

## Binding energy of neutral bound excitons in GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As quantum wells

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The binding energy of an exciton bound to a neutral donor ( $D^0, X$ ) in a GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As quantum well is calculated variationally by using a two-parameter wave function. There is no artificial parameter added in our calculation. Our results agree fairly well with previous experimental results, except that our position of the binding energy maximum is at about 15 Å, not at 100 Å as shown by Reynolds *et al.* [Phys. Rev. B **40**, 6210 (1989)]. [S0163-1829(97)05703-2]

There is a great amount of experimental data about donor-bound exciton ( $D^0, X$ ) states in GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As quantum wells (QW's).<sup>1-3</sup> The original report of donor-related complexes in QW's was first proposed by Shanabrook and Comas.<sup>4</sup> Reynolds *et al.*<sup>5</sup> reported sharp lines observed in the photoluminescence (PL) associated with  $D^0, X$  transitions in nonintentionally doped GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As multiple quantum wells.  $D^0, X$  transitions are also reported by Nomura, Shinozaki, and Ishii<sup>1</sup> in Si-doped GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As single QW's (SQW's). Liu *et al.*<sup>2</sup> observed transitions in PL associated with excitons bound to neutral and ionized donors located at the center of the quantum wells. The results reported by Nomura *et al.*<sup>1</sup> or Liu *et al.*<sup>2</sup> both reveal that the value of the binding energy of  $D^0, X$  decreases as the well size is increased. Reynolds *et al.*<sup>3</sup> observed the binding energy of  $D^0, X$  as a function of well size from 75 to 350 Å, when donors are located in the center of the well, or at the edge of the well in the interface region in GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As QW's. They found the binding energies increased as well size was reduced until about 100 Å, after which they decreased. As far as we know, however, there have been few theoretical studies of  $D^0, X$  states in QW's. Some authors<sup>6,7</sup> calculated the binding energy of  $D^0, X$  in bulk (e.g., GaAs), and only Kleinman<sup>8</sup> calculated the binding energy of  $D^0, X$  in SQW's. Using the six-parameter wave function of Brinkman, Rice, and Bell,<sup>9</sup> Kleinman<sup>8</sup> calculated variationally the binding energy of the biexciton and  $D^0, X$  as a function of well thickness in an infinite semiconductor (e.g., GaAs) quantum well. The wave function used by Kleinman<sup>8</sup> is good for calculating the binding energy of the biexciton. As regards calculating the binding energy of  $D^0, X$  in SQW's, although his results agreed with the experimental results<sup>1,2</sup> very well, an artificial parameter had to be added in his calculating the binding energy of  $D^0, X$  (other than variational parameters completely determined by requirement of maximizing  $E$ ), or a bound state could not be found with his wave function. So, it is necessary to make further theoretical study for the binding energy of  $D^0, X$  in SQW's.

In the effective-mass approximation, the Hamiltonian of  $D^0, X$  in SQW's can be written

$$H = -c_e(\nabla_1^2 + \nabla_2^2) - c_h\nabla_3^2 - \frac{2}{\sqrt{\rho_1^2 + z_1^2}} - \frac{2}{\sqrt{\rho_2^2 + z_2^2}} + \frac{2}{\sqrt{\rho_3^2 + z_3^2}} + \frac{2}{\sqrt{\rho_{12}^2 + (z_1 - z_2)^2}} - \frac{2}{\sqrt{\rho_{13}^2 + (z_1 - z_3)^2}} - \frac{2}{\sqrt{\rho_{23}^2 + (z_2 - z_3)^2}} + V_{e1} + V_{e2} + V_{h3}, \quad (1)$$

where 1, 2 are the electrons and 3 is the hole,  $\vec{\rho}_i$  is the relative coordinate to the origin in the two-dimensional (2D) plane,  $\rho_{ij}$  is the distance between the  $i$ th and the  $j$ th particles in 2D plane,  $c_e = m_{ew}/m_e$ ,  $c_h = m_{eh}/m_h$ ,  $m_{ew}$  is the effective mass of conduction electron in GaAs,  $m_e$  ( $m_h$ ) is the effective mass of the conduction electron (the heavy-hole) in GaAs or Al<sub>x</sub>Ga<sub>1-x</sub>As. The potential wells for the conduction electron  $V_{e1}$ ,  $V_{e2}$  and for the heavy-hole  $V_{h3}$  are assumed to be square wells of width  $d$ . Here we have chosen, without any loss of generality, the origin of the coordinate system to be the center of the GaAs well. The values of the potential-well heights  $V_e$  and  $V_h$  are determined from the Al concentration in Al<sub>x</sub>Ga<sub>1-x</sub>As.

