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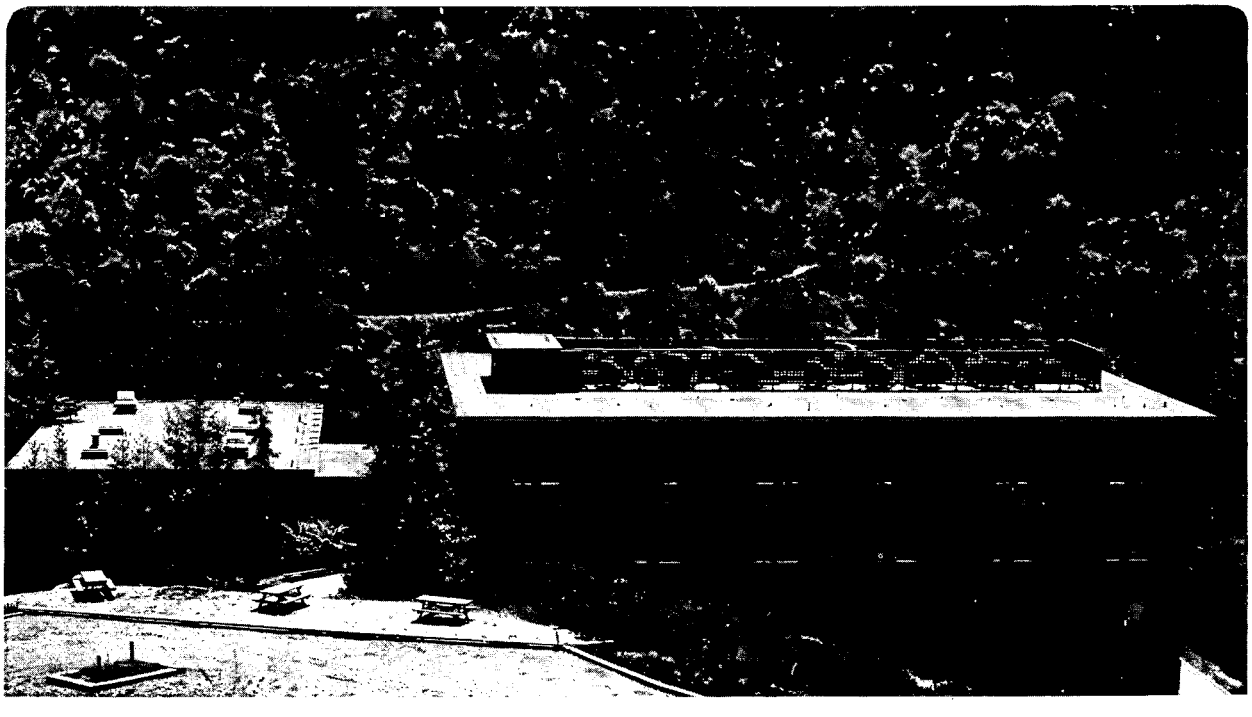

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ENERGIES OF X CONDUCTION BAND MINIMA IN DISORDERED AND ORDERED $GaInP_2$ ALLOYS

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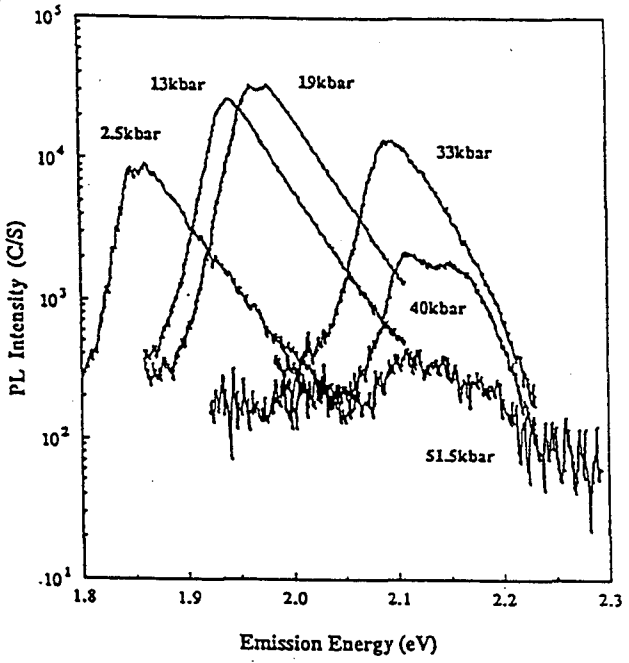
ABSTRACT

