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Band offsets and exciton binding energies in $Zn_{1-x}Cd_xSe$-ZnSe quantum wells grown by metal-organic vapor-phase epitaxy

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We present a joint study of the band offsets and exciton binding energies in $Zn_{1-x}Cd_xSe$-ZnSe quantum wells grown by metal-organic vapor-phase epitaxy with cadmium composition ranging up to 22%. The optical-spectroscopy data presented here are the wavelength derivative of the 2-K reflectance. The strained band-gap difference is divided as follows: the heavy-hole valence-band share deduced from the calculation is $32\pm1\%$; the remainder is allotted to the electron conduction band. The exciton binding energy has been calculated within the context of two methods: first, we propose a variational calculation using an exciton wave function written as the product of the envelope-function solutions of the square-well problem with a hydrogenlike two-parameter trial function. Second, as the light-hole potential is marginally type I, we lay out a more sophisticated computation based on a self-consistent variational approach that gives both the exciton binding energies and the self-consistent light-hole densities of probability. We compare the full information given by these two approaches.

Interest in the study of wide-band-gap $Zn_{1-x}Cd_xSe$-ZnSe quantum wells continues to increase since the effective p-type doping of ZnSe has been demonstrated by molecular-beam epitaxy and since several blue-light emitters based on such II-VI compounds have been realized.[1] The last few years have essentially been devoted to the improvement of the laser characteristics: lifetime, operating wavelengths, etc. Until quite recently, few efforts were oriented towards basic physics investigations, with the exception of the lasing mechanism for which several models have been proposed, based either on localized exciton, exciton-exciton scattering, or plasma assistance.[2–4] Besides this, only a few examinations of the band-offset problem and exciton binding energies are available in the literature of this field. Such knowledge is valuable for designing any optoelectronics device, either a light emitter or a light modulator. This work also inserts itself in the context of the recent progress achieved in the growth of zinc-blende CdSe (Ref. 5) and its zinc-based alloys and the subsequent improvements in the knowledge of their physical properties.

We first examine the band-offset problem by studying the spectroscopy properties of a series of $Zn_{1-x}Cd_xSe$-ZnSe quantum wells having nominal well widths of 7 nm and nominal cadmium compositions ranging up to 22%. Mircoprobe microanalysis has been performed and x-ray and spectroscopic data have been used on thick alloy epilayers to assess the cadmium composition. The samples were grown by low-pressure metal-organic vapor-phase epitaxy, using hydrogen selenide, triethyl-amine-dimethylzinc, and dimethyl cadmium as precursors. A buffer layer of 300 nm is grown onto the GaAs (001) epiready substrate, prior to the deposition of the $Zn_{1-x}Cd_xSe$ quantum well. The upper ZnSe barrier layer thickness was 200 nm.

Here, we have limited our paper to the alloy compositions we can grow with low dislocation densities; our theory based on an elastic model assumes the alloy layers are not relaxed. Figure 1 summarizes the wavelength-derivative reflectivity spectra taken on four samples. All our spectra display sharp, well-resolved transitions, at the energy of the band gap of ZnSe ($\sim$2.8 eV at 2 K). This is the signature of the ZnSe buffers that display a doublet substructure. Lower in energy, one detects structures related to the existence of a quantum well. These structures broaden when the alloy composition increases; we attribute this to the increase of both the intrinsic alloy disorder and a greater dislocation density. The observation of a series of excited states is evidence that our best results are obtained for a cadmium composition of 14%. In this case, one observes three marked transitions and a fourth one, vanishingly weak.

The identification of the transitions has been made within the context of the envelope-function approximation, including the interaction of the light-hole band with the spin-orbit split-off hole as a perturbation in the Bir-Pikus Hamiltonian. Moreover, we have assumed a pseudomorphic growth of the alloy layer onto the ZnSe buffer. The relevant parameters of the calculation were taken from Table I of Ref. 6. A linear interpolation was made between the CdSe and ZnSe values. Concerning the composition dependence of the band-to-band gap of the bulk unstrained alloy we used the following variation relationship:[7] $E_g(Zn_{1-x}Cd_xSe)=2820-1530x+510x^2$. We also accounted for a possible small deviation ($\sim$1%) between the nominal cadmium composition and the value of the fitting. Timing was employed during the growth to control the thicknesses and wedge TEM experiments on cleaved edges are employed to check the samples studied by spectroscopy. A discrepancy of 3 Å consistent with the structural investigations made on the samples was assumed for the well thickness. Then the full set of data can be fitted correctly, assuming the strained-electron and heavy-hole potentials are $V_e(x)\approx 925x$ (meV) and $V_{hh}(x)\approx 435x$ (meV) for $x\leqslant 0.22$. In this context, the electron-to-light-hole transition is type I, provided the depth of the light-hole potential is weakly nonlinear with cadmium composition $V_{lh}(x) \approx 55x$ (meV). We note that the transition labeled $e_1hh_3^*$ on Fig. 1 detected for the 14% sample involves a hole resonant state above the top of the heavy-hole potential. Resonant states, which are rather difficult to observe, can

