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Band offsets of $Ga_{0.5}In_{0.5}P/GaAs$ single quantum wells from pressure-induced type-II transitions

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We report on high-pressure, low-temperature photoluminescence of $Ga_{0.5}In_{0.5}P/GaAs$ single quantum wells grown by metalorganic-molecular-beam epitaxy. A type-I–type-II (and Γ-X) transition occurs at $P=3.25\pm0.1$ GPa for all well widths (from 10 to 70 Å), in contrast to what is observed in (Al,Ga)As/GaAs quantum wells. Using envelope-function calculations for the type-II transitions, a valence-band offset of 330 ± 20 meV is deduced independent of pressure, within experimental precision. This is in good agreement with a previous photoreflectance study and with recent theoretical predictions on such heterostructures.

The solid-state alloy $Ga_xIn_{1-x}P$ is lattice matched to GaAs for $x\approx0.5$. Due to its high direct band gap of 1.97 eV at 4 K, this material is attractive as a substitute to the (Al,Ga)As alloy for heterostructure devices, such as heterojunction bipolar transistors (HBT's), because of its large valence-band offset, and because of the elimination of Al, with the related problems due to its chemical reactivity in crystal growth and also in the later device processing steps. Furthermore, it seems that problems associated with *DX* centers are less crucial in $Ga_{0.5}In_{0.5}P$ than in (Al,Ga)As, though this last point is controversial. As far as minority carrier devices are concerned (such as solar cells), it should also be noted that this alloy allows one to obtain ultralow interface recombination velocities with GaAs ($s=1.5$ cm/s).[1] However, in spite of its great technological interest, agreement still does not exist regarding the problem of band lineup. A wide range of experimental values exists for the conduction-band offset C_{BO}, ranging from 30[2] to 390[3] meV (the band-gap difference being 450 meV). Recent studies by internal photoemission on *p-i-n* (Ref. 4) or HBT (Ref. 5) structures gave values of 108 and 190 meV, respectively. By fitting the ground and excited excitonic states of metalorganic molecular-beam epitaxially (MOMBE) -grown quantum wells (QW's) of various thicknesses, we determined a value of 320 meV for the valence-band offset V_{BO} (Ref. 6) (i.e., $C_{BO}=130$ meV). From the theoretical point of view, a tight-binding calculation by Foulon *et al.*[7] gave values of 320 and 355 meV for the valence-band offset at the two kinds of interfaces [Ga-P-(Ga,In) or Ga-As-(Ga,In)] that may exist in this system. The inequivalence of interfaces in heterostructures sharing neither common anion nor cation has been evidenced in a recent ultraviolet-photoemission-spectroscopy (UPS) study, performed *in situ*, on MOMBE-grown (Ga,In)As/InP interfaces,[8] though the results on $Ga_{0.5}In_{0.5}P/GaAs$ heterostructures were not conclusive.

It is worth recalling that such discrepancies in band-offset values have long been the case in the GaAs/(Al,Ga)As system. One of the earliest precise determinations was achieved through high-pressure photoluminescence (PL) spectroscopy.[9,10] Indeed, in the GaAs/(Al,Ga)As system, high pressure induces a type-I–type-II transition, and in the type-II regime transition energies are functions of the valence-band offset only. Chen *et al.*[11] have studied, under pressure, the PL of a gas-source MBE-grown $Ga_{0.5}In_{0.5}P/GaAs$ multiple-quantum-well structure, with a well width of 59 Å, together with a bulk $Ga_xIn_{1-x}P$ sample. From the pressure dependence of type-II transitions in the MQW, they deduced a value of 400 ± 20 meV for the valence-band offset. This is significantly larger than our own determination,[6] and a similar high-pressure investigation of MOMBE-grown QW's appears necessary.