A pressure-induced change from a direct bandgap to an indirect bandgap semiconductor has been observed in both partially ordered and disordered $GaInP_2$. By extrapolating back to ambient pressure the indirect Γ-X band gap energy has been deduced. It was found that the Γ-X conduction band separation remains almost constant between the ordered and disordered phases. A phenomenological model is proposed to explain this result.

$GaInP_2$ grown by MOVPE on GaAs can form either a disordered or partially ordered alloy depending on the growth conditions.[1-4] Both types of materials have direct bandgaps at the Brillouin zone center (Γ point). The bandgap in the ordered alloy is smaller than that in the disordered phase by as much as 100 meV. It is generally believed that the structure of the ordered phase is CuPt with ordering along the [111] direction. This causes the conduction band valleys at the L point to fold into Γ. Mixing of these folded bands with the Γ conduction minimum is responsible for the smaller bandgap in the ordered phase.[5] This model has received support from electroreflectance measurements.[6] A new peak attributed to the folded L transition has been observed in the ordered phase. In this model the location of the X conduction band valleys are not expected to be affected. However, Kurtz[6] observed also a peak in the electroreflectance spectra in the ordered phase which was attributed to a transition to the X conduction band minima. The surprising result was that the X minima followed the Γ minimum as the bandgap was varied by ordering. To understand further the properties of the X conduction band minima, we have studied the pressure dependence of photoluminescence (PL) in both phases of $GaInP_2$ alloys at room temperature. It is well-known that the X conduction valleys have a negative pressure coefficient while the corresponding coefficient for the Γ valley is positive. At high enough pressure the X valleys will lie below the Γ valley and the semiconductor bandgap changes from direct to indirect. By performing the experiment at room temperature, emission from both the direct and

Figure 1 Photoluminescence spectra of ordered $GaInP_2$ at room temperature.



indirect transitions can be observed simultaneously near this pressure-induced Γ-X cross-over. Our results which agree with those of Kurtz can be qualitatively understood within a model involving partial ordering along the [001] direction.

Our samples were grown by low pressure OMVPE on semi-insulating [001] oriented GaAs substrates. The degree of ordering in the GaInP epilayers was varied by

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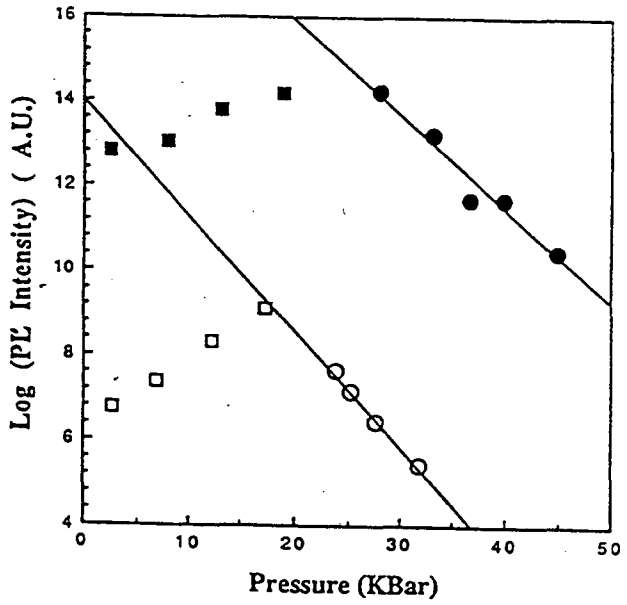
Figure 2 The direct gap emission in ordered (solid symbols) and in disordered (open symbols) $GaInP_2$ as a function of pressure.