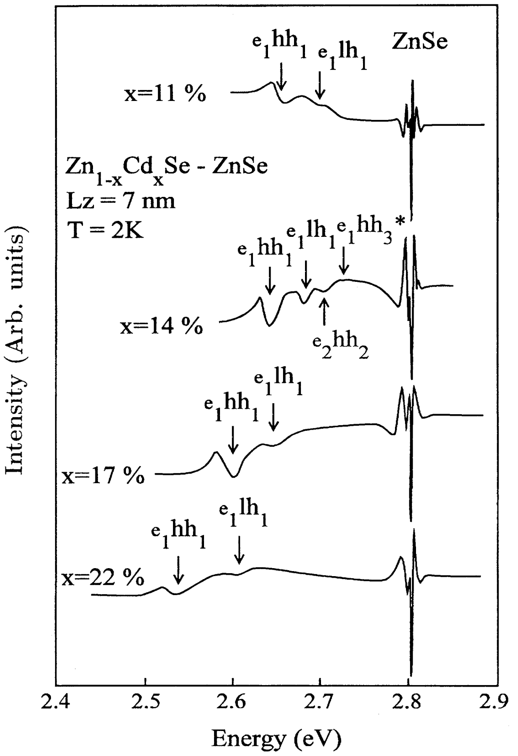

FIG. 1. Typical derivative spectra of the 2-K reflectance for a series of (Zn,Cd)Se-ZnSe quantum wells with identical thickness and varying cadmium composition. The transitions are labeled according to the predictions of an envelope-function calculation. The 2.8-eV structures are related to the ZnSe buffer layer.

only be detected in high-quality samples. We believe that the observation of such a state is linked to (i) a good interface quality and alloy uniformity, and (ii) the fact that the barrier layer where the hole wave function spreads is ZnSe, a binary compound whose growth we master rather well.

At this stage of the paper, we present the calculations of the exciton binding energies using two different models. In the first one, the exciton eigenfunction Ψ is the product of three terms: the envelope functions $\chi_e(z_e)$ and $\chi_h(z_h)$ of the electron and heavy hole, which depend on z_e and z_h, respectively, and $\Phi(\rho,z_e,z_h)=\exp\{-\sqrt{[\rho^2+\alpha^2(z_e-z_h)^2]}/\lambda\}$ is the trial function with two variational parameters (α,λ). The range of applicability of this method is limited to the treatment of sufficiently deep wells having widths L_z lying below two Bohr radii ($L_z \leq 80$ Å). Figure 2(a) displays the dependence of the heavy-hole Rydberg energies computed for well widths ranging up to 80 Å for typical cadmium compositions. For the sake of completeness, we have also reported the position of the LO phonon (31.3 meV). We note that the heavy-hole exciton binding energy is in general larger than the thermal energy at room temperature (25.7 meV) and that it rapidly exceeds the energy of the LO phonon. A similar calculation has been performed for the light-hole exciton. The results exhibited on Fig. 2(b) are limited to computations performed for cadmium composition of 5%, 10%, and 25% and are plotted using dashed lines.

We can make an analogy with the (Ga,In)As-GaAs combination (for which the electron light-hole band gap is marginally type II), where, due to the marginal nature of the light-hole potential, this exciton is weaker than the heavy-hole exciton.[8] We have the same phenomenon here but with a marginal type-I configuration. Besides this, we never find, for this range of cadmium composition, light-hole Rydberg values larger than the LO energy. We have next calculated the light-hole exciton binding energy in the spirit of the theories developed earlier to study excitons in marginally confined conditions, for various II-VI semiconductor heterostructures.[9–11] Within such an approach, the light-hole eigenfunction is obtained self-consistently from the resolution of a Schrödinger equation, where the square-well light-hole potential is deformed by the presence of the density of charges of the electron. The previous works were performed using a bidimensional trial function with one single variational parameter (case $\alpha=0$, in the above notations). In a previous paper we made on ZnS-ZnSe heterostructures (the *electron*

