RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 11 15 SEPTEMBER 1992-I

Valence-band splitting in ordered $Ga_{0.5}In_{0.5}P$ measured by polarized photoluminescence excitation spectroscopy

D. J. Mowbray, R. A. Hogg, and M. S. Skolnick
Department of Physics, University of Sheffield, Sheffield S3 7RH, United Kingdom

M. C. DeLong
Department of Physics, University of Utah, Salt Lake City, Utah 84112

S. R. Kurtz and J. M. Olson
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393
(Received 5 June 1992)

The spontaneous long-range-order-induced splitting of the valence band of $Ga_{0.5}In_{0.5}P$ is studied by polarized near-gap-excited photoluminescence and photoluminescence excitation. The results allow a direct determination of the size of the valence-band splitting and the relative ordering of the resultant states. Values obtained for the splitting are compared with recent calculations.

There is considerable contemporary interest in the spontaneous long-range ordering exhibited by the metal-organic vapor phase epitaxy (MOVPE) grown, III-V ternary semiconductor $Ga_{0.5}In_{0.5}P$.[1] This ordering, the degree of which depends critically upon the growth conditions,[2] consists of alternate group-III sublattice layers composed preferentially of In and Ga.[3] The ordering axis is along two of the four $\langle 111 \rangle$ directions, $[\bar{1}11]$ and $[1\bar{1}1]$, both of which lie in the (110) plane. Such ordering results in the so-called CuPt structure.

The crystal ordering has dramatic effects upon the electronic, and hence optical, properties of the material. The band gap of the ordered material is considerably smaller (up to 100 meV) than that of disordered, random material with the size of band-gap reduction being related to the degree of ordering.[1] Furthermore, the energy of one of the principal photoluminescence (PL) peaks (the "moving" emission) increases with increasing incident laser power density; the rates at which the emission moves is also related to the degree of sample ordering and, in addition, substrate orientation.[4,5]

First-principles calculations of the electronic structure of perfectly ordered GaInP (equivalent to a 1-1 monolayer, [111] orientated GaP-InP superlattice) have been performed by Zunger and co-workers[6,7] and Kurimoto, Hamada, and Oshiyama.[8] The band-gap reduction is explained in terms of the folding of electronic states, at the L point in the random alloy, to the zone center, which then repel the valence band upwards and the conduction band downwards. The moving PL is not understood but may be a consequence of the fact that the ordering does not extend continuously through the sample but is confined to small [$\sim$100 Å (Ref. 9)] isolated regions or domains. Any resultant potential fluctuations may cause a spatial separation of the electrons and holes which in turn would partially screen the potential as the photoexcited carrier density increases. A variable band gap, similar to that found in *nipi* low-dimensional semiconductor structures, would result.

In addition to the band-gap reduction, the lowered symmetry of the ordered material will cause a splitting of the zone-center valence-band states which are fourfold degenerate in the random alloy. This splitting should manifest itself as an anisotropy of the optical properties about an axis normal to the surface of samples grown on (001) substrates. Such an anisotropy has been observed by Mascarenhas *et al.*[10] in the room temperature PL of GaInP and by Kanata *et al.*[11] in the PL over a range of temperatures. From the temperature dependence of the relative PL intensities, the latter authors deduced values for the size of the valence-band splitting in a number of samples.

In this paper we present results of a study of the polarized near gap excited PL and photoluminescence excitation (PLE) of ordered GaInP. In contrast to PL, PLE provides an unambiguous measurement of both the valence-band splitting and the relative oscillator strengths of the resultant optical transitions. In particular, problems associated with the moving emission, valence-band state populations and carrier localization induced Stokes shifts are absent in PLE. The form of the PLE spectra is found to depend strongly on the incident laser polarization in a manner consistent with the predictions of a group-theory analysis. Our results allow a direct determination of the valence-band splitting and the values obtained are compared with recent theoretical calculations.

The samples studied were grown by MOVPE on undoped (001) GaAs substrates misorientated by 2° towards (011). The growth temperature and III/V ratio were 675 °C and 64, respectively. These are conditions which typically yield material with the lowest band gap.[2,12] Selectively excited PL and PLE spectra were measured at 4.2 K using excitation from an Ar^+ pumped dye laser equipped with DCM (4-dicyano-methylene-2-methyl-6-*p*-dimethylaminostyryl-4*M*-pyran) dye. The luminescence was dispersed by a double grating spectrometer and detected by a cooled GaAs photomultiplier. All spectra were recorded in a normal incidence geometry with a power density of $\sim$1 W cm^{-2}. The samples were mounted so that the two ordering axes $[\bar{1}11]$ and $[1\bar{1}1]$ lay in the horizontal plane (110) ([110] crystal direction vertical).

