more applied (band-structure engineering) point of view there is a need for a more detailed understanding of excitonic binding energies in quantum wells. Here we address ourselves, both theoretically and experimentally, to some symmetry aspects of the excitonic transitions. We discuss the effects of crystal symmetry as reflected in the anisotropy of excitonic binding energy for wells grown along different crystal directions. We report the first observation of 2*s*-excitonic emission for a non-(001)-oriented sample. Also, we consider the effects of the symmetry of the excitonic envelope function as related to the so-called "forbidden" transitions, resulting in a clear assignment of 2*p*-excitonic features in our excitation spectra.

Our (Al,Ga)As multiple-quantum-well samples were grown in a Varian Gen II molecular-beam-epitaxy machine, as described previously.[4] Two sets of multiple-quantum-well structures were grown, each consisting of three samples, grown respectively, along the [001], [310], and [111] crystal directions. In set I the (310)- and (111)*B*-oriented substrates were misoriented by 4° towards the (001) plane to facilitate nucleation; in set II the misorientation was 2°. X-ray diffraction and photoluminescence were used to determine the well widths and barrier composition. All samples have wells and barriers of the same thickness, as evidenced by the absence of second-order x-ray satellites. In all cases, the superlattice period found in the x-ray measurements equals twice the well width found by fitting the excitation spectra, yielding values for the well width of 76 Å for the samples of set I and of 71 Å for those of set II. Both x-ray (from the average alloy composition) and excitation spectra evidence that the barriers consist of $\mathrm{Al_{0.33}Ga_{0.67}As}$.

The photoluminescence and photoluminescence-excitation experiments were done using an argon-ion-laser–pumped pyridine-2 dye laser as the excitation source. Excitation density was always below 5 W/cm^2; in the luminescence measurements the excitation energy was 1.697 eV, i.e., below the band gap of the barriers. The samples were kept at a temperature of 6 K in an optical cryostat. The luminescence was dispersed through a double monochromator and detected by a cooled photomultiplier with a GaAs photocathode, using photon-counting techniques.

We investigated the anisotropy of exciton binding energies theoretically within an effective-mass approximation.[5] We expand the exciton envelope function into a large set of nonorthogonal two-dimensional hydrogen-atom-like wave functions to describe the behavior in the plane of the well and subband eigenfunctions obtained from a parabolic-band calculation for the out-of-plane components. This basis set allows for a classification of the exciton eigenstates in terms of its in-plane symmetry components. The valence-band mixing is described by the Luttinger Hamiltonian and the effect of the conduction-band nonparabolicity is approximated by employing electron effective masses at the first subband as obtained by an eight-band $\mathbf{k}\cdot\mathbf{p}$ method.[6] The effect of the deviations from axial symmetry along the growth axis ("warping") on the exciton binding energy is calculated to be very small for the (001) quantum well (<0.01 meV).[5] Since the effect of warping on the in-plane subband dispersion for quantum wells grown along the other crystal directions is very similar to that for the (001) case, it may be neglected altogether in the calculation of exciton binding energies. Using the set of previously[4] deter-

TABLE I. The material parameters used in our calculations and the parameters derived from them. All effective masses (in units of the free-electron mass) refer to the center of the Brillouin zone and all but $m^*_{\rm hh}(111)$, the heavy-hole mass along [111], are in the [001] direction.

	$E_{\rm gap}$	m^*_e	$m^*_{\rm hh}$	$m^*_{\rm lh}$	$m^*_{\rm hh}(111)$
GaAs	1.519	0.0665	0.34	0.094	0.7
AlAs	2.766	0.15	0.752	0.16	1.0