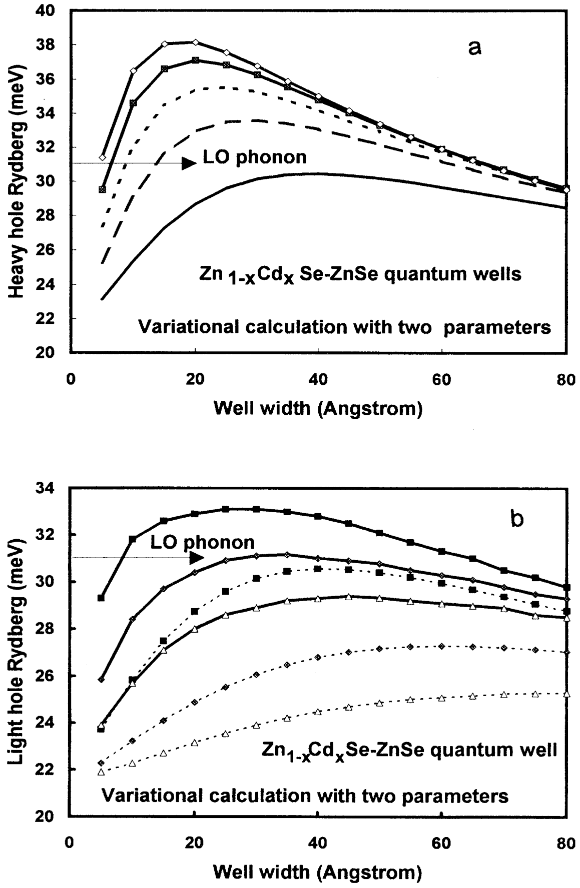

FIG. 2. (a) Heavy-hole excitons calculated with a two-parameter trial function for cadmium compositions of 5%, 10%, 15%, 20%, and 25% (full line, long-dashed line, dotted line, squares on full line, and diamonds on full line). The position of the LO phonon is also reported. (b) Dashed lines are the results of the calculation of the light-hole exciton binding energy for cadmium compositions of 5%, 10%, and 25% (triangles on dashed line, diamonds on dashed line, and squares on dashed line). The result of the calculation including the deformation on the light-hole lineup is given by using full lines.

potential is marginal),[12] we have shown that the two-parameter trial functions and the standard variational procedure give larger binding energy than the self-consistent method with a two-dimensional trial function. For this reason, we increase the degree of sophistication of the calculation by using a *two-parameter* trial function *and a self-consistent* treatment. We leave the mathematical details elsewhere and give the result of this second calculation in Fig. 2(b), using full lines. The self-consistent treatment significantly improves the calculation as expected, and we note that for the cadmium compositions we investigate here, the light-hole Rydberg may be larger than the energy of the LO phonon, on the one hand, and often larger than kT at room temperature. The latter point is not so obvious from the point of view of non-self-consistent calculations. Performing a similar treatment at the scale of the heavy-hole exciton does not significantly modify the above-mentioned conclusions.

These results are relevant since various lasing mechanisms have been invoked for II-VI compounds, depending on the relative strengths of both the LO-phonon energy and exciton binding energies.[2–4] We have shown that values of the binding energies are strongly related to the degree of sophistication of the model calculation used to obtain them. The results on (Zn,Cd)Se-ZnSe quantum wells are not so numerous compared to the amount of data collected for the GaAs-$Ga_{1-x}Al_xAs$ system. Then comparatively, the physics of excitons in $Zn_{1-x}Cd_xSe$-ZnSe remains quite embryonic. For the GaAs-(Ga,Al)As combination, the most sophisticated calculations predicted that the binding energy in similar quantum wells could exceed four times the value in bulk GaAs.[13] Obtaining the experimental evidence required several years of experimental investigations.[14] It is plausible that better descriptions of the exciton problem in (Zn,Cd)Se-ZnSe quantum wells may appear with the increase of experimental information and thus require even more subtle effects (such as valence-band mixings, mismatch of dielectric constants, etc.) in the theory.

To illustrate concretely the influence of the self-consistent treatment, we plot in Fig. 3 the density of probability for the electron (full line), heavy hole (dotted line), and light hole (dashed line) obtained by the standard envelope calculation. Results are given for a typical well width of 40 Å (~1 Bohr radius), and a cadmium composition of 10%. The position of the confining layer is also given at the bottom of the figure, using a full bold line. We note the strong spreading of the light-hole wave function in the barrier layers. Such a spreading is quenched when a self-consistent calculation is performed as shown by comparing the spatial extension of the bold dashed line (self-consistent light-hole envelope function) and the dashed line in Fig. 3.

