Photoluminescence in (Ga,In)P at high pressure

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Room-temperature photoluminescence measurements have been carried out at high pressure on (Ga,In)P layers grown by two different methods. The pressure dependence of the direct energy-band gap was fitted with a second-order function. Evidence of the direct-indirect band crossing has been observed from the reduction in the photoluminescence efficiency at about 2.8 GPa pressure.

I. INTRODUCTION

(Ga,In)P has attracted considerable interest for its uses in optoelectronic devices. Recently, the material has been employed[1-8] to show the spontaneous long-range ordering in III-V compound semiconductors. The band gap of (Ga,In)P has been shown to vary by as much as 80 meV depending on deposition conditions.[1,2,9,10] The variation of the band gap is believed to be related to the spontaneous ordering. It is of interest to ascertain whether other parameters are altered by the ordering, also. So far, only photoluminescence (PL)[2,9,11] electroreflectance, photoreflectance,[9] Raman,[11] and structural[1,2,4-8] (electron diffraction) results have been reported.

Pressure measurements can give useful information on these systems. From such studies, important parameters can be obtained such as the pressure coefficient of the conduction-band minima, $\Gamma-X-L$ conduction-band minima separation, and effective masses. Hall measurements on vapor-phase epitaxially grown $Ga_xIn_{1-x}P$ have been reported by Pitt *et al.*[12] at 90 K temperature in a pressure device other than a diamond-anvil cell. They speculated that for all compositions x, a $\Gamma-L$ and then an $L-X$ transition occurred at high pressure. Two points require clarification, however. A solid pressure-transmitting medium was used for their higher-pressure data, which would imply nonhydrostatic pressure. Also, the pressure coefficient of the Γ minimum was interpolated between InP and GaP, which may not be strictly correct, as shown by the work on (GaIn)(AsP).

In this work, room-temperature PL measurements in a diamond-anvil (high-pressure) cell[14] (DAC) are reported for (Ga,In)P ternary alloys grown on GaAs by two different techniques. The shift in the PL peak energy is tracked with pressure. It was assumed that the PL energy tracks the band edge.

II. EXPERIMENTAL TECHNIQUES

The (Ga,In)P samples used in the present studies were grown by metal organic chemical vapor deposition[15] (MOCVD) and molecular-beam epitaxy[16] (MBE) techniques. The MBE sample, $Ga_{0.49}In_{0.51}P$, as used in our Hall measurements with pressure,[17] was grown at 490 °C. The MOCVD layer of composition $Ga_{0.52}In_{0.48}P$ was grown at 670 °C. This sample had characteristics indicating some ordering of atoms on the group-III sublattice, which is believed to be Ga and In $\{111\}$ planes.[4] Although the composition of these two samples differ slightly, the difference should be minimal in determining the pressure dependence of the direct band gap. Both samples were essentially lattice matched to the GaAs substrate (the lattice mismatch was $\sim 0.2\%$ for the MBE sample and $< 0.05\%$ for the MOCVD sample) as measured by double-crystal x-ray diffraction. In neither case was the lattice mismatch large enough to cause a significant number of dislocations. Both samples were n-type with free-carrier concentrations of 10^{18} and 10^{16} cm^{-3}, respectively.

The back surface of the sample was chemomechanically thinned to obtain total thickness of 30 μm. No degradation of the PL signal was observed from this thinning process. A small region was cleaved and placed in a gasketed[14] DAC together with a small ruby chip. A 4:1 methanol-ethanol alcohol mixture was employed as the pressure-transmitting medium to apply hydrostatic pressure. This procedure was repeated for both samples.

The PL was excited with the 514.5-nm line of a cw Ar-ion laser, and detected by a cooled GaAs photomultiplier tube via a $\frac{1}{4}$-m Jarrel-Ash spectrometer. Pressure was monitored by the ruby fluorescence scale.[18] In all the spectra, known Ne lines were used for calibration of the wavelength. PL measurements were obtained with increasing and decreasing pressures.

III. EXPERIMENTAL RESULTS

As an example of the PL spectra, Fig. 1 shows the shift in the PL peak with increasing pressure for the MBE sample. Similar spectra were obtained for the MOCVD sample. The Ne line, at 6143.1 Å, used in this set of spectra as the reference can be seen, and the remaining spikes are from noise.

