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Size quantization and band-offset determination in GaAs-GaAlAs separate confinement heterostructures

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We have investigated the photoluminescence excitation spectroscopy of GaAs-$Ga_{1-x}Al_xAs$ separate confinement heterostructures consisting of a narrow GaAs quantum well embedded in a larger $Ga_{1-x}Al_xAs$ one. Quantization of the energy in the "upper" large well is observed for thicknesses smaller than 750 Å. The peculiar structure configuration allows the observation of transitions which are strongly dependent on the conduction- and valence-band discontinuities. Comparison between theory and experiment gives a conduction-band offset between GaAs and $Ga_{1-x}Al_xAs$ equal to $(59 \pm 3)\%$ of the total band-gap difference for $x = 0.13$. This determination is also strongly supported by the good agreement between the observed and calculated transition energies in asymmetrical structures in which strong *odd* Δn transitions appear.

We report here the results of photoluminescence excitation spectroscopy experiments done at low temperature on symmetrical and asymmetrical quantum-well separate confinement heterostructures (QWSCH). These structures consist of a GaAs quantum well embedded in $Ga_{1-x_1}Al_{x_1}As$ layers, the latter being clad between thick $Ga_{1-x_2}Al_{x_2}As$ layers with $x_2 > x_1$ (see Fig. 1). The $Ga_{1-x_1}Al_{x_1}As$ layer with intermediate Al concentration will hereafter be termed the barrier. Delocalized excitons associated with lower-lying barrier states have recently been observed in multiple quantum-well structures by Zucker *et al.*[1] Structures in the energy spectrum of QWSCH barriers are also expected to show up.[2] One of our purposes is to report the observation of excitonic recombination associated with these quantized levels in the barrier. The structures under study have been grown either symmetrical, i.e., the GaAs quantum well being located at the center of the structure ($L = R$), or asymmetrical, i.e., one of the $Ga_{1-x_1}Al_{x_1}As$ layers being thicker than the other one ($R > L$).

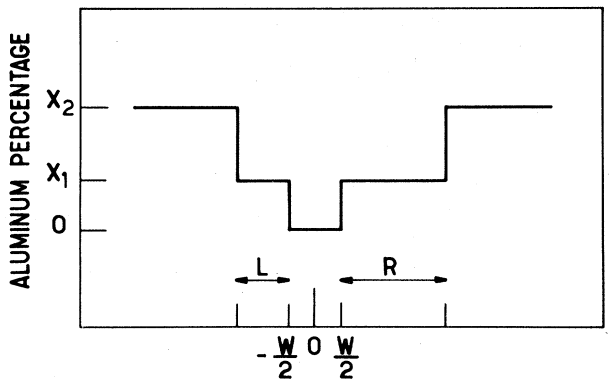

FIG. 1. Aluminum percentage profile in a QWSCH. The values of the parameters for the structures investigated here are summarized in Table I.

We observe actually three different kinds of optical transitions in our QWSCH's, i.e., transitions involving quantized levels (i) both essentially localized within the narrow GaAs well, (ii) with one state (initial or final) confined within the GaAs quantum well and the other one (final or initial) in the barrier, and (iii) both in the barrier. The difference in energy spacing between adjacent levels of the 50-Å GaAs well and of the thicker $Ga_{1-x_1}Al_{x_1}As$ barrier induces a strong dependence on the conduction and valence barrier heights for the energies of the second kind of transitions. Thus, these peculiar structures should be well suited for a determination of the band offsets between GaAs and $Ga_{1-x}Al_xAs$, a topic of present controversy.[3-6]

The energy levels of QWSCH's have been calculated within the three-band[7] envelope-function approximation.[8,9] The 8×8 effective Hamiltonian acting on the envelope functions has been projected onto the *S*-like band edge, resulting in an effective scalar Hamiltonian acting on the associated envelope function. Since the band edges are piecewise constant in QWSCH, analytical solutions can be obtained. The calculations are a little tedious but straightforward, and they will not be detailed here. By fitting the observed optical transition energies to the theoretical results we are able to determine that for $x = 0.13$ the conduction-band discontinuity is $(59 \pm 3)\%$ of the total band-gap difference between the two materials. This value is not in agreement with that of Dingle (85% for $x = 0.2$),[3] or Dawson, Duggan, Ralph, and Woodbridge (75%, $x \sim 0.3$),[6] but is close to the result obtained recently by Miller, Kleinman, and Gossard (57%, $x = 0.3$),[4] and by Wang, Mendez, and Stern (62%, $x = 0.5$).[5]

The structures investigated were grown on (100) oriented Si-doped GaAs substrates by molecular beam epitaxy (MBE). The growth was carried out in a second-generation MBE system. The background pressure in the growth chamber was 5×10^{-11} Torr. The source of elemental arsenic produced primarily an As_4 flux. The growth conditions used are a high substrate temperature ($T_s = 680\,°C$),

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TABLE I. Parameters of samples A, B, and C as defined in Fig. 1.

