

High-pressure photoluminescence study of ordered Ga_{0.5}In_{0.5}P alloys grown on GaAs by organometallic vapor phase epitaxy

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Photoluminescence (PL) measurements on Ga_{0.5}In_{0.5}P grown by organometallic vapor phase epitaxy on GaAs substrates at various growth temperatures have been made as a function of pressure up to about 4.5 GPa. In the pressure range 0–3.8 GPa the PL spectrum exhibits a shift to higher energies. It is found that the pressure coefficient of the PL peak energy depends significantly on the growth temperature and hence on the degree of ordering. These results are partly explained in terms of repulsion between the Γ -folded energy states in the CuPt-type ordered structure.

Recently, it has been found that the band-gap energy of Ga_{0.5}In_{0.5}P alloys grown on (001) GaAs substrates by organometallic vapor phase epitaxy (OMVPE) strongly depends upon growth conditions such as growth temperature and V/III ratio.^{1–3} The direct band-gap energy, which was determined by photoluminescence (PL) measurements, is significantly smaller (about 50 meV) than the previously reported values of this alloy grown by other methods, such as liquid phase epitaxy (LPE). This anomaly in band-gap energy has been attributed previously to the existence of an ordering in the atomic (Ga, In) arrangement on the Group III sublattice in OMVPE-grown Ga_{0.5}In_{0.5}P.^{1,2} The ordered structures in these alloys, grown under various growth conditions, have also been investigated using transmission electron microscopy (TEM),^{4–6} Raman scattering,^{6,7} and electroreflectance (ER)^{6,8} measurements. The relationship between the direct band gap and ordering was found to be more complex than previously thought. From TEM studies it has been found that a short-range ordered structure forms at lower growth temperatures and gradually changes into a long-range ordered structure having a high degree of ordering with an increase in growth temperature. The anomalous change in direct band gap found in PL and ER measurements correlated with the anomalous broadening in the Raman spectrum, but was not directly related to the degree of ordering. The atomic structures and ordering in pseudobinary isovalent semiconductor alloys have also been theoretically investigated^{9,10} and predicted to be accompanied by a reduction in the direct band gaps.^{11,12} The mechanism for this band-gap narrowing is explained as band folding followed by repulsion between the folded states absent in disordered alloys. However, the details of electronic band structure including higher-lying conduction band states and their effects on optical spectra are still not accurately known. The structural ordering and its relationship to PL properties is not yet completely understood.

Many of the optical investigations described so far were performed at atmospheric pressure. Hydrostatic pressure can change the energies of the electronic states, preserving crystal symmetry. Thus, application of high pres-

sure for systematic and controllable adjustment of tuning of electronic states in semiconductors seems ideally suited to fundamental studies of electronic band structure, such as the folded states in the ordered semiconductor alloys.^{11,12}

In this letter we have measured PL spectra for a series of OMVPE Ga_{0.5}In_{0.5}P alloys grown using different growth temperatures, as a function of pressure up to 4.5 GPa at a temperature of 77 K, with the intention of observing distinct effects of growth conditions on the PL spectra. We report for the first time that the pressure dependence of the PL peak energy is closely related to the growth temperature and hence to the degree of ordering in this alloy system. These experimental results are also discussed in connection with the recent theoretical predictions to the physical mechanism for the characteristic changes in the energies of the electronic states in the CuPt-type crystalline structure absent in disordered alloys.

Samples were grown at one atmosphere from triethylgallium, trimethylindium, and phosphine using a conventional horizontal OMVPE system.⁵ Growth temperatures (T_g) of 600, 650, and 700 °C were used. The V/III ratio was held constant at 160. Undoped Ga_{0.5}In_{0.5}P epitaxial layers with a thickness of 0.7 μm were grown on Si-doped GaAs wafers with (001) orientation after the growth of a 0.4 μm GaAs buffer layer. The lattice mismatch was less than 10^{-3} for all the samples studied. PL measurements at 77 K were made with a diamond-anvil high-pressure cell,¹³ using argon as a pressure-transmitting medium. The substrate was thinned to a total thickness of less than 50 μm . A small piece of about 150 μm across was loaded into a 450 μm hole of metal gasket. Luminescence was excited using the 488 nm line of an Ar⁺ laser, and the data were taken with an incident power of 10 mW or below.