It is known that E_0 of $Ga_xIn_{1-x}P$ increases[19] with the Ga composition x. Thus a sample with $x=0.52$ should have a larger E_0 than a sample with $x=0.49$. However, it is found that with no applied pressure, $E_0=1.862\pm0.010$ eV for the MBE sample and $E_0=1.821\pm0.008$ eV for the MOCVD sample assuming that there is approximately $0.5kT$ difference between the PL peak energy and the band gap as reported by Zarrabi *et al.*[20] This discrepancy is related to the fact that E_0 of $Ga_xIn_{1-x}P$ at a given composition varies by 50–80 meV as a function of growth conditions, such as the growth temperature. This variation is believed to be related to the ordering of the Ga and In on the group-III sublattice.[1,2,9,10]

The shift in the peak with pressure is shown in Fig. 2 for the two samples of (Ga,In)P. Each PL spectrum was fitted with a polynomial to determine the PL peak position. Data are shown for both increasing and decreasing pressure. The PL efficiencies fell steeply with pressure for both samples above ~2 GPa, and the experimental data are plotted in Fig. 3.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

A. The variation of PL peak energy with pressure

In Fig. 2 (pressure dependence of the PL peak energy) the solid lines represent least-squares second-order fits to the data with

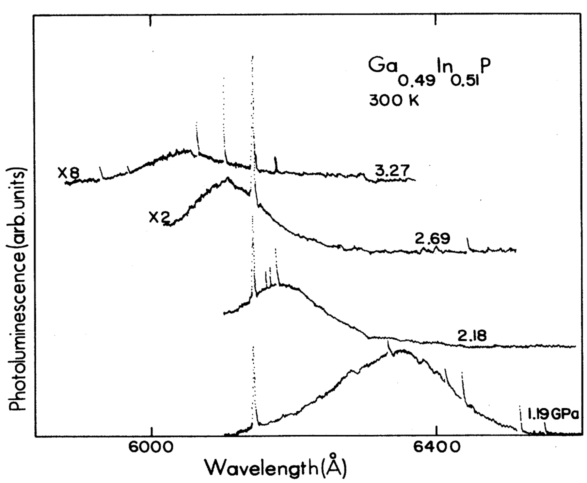

FIG. 1. Room-temperature photoluminescence spectra of disordered $Ga_{0.49}In_{0.51}P$ (grown by MBE) at four different pressures. A 6143.1-Å Ne line is a reference. Remaining noise spikes were removed during PL peak analysis. The decrease in efficiency at the higher pressure is due to the carrier transfer to the indirect X conduction band.

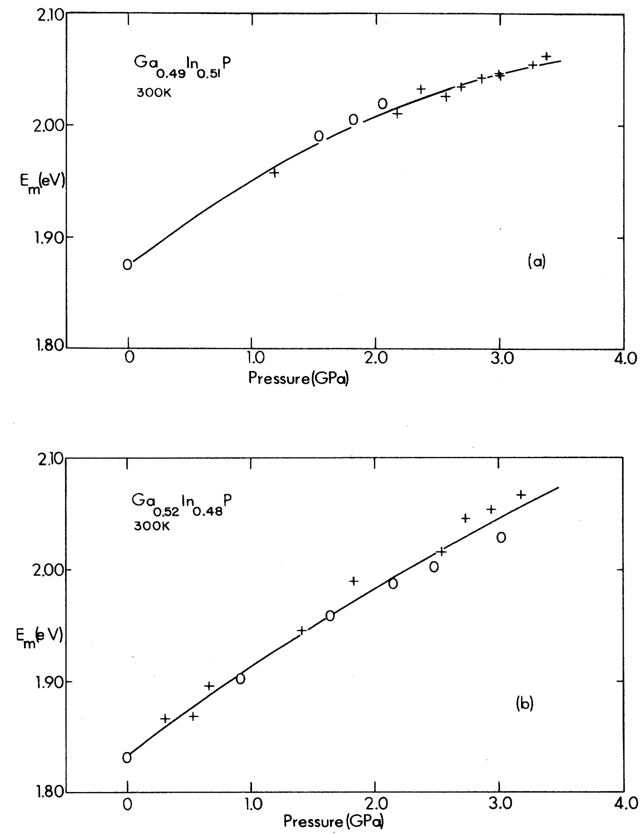

FIG. 2. (a) Photoluminescence peak energy [E_m (eV)] is plotted against pressure for the same sample as shown in Fig. 1. The open symbols are for decreasing pressure measurements. The solid line is a second-order least-squares fit to the data. (b) Shift in the photoluminescence peak energy with pressure for the ordered $Ga_{0.52}In_{0.48}P$ sample (grown by MOCVD). Measurements for descending pressure are shown by the open symbols. The solid line represents a second-order least-squares fit to the data.

