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Effect of band hybridization on exciton states in GaAs-Al$_x$Ga$_{1-x}$As quantum wells

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Binding energies and oscillator strengths of ground-state Wannier excitons in GaAs-Al$_x$Ga$_{1-x}$As quantum wells are studied by a multiband effective-mass method. The present calculation incorporates valence-band nonparabolicity resulting from the hybridization of heavy and light holes. The variation of the exciton binding energy and oscillator strength as a function of the GaAs well width and the aluminum mole fraction of the Al$_x$Ga$_{1-x}$As barrier is discussed.

In recent years GaAs-Al$_x$Ga$_{1-x}$As superlattices and quantum wells have been extensively studied both experimentally and theoretically and it is known that excitons play an important role in optical absorption in these systems.[1,2]

Greene and Bajaj have studied free-exciton binding energies in GaAs-Al$_x$Ga$_{1-x}$As quantum wells in a two-band effective-mass model where the light- (LH) and heavy-hole (HH) subbands are decoupled and the effective masses in GaAs and Al$_x$Ga$_{1-x}$As are taken to be equal.[3,4] The method of Greene and Bajaj has recently been extended by Priester, Allan, and Lannoo.[5] These authors consider the effects of effective-mass mismatches between GaAs and Al$_x$Ga$_{1-x}$As and find significantly enhanced exciton binding energies for well thicknesses below 100 Å and binding energies essentially identical to those calculated by Greene and Bajaj for thicker wells.

In quantum wells and superlattices it has been shown that heavy- and light-hole states are strongly hybridized.[6,7] Mixing of heavy- and light-hole states of both parities gives rise to dipole-allowed transitions between all pairs of valence and conduction subbands. Strong exciton structures corresponding to "forbidden" transitions have been observed in luminescence studies of GaAs-Al$_x$Ga$_{1-x}$As multilayer structures[8] and have been reproduced in theoretically calculated absorption spectra taking valence-band hybridization into account.[6,7]

In this paper we present a theoretical calculation of the binding energies and oscillator strengths of Wannier excitons in GaAs-Al$_x$Ga$_{1-x}$As quantum wells that takes into account the effects of valence-band hybridization. This approach allows us to calculate oscillator strengths of the forbidden transitions which violate the $\Delta n=0$ selection rule. The valence bands in quantum wells are highly nonparabolic[6,7,9] and this we take explicitly into account. It has been shown that several of the hole subbands can have negative zone-center effective masses and we find that excitons corresponding to these valence subbands have enhanced binding energies due to the reduction in kinetic energy brought about by their large joint density of states.

In our model we first solve the free-carrier problem in the envelope-function approximation for electrons and holes separately. The free conduction-band (CB) states are given by $|\mathbf{k}_\parallel,n\rangle=f_n(z)U_0(\mathbf{r})e^{i\mathbf{k}_\parallel\cdot\boldsymbol{\rho}}$, where $f_n(z)$ is the envelope function of the nth conduction subband, $U_0(\mathbf{r})$ is the zone-center conduction-band Bloch function for bulk GaAs. The growth axis is taken to be in the [001] direction. The envelope function $f_n(z)$ satisfies an effective-mass equation $H_e f_n(z)=E_n(\mathbf{k}_\parallel)f_n(z)$, where $H_e=\hbar^2k_\parallel^2/2m_e^*+p_z^2/2m_e+V_e(z)$. Here m_e^* is the effective electron mass, taken to be $0.067m_0$, and $V_e(z)$ is a finite square-well potential.

Unlike the case for the conduction band, the valence band in bulk GaAs, in the limit of infinite spin-orbit splitting, is fourfold degenerate at the band edge with total spin $J=\frac{3}{2}$. The heavy-hole ($J_z=\pm\frac{3}{2}$) and light-hole ($J_z=\pm\frac{1}{2}$) subband states are thus strongly hybridized. The free hole states in the envelope-function approximation for the mth hole subband are

$$|\mathbf{k}_\parallel,m\rangle=\sum_\nu g_m^\nu(\mathbf{k}_\parallel,z)U_0^\nu(\mathbf{r})e^{i\mathbf{k}_\parallel\cdot\boldsymbol{\rho}} .$$