mined parameters for well and barrier materials that is summarized in Table I, we have calculated the exciton binding energies for 76 Å-wide quantum wells. Table II lists the results for the main crystal directions; sufficiently accurate values for the binding energy in other directions can be obtained by interpolation of these data. Our calculations predict a markedly different anisotropy of the binding energy for excitons derived from heavy and light holes. While the largest difference in the heavy-hole exciton binding energy for the different orientations is less than 0.3 meV, it is more than 5 times as much for light-hole excitons. This behavior is caused by the fact that, within the symmetry group of the quantum-well exciton Hamiltonian,[5] *s*-like excitons associated with the lowest heavy- (light-) hole subband mix predominantly, through the crystal field, with *p* excitons derived from the second light- (heavy-) hole state. Upon going from (001)- to (111)-oriented samples, the difference in confinement energy, $\Delta E(2h\text{-}1l)$, between second heavy- and first light-hole subbands decreases, due to the strong anisotropy of the heavy-hole effective mass. This causes an increase of the mixing between second heavy- and first light-hole subbands. Thus, the changes in $\Delta E(2h\text{-}1l)$ result in the anisotropy of the light-hole binding energy. At the same time, oscillator strength is transferred to the "forbidden" second heavy-hole exciton, as we will discuss below. On the other hand we have $\Delta E(2l\text{-}1h)$, the confinement-energy difference between first heavy hole and second light hole, larger than $\Delta E(2h\text{-}1l)$ and much less anisotropic. This explains the absence of a significant anisotropy in the heavy-hole exciton binding energy.

TABLE II. Theoretical exciton binding energies (in meV) for a 76-Å-wide quantum well.

Growth direction	1-1*h* (1*s*)	1-1*h* (2*s*)	1-1*l* (1*s*)
[001]	9.82	1.57	11.7
[110]	9.55	1.50	12.2
[310][a]	9.76	1.55	11.8
[111]	9.59	1.50	13.3

[a] From interpolation.

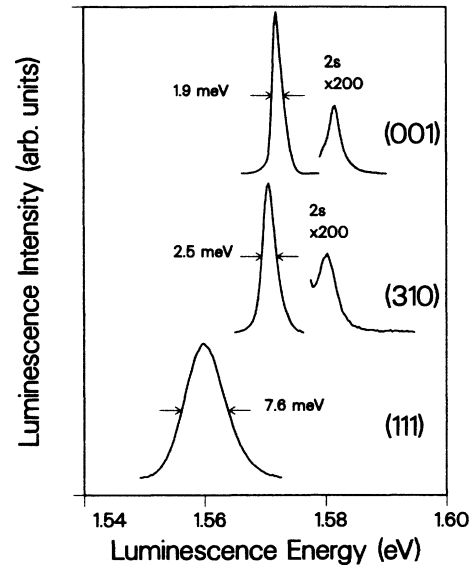

FIG. 1. Photoluminescence spectra at 6 K of the three samples with 4° misorientation. Substrate orientation is as indicated. Excitation energy is in all cases 1.697 eV, with a power density of 4 W/cm^2.

The photoluminescence spectra obtained from the second set of samples are shown in Fig. 1. The dominant emission features are due to radiative recombination of the 1*s* excitonic state associated with the lowest electron and heavy-hole confinement levels (which from now on will be referred to as 1-1*h*; we use a similar notation for the other transitions). Apart from these well-known 1-1*h* lines, a much less intense feature is observable at the high-energy edge of the emission band for the (001)- and (310)-oriented samples. For (001)-oriented samples this feature was previously identified[1] as originating from the 2*s* state of the 1-1*h* associated exciton. From the similarity of the spectra of the (001)- and (310)-oriented samples we conclude that also for the (310) quantum well the high-energy feature is due to the radiative recombination of a 2*s* exciton. This is the first observation of 2*s* excitons in non-(001)-oriented quantum wells and it furnishes a direct measure of the anisotropy of the exciton binding energy. In Table III we summarize the experimentally obtained positions (both in photoluminescence and excitation spectra) of the 1*s*- and 2*s*-excitonic features we have observed for our samples, as well as the half-width's [full width at half maximum (FWHM)] of the photoluminescence. As an example of the excitation spectra, Fig. 2 gives the data obtained from the first set of samples. Below, we will discuss the higher-energy part of these spectra. From Table III several conclusions can be drawn.

First, the above assignments of 2*s*-excitonic luminescence are substantiated by a comparison of the positions of the luminescence lines with those of the 1*s* and 2*s* excitons as observed in the excitation spectra. [For the (310)-oriented samples we assume the 2*s* exciton in the excitation spectra to be situated at the position indicated in the figure.] The observation of 2*s*-excitonic luminescence in the (111)-oriented wells is hindered by the relatively large FWHM of the 1-1*h* luminescence found for these samples.