Figure 1 shows typical PL spectra in the region of the E_0 band gap of OMVPE-grown Ga_{0.5}In_{0.5}P for a series of pressures up to 4.5 GPa at 77 K. The growth temperature was $T_g = 650$ °C. At atmospheric pressure the PL peak energy was observed to be very sensitive to the growth temperature and was considerably lower (50–80 meV) than the normal value for crystals grown by LPE (1.98 eV).^{6,8,14} It has a minimum value at around 650 °C as shown in Fig. 2. With increasing pressure the PL spectrum exhibits a rapid shift to higher energies. The energy shift of

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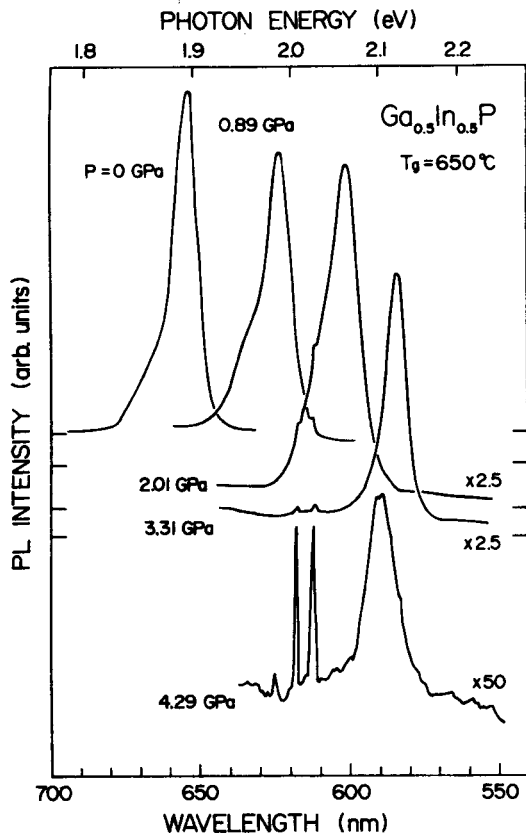


FIG. 1. Typical PL spectra of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ taken at several pressures with a temperature of 77 K. The growth temperature is 650 °C.

the main PL peak is directly related to the pressure dependence of the direct E_0 band gap. The sample grown at the lowest growth temperature ($T_g = 600$ °C) exhibits a larger rate of PL peak shift than the sample grown at the highest growth temperature ($T_g = 700$ °C). No significant change in the PL intensity is noticed for pressures up to about 3.0 GPa, while an order of magnitude decrease in the intensity is observed for higher pressures near 3.5 to 3.8 GPa. At a certain pressure 3.8–4.0 GPa the shift of PL spectra satu-

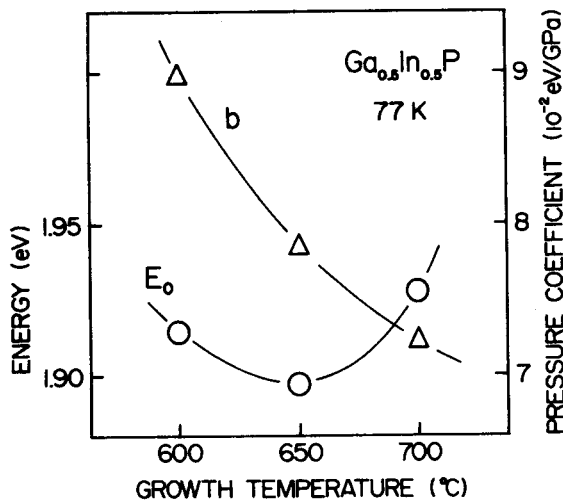


FIG. 2. Growth temperature dependence of the PL peak energy at atmospheric pressure and of the linear pressure coefficient of the PL peak energy.

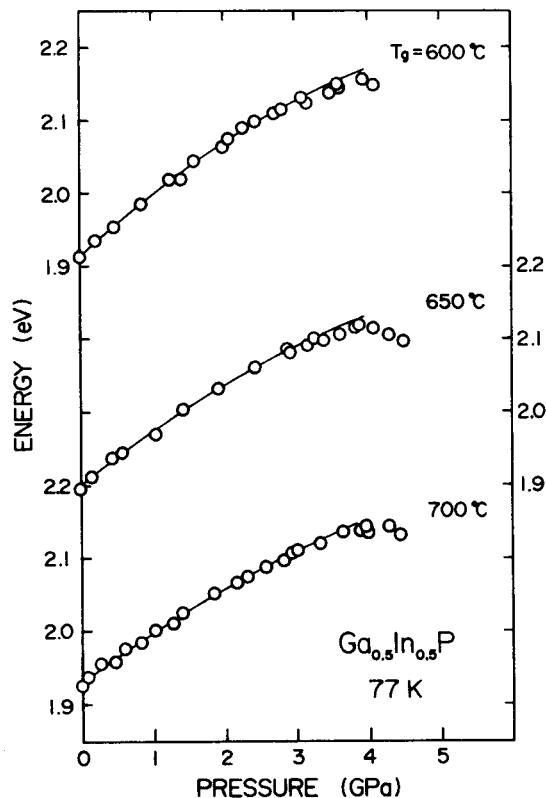


FIG. 3. Pressure dependence of the PL peak energy in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. The growth temperatures are 600, 650, and 700 °C. The solid lines represent the least-squares fits to the experimental data.

rates, and then the PL spectrum tends to shift to lower energies, followed by complete disappearance of this emission at 4.5 GPa. No emission line near the main PL peak has been detected in the present study even in the pressure range 2.7–4.5 GPa for all the samples evaluated.