Figure 1 shows selectively excited PL spectra of an ordered GaInP sample. Spectra are shown for different excitation energies and for both vertical (Y) (crystal direction [110]) and horizontal (X) (crystal direction [1$\bar{1}$0]) incident laser polarization. Unlike the higher-temperature measurements of Mascarenhas *et al.*[10] and Kanata *et al.*[11] the form (peak position and linewidth) of the PL (and PLE) spectra is found to be independent of the detection polarization in all the samples studied. This is because at low temperature the photocreated holes thermalize to the lowest-energy valence band. The intensity of the PL, however, is found to be anisotropic in all GaInP samples we have studied, both ordered and disordered MOVPE grown and also MBE grown GaInP, the latter being at most only very weakly ordered. In contrast the PL from a MBE grown, AlGaAs sample showed no PL intensity anisotropy. Referring to Fig. 1 it can be seen that for high-energy excitation the PL spectra for X and Y incident polarizations are identical. However, as the excitation energy is reduced the X incident polarized PL occurs at a lower energy and is significantly weaker than the Y incident polarized PL.

Figure 2 shows a series of PLE spectra, of the same ordered sample, for X and Y incident polarizations and a range of detection energies. As stated earlier the PLE spectra are independent of detection polarization. The large Stokes shift (≈ 60 meV) between the PL and PLE emphasizes the importance of using an absorption related technique to measure accurately the sample band gap. The PLE spectra show considerable polarization dependence with a difference of ≈ 19 meV between the excitonic transition energies of the two polarizations (A and B in Fig. 2). The lowest-energy transition (A) appears strongly in the Y polarization and is reduced in intensity by a factor ≈ 2.5 in the X polarization. The higher-energy transition (B) is visible in the X polarization. For energies ≥ 1.94 eV the PLE is essentially unpolarized. Similar incident polarization dependent PLE (and PL) has been observed in other ordered samples. In contrast, the PLE of very weakly ordered or disordered samples (MOVPE grown at 750 °C and MBE grown) showed no incident polarization dependence.

Of further note in the PLE spectra is that as the detection energy is decreased, the onset and excitonic features of the PLE also decrease in energy. This behavior, which has also been observed in other ordered samples but not in disordered ones, is probably related to the existence of a high density of band-tail states in the ordered material

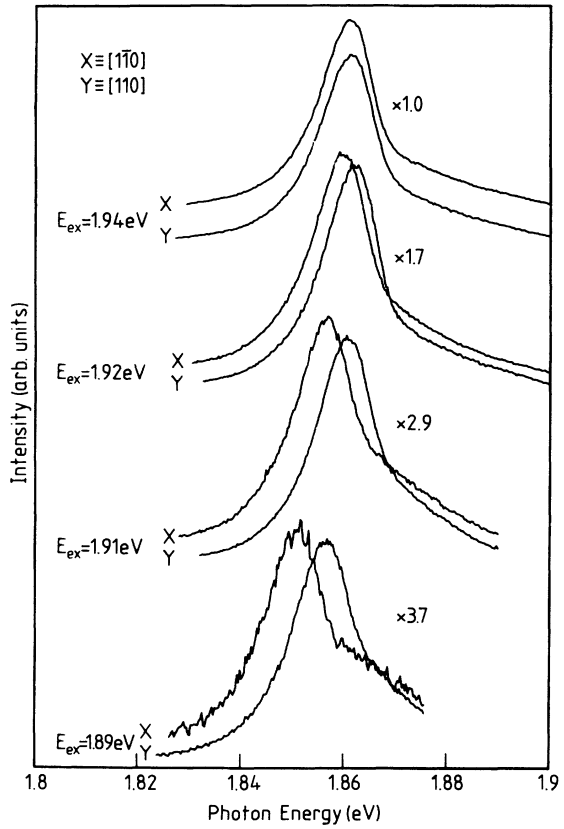

FIG. 1. Near gap excited PL spectra of an ordered (T_g=675 °C) GaInP sample for horizontal (X≡[1$\bar{1}$0]) and vertical (Y≡[110]) incident polarization and various excitation energies. The numbers by the spectra give the relative gain increases for the X incident polarization spectra. The sample temperature was 4.2 K and the PL was excited using an incident laser power density of ≈ 0.7 W cm^{-2}.