Samples	W (Å)	L (Å)	R (Å)	x_1 (%)	x_2 (%)
A	45	100	100	13.3	32
B	50	50	100	13	34
C	45	100	300	13.3	32

and a low effective flux ratio ($T_{As_4}/T_{Ga}=3.6$), with a growth rate of 1.4 μm per hour. The layers were not intentionally doped, which for bulk GaAs means a background p-type doping of about 2×10^{14} cm^{-3}. We report here results obtained on three sets of structures whose parameters are summarized in Table I. Structures A are symmetrical whereas structures B and C are not. Photoluminescence excitation spectroscopy measurements were performed at low temperatures (~ 2 K), using standard cw laser excitation and lock-in techniques. All the spectra present a large number of peaks attributed to excitonic transitions between an electron level E_n and a heavy- or light-hole level H_m or L_m. In most of the spectra we were able to observe a weak shoulder between E_1H_1 and E_1L_1 related excitons, and a small peak lying a few meV above E_1L_1. These features are attributed either to the excited "2s" state or to the onset of the exciton continuum.[10] We can thus deduce within 2 meV (which is approximately the binding energy of the "2s" exciton state) a binding energy of 9.5 meV, and 11 meV for the E_1H_1 and E_1L_1 excitons, respectively. The Al percentage of the barrier x_1 was determined from growth calibration, and cross checked by means of photoluminescence and excitation spectroscopy of thick $Ga_{1-x_1}Al_{x_1}As$ layers. We estimate our accuracy to be 0.4% for x_1. Knowing x_1 and the nearly exact energies of the E_1H_1 and E_1L_1 transitions, we could adjust the well thickness W since these transitions depend strongly on this parameter (because W is small), but less on the barrier heights. The precision on W is estimated to be ±1 monolayer (2.83 Å).

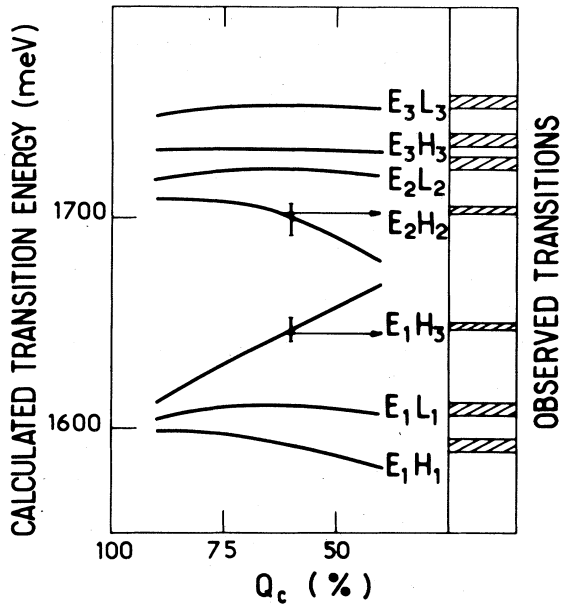

FIG. 2. Calculated dependence of the transition energies (Ref. 13) on the conduction-band discontinuity $Q_c=\Delta E_c/\Delta E_g$. The observed transitions, corrected for the binding energies of the excitons, are indicated in the right side of the figure. The structure parameters are those of samples A.

For samples A, Fig. 2 displays the theoretical dependence of the various possible and observed $\Delta n=0$ and $\Delta n=2$ transitions on the conduction-band offset ΔE_c, expressed as a percentage Q_c of the total band-gap difference ΔE_g between GaAs and $Ga_{1-x_1}Al_{x_1}As$, i.e., $Q_c=\Delta E_c/\Delta E_g$. It is worth noticing the strong dependence of the E_1H_3 transition on Q_c, which involves a state (E_1) essentially localized in the GaAs well, and the other one (H_3) delocalized over the barrier. The same effect appears for E_2H_2 (E_2 delocalized over the barrier, H_2 mostly localized in the well), if $Q_c\lesssim 75\%$. The error bars drawn at $Q_c=60\%$ account for the uncertainties on the well thickness W (±2.83 Å) and the aluminum concentration x_1 ($\pm0.4\%$), while the error bars for each of the observed transitions account for the uncertainty on the exciton binding energy involving excited QWSCH levels.[11,12] The material parameters used in the calculations are summarized in Table II.

The strong dependence of the E_1H_3 and E_2H_2 transitions on Q_c allows us to determine a conduction-band discontinuity of $(60\pm4)\%$ of the total band-gap difference between GaAs and $Ga_{0.87}Al_{0.13}As$. Let us point out that we also observe two weak shoulders in the spectra attributed to E_1L_3 and E_2H_4 transitions, whose energies are also in very good agreement with the theoretical predictions for $Q_c=60\%$.