Here $U_0^\nu(\mathbf{r})$ is the zone-center valence-band Bloch state for spin component $J_z=\nu=-\frac{3}{2},\ldots,\frac{3}{2}$ in bulk GaAs and $g_m^\nu(\mathbf{k}_\parallel,z)$ is the corresponding envelope function. The effective-mass Hamiltonian is a 4×4 matrix operator whose entries are labeled by ν:

$$(H_h)_{\nu,\nu'}=T_{\nu,\nu'}(\mathbf{k}_\parallel)+V_h(z)\delta_{\nu,\nu'} ,$$

where $T_{\nu,\nu'}(\mathbf{k}_\parallel)$ is the $\mathbf{k}\cdot\mathbf{p}$ expression of Luttinger and Kohn[10] with k_z replaced by the operator $p_z/\hbar$ and $V_h(z)$ is a finite square well. In our model the well potential is diagonal in the basis used. It can be shown by detailed tight-binding studies that the off-diagonal components are very small.[6] Our treatment of the valence bands is similar to that of Fasolino and Altarelli.[9]

The square-well potentials arise as a result of the band-gap mismatch between GaAs and Al$_x$Ga$_{1-x}$As which we take to be $\Delta E_g=(1.115x+0.37x^2)$ eV.[11] This band-gap mismatch is divided between the conduction and valence bands to form the confining potentials, and thus $V_e(z)$ has a height $Q_e\Delta E_g$ and $V_h(z)$ has a height $Q_h\Delta E_g=(1-Q_e)\Delta E_g$. The band offset parameters Q_e and Q_h are taken to be 0.6 and 0.4, respectively,[12] and for the Luttinger parameters we adopt values of $\gamma_1=6.93$, $\gamma_2=2.15$, and $\gamma_3=2.81$.[13]

The free-carrier problems are solved by expanding the envelope functions in variational Gaussian basis states and the solutions have been discussed elsewhere.[7]

The free-electron and hole-carrier states interact through the screened Coulomb force to form excitons. The exciton wave function is made up of linear combinations of direct products of quantum-well electron and hole eigenstates,

$$\psi_x=\sum_{n,m}\sum_{\mathbf{k}_\parallel,\mathbf{k}'_\parallel}F_{nm}(\mathbf{k}_\parallel,\mathbf{k}'_\parallel)|\mathbf{k}_\parallel,n\rangle|\mathbf{k}'_\parallel,m\rangle ,$$

where n and m are subband indices for electron and hole, respectively. It can be shown that the exciton envelope function satisfies a two-dimensional effective-mass equation. The envelope function is given by

$$F_{nm}(k_{\parallel},k'_{\parallel})=\delta(\mathbf{k}_{\parallel}+\mathbf{k}'_{\parallel})G_{nm}(\mathbf{k}_{\parallel}) \ ,$$

where $G_{nm}(\mathbf{k}_{\parallel})$, the exciton relative motion envelope function, satisfies

$$[E^{e}_{n}(\mathbf{k}_{\parallel})+E^{h}_{m}(\mathbf{k}_{\parallel})]G_{nm}(\mathbf{k}_{\parallel})+\sum_{n',m'}\sum_{k'_{\parallel}}V^{nm}_{n'm'}(\mathbf{k}_{\parallel},\mathbf{k}'_{\parallel})G_{n'm'}(\mathbf{k}'_{\parallel})=EG_{nm}(\mathbf{k}_{\parallel}) \ . \tag{1}$$

In this expression $E^{e}_{n}(\mathbf{k}_{\parallel})$ and $E^{h}_{m}(\mathbf{k}_{\parallel})$ are the energies for the nth conduction and mth valence subbands and the Coulomb interaction term $V^{nm}_{n'm'}(\mathbf{k}_{\parallel},\mathbf{k}'_{\parallel})$ is given by (within the effective-mass approximation)

$$V^{nm}_{n'm'}(\mathbf{k}_{\parallel},\mathbf{k}_{\parallel})=\frac{-e^{2}}{\epsilon|\mathbf{k}_{\parallel}-\mathbf{k}'_{\parallel}|}\int\int dz_e\,dz_h f^{*}_{n'}(z_e)f_n(z_e)\sum_{\nu}[g^{\nu}_{m'}(\mathbf{k}'_{\parallel},z_h)]^{*}g^{\nu}_{m}(\mathbf{k}_{\parallel},z_h)\exp(-|\mathbf{k}_{\parallel}-\mathbf{k}'_{\parallel}||z_e-z_h|) \ . \tag{2}$$