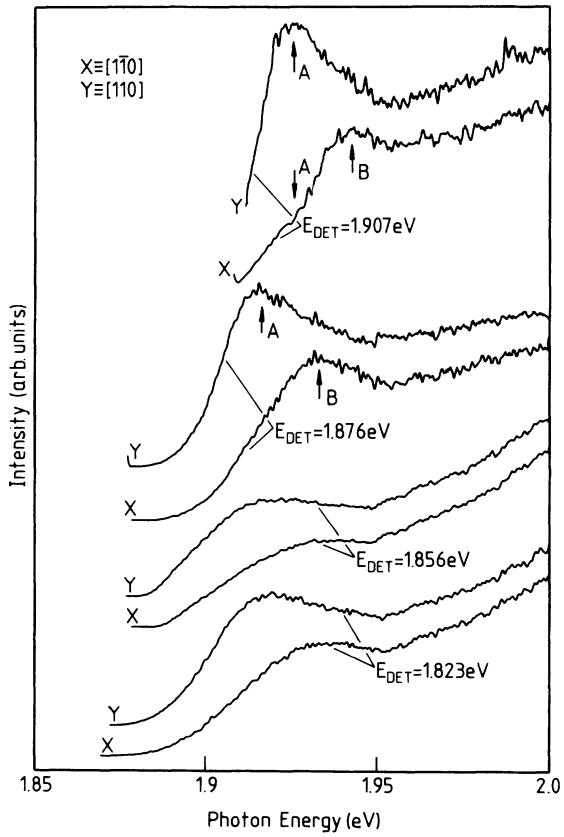

FIG. 2. PLE spectra, recorded at 4.2 K, of the ordered sample of Fig. 1 for the two incident polarizations and various detection energies. For each pair of spectra the Y polarization has been displaced vertically for clarity. For energies ≥ 1.95 eV the PLE is incident polarization independent.

and will be discussed in greater detail in a separate publication.

The CuPt ordering of GaInP reduces the crystal symmetry from T_d to C_{3v}. In the T_d double group the highest-energy valence band is fourfold degenerate and transforms as the Γ_8 irreducible representation. The reduced symmetry partially lifts this degeneracy to give Γ_5 and Γ_6 states ($m_J = \pm \frac{3}{2}$) which remain degenerate (henceforth referred to as $\Gamma_{5,6}$) and a doubly degenerate Γ_4 ($m_J = \pm \frac{1}{2}$) state. The lowest conduction band transforms as Γ_4 so that possible transitions are $\Gamma_4 \rightarrow \Gamma_4$ and $\Gamma_{5,6} \rightarrow \Gamma_4$. For light polarized normal to the symmetry (ordering) axis both transitions are allowed whereas for parallel polarized light only the former is possible. In the absence of significant band mixing the relative oscillator strengths of the transitions are $I_\perp(\Gamma_4 \rightarrow \Gamma_4):I_\perp(\Gamma_{5,6} \rightarrow \Gamma_4):I_\parallel(\Gamma_4 \rightarrow \Gamma_4) = 1:3:4$. Experimentally, the ordering axes lie in the $(1\bar{1}0)$ horizontal plane and make angles of 54.7° to the [001] surface normal. Hence Y incident polarized light produces only a component normal to the symmetry axis whereas X incident polarized light produces both parallel and normal components.

Allowing for the relative oscillator strengths and for the projections of the incident polarizations onto directions perpendicular or parallel to the symmetry axis results in the relative transition intensities for the two polarizations given in Table I.[10,13] These results allow the unambiguous identification of $\Gamma_{5,6} \rightarrow \Gamma_4$ as the lowest-energy transition; its measured reduction in intensity of ≈ 2.5 between Y and X being close to the calculated value of 3. The relative polarized intensities of the higher energy, $\Gamma_4 \rightarrow \Gamma_4$ transition are difficult to measure as the excitonic feature lies on top of the continuum states of the lower-energy transition. The sum of the two transition intensities is polarization independent in agreement with the experimental observation that, for energies above the excitonic features, the PLE is unpolarized.

