Pressure-induced Γ-X transition in (Ga,In)P

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(Received 13 June 1988)

Transport properties of (Ga,In)P are reported to 6 GPa pressure. Room-temperature Hall and resistivity measurements show a transition in mobility from Γ- to X-band conduction and a corresponding maximum in the Hall constant at 2.8 GPa. Room-temperature photoluminescence was measured to determine the increase in the Γ-band gap with pressure at a rate of 0.096 ± 0.005 eV/GPa. A two-band model was used to explain the transport measurements.

INTRODUCTION

Steady progress has been reported in the development of the alloy (Ga,In)P. The alloy has applications for optoelectronic devices operating in the visible spectrum, such as light-emitting diodes and room-temperature continuous-wave operation[1] (Ga,In)P multiple-quantum-well lasers. The $Ga_xIn