Here ϵ is the static dielectric constant. $f_n(z_e)$ and $g^{\nu}_{m}(\mathbf{k}_{\parallel},z_h)$ are the electron and hole envelope functions, respectively. The Coulomb interaction couples excitons from different subbands. For thin wells the subband energies are well separated and the coupling is weak, but for thick wells ($W>300$ Å) the subband energies are closely spaced and coupling between excitons from different subbands could be significant. We adopt a two-band model keeping only one valence and one conduction subband and examine the effect on the HH1-CB1 exciton biinding energy of coupling to the other excitons. We further approximate $\sum_{\nu}[g^{\nu}_{m}(\mathbf{k}'_{\parallel},z_h)]^{*}g^{\nu}_{m}(\mathbf{k}_{\parallel},z_h)$ in (2) by its value at the zone center. This is a fairly good approximation, since the dominating contribution in (2) comes from the $\mathbf{k}_{\parallel}\simeq\mathbf{k}'_{\parallel}$ term and we find that $\sum_{\nu}|g^{\nu}_{m}(\mathbf{k}_{\parallel},z_h)|^{2}$ is a smooth function of $\mathbf{k}_{\parallel}$, even though $g^{\nu}_{m}(\mathbf{k}_{\parallel},z_h)$ varies quickly with $\mathbf{k}_{\parallel}$. The validity of this approximation has, in fact, been examined numerically by evaluating $\langle\psi_x|V^{nm}_{nm}|\psi_x\rangle$ with and without replacing $g^{\nu}_{m}(k_{\parallel},z_h)$ by its zone-center value. We found that the difference is only about 5%.

The two-band model allows us to ignore Fano resonances[14] of high-lying excitons with the continuum levels of lower-lying excitons. We solve (1) variationally by expanding G_{nm} as a sum of nine Gaussians with exponents chosen to cover a broad physical range. The exciton energies and envelope wave functions are then obtained by solving a generalized eigenvalue problem for the expansion coefficients. All of the matrix elements are evaluated numerically and, in particular, we use the computed free-carrier band structures in the evaluation of the kinetic energy matrix. The energy bands are nearly isotropic in the region of interest near the band edges and with this approximation all the numerical integrals are one dimensional.

Having obtained the exciton wave function, the oscillator strength for light propagating along the z direction can be determined by[15]

$$f_{nm}=\frac{2}{E_g m_0}\left|\sum_{\mathbf{k}_{\parallel}}G_{nm}(\mathbf{k}_{\parallel})\hat{\mathbf{x}}\cdot\mathbf{p}_{nm}(\mathbf{k}_{\parallel})\right| \ ,$$

where E_g is the fundamental energy gap of bulk GaAs. $\hat{\mathbf{x}}$ denotes the direction of polarization which is perpendicular to the z direction. In the envelope-function approximation we have

$$\mathbf{p}_{nm}(\mathbf{k}_{\parallel})=\sum_{\nu}\int d\mathbf{r}\,U_0(\mathbf{r})\mathbf{p}U^{\nu}_{0}(\mathbf{r})\int_{-\infty}^{\infty}dz\,f^{*}_{n}(z)g^{\nu}_{m}(\mathbf{k}_{\parallel},z) \ .$$

The integral involving the Bloch functions is just the optical matrix element between the s-like spin-$\frac{1}{2}$ conduction Bloch state $U_0(\mathbf{r})$ and the p-like spin-$\frac{3}{2}$ hole Bloch state $U^{\nu}_{0}(\mathbf{r})$, which is proportional to the optical matrix element defined in Ref. 16.

The effect of band hybridization on the binding energies of ground-state HH1-CB1 and LH1-CB1 excitons is shown in Fig. 1 for GaAs-$\mathrm{Al_{0.25}Ga_{0.75}As}$ quantum wells. In this figure the calculated exciton binding energy is shown versus the well width for two cases: uncoupled parabolic bands (dashed curves) and coupled nonparabolic valence bands (solid curves). For the case of uncoupled bands our formalism is identical to that of Greene and Bajaj.[3,4] Inclusion of valence-band hybridization gives larger exciton binding energies for both heavy- and light-hole excitons for all well