changing the GaAs substrate orientations. Photoluminescence (PL) spectra were excited by an Ar ion laser and measured as a function of pressure using a gasketed diamond anvil high pressure cell. Methanol/ethanol mixture is used as the pressure medium and the pressure determined with the ruby fluorescence scale. Some representative PL spectra in the ordered GaInP sample are shown in Fig. 1. At low pressures the emission consists of a single asymmetric peak due to recombination of electrons and holes at Γ. At pressures above 33 Kbar, the emission splits into two peaks. The intensity of the Γ transition weakens rapidly with pressure as shown in Fig. 2. The pressure dependence of all the observed emission peak energies can be found in Ref. 7. The second peak which appears only at high pressures has been identified with recombination from an electron in the X conduction valleys with a hole at Γ based on its negative pressure coefficient. From these peak energy and intensity dependence we extrapolated the ambient pressure

energy of the indirect Γ-X transition to be 2.132 eV and the X-Γ conduction valley separation to be 0.28 eV in our partially ordered sample. The corresponding values obtained by Kurtz are 2.16 eV and 0.36 eV. The PL intensity in our disordered sample was much lower and consequently we did not observe any indirect gap emission. The pressure dependence of the direct gap emission intensity is shown in Fig. 2. The X-Γ indirect emission in disordered $GaInP_2$ has been reported previously by Chen et al.[8] They extrapolated the Γ-X transition energy to be 2.26 eV and the Γ-g conduction band separation to be 0.29 eV. Although their measurements were performed at 25 K, the *difference* in the temperature coefficients of the direct Γ-Γ and indirect Γ-X transitions in both InP and GaP is rather small.[9] We estimated that the correction for the temperature dependence to the X-Γ separation to be less than 20 meV. Thus we are led to the same conclusion as Kurtz[6] that the Γ-X separation is the same for both ordered and disordered phases in $GaInP_2$.

To explain the appearance of the Γ-X indirect transition in the electroreflectance spectra, Kurtz[6] pointed out the possible existence of ordering along the [001] direction. Such ordering can be regarded as stacking faults of the [110] oriented chains containing alternate rows of Ga or In. Figure 3 compares the arrangement of the Ga and In atoms in the CuPt and the so-called Y2 structures.[6] In both structures we find [001] oriented planes containing alternate rows of In and Ga atoms along the [110] direction. The stacking order of these planes determines whether the structure is CuPt or Y2. The electron diffraction patterns of ordered $GaInP_2$ typically exhibit strong ordering along the [I11] and [1I1] directions. However, this does not rule out the possible existence of stacking faults within the ordered domains. These stacking faults can couple the conduction band states at zone center and at the L point with those at the X point. We propose therefore the following model to explain our results qualitatively.

We use the virtual crystal approximation as our starting point. In this approximation the ordering of the various conduction band minima in the random alloy is sketched in Fig. 4(a). Introduction of ordering along the [111] direction produces a coupling between the Γ and L minima resulting in the band scheme in Fig. 4(b). This coupling raised the L valleys to above the X valleys. Finally, the stacking faults are introduced as a perturbation which mixes the Γ, L and X valleys. This mixing produces a much bigger effect on the X and L valleys than on the Γ valley since they are closer together. The net effect is to lower the