The present results allow us to conclude that in ordered GaInP the $\Gamma_{5,6}$ valence band lies above Γ_4, in agreement with the theoretical predictions of Wei and Zunger.[6,14] These authors calculate a valence-band splitting of 62 meV,[6] somewhat larger than our experimental value of 19 meV which includes possible small excitonic corrections. A similar value (22 meV) is found in a second ordered sample also grown at 675 °C. The reason for this discrepancy between theory and experiment is likely to be due in part to the existence of less than perfect ordering in the present samples which, instead of containing pure Ga and In layers, probably consist of alternate group-III layers which are either preferentially Ga or In rich. Calculations of the dependence of the valence band splitting upon the degree of ordering are not available although Kanata *et al.*[11] experimentally deduce a linear dependence based on the unproven assumption that the amount of band-gap reduction is also a linear function of the degree of ordering. The ordering parameter δ in this work is defined by describing the material as a [111] $Ga_{0.5+\delta}In_{0.5-\delta}P/Ga_{0.5-\delta}In_{0.5+\delta}P$ monolayer superlattice. Application of this model to the present results gives a value of $\delta = 0.31 (\equiv 19 \text{ meV}/62 \text{ meV})$ from the size of the valence-band splitting and $\delta \approx 0.24 \sim 0.32$ (Ref. 15) from the band-gap reduction where again the measured value of ≈ 70 meV (Ref. 16) is less than the value of 260 meV calculated by Wei and Zunger.[6] Our results for the valence-band splitting are, however, similar in magnitude to the range of values ~20–40 meV deduced in a less direct manner by Kanata *et al.*[11] from the temperature dependence of the PL.

TABLE I. Relative transition intensities for the two incident laser polarizations ($X \equiv [1\bar{1}0]$, $Y \equiv [110]$).

Polarization	Transition $I(\Gamma_4 \rightarrow \Gamma_4)$	$I(\Gamma_{5,6} \rightarrow \Gamma_4)$
X	3	1
Y	1	3

Finally the behavior of the PL (Fig. 1) can be understood by a consideration of the form of the PLE spectra. For energies ≥ 1.94 eV the PLE, and hence the sample absorption, is incident-polarization independent. For lower energies, however, the absorption is greater for Y polarization than for X. Because the PL of the ordered sample has an excitation intensity dependent energy[4] (9 meV/decade for the present sample), the lower absorption for X incident polarization results in a lower energy, weaker PL peak. This explanation was confirmed by increasing the incident power for the X polarization to compensate for the lower PL intensity. The X and Y incident PL were then found to occur at the same energy. This result indicates that any anisotropy in the low-temperature, near gap excited PL cannot be taken as a measure of the valence-band splitting.

To conclude, polarized PLE has allowed a direct determination of the ordering induced valence-band splitting of GaInP. Values of 19 and 22 meV are found for two samples both grown at 675 °C, less than predicted by recent calculations. Part of this discrepancy is probably due to there being less than perfect crystal ordering.

We wish to thank G. A. Gehring and K. J. Nash for useful discussions and SERC (United Kingdom) for financial support (Grant No. GR/H08082).

[1] A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. **60**, 2645 (1988).

[2] S. R. Kurtz, J. M. Olson, and A. Kibbler, Appl. Phys. Lett. **57**, 1922 (1990).

[3] O. Ueda, M. Takikawa, J. Komento, and I. Umebu, Jpn. J. Appl. Phys. **26**, L1824 (1987).

[4] M. C. DeLong, P. C. Taylor, and J. M. Olson, Appl. Phys. Lett. **57**, 620 (1990).

[5] J. E. Fouquet, V. M. Robbins, and J. Rosner, Appl. Phys. Lett. **57**, 1566 (1990).

[6] S. H. Wei and A. Zunger, Appl. Phys. Lett. **56**, 662 (1990).

[7] J. E. Bernard, S. Froyen, and A. Zunger, Phys. Rev. B **44**,

11 178 (1991).

[8]T. Kurimoto, N. Hamada, and A. Oshiyama, Superlattices Microstruct. **5**, 171 (1989).

[9]M. Kubo, M. Mannoh, and T. Narusawa, J. Appl. Phys. **66**, 3767 (1989).

[10]A. Mascarenhas, S. Kurtz, A. Kibbler, and J. M. Olson, Phys. Rev. Lett. **63**, 2108 (1989).

[11]T. Kanata, M. Nishimoto, H. Nakayama, and T. Nishino, Phys. Rev. B **45**, 6637 (1992).

[12]T. Suzuki, A. Gomyo, S. Iijma, K. Kobayashi, S. Kawata, I. Hino, and T. Yuasa, Jpn. J. Appl. Phys. **27**, 2098 (1988).

[13]A. Mascarenhas and J. M. Olson, Phys. Rev. B **41**, 9947 (1990).

[14]S. H. Wei and A. Zunger, Phys. Rev. B **39**, 3279 (1989).

[15]The precise value depends upon the value taken for the band gap of the ordered material from the PLE spectra of Fig. 2.

[16]The excitonic band gap of totally disordered GaInP is taken as 2.003 eV. C. T. H. F. Liedenbaum, A. Valster, A. L. G. J. Severens, and G. W. 't Hooft, Appl. Phys. Lett. **57**, 2698 (1990).