In our calculations, the units of distance and energy are the electron Rydberg and Bohr radius in GaAs, respectively, i.e.,  $a_B = \epsilon_w \hbar^2 / e^2 m_{ew}$ ,  $R_y = e^2 / 2\epsilon_w a_B$ , where  $\epsilon_w$  is the dielectric constant in GaAs.

For the  $D^0, X$  we use the wave function<sup>8</sup>

$$\Psi = \Phi(\vec{\rho}_1, \vec{\rho}_2, \vec{\rho}_3) f_e(z_1) f_e(z_2) f_h(z_3), \quad (2)$$

where  $f_e(z)$  and  $f_h(z)$  are taken to be ground-state solutions of an electron and a hole for the finite square-well potentials, respectively. To simplify the calculation we have not included an explicit  $z$  dependence in  $\Phi$ . The Hamiltonian of interest is then just  $H_{\text{eff}}$ , which we write in dimensionless form

$$H_{\text{eff}} = -c_e(\nabla_1^2 + \nabla_2^2) - c_h\nabla_3^2 - 2(U_{1D} + U_{2D} - U_{3D} - U_{12} + U_{13} + U_{23}), \quad (3)$$

where  $c_e = m_{ew}/m_{e\parallel}$ ,  $c_h = m_{eh}/m_{h\parallel}$ .  $m_{e\parallel}$  ( $m_{h\parallel}$ ) is the effective 2D mass of the electron (the heavy hole), which can be

calculated from Ref. 10.  $U_{1D}$ ,  $U_{2D}$ ,  $U_{3D}$ ,  $U_{12}$ ,  $U_{13}$ ,  $U_{23}$ , which come from the effective 2D Coulomb interaction,  $U_{1D}$ ,  $U_{2D}$ , and  $U_{3D}$  are defined by<sup>8</sup>

$$U_D(\rho) = \int \frac{f_e^2(z_e)}{\sqrt{\rho_e^2 + z_e^2}} dz_e = \frac{1 - e^{-\gamma_D \rho_e}}{\rho_e}, \quad (4)$$

and  $U_{12}$ ,  $U_{13}$ , and  $U_{23}$  are defined by<sup>8,11</sup>

$$U_X(\rho) = \int \int \frac{f_e^2(z_e) f_h^2(z_h)}{\sqrt{\rho^2 + z^2}} dz_e dz_h = \frac{1 - e^{-\gamma_X \rho}}{\rho}, \quad (5)$$

where  $z = z_e - z_h$ ,  $\vec{\rho} = \vec{\rho}_e - \vec{\rho}_h$  is the relative coordinate in the 2D plane,  $\gamma_D^{-1}$ ,  $\gamma_X^{-1}$  is a measure of the well width  $d/a_B$ . In Eqs. (4) and (5), we have chosen<sup>8</sup>  $\gamma_{1D} = \gamma_{2D} = \gamma_{3D} = \gamma_D$ ,  $\gamma_{12} = \gamma_{13} = \gamma_{23} = \gamma_X$ .

In order to obtain the values of  $\gamma_X$ , we follow a variational approach and use the trial wave function,  $\psi = f_e(z_e) f_h(z_h) g(\rho, z, \phi)$ , to seek out the binding energies of an exciton in SQW. For the function  $g(\rho, z, \phi)$ , we have chosen the simple form,  $g(\rho, z, \phi) = A_X \exp(-\lambda \sqrt{\rho^2 + z^2})$ , where  $\lambda$  is a nonlinear variational parameter, which is adjusted to minimize the energy,  $A_X$  is the normalized constant.

The variational binding energy  $E_{XB}$  of the  $1s$  exciton state is obtained by subtracting the energy  $E_X$  of the exciton system from the lowest electron and hole subband energies ( $E_e$  and  $E_h$ ). We assumed an infinite mass for the donor. A similar calculation is made for the impurity state in SQW's, from which the binding energy  $E_{DB}$  of the  $1s$  impurity state is obtained.