Figure 3 shows the pressure dependence of the PL peak energy of samples grown at 600, 650, and 700 °C. In this figure one can clearly observe the sublinear dependence in the pressure range 0–3.8 GPa for all the samples. A least-squares fit to the data shows a quadratic dependence

$$E_0(P) = E_0 + bP + cP^2. \quad (1)$$

The linear and quadratic pressure coefficients b and c so obtained with emphasis on pressures below 3.5 GPa are given in Table I. The linear pressure coefficient, b , obtained at the lowest growth temperature ($T_g = 600$ °C) is found to be significantly larger than at the highest growth temperature ($T_g = 700$ °C), as shown in Fig. 2. There is, however, no significant correlation between the band-gap energy at atmospheric pressure and the linear pressure coefficient. The pressure at which the PL peak energy reaches a maximum (denoted P_m) and the corresponding energy $E_0(P_m)$ are also given in Table I. It should be noted that the maximum shift of the PL peak energy with pressure, $E_0(P_m) - E_0$, obtained at the lowest growth temperature ($T_g = 600$ °C) is larger than at the highest growth temperature ($T_g = 700$ °C). From TED and ER studies,⁴⁻⁸ it is known that the ordering in $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ is not perfect

TABLE I. Data related to the band gap of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ at high pressures: direct band gap E_0 at atmospheric pressure, its linear and quadratic pressure coefficients b and c , and pressure P_m at which direct band gap reaches a maximum $E_0(P_m)$.

T_g (°C)	E_0 (eV)	b (10^{-2} eV/GPa)	c (10^{-3} eV/GPa ²)	P_m (GPa)	$E_0(P_m)$ (eV)	$E_0(P_m) - E_0$ (eV)
600	1.91(5)	9.0	-6.4	3.9(4)	2.15(6)	0.24(1)
650	1.89(5)	7.8	-5.1	3.8(2)	2.12(8)	0.23(3)
700	1.92(6)	7.2	-4.1	4.0(0)	2.14(4)	0.21(8)

nor homogeneous but rather consists of a composite of domains of ordered and disordered phases depending on growth conditions. Therefore, the present results strongly suggest that they directly reflect the degree of ordering in this alloy system.

For pressures above 4.0 GPa there appears to be a decrease in the PL peak energy for all the samples measured in this study. In recent Hall and PL¹⁵ and optical absorption¹⁶ measurements on bulk GaInP alloys at 300 K, it is reported that the pressure-induced Γ - X crossover takes place at around 2.7 GPa. This is slightly lower than the pressure (~ 3.0 GPa) for the PL intensity to start to decrease and significantly lower than the pressure region 4.0–4.5 GPa for the observed decrease in the PL peak energy of OMVPE-grown $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. In addition, as mentioned above, no new emission has been detected even in the pressure range 2.7–4.5 GPa. It is plausible that the PL peak observed above 4.0 GPa arises from the direct transition across the E_0 band gap.

Recently, Bernard *et al.*¹¹ and Wei and Zunger¹² have presented a theory for the reduction in the direct band gaps of the ordered $\text{A}_{0.5}\text{B}_{0.5}\text{C}$ alloys. The $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloys can order into CuPt-like structure, which is a $(AC)_1(BC)_1$ superlattice along $\langle 111 \rangle$ directions. Hence, the L states in the binary constituents can fold into $\bar{\Gamma}$ states in the CuPt-type ordered structure. For example, the conduction band $\bar{\Gamma}_{1c}$ of the superlattice and Γ -folded L_{1c} states, $\bar{\Gamma}(L_{1c})$, can interact and, hence, repel each other by an amount that is inversely proportional to their unperturbed energy difference $\Gamma_{1c} - L_{1c}$ and directly proportional to the square of the coupling matrix $(\Delta V)^2$. This repulsion lowers $\bar{\Gamma}_{1c}$ of the superlattice state and raises $\bar{\Gamma}(L_{1c})$. At atmospheric pressure the Γ_{1c} and L_{1c} conduction bands of disordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloys are located at 1.97 and ~ 2.1 eV above the valence-band maximum, respectively.^{17,18} Therefore, the direct band gap $\bar{\Gamma}_v - \bar{\Gamma}_{1c}$ of the ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloys should be below 1.97 eV and new pseudodirect transitions $\bar{\Gamma}_v - \bar{\Gamma}(L_{1c})$ above ~ 2.1 eV will occur due to repulsion between these two states. Similar repulsion also affects the valence-band states $\bar{\Gamma}_v$ and reduces the band gap.