Similar results are presented in Fig. 3 for samples B, i.e., asymmetrical structures with total barrier thickness equal to 200 Å. Again, the energies of the E_1H_3 and E_2H_2 transitions depend strongly on Q_c. In addition, the E_1L_3 transition (E_1 localized in the well, L_3 delocalized over the barrier) appears more clearly, so that we can determine Q_c by fitting three different transition energies. We get from the two sets of measurements a final value for Q_c of $(59\pm3)\%$.

The error bars on Q_c ($\pm3\%$) mostly arise from the well-width uncertainty (±1 monolayer), and the Al percentage of the intermediate barrier ($\pm0.4\%$). Another uncertainty

TABLE II. Material parameters used in the calculations (Ref. 13).

$Ga_{1-x}Al_xAs$ band gap (meV)	$1519.2+1247x$
$Ga_{1-x}Al_xAs$ spin-orbit energy at Γ point (meV)	$341-66x$
GaAs conduction-band effective mass	$0.067m_0$
$Ga_{1-x}Al_xAs$ heavy-hole effective mass	$(0.48\pm0.31x)m_0$
GaAs light-hole effective mass (derived from the Kane three-band model)	$0.094m_0$

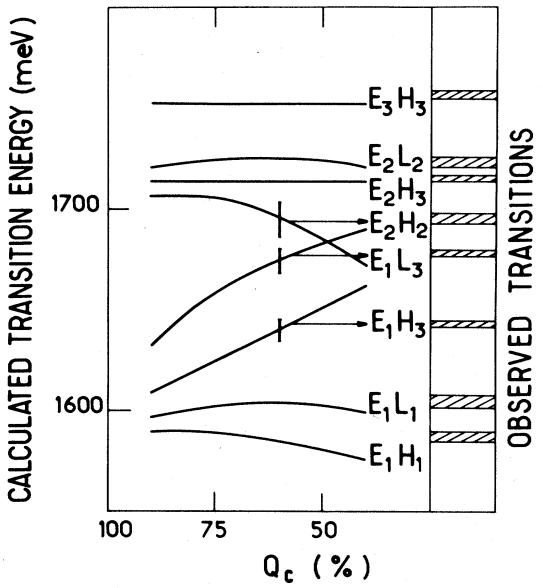

FIG. 3. Same as Fig. 2 for the samples B structure parameters.

arises from the ambiguity about the heavy-hole mass. We have chosen here to use a density-of-states effective mass $(0.48+0.31x)m_0$ (Ref. 13) rather than a (001) effective mass $(0.38+0.12x)$,[14,15] also employed for (001) GaAs quantum wells. We checked that the difference between the E_1H_3 and E_2H_2 transition energies calculated for these two values was smaller than 1 and 6 meV, respectively, which is somewhat smaller than the error bars quoted in Fig. 2.

Another interesting feature of samples B is their asymmetry, i.e., the eccentric position of the well is expected to partially break down the parity selection rule Δn even, which is valid for symmetrical structures. However, note that the effect of the asymmetry is effective only for states lying in the barrier, since the strongly localized states (E_1,H_1,L_1) of the GaAs well do not in practice experience it. Figure 4 shows a typical photoluminescence excitation spectrum obtained in a B sample. The determined value of Q_c allows the assignment of all the transitions as indicated on the spectrum. As expected, the transitions involving two states mostly localized in the GaAs well fulfill the $\Delta n=0$ selection rule. For the states delocalized over the barrier, however, this rule is broken down, and we observe a strong $\Delta n=1$ transition, E_2H_3. Simultaneously, the $\Delta n=0$ transition involving lower-lying barrier states, i.e., E_2L_2, weakens as compared to the symmetrical situation. We believe these effects are due to the strong perturbation induced by the eccentricity of the well on the symmetry of the structure for the lower-lying barrier states. It is predictable that, with increasing energy, the behavior of the spectrum will approach that of a 200-Å-thick $Ga_{1-x_1}Al_{x_1}As$ quantum well, which is a symmetrical structure. Actually, we have not observed any sizable difference between the intensities of the $\Delta n=0$, $n=3$ transitions observed in A or B samples. For the C samples, which are much more asymmetrical than the B ones, we get even more experimental evidence of these effects since the $n=2$, $\Delta n=0$ transitions fade away to be replaced by odd Δn transitions between lower-lying barrier states. Finally, no barrier quantization was observable in samples with a thicker barrier ($L+R+W>750$ Å).