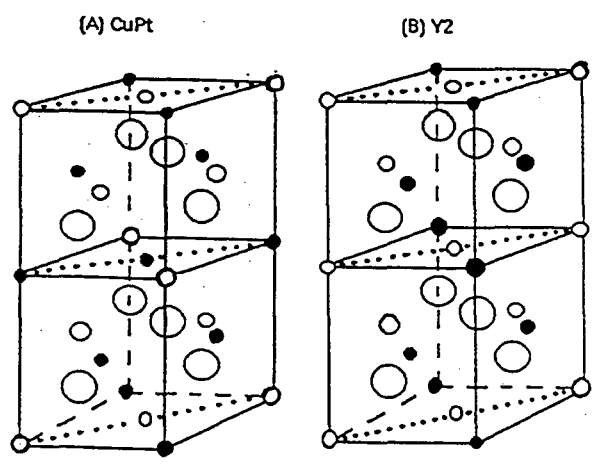


Figure 3 Crystal structures of ordered $GaInP_2$. Solid circle: Ga; small open circle: In; large open circle: P. The dotted line shows the chains of Ga or In atoms along the [110] direction.

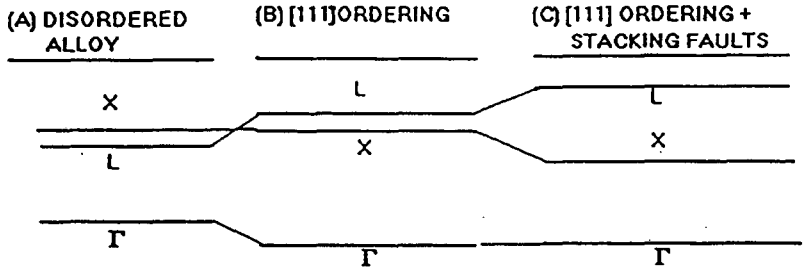


Figure 4 Schematic model for the conduction band orderings in $GaInP_2$

X valley and raise the L valley further while keeping the Γ valley unchanged. This is shown schematically in Fig. 4(c). However, this model cannot explain why the X valleys always seem to follow the Γ valley as found by Kurtz.[6]

In conclusion, we found from photoluminescence measurements in $GaInP_2$ under pressure that the energy separations between its Γ and X conduction band valleys are the same in both ordered and disordered phases.

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REFERENCES

1. A. Gomyo, K. Kobayashi, S. Kawata, I. Hino, T. Suzuki, and T. Yuasa, J. Cryst. Growth 77, 367 (1986);A. Gomyo, T. Suzuki, K. Kobayashi, S. Kawata, and I. Hino, Appl. Phys. Lett. 50, 673 (1987).
2. M. Kondow, H. Kakibayashi, and S. Minagawa, Appl. Phys. Lett. 53, 2053 (1988); T. Nishino, Y. Inoue, Y. Hamakawa, M. Kondow, and S. Minagawa, Appl. Phys. Lett. 53, 583 (1988).
3. T. Kobayashi, and R. S. Deol, Appl. Phys. Lett. 58, 1289 (1991).
4. M. C. DeLong, W. D. Ohlsen, I. Viohl, P. C. Taylor and J. M. Olson, J. Appl. Phys. 70, 2780 (1991); M. C. DeLong, D. J. Mowbray, R. A. Hogg, M. S. Skolnick, M. Hopkinson, J. P. R. David, P. C. Taylor, S. R. Kurtz, and J. M. Olson, J. Appl. Phys. 73, 5163 (1993).
5. S-H. Wei and A. Zunger, Appl. Phys. Lett.56, 662 (1990); J. E. Bernard, S.-H. Wei, D. M. Wood and A. Zunger, Appl. Phys. Lett. 52, 311 (1988).
6. S. R. Kurtz, J. Appl. Phys. 74, 4130 (1993).
7. K. Uchida, P. Y. Yu, N. Noto, and E. R. Weber, Appl. Phys. Lett.64, 2858 (1994).
8. J. Chen, J. R. Sites, I. L. Spain, M. J. Hafich and G. Y. Robinson, Appl. Phys. Lett. 58, 744 (1991).
9. See data listed in Landolt-Börnstein New Series Group III: Crystal and Solid State Physics, Vol. 22 *Semiconductors Subvolume a. Intrinsic Properties of Group IV. Elements, and III-V, II-VI and I-VII Compounds*, ed. by O. Madelung (Springer-Verlag, Berlin, 1987).

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