Furthermore, the small difference in the 1*s*-2*s* splittings as observed for the (001)- and (310)-oriented samples is a good confirmation of the theoretical predictions concerning the small anisotropy of the heavy-hole exciton bind-

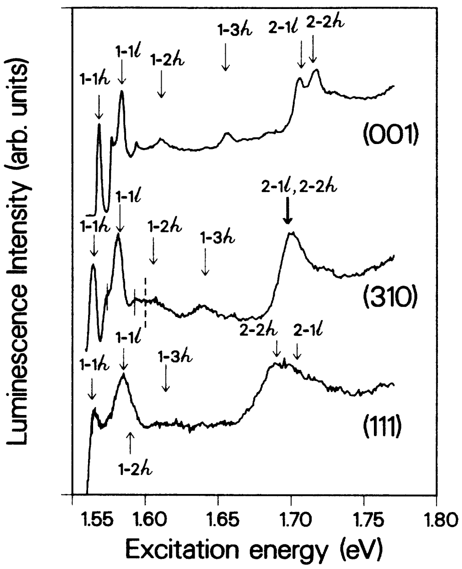

FIG. 2. Photoluminescence excitation spectra at 6 K obtained from the 2°-misoriented samples, with substrate orientation as indicated. For clarity, the vertical scale for the spectrum (310)-oriented well was enlarged by a factor of 3 for photon energies larger than indicated by the dotted line. Detection is always at the low-energy edge of the luminescence spectrum.

ing energy. However, for both well widths the theoretically obtained value for the 1*s*-2*s* term splitting is 1.5 meV smaller than that found experimentally. This is a general, but not very well understood, feature of most of the recent theories of exciton binding in quantum wells when using appropriate effective masses and barrier heights.[3,5,7]

Finally, we remark that the 2° off-oriented samples have a smaller FWHM for quantum wells in the [310] direction, while the situation is opposite for the (111)-oriented wells. This may indicate different nucleation mechanisms for the two cases and is under further investigation.

Next, we will discuss the "forbidden" excitonic transitions (between the hole and electron subband states with unequal subband index *i*, $\Delta i \neq 0$) observed in the photoluminescence excitation spectra, cf. Fig. 2. Here the arrows indicate the calculated positions of the various transitions.[8] We now focus at the $\Delta i \neq 0$ transitions 1-2*h*, 1-3*h*, and 2-1*l*. Both 1-2*h* and 1-3*h* lines have a much smaller oscillator strength than the $\Delta n = 0$ transitions. For the 1-3*h* transition this can be explained by the small overlap of first electron and third heavy-hole envelope functions. We calculate a band-to-band oscillator strength for the 1-3*h* line in the (001) sample of about 1% of that of the 1-1*h* transition. This is somewhat smaller than the experimentally observed ratio. It was suggested by Chan[9] that the 1-3*h* exciton could possess some *d* character, enabling mixing with the 1-1*l* exciton, which would then lead to a larger oscillator strength and, consequently, a smaller exciton binding energy than that found for the 1-1*h* line. However, our calculations do not confirm such an effect: binding energies and in-plane symmetries of 1-1*h* and 1-3*h* excitons are very similar. This is also borne out by our study of the excitation spectra of these samples, where we assumed equal binding energies for both excitons, leading to a consistent fit of all spectra and a determination of the valence-band anisotropy.[4] While the 1-3*h* oscillator strength is small but not zero, the 1-2*h* band-to-band transition is parity forbidden when valence-band mixing is not taken into account. In the terminology associated with the basis set we use in our calculations, this means that the observed line corresponds to the creation of an exciton with an odd-parity (in the plane of the well) envelope function, most probably in a 2*p* state, which through the cubic crystal field is mixed with the 1-1*l* 1*s* exciton.[3,5,9,10] This is, of course, the same mechanism as the one that causes the enhanced anisotropy of the 1-1*l* exciton binding energy. Convincing evidence for this assertion can be found in the spectral position of the 1-2*h* line. When we use an exciton binding energy of 10.8 meV, as was measured for the 1-1*h* line, the calculated transition energy is 9 meV lower than the experimental value. This implies that the 1-2*h* exciton is bound only by some 2 meV, and thus in a state with predominantly $n = 2$ character (n is the principal quantum number of the in-plane exciton envelope function). The above symmetry argument then leads to the 2*p* assignment. Of course, the same argument holds for the 2-1*l* and 2-2*h* transitions.[8,10,11] Since the difference in energy between the two lines is smaller than that between 1-1*l* and 1-2*h*, a larger oscillator strength is now expected for the "forbidden" transition, again in qualitative agreement with the experiment. Previously, Miller *et al.*[11] discussed the mixing of the 2-1*l* and 2-2*h* excitonic transi-