The sample studied consists of five QW's of widths 10, 15, 25, 35, and 70 Å separated by 350-Å $Ga_{0.5}In_{0.5}P$ barriers (i.e., the wells are isolated) on a GaAs substrate. Details of the MOMBE growth and also evidence of the importance of the growth procedure on QW properties are given in Ref. 12. After thinning, the sample is inserted, together with a ruby chip for pressure calibration, in a diamond-anvil cell filled with argon and placed in a liquid-helium Dewar.[13] PL was excited with the 4880-Å line of an argon laser and detected by a cooled GaAs photomultiplier.

High-pressure PL spectra of the QW structure are displayed in Figs. 1(a) and 1(b). Figure 1(a) corresponds to the low-pressure range, where transitions are direct type I. Intense emission from the QW's is observed. A blueshift of typically 10 meV for two decades of excita-

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tion intensity is observed for the QW PL energies. At atmospheric pressure, the PL energies under high excitation power (≈ 100 W/cm^2) are in good agreement with the ground-state $e1hh1$ exciton energies measured by photoreflectance (PR),[6] allowing us to assume that intrinsic excitonic QW transitions are measured through PL. Other PL features in Fig. 1(a) are electron-to-acceptor and bound-exciton recombinations in the GaAs buffer (eA^0 and D_Γ, respectively), and barrier PL. At atmospheric pressure, the barrier PL energy is 1.94 eV, whereas PL excitation has shown that the barrier gap is 1.97 eV (in agreement with PR). On the other hand, since no blueshift of barrier PL with excitation intensity is detected, it is attributed to electron-to-acceptor recombinations in the alloy (this is consistent with the fact that the GaAs buffer PL is also dominated by eA^0 transitions). The alloy band gap is that of a disordered alloy with composition $x_{Ga}=0.50-0.51$,[14] in agreement with x-ray-diffraction results.

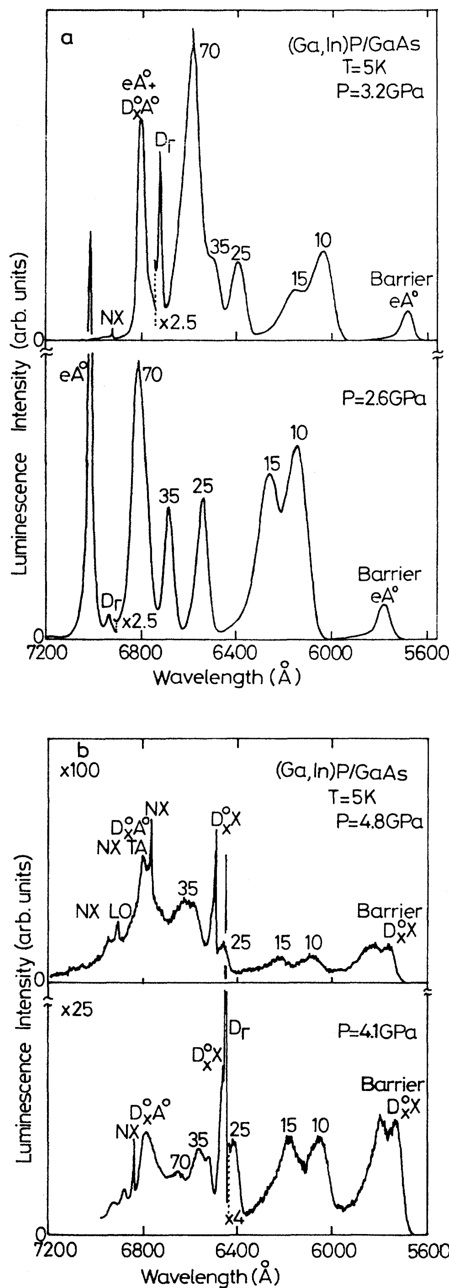

FIG. 1. (a) and (b) High-pressure photoluminescence spectra of GaAs/Ga$_{0.5}$In$_{0.5}$P single quantum wells.