$$E_m(P)=E_m(0)+\alpha P+\beta P^2 , \tag{1}$$

where $\alpha=86\pm6$ meV/GPa and $\beta=-10\pm2$ meV/GPa^2 for the MBE disordered sample and $\alpha=84\pm6$ meV/GPa and $\beta=-4\pm2$ meV/GPa^2 for the MOCVD ordered sample. The β coefficients or the curvature of the curves in Fig. 2 indicate that the pressure dependence (up to ~3 GPa) of the PL peak energy of the two samples are different. However, further measurements on samples of different composition are required to establish any trend in the compositional dependence of the pressure coefficient $\alpha=dE_0/dP$ and the curvature β. For comparison, Hakki *et al.*[21] report dE_0/dP to be 130 and 120 meV/GPa for samples of composition $Ga_{0.5}In_{0.5}P$ and $Ga_{0.54}In_{0.46}P$, respectively. Their values are possibly in error because of their indirect determination of dE_0/dP from current-voltage measurements on *p-n* diodes which have complications due to interface effects, current leakage, and nonuniformity of the diode and also pressure effect on the electrical contacts for the I-V measurements.

B. The variation of PL efficiency with pressure

From the analysis of Hakki[22] on the luminescence efficiency in alloy semiconductors with different compositions, the PL efficiency has been calculated here as a function of pressure for the (Ga,In)P ternary alloy. At the composition of interest here, it is easily shown from Pitt *et al.*[12] that Γ–L, Γ–X, and L–X transitions all occur within ~ 0.5 GPa pressure. Thus it is possible that a Γ–L transition precedes one involving X minima. However, the closeness of these transitions in pressure, the fact that X minima would be the lowest very quickly with pressure, and the higher density of states of the X minima at room temperature would all favor a transition involving the X band at high pressure in this material. In a two-band model with Γ and X conduction-band minima, the quantum efficiency can be written[22] as

$$\eta = L / I_0 \,, \tag{2}$$

where L is the rate of photon generation in the semiconductor and I_0 is the net rate of generation of carriers. From the transfer rate balance equations,[22] the efficiency in a direct-band-gap semiconductor with a two-band model is given in Eq. (3) in terms of intravalley and intervalley lifetimes τ_Γ, τ_X and $\tau_{\Gamma X}, \tau_{X\Gamma}$, respectively:

$$\eta = A\,[1 + (\tau_\Gamma/\tau_X)(\tau_{X\Gamma}/\tau_{\Gamma X})(1 + \tau_{X\Gamma}/\tau_X)^{-1}]^{-1} \,. \tag{3}$$

The factor A accounts for the internal efficiency of the Γ and the X band. The value of A is a small correction to the drop in the PL efficiency at the end of the carrier transfer to the X conduction-band minima, and is given by

$$A = \eta_\Gamma + \eta_X (\tau_\Gamma/\tau_X)(\tau_{X\Gamma}/\tau_{\Gamma X})(1 + \tau_{X\Gamma}/\tau_X)^{-1} \,, \tag{4}$$

where the efficiencies η_Γ and η_X are of the order of 10^{-4} and 10^{-6}, respectively.

In order to explain the PL efficiency behavior with pressure, the pressure dependences of these lifetimes are required. The intervalley lifetime ratio is given by[22]

$$\tau_{X\Gamma}/\tau_{\Gamma X} = (m_X^*/m_\Gamma^*)^{3/2} e^{-\Delta E/kT} \,, \tag{5}$$

where $\Delta E = (E_X - E_\Gamma) \sim 0.2$ eV, with k as Boltzmann's constant, T the temperature of 300 K, and $m_X^* \sim 0.38$ (Ref. 23) and $m_\Gamma^* \sim 0.096$ (Ref. 23) are the effective masses of the X and the Γ conduction-band minima, respectively, at zero pressure.