TABLE III. Positions[a] of the observed 1*s* and 2*s* 1-1*h* excitonic features.

Growth direction	Luminescence (1*s*)	Luminescence (2*s*)	Luminescence Splitting	FWHM	Excitation (1*s*)	Excitation (2*s*)	Excitation Splitting
[001][b]	1.5665	1.5754	8.9±0.5	2.14	1.5682	1.5768	8.6±0.5
[310][b]	1.5612	1.5705	9.3±0.7	2.83	1.5638	1.5733	9.5±1.0
[111][b]	1.5578			4.75	1.5645		
[001][c]	1.5721	1.5816	9.5±0.4	1.86	1.5741	1.5827	8.6±0.5
[310][c]	1.5709	1.5805	9.6±0.6	2.48	1.5738	1.5826	8.8±1.0
[111][c]	1.5600			7.62	1.5730		

[a] Term splittings and FWHM are in meV, all others energies in eV.

[b] First set of samples; (310) and (111) orientations 4° misoriented towards (001). Well width 76 Å.

[c] Second set of samples; (310) and (111) orientations 2° misoriented towards (001). Well width 71 Å.

tions and provided evidence for the heavy-hole character of the 2-1*l* line by polarization analysis. The shift of the 2-1*l* line due to the marked anisotropy of the heavy-hole mass causes a near coincidence of the 2-1*l* and 2-2*h* transitions in the (310) sample. For the (111)-oriented sample theory even predicts interchanging of the 2-1*l* and 2-2*h* transitions, leading to the tentative assignments given for that excitation spectrum.

Our exciton calculations confirm the above assignments. However, the experimentally observed oscillator strength of the "forbidden" transitions is, still, somewhat larger than that found in our calculations. This difference might be caused by the presence of some residual electric field across the sample.[12]

In conclusion, we have shown that the binding energy of heavy-hole excitons in quantum wells does not depend significantly on the orientation of the wells. However, mixing between the first light-hole and second heavy-hole subbands causes a considerable anisotropy in the binding energy of the light-hole exciton. Furthermore, we have presented clear evidence that the excitons associated with the 1-2*h* and 2-1*l* transitions have *p* symmetry in the plane of the well. The 1-3*h* line corresponds to a 1*s* exciton.

Note added in proof. Very recently, Hayakawa *et al.* [Phys. Rev. B **38**, 1526 (1988)] reported 1*s*-2*s* splittings in excitation spectra of (111)-oriented quantum wells which were interpreted as indicative of an increase of the exciton binding energy of 10% relative to (001)-oriented wells. This would imply that the in-plane hole mass of (111) quantum wells should be larger than that of (001) quantum wells, which is at variance with an effective hole-mass tensor with its largest element in a direction perpendicular to the (111) plane of the well. At present, we cannot offer an explanation for this discrepancy.

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[7] Note that upon modeling the excitonic binding energy in a well with infinitely high barriers the authors of Ref. 2 obtain results from their calculation that are in good agreement with the experimental data. However, more advanced calculations using realistic using realistic values for barrier height and effective masses seem to yield binding-energy values that are too small in comparison with the experimental findings. See also Refs. 3 and 5.

[8] It should be noted here that, as our $\mathbf{k}\cdot\mathbf{p}$ theory does not fully incorporate the nonparabolicity of the conduction band, it does not predict the correct confinement energy for the second electron level. We have therefore lowered the calculated transition energies involving the second electron level for all three orientations by 10 meV, which is the difference between calculated and observed transition energies of the 2-2*h* line in the (001)-oriented sample. This procedure does, of course, not influence the relative positions of the 2-1*l* and 2-2*h* transitions which is our only issue of discussion here.

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