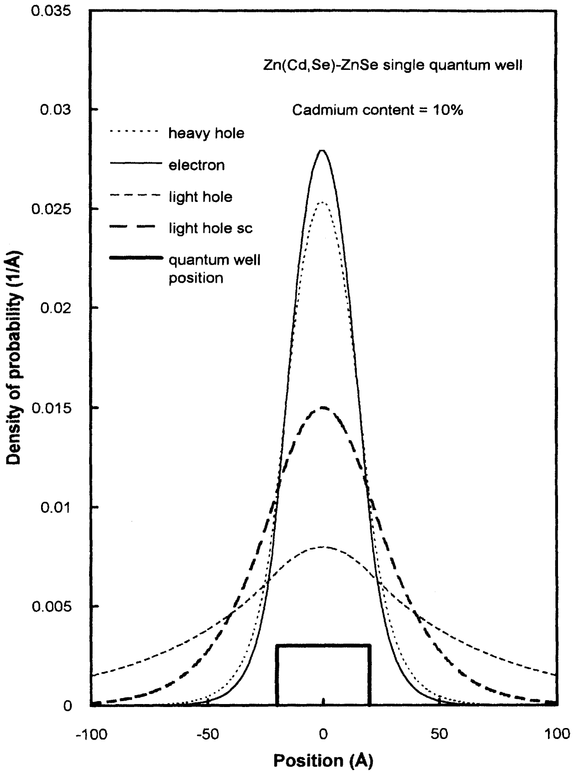

FIG. 3. Typical electron (full line), heavy-hole (dotted line), and light-hole (dashed line) envelope functions calculated for a 40-Å-wide well with 10% cadmium. The results of the more complete calculation is given using a bold dashed line. See text for details.

In conclusion, we have grown (ZnCd)Se-ZnSe quantum wells by metal-organic vapor-phase epitaxy. These samples have revealed several type-I excitonic resonances. The heavy-hole exciton is large in these materials due to good electron and heavy-hole confinements. The light-hole potential is marginally type I and leads to weaker exciton binding energies. A significant description of the light-hole exciton and envelope function requires us to calculate these quantities, taking into account the deformation of the light-hole potential produced by the electron wave function.

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[1] For a review, see, for instance, Jung Han, Li He, Robert L. Gunshor, and Arto V. Nurmikko, IEEE Circuits Devices Mag. **18** (1994); Arto V. Nurmikko and R. L. Gunshor, Solid State Commun. **92**, 113 (1994), and references therein.

[2] J. Ding, H. Jeon, T. Ishihara, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna, Phys. Rev. Lett. **69**, 1707 (1992); J. Ding, M. Hagerott, P Kelkar, A. V. Nurmikko, D. C. Grillo, L. He, J. Han, and R. L. Gunshor, Phys. Rev. B **50**, 5787 (1994).

[3] Y. Kawakami, I. Hauksson, H. Stewart, J. Simpson, I. Galbraith, K. A. Prior, and B. C. Cavenett, in Proceedings of the 3rd International Conference on Excitons in Confined Systems, edited by G. Bastard and B. Gil [J. Phys. (France) IV **3**, C5-83 (1993)].

[4] R. Cingolani, R. Rinaldi, L. Calcagnile, P. Prete, P. Sciacovelli, L. Tapfer, L. Vanzetti, G. Mula, F. Bassani, L. Sorba, and R. Fran-

ciosi, Phys. Rev. B **49**, 16 679 (1994).

[5] N. Samarth, L. Luo, J. K. Furdyna, Y. R. Lee, A. R. Ramdas, and N. Otsuka, Appl. Phys. Lett. **56**, 2413 (1990).

[6] P. M. Young, E. Runge, M. Ziegler, and H. Ehrenreich, Phys. Rev. B **49**, 742 (1994).

[7] O. Briot, N. Briot, T. Cloitre, R. L. Aulombard, F. Liaci, P. Bigenwald, B. Gil, L. M. Smith, S. A. Ruthworth, A. C. Jones, A. Huber, M. Gailhanou, and J. M. Sallese, Proc. SPIE **2346**, 80 (1994).

[8] P. Bigenwald and B. Gil, Solid State Commun. **91**, 33 (1994).

[9] E. Deleporte, G. Peter, J. M. Berroir, and C. Delalande, Surf. Sci. **267**, 137 (1992).

[10] G. Peter, E. Deleporte, G. Bastard, J. M. Berroir, C. Delalande, B. Gil, J. M. Hong, and L. L. Chang, J. Lumin. **52**, 147 (1992); E. Deleporte, J. N. Berroir, G. Bastard, C. Delalande, J. M. Hong, and L. L. Chang, Phys. Rev. B **42**, 5891 (1990).

[11] E. Deleporte, T. Lebihen, B. Ohnesorge, P. Roussignol, C. Delalande, S. Guha, and H. Munekata, Phys. Rev. B **50**, 4514 (1994).

[12] B. Gil, T. Cloitre, M. Di Blasio, P. Bigenwald, L. Aigouy, N. Briot, O. Briot, D. Bouchara, R. L. Aulombard, and J. Calas, Phys. Rev. B **50**, 18 231 (1994).

[13] L. C. Andreani and A. Pasquarello, Phys. Rev. B **42**, 8928 (1990).

[14] M. Gurioli, J. Martinez-Pastor, M. Colocci, A. Bosacchi, S. Franchi, and L. C. Andreani, Phys. Rev. B **47**, 15 755 (1993).