The intervalley lifetime $\tau_{X\Gamma}$ at the temperature of interest is given[22] by

$$\tau_{X\Gamma} \propto [\exp(\hbar\omega_i/kT) - 1]\, m_\Gamma^{*\,-3/2} \,, \tag{6}$$

where $\hbar\omega_i$ is the phonon energy. Complete expressions and definitions are given by Hakki *et al.*[22]

The pressure-dependent terms in Eq. (3) for the efficiency are the effective masses and the energy-band gaps. The variation of the band gap, ΔE, is obtained from the differences in the PL peak energy and a shift of

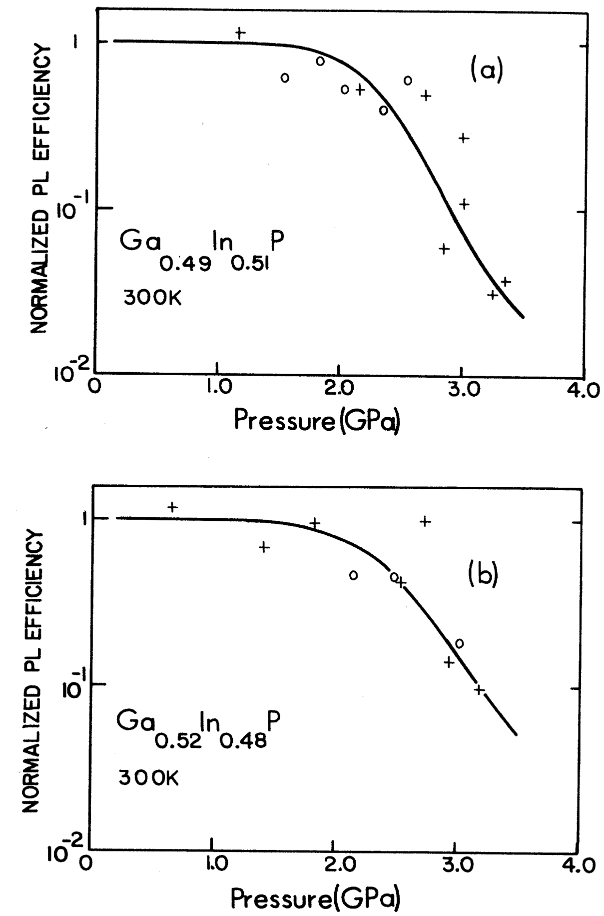

FIG. 3. Photoluminescence efficiency data of (a) $Ga_{0.49}In_{0.51}P$ (grown by MBE) are shown at high pressure. The drop in the efficiency between 2 and 3 GPa is due to the Γ–X inversion. The open symbols represent the data for decreasing pressure. A two-band model fit is shown by the solid line. Similarly, efficiency data for the $Ga_{0.52}In_{0.48}P$ sample (grown by MOCVD) are shown in (b).

-20 meV/GPa for the X minimum.[12] $\mathbf{k}\cdot\mathbf{p}$ theory was used to determine the increase in m_Γ^* with pressure from the increase in E_0. The pressure dependence of m_X^* was assumed to be zero. These values are consistent with a direct-indirect band crossover of 2.8 GPa pressure as given in our earlier paper.[17]

The solid line in Fig. 3(a) shows the efficiency of (Ga,In)P fitted to the experimentally measured PL intensities for the MBE sample using $\beta = -5$ meV/GPa^2 rather than a value of -10 meV/GPa^2 found experimentally [from Fig. 2(a)]. The reason for the unusually high β for the MBE sample is unknown. The result of the fit using the experimentally observed coefficients α and β is in good agreement for the MOCVD sample as shown in Fig. 3(b). The experimental points in Fig. 3 correspond to all but a few data points in Fig. 2; the missing intensity data points were not recorded. The scatter in the data is inherent in PL efficiency data even at low temperatures.[24]

The main decrease in the PL efficiency is due to the pressure dependence of the intervalley lifetimes, the energy-gap difference $(E_X - E_\Gamma)$, and the effective masses. The small amount of negative bowing in the curves at the higher end of the pressure range is the leading edge to PL quenching when all the carriers are in the indirect X minima. It was not possible to reasonably fit the PL efficiency data using the model proposed by Pitt *et al.*[12] which involved a $\Gamma - L$ and an $L - X$ transition.

V. SUMMARY

Room-temperature photoluminescence data of (Ga,In)P/GaAs have been obtained in a diamond-anvil high-pressure cell. Measurements were made on samples grown by two different techniques. The pressure dependence of the PL peak energy for both samples was sublinear. The PL efficiency was found to be quenched due to direct-indirect transition at high pressure. A two-band model was used to fit the PL efficiency data.

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