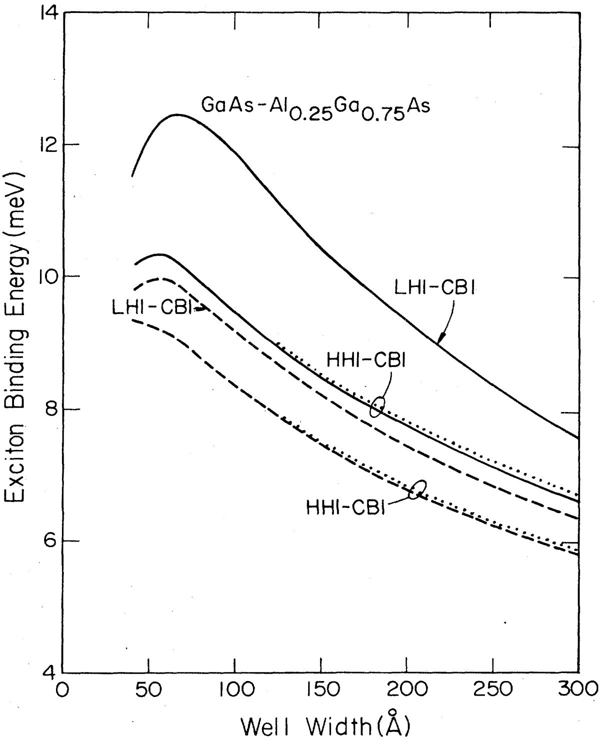

FIG. 1. Exciton binding energy vs well width calculated in two different models, one using nonparabolic (solid) and another using parabolic (dashed) valence bands. The dotted curves show the effect on the HH1-CB1 exciton binding energy of coupling with the neighboring exciton states.

widths. This is due to the enhancement in the joint densities of states of the two exciton states via band hybridization, especially for the ligh-hole exciton. If one includes the effects of effective-mass mismatches between GaAs and $Al_xGa_{1-x}As$ as done in Ref. 5, the exciton binding energies will probably be further enhanced for well thicknesses below 100 Å.

To examine the effect of coupling with various excitons obtained in the two-band model, we use the degenerate first-order perturbation theory. We choose the four lowest-lying exciton states, HH1-CB1, LH1-CB1, HH2-CB1, and HH3-CB1, and calculate their coupling using the expression

$$V_{mm'} = \sum_{\mathbf{k}_\parallel,\mathbf{k}'_\parallel} G^*_{1m}(\mathbf{k}'_\parallel) G_{1m'}(\mathbf{k}_\parallel) V^{1m}_{1m'}(\mathbf{k}_\parallel,\mathbf{k}'_\parallel) \ ,$$

where m, $m' = 1, 2, 3, 4$ for HH1, LH1, HH2, and HH3. The new exciton state energies are obtained by diagonalizing the Hamiltonian given by $H_{mm'} = E_m \delta_{mm'} + V_{mm'}$, where E_m is the zone-center energy (E^h_m) minus the mth exciton binding energy obtained in the two-band model. The HH1-CB1 exciton binding energies including the coupling with the neighboring exciton states are also shown (dotted curves) in Fig. 1. It is seen that such effect is negligible ($< 1\%$) for $W < 200$ Å and our use of a two-band model is justified. For $W > 200$ Å, such coupling gradually becomes important.

For quantum wells whose widths lie in the range from 60 to 300 Å, the most pronounced exciton absorption peaks are the ground-state HH1-CB1, LH1-CB1, HH2-CB2, and LH1-CB2 excitons.[6,7] Binding energies of these excitons as functions of well width are shown in Fig. 2 for $x = 0.25$ (solid curves) and 0.4 (dashed curves). Those excitons associated with hole bands having negative zone-center effective masses, i.e., LH1-CB1 and LH1-CB2, are seen to have significantly enhanced binding energies relative to other excitons. This is because the effect of a large joint density of states is to lower the kinetic energy for the exciton. There is also a general trend toward decreasing binding energies with increasing principle quantum numbers due to tunneling by the zone-center carrier wave functions into the barrier. This tends to reduce the exciton potential in (2).

The oscillator strengths calculated within the two-band model for the four most pronounced excitons are shown versus well width (W) for $x = 0.25$ in Fig. 3. The oscillator strengths are found to be complicated functions of well width. In general, there is a trend toward decreasing oscillator strength with increasing well width for moderately wide wells, on account of wave-function spreading. Note that in the absence of band hybridization, the oscillator strength for $\Delta n = 0$ excitons is proportional to $|G(0)|^2$. For narrow wells this trend is reversed as the exciton wave function spills out of the well into the surrounding $Al_xGa_{1-x}As$ barrier and thus the oscillator strength typically has a maximum at some critical well width.