While the recent theory does not give a full understanding of the relationship between the direct band gap and ordering at atmospheric pressure, it is still a useful guide for interpreting high-pressure PL behavior. At high pressures we can expect that an ascending $\bar{\Gamma}_{1c}$ conduction-band minimum approaches the $\bar{\Gamma}(L_{1c})$ conduction-band minima from the lower energy side. This will cause an additional repulsion between two energy states due to a decrease in their energy difference, thereby lowering the

rate at which the $\bar{\Gamma}_{1c}$ of the superlattice state shifts to higher energies as compared with that for disordered alloys. We propose that the degree of ordering will influence the rate of the $\bar{\Gamma}_{1c}$ shift. The existence of such a repulsion will result in an eventual decrease in the $\bar{\Gamma}_{1c}$ state above a certain pressure P_m . This physical mechanism seems to be responsible for the observed shift of the PL peak energy with pressure. Experimental results have indeed indicated noticeable differences in pressure coefficient b and in the maximum shift of the PL peak energy $E_0(P_m) - E_0$ (Table I) between $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloys grown at different temperatures. Currently available $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloys are not only imperfectly ordered, but also show domains of ordered and disordered phases. We expect that as the degree of ordering and sample uniformity improve, ordering-induced effects shown above will become more pronounced.

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- ¹A. Gomyo, K. Kobayashi, S. Kawata, I. Hino, T. Suzuki, and T. Yuasa, *J. Cryst. Growth* **77**, 367 (1986).
- ²A. Gomyo, T. Suzuki, K. Kobayashi, S. Kawata, I. Hino, and T. Yuasa, *Appl. Phys. Lett.* **50**, 673 (1987).
- ³Y. Ohba, M. Ishikawa, H. Sugawara, M. Yamamoto, and T. Nakanishi, *J. Cryst. Growth* **77**, 374 (1986).
- ⁴O. Ueda, M. Takikawa, J. Komeno, and I. Umebu, *Jpn. J. Appl. Phys.* **26**, L1824 (1987).
- ⁵M. Kondow, H. Kakibayashi, and S. Minagawa, *J. Cryst. Growth* **88**, 291 (1988).
- ⁶M. Kondow, H. Kakibayashi, S. Minagawa, Y. Inoue, T. Nishino, and Y. Hamakawa, *Appl. Phys. Lett.* **53**, 2053 (1988).
- ⁷M. Kondow and S. Minagawa, *J. Appl. Phys.* **64**, 793 (1988).
- ⁸T. Nishino, Y. Inoue, Y. Hamakawa, M. Kondow, and S. Minagawa, *Appl. Phys. Lett.* **53**, 583 (1988).
- ⁹G. P. Srivastava, J. L. Martins, and A. Zunger, *Phys. Rev. B* **31**, 2561 (1985).
- ¹⁰A. A. Mbaye, A. Zunger, and D. M. Wood, *Appl. Phys. Lett.* **49**, 782 (1986).
- ¹¹J. E. Bernard, S.-H. Wei, D. M. Wood, and A. Zunger, *Appl. Phys. Lett.* **52**, 311 (1988).
- ¹²S.-H. Wei and A. Zunger, *Appl. Phys. Lett.* **56**, 662 (1990).
- ¹³T. Kobayashi, *Rev. Sci. Instrum.* **56**, 255 (1985).
- ¹⁴T. Kato, T. Matsumoto, and T. Ishida, *J. Cryst. Growth* **71**, 728 (1985).
- ¹⁵D. Patel, J. Chen, I. L. Spain, J. H. Quigley, M. J. Hafich, and G. Y. Robinson, *Phys. Rev. B* **38**, 13206 (1988).
- ¹⁶A. R. Goñi, K. Syassen, K. Strössner, and M. Cardona, *Phys. Rev. B* **39**, 3178 (1989).
- ¹⁷G. D. Pitt, M. K. R. Vyas, and A. W. Mabbitt, *Solid State Commun.* **14**, 621 (1974).
- ¹⁸D. Auvergne, P. Merle, and H. Mathieu, *Solid State Commun.* **21**, 437 (1977).