In our calculation, we have used the varying values for the conduction- and valence-band mass parameters and the dielectric constants in GaAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . We find that our results, the binding energies of excitons and impurity states in SQWs, agree fairly well with those of the predecessors'.<sup>11-13</sup>

The exciton in SQW's can be described by the effective 2D exciton in the plane perpendicular to the  $z$  axis.<sup>8,10</sup> The eigenequation of its Hamiltonian is

$$\left[ -c_X \left( \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) - 2U_X(\rho) \right] F(\rho, \phi) = E_{XB} F(\rho, \phi). \quad (6)$$

Here  $c_X = m_{ew}/\mu_{\parallel}$ ,  $\mu_{\parallel} = m_{e\parallel} m_{h\parallel} / (m_{e\parallel} + m_{h\parallel})$  is the 2D reduced mass. The effective-mass mismatch between the well and barrier materials is taken into account.

The wave function  $F(\rho, \phi)$  can be written in simple form<sup>10</sup> for the lowest states,  $F(\rho, \phi) = N e^{-\alpha_X \rho}$ . Changing the nonlinear variational parameter  $\alpha_X$  to maximize the energy  $E_{XB}(\alpha_X)$  of the effective 2D exciton, we have the following equations:

$$c_X^2 \alpha_X^4 - 8c_X \alpha_X^3 - 2c_X E_{XB} \alpha_X^2 + E_{XB}^2 = 0, \quad (7)$$

$$\gamma_X = \frac{2c_X \alpha_X^3 - 2E_{XB} \alpha_X}{E_{XB} - c_X \alpha_X^2 + 4\alpha_X}. \quad (8)$$

By requiring that Eqs. (7) and (8) give the  $E_{XB}$  obtained previously, we gain the  $\gamma_X(d)$  shown in Table II. A similar

calculation is made for the impurity state, from which we gain the  $\gamma_D(d)$  shown in Table II.

Sanders and Yia-Chung Chang's<sup>6</sup> presented the wave function of the bound exciton in bulk and calculated variationally the binding energy of the bound exciton. In our effective 2D bound exciton system,  $\sigma = m_{e\parallel}/m_{h\parallel}$  is about 0.6. Therefore, it is reasonable that we use a wave function in the effective 2D bound exciton system, which has a similar form as that in bulk materials, i.e.,

$$\Phi(\vec{\rho}_1, \vec{\rho}_2, \vec{\rho}_3) = N [\phi_D(\vec{\rho}_1) \phi_c(\vec{R}_{23}) \phi_X(\vec{\rho}_{23}) + (1 \leftrightarrow 2)], \quad (9)$$

where  $N$  is the normalization constant,  $\phi_D(\vec{\rho}) = e^{-\alpha_D \rho}$  and  $\phi_X(\vec{\rho}) = e^{-\alpha_X \rho}$  are Slater  $1s$  orbitals describing the effective 2D donor and exciton, respectively, and  $\phi_c$  is a wave function describing the center-of-mass motion of the effective 2D exciton.  $\vec{R}_{23} = (m_{e\parallel} \vec{\rho}_2 + m_{h\parallel} \vec{\rho}_3) / (m_{e\parallel} + m_{h\parallel}) = (\sigma \vec{\rho}_2 + \vec{\rho}_3) / (1 + \sigma)$  is the center-of-mass coordinate for the effective 2D exciton, and  $\vec{\rho}_{23} = \vec{\rho}_2 - \vec{\rho}_3$  is the relative coordinate of electron and hole in the effective 2D exciton. The symbol  $(1 \leftrightarrow 2)$  in the above equation represents the exchange term, in which the roles of particles 1 and 2 are interchanged. The energy of the bound exciton system

$$E = \frac{\int \Phi^* H_{\text{eff}} \Phi d\tau}{\int |\Phi|^2 d\tau}, \quad (10)$$

where  $d\tau = d^2 \vec{\rho}_1 d^2 \vec{\rho}_2 d^2 \vec{\rho}_3$  is the total volume element. We assumed  $\phi_c(R) = R^\alpha e^{-\beta R}$ , where  $\alpha$  and  $\beta$  are the nonlinear variational parameters, which are adjusted to minimize the energy  $E$  of the bound exciton system. Using the values of  $\alpha_D$ ,  $\alpha_X$ ,  $\gamma_D$ ,  $\gamma_X$ , obtained previously, we obtained the binding energy of  $D^0, X$ :

$$E_{XD} = E - E_{DB} - E_{XB}. \quad (11)$$

The material parameters used in the calculation are listed in Table I. Both the heavy-hole mass along the  $z$  direction and the reduced mass corresponding to heavy-hole bands in the plane perpendicular to the  $z$  axis can be expressed in terms of the well-known Kohn-Luttinger band parameters  $\gamma_1$  and  $\gamma_2$ .<sup>14</sup> The complete results for  $D^0, X$  in a GaAs-Al<sub>0.25</sub>Ga<sub>0.75</sub>As SQW as a function of  $d$  are given in Table II.