This picture is complicated by hybridization of the hole wave functions however. In addition to $\Delta n = 0$ excitons there are $\Delta n \neq 0$ forbidden excitons which share oscillator strength with the $\Delta n = 0$ allowed excitons through mixing of their wave functions. Thus the LH1-CB2 exciton corresponding to a parity-forbidden $\Delta n \neq 0$ transition acquires a giant oscillator strength at the expense of HH2-CB2, where the LH1 and HH2 states are nearly degenerate in energy

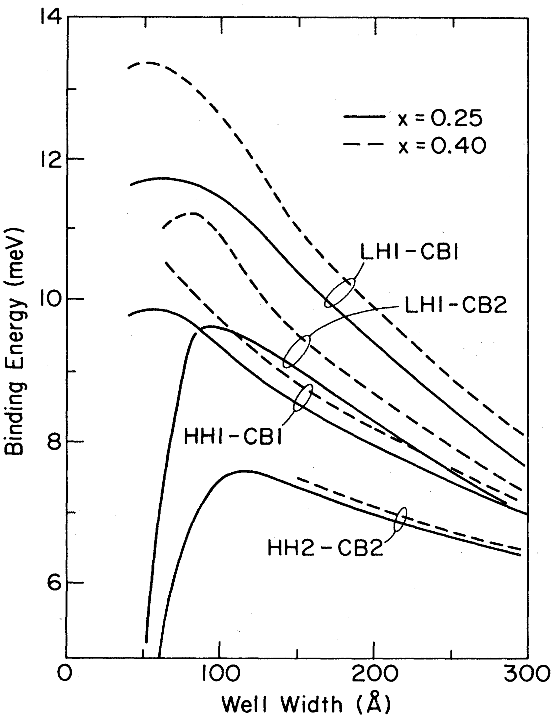

FIG. 2. Exciton binding energy vs well width for several prominent excitons in $GaAs\text{-}Al_xGa_{1-x}As$ quantum wells for aluminum mole fractions x of 0.25 (solid) and 0.4 (dashed).

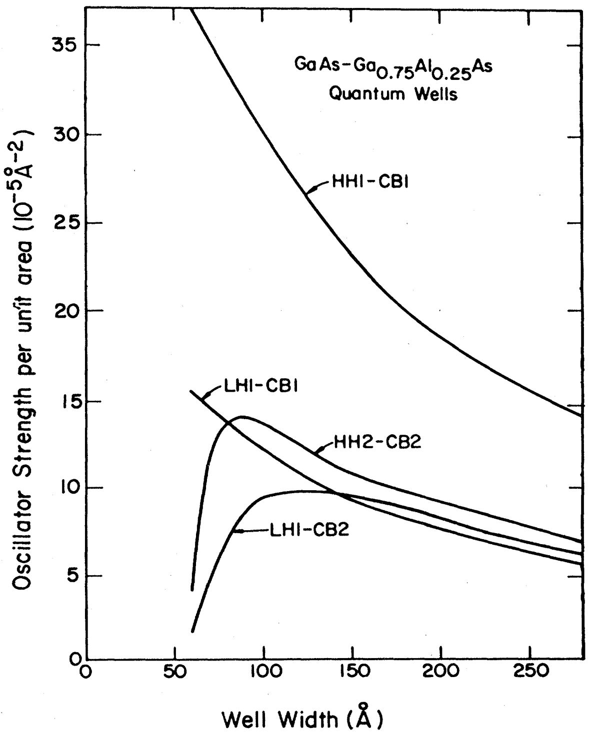

FIG. 3. Exciton oscillator strengths per unit area vs well width in $GaAs\text{-}Al_{0.25}Ga_{0.75}As$ quantum wells for several prominent excitons.

and strongly mixed. In this situation the LH1-CB2 peak rivals the HH2-CB2 peak resulting in a pair of exciton lines in the absorption spectrum.[7]

In conclusion, we have studied the binding energies and oscillator strengths for Wannier excitons in GaAs-$Al_xGa_{1-x}As$ quantum wells as functions of well width using a multiband effective-mass theory. We find that valence-band hybridization can lead to significant enhancement in computed binding energies and that mixing of hole wave functions results in sharing of oscillator strength between allowed and forbidden excitons.

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