In conclusion, we have presented the first experimental evidence of the barrier-states quantization in QWSCH's, with barrier thicknesses ranging from 200 to 500 Å. These structures allow the observation of optical transitions involving states localized in the well and/or the barrier. Among these transitions, those involving one state in the well and the other in the barrier are very sensitive to the band offset between the well and the barrier materials. Comparison between the observed transition energies and the calculated levels for three sets of QWSCH's yield a conduction-band discontinuity equal to $(59\pm3)\%$ of the total band-gap difference between GaAs and $Ga_{0.87}Al_{0.13}As$, in agreement with previous determinations. Moreover, we have studied for the first time the effect of the asymmetry of the structure on the transitions involving lower-lying barrier states and have observed odd Δn transitions.

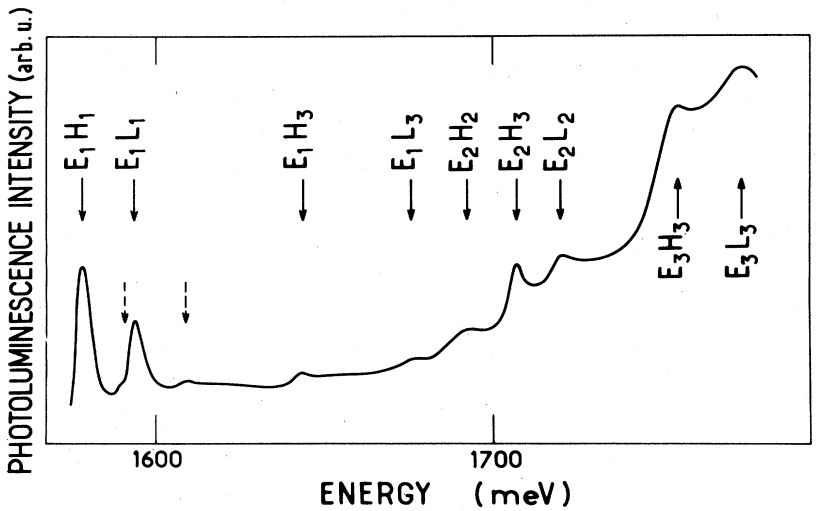

FIG. 4. Excitation spectrum of a B sample. The arrows indicate the peak maxima and the corresponding transition. The two dashed arrows indicate the shoulders assigned to the excited 2s level or onset of the continuum of the E_1H_1 and E_1L_1 excitons.

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[1]J. E. Zucker, A. Pinczuk, D. S. Chemla, A. C. Gossard, and W. Wiegmann, Phys. Rev. B **29**, 7065 (1984).

[2]G. Bastard, Phys. Rev. B **30**, 3547 (1984).

[3]R. Dingle, in *Festkörperprobleme,* edited by H. J. Queisser, Advances in Solid State Physics, Vol. 15 (Pergamon/Vieweg, Braunschweig, 1975), p. 21.

[4]R. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1984).

[5]W. I. Wang, E. E. Mendez, and F. Stern, Appl. Phys. Lett. **45**, 639 (1984).

[6]P. Dawson, G. Duggan, H. I. Ralph, and K. Woodbridge, in *Proceedings of the First International Conference on Superlattices, Microstructures and Microdevices,* Champaign-Urbana, 1984 [Superlattices Microstruct. **1**, 173 (1985)].

[7]G. Bastard, U. O. Ziemelis, C. Delalande, M. Voos, A. C. Gossard, and W. Wiegmann, Solid State Commun. **49**, 671 (1984).

[8]S. R. White and L. J. Sham, Phys. Rev. Lett. **47**, 879 (1981).

[9]M. Altarelli, Phys. Rev. B **28**, 842 (1983).

[10]R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B **24**, 1134 (1981).

[11]For $\Delta n = 0$, E_nH_n, or E_nL_n transitions involving states which are both in the barrier, we assumed this energy to be larger than the corresponding energy of a E_1H_1 or E_nL_n related exciton in a 200-Å rectangular $Ga_{0.87}Al_{0.13}As$ well, and smaller than that of a 50-Å rectangular GaAs well. These energies have been estimated [J. A. Brum (private communication)] following the treatment of Green and Bajaj (see Ref. 12). For the E_1H_3 and E_2H_2 transitions, for which the initial and final states are localized at different places in the structure, we assumed exciton binding energies ranging from 3 to 6 meV.

[12]R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 831 (1983).

[13]Band parameters are taken from H. C. Casey and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978).

[14]D. Bimberg, in *Festkörperprobleme,* edited by J. Treusch, Advances in Solid State Physics, Vol. 17 (Pergamon/Vieweg, Braunschweig, 1977), p. 195.

[15]The AlAs heavy-hole effective mass ($0.5m_0$) is quoted in *Semiconductors,* edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. 17 (Springer-Verlag, Berlin, 1982).