We discuss our results as follows:

(1) In comparison with the theoretical results obtained by Kleinman,<sup>8</sup> (i) It can be seen from Fig. 1 that the binding energy of  $D^0, X$  obtained by us basically agrees with the results of Ref. 8. Because Kleinman<sup>8</sup> used the model of the infinite quantum well, his binding energies of  $D^0, X$  do not have a maximum. But our results show that the peak of the binding energy of  $D^0, X$  in SQW's appears, which is an inevitable outcome for SQW's with finite potential barriers. The position of the peak appears at around  $d = 15 \text{ \AA}$ , this is also the position of the peak for the exciton or the impurity states. It is easy to understand, since the electrons and hole are bounded by the same potentials both in the case of  $D^0, X$  and in the case of the exciton or the impurity states. The peak value is about 3.1 meV, which is reasonable. (ii) The two-parameter wave function we used has a clear physi-

TABLE I. Material parameters of GaAs and  $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$  used in the calculation.

Material	$\Delta E_g$ (meV)	$\Delta E_c/\Delta E_g$	$\gamma_1$	$\gamma_2$	$m_e$	$\epsilon$
GaAs <sup>a</sup>	311.88 <sup>b</sup>	60% <sup>a</sup>	6.85	2.1	0.0665	12.5
$\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$			5.49 <sup>c</sup>	1.52 <sup>c</sup>	0.0873 <sup>d</sup>	11.9 <sup>d</sup>

<sup>a</sup>Reference 12.<sup>b</sup>Reference 13.<sup>c</sup>Reference 16.<sup>d</sup>Reference 15.

cal idea and a simple mathematical form, and incorporates important interparticle correlation effects. (iii) When we calculate the binding energy of  $D^0, X$ , only the two variational parameters in the wave function are determined completely by minimizing the value  $E$  of the total energy of the bound exciton. The correct results have been obtained without adopting any adjustable parameters in our theory. Whereas in Ref. 8, if his artificial adjustable parameter had not been introduced in the wave function to correct his calculated results, the bound states would not have been obtained. Therefore we can conclude that our wave function has better ability to describe the properties of a neutral bound exciton in SQW's than that in Ref. 8. (iv) The Haynes factor  $f_H$ <sup>8,17</sup> is calculated for 12 well thicknesses. It is reasonable that the value  $f_H$  is from 0.09 to 0.23.

(2) In comparison with experiments: (i) Our results agree rather well with the results observed by Nomura, Shinozaki, and Ishii<sup>1</sup> and Liu *et al.*<sup>2</sup> (Fig. 1). And they also agree qualitatively with those observed by Reynolds *et al.*<sup>3</sup> (Fig. 1), in addition, though our values ranging from 90 to 300 Å are smaller than those determined by Reynolds *et al.*,<sup>3</sup> yet their general changing tendency is nearly the same. (ii) The maximum value of the binding energy of  $D^0, X$  in Ref. 3 is at well sizes of about 100 Å, which is considerably larger than that of ours, about 15 Å. We think that the reason for the binding energy of  $D^0, X$  reaching a maximum at well sizes of about 100 Å is possibly due to the doping way of the samples, but not caused by the finite potential barrier. The doping samples

TABLE II. Summary of the optimized results for the bound exciton in a GaAs- $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$  SQW.  $z_i$  indicates the position of the donor and the unit of  $E_{XD}$  is meV.

$d$ (Å)	$z_i=0$			$z_i=d/2$		
	$\gamma_D$	$\gamma_X$	$E_{XD}$	$\gamma_D$	$\gamma_X$	$E_{XD}$
8	5.91	5.06	2.684	5.88	5.06	2.683
10	6.32	5.49	2.906	6.25	5.49	2.875
15	6.83	6.01	3.091	6.60	6.01	2.993
20	6.97	6.10	3.037	6.43	6.10	2.734
30	6.95	5.96	2.847	5.66	5.96	2.387
50	6.64	5.52	2.521	4.21	5.52	1.737
80	5.92	4.83	2.094	2.93	4.83	1.261
100	5.45	4.41	1.854	2.42	4.41	1.085
150	4.51	3.57	1.396	1.67	3.57	0.828
200	3.84	3.01	1.106	1.28	3.01	0.700
250	3.37	2.63	0.915	1.04	2.63	0.624
300	3.03	2.36	0.790	0.89	2.36	0.580