Up to 3.2 GPa, the QW emission energies increase with pressure, while the PL intensity is nearly constant. For pressures higher than 3.2 GPa [Fig. 1(b)], the QW and barrier PL energies now decrease with pressure, and the PL intensity undergoes a strong quenching. New transitions also shown in Fig. 1(b) are indirect donor-to-acceptor ($D^0_XA^0$) (Ref. 15) and indirect bound-exciton (D^0_XX) (Ref. 16) recombinations in the GaAs buffer. Analogous to the buffer PL, the high-energy indirect PL band in the barriers can also be attributed to bound-exciton recombinations. Line NX and its phonon replica correspond to nitrogen bound excitons.[17,18] It may originate from the substrate or be due to the use of high-temperature BN cracker cells in MOMBE growth.

Figure 2 displays the pressure dependence of the PL energies of the various transitions observed in this work. Table I is a summary of the data from Fig. 2. As usual, it is assumed that indirect transition energies vary linearly with pressure, but that direct ones vary quadratically. Figure 2 shows that the alloy direct gap varies less steeply with pressure than that of GaAs and also exhibits a stronger quadratic pressure coefficient (Table I). The pressure coefficient of the alloy is within the range of existing values for similar composition, both at low temper-

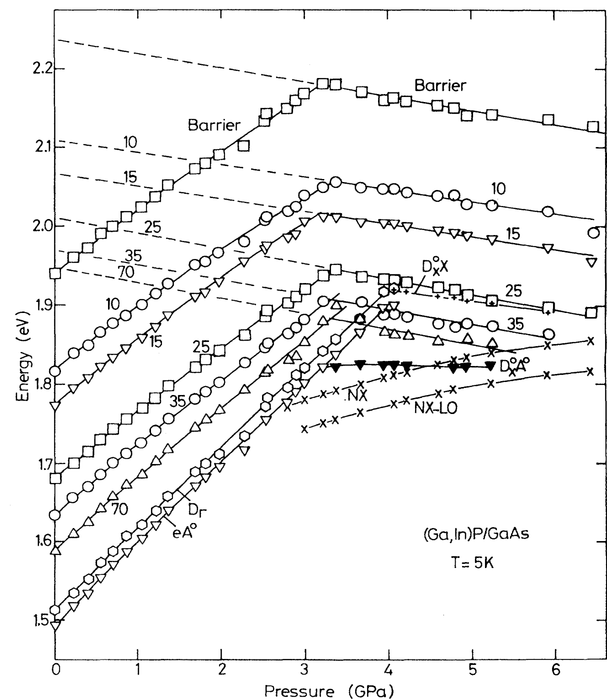

FIG. 2. Pressure dependence of the luminescence energies of GaAs/Ga$_{0.5}$In$_{0.5}$P quantum wells.

TABLE I. Pressure dependence of the transition energies in the $Ga_{0.5}In_{0.5}P$/GaAs quantum wells studied.

Transition	$E_\Gamma(0)$ (eV)	α_Γ (meV/GPa)	β_Γ (meV/GPa^2)	$E_X(0)$ (eV)	α_X (meV/GPa)
GaAs (D_Γ, D_X^0X)	1.513	107	−1.5	1.975	−14
Barrier (eA_Γ^0, D_X^0X)	1.941	83	−2.6	2.236	−18
QW70	1.591	92	−1.3	1.947	−19
QW35	1.635	91	−2.8	1.97	−19
QW25	1.681	88	−2.9	2.01	−19
QW15	1.775	86	−3.3	2.07	−16
QW10	1.819	83	−3.7	2.11	−16

ature ($T \leq 80$ K) (Refs. 11, 19, and 20) and at room temperature.[21,22] The Γ-X crossover occurs at 3.2 GPa in the barrier, in agreement with a Ga composition close to 0.5.[19] Also from Fig. 2, it can be seen that direct-to-indirect QW transitions occur at 3.25±0.1 GPa whatever the well width. This is in contrast with (Al,Ga)As QW's, where the direct-to-indirect crossover pressures are well width dependent (due to differences in electron confinement energies),[10,23] and will be given a natural explanation below.

We now turn to the band-offset problem. In Figs. 1 and 2, it can be seen that, thanks to high sample quality, i.e., low nonradiative recombination rates, indirect transitions with an X-like pressure coefficient (≈ -15 meV/GPa) originating from the GaAs buffer, the barrier and the five QW's can be followed over the whole pressure range. In particular, the indirect emission energy from wells of width 35 and 70 Å lies below the GaAs indirect bound-exciton PL energy. This indicates that electrons involved in these QW transitions are not confined in the X conduction band of GaAs, allowing us to assume that the indirect QW transitions observed are type II, i.e., electrons are in the $Ga_{0.5}In_{0.5}P$ barrier (see also Ref. 11). For type-II transitions, the emission energy E is given, as sketched in the inset of Fig. 3, by

$$E = E_{gb} - V_{BO} + E_{hh} - E_{Ry} - E_{loc} , \tag{1}$$

where E_{gb} is the barrier band gap, E_{hh} is the heavy-hole confinement energy, E_{Ry} is the exciton Rydberg, and E_{loc} stands for possible localization of the exciton. The theoretical binding energy of excitons in type-II GaAs/AlAs heterostructures varies from ≈ 10 meV in short-period superlattices[24] to 0 in large heterojunctions.[25] Since barriers are large in our sample, we shall neglect E_{Ry}. E_{loc} is difficult to evaluate for type-II transitions. As mentioned previously, it is small in the type-I pressure range, and we shall also neglect it in the type-II regime. As in the case of GaAs,[16] the barrier indirect band gap is assumed to be 30±10 meV above the indirect bound exciton energy.

With the above assumptions, and since the heavy-hole confinement energy is only a function of V_{BO}, using the envelope-function formalism we can straightforwardly compute the difference $E_{gb} - E$ as a function of well width L for various values of V_{BO}. The results are plotted on Fig. 3 and compared with the experimental results at 3.7 and 4.9 GPa. Values of V_{BO} in the 320–340-meV range are shown to give good agreement with the data at both pressures (yielding, taking E_{gb} uncertainty into account, $V_{BO} = 330 \pm 20$ meV). It can be argued that such a determination relies on the value of E_{gb}. This can be answered by plotting the difference between QW luminescence energies [$E(10) - E(L)$, for instance]. This eliminates E_{gb} from Eq. (1), and diminishes the effect of possible variations in E_{Ry} and E_{loc}. Comparison with experimental values on such a plot (not reported) gives also $V_{BO} = 330$ meV.

The fact that the valence-band offset is independent of pressure within experimental uncertainty is important: using the band-gap pressure variations of the barrier and well materials given in Table I, and the above determination of V_{BO}, we find that the Γ conduction-band offset at

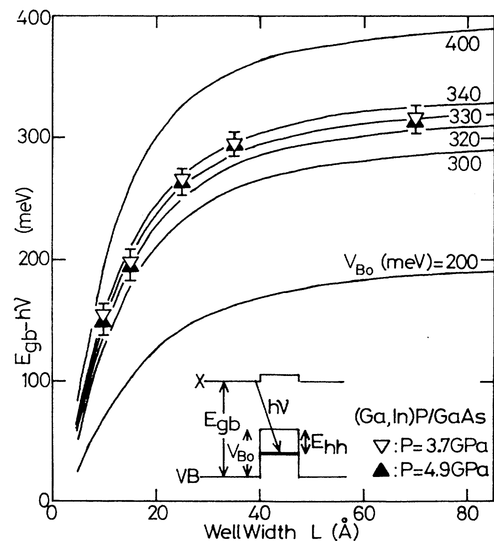

FIG. 3. Calculated type-II recombination energy relative to the barrier band gap as a function of well width for various valence-band offset values. Symbols are experimental values at 3.7 and 4.9 GPa.