were doped over the central range in proportion of the well sizes in Refs. 1 and 2. But in Ref. 3, the doping range in the wells was fixed. The samples for well widths ranging from 75 to 100 Å were doped over the central 25 Å and for well widths ranging from 150 to 300 Å were doped over the central 50 Å, thus, the doping proportion is different for different well widths. Since the influence of the proliferate extent of impurities on the narrow well width is greater than on the wide well width, it seems that it is this influence that makes the maximum value of the binding energy appear at about 100 Å. We also note that the binding energy in Ref. 2 (1.9 meV) is the same as that in Ref. 3 for the well width  $d=80$  Å or so. In this case, the sample doped in proportion in Ref. 2 is the same as that in Ref. 3, where the proportions of doping are one-third of the wells. However, at  $d=150$  Å or so, it is not clear why the binding energy (1.5 meV) in Ref. 2 is considerably smaller than that (1.95 meV) in Ref. 3, although the doping samples are the same. (iii) Our value is much smaller than those of the experiment for the wide wells, but there is hardly any difference for the narrow wells

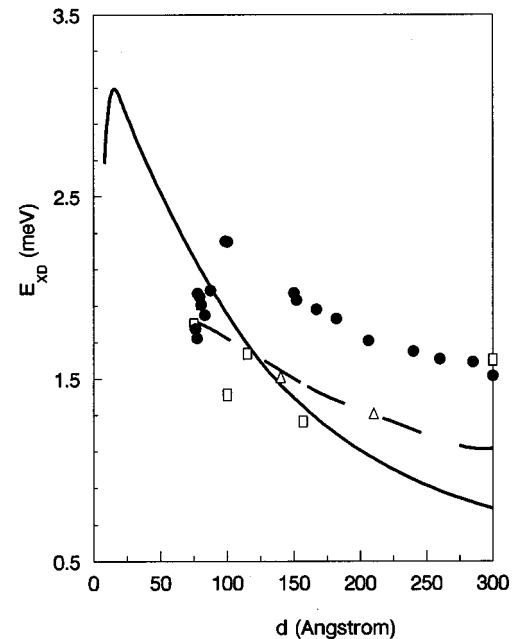


FIG. 1. Binding energy  $E_{XD}$  of excitons to neutral donors located at the center of the well as a function of well thickness  $d$  of GaAs. The solid curve is our result and the dashed curve is the previous result of Ref. 8. Squares indicate the experimental values of Ref. 1 and triangles indicate the experimental values of Ref. 2. Circles indicate the experimental points of Ref. 3.

(Fig. 1). This is because our wave function is made up of the product of the envelope function and the 2D wave function, and in fact, this is an adiabatic treatment. This approximation is reasonable for narrow wells but it may produce a greater error for wide wells. (iv) For well width ranging from 75 to 90 Å, the binding energy obtained by us is much greater than that of the experiment, when compared with Ref. 3 (Fig. 1), this is because our model is a single donor bound exciton in the center of the finite SQW's, but the sample at test is doped over the central range in a certain proportion.

(3) The binding energy of  $D^0, X$  when the dopant was located at the edge of the well: (i) We have calculated the binding energy of  $D^0, X$  when donors are located at the edge of the well in the interface region. The binding energies are investigated as a function of well size (Table II). Theoretically, since the binding energy of  $D^0, X$ , when donors are located at the edge of the well, is smaller than that when

donors are located at the center of the well for the same material and well size, our results are qualitatively reasonable. (ii) So far there have been few reports about the experimental data of the binding energy when donors are located at the edge of the well. The binding energy obtained by us may be small, for the well width ranging from 100 to 300 Å, when compared with those observed by Reynolds *et al.*<sup>3</sup> Our binding energy maximum is not the same as that in Ref. 3 at well sizes of about 100 Å, but at about 15 Å, which is about 2.99 meV. Yet their basic changing tendency is almost the same.

In conclusion, we have determined the binding energy of  $D^0, X$  in GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As SQW's and calculated the changes when the dopant was located in the center of the well, at the edge of the well. This was calculated as a function of well size from 8 to 300 Å, which yielded an increase in binding energy as the well size was increased to about 15 Å, after which the binding energy decreased.

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