3.2 GPa is only 33 meV. This shallowness and the small electron effective mass at Γ leads to small variations with the well width of electron confinement energies. This explains the similar crossover pressures observed for each well. Indeed, the type-I–type-II crossover pressures calculated for each QW are 3.20 ± 0.05 GPa, comparing well with experimental observation.

Such a value of the valence-band offset is in very good agreement with our previous atmospheric determination through PR (a slight pressure variation of V_{BO} with pressure, as in the case of the AlAs/GaAs system,[26] would improve the agreement). It also agrees with the internal photoresponse result of Haase, Hafich, and Robinson,[4] and the theoretical calculation of Foulon *et al.*[7]

It is necessary at this point to try to discuss the large variations of band-offset values in the literature. Since experimental methods are diverse, we shall first examine the results of Chen *et al.*,[11] who used a high-pressure method as we do here. The type-II pressure coefficient of multiple quantum wells (MQW's) found in Ref. 11 is 30 meV/GPa, higher than the barrier pressure coefficient, and also higher than the values obtained in this work (≤ 20 meV/GPa). It is also stated in Ref. 11 that this could be due to residual stress. Such a residual stress, likely to act along the (001) axis of the crystal in a diamond-anvil cell, will lower one (or two) of the barrier X band gaps.[15] Using Eq. (1) with a lowered barrier band gap leads directly to larger valence-band offset values. In our experiment, we could measure buffer, QW, and barrier PL in the same sample. Table I shows that the pressure variation of the transitions in the GaAs buffer are in very good agreement with the most recent data regarding GaAs,[15,16,27] both for direct and indirect transitions. Since it is known that bulk moduli, in a family of compounds (e.g., III-V's) are only functions of the lattice parameter,[28] we conclude that the lattice-matched $Ga_{0.5}In_{0.5}P$ barriers are under hydrostatic compression in this work.

But other reasons can be invoked for the discrepancy between the results of Chen *et al.* and ours, principally the difference in the growth method (gas-source MBE instead of MOMBE), possibly leading to different interface properties. First, there is a fundamental reason in the present system for interface nature to influence the band offset: in III-V heterojunctions sharing neither common anion nor common cation, two different kinds of interfaces may exist, i.e., GaP or (Ga,In)As in our case. This leads to different interface strain and dipole and hence different valence-band offset.[7,29]

Other elements more directly related to the growth method must be taken into account. Switching two group-V species is difficult,[2] and may lead to some intermixing. In contrast, growth interruptions, as performed in MOMBE, may lead to the formation of a GaP interface layer.[12] Also to be taken into account is the well-known phenomenon of In segregation in the growth of (Ga,In) compounds,[30,8] that may lead to asymmetry in barrier composition. Last but not least, $Ga_{0.5}In_{0.5}P$ is known to form an ordered phase, with a CuPt-like structure, depending on growth method and procedure.[2,20] The variation of band gap associated with ordering directly modifies band offsets. All these facts may explain discrepancies in band-offset values reported for $Ga_{0.5}In_{0.5}P$/GaAs heterostructures grown by various methods such as chloride vapor-phase epitaxy (VPE),[3] metalorganic VPE,[2] MBE,[5] gas-source MBE,[4,11] or MOMBE.[6,12] This discussion leaves us with the rather disappointing conclusion that the band-offset value measured in this work, which is an average value, might only be valid for MOMBE-grown samples, using the growth procedure described in Ref. 12. On the other hand, the above valence-band offset value describes well the ground and excited states of QW's of various widths.[6]

In conclusion, the pressure-induced type-II photoluminescence energies of GaAs/$Ga_{0.5}In_{0.5}P$ QW's have been found to be consistent with a valence-band offset of 330 ± 20 meV. Such a value, allowing the description of ground and excited QW's states,[6] and in agreement with recent theoretical calculations,[8] should prove useful in the modeling of MOMBE-grown devices based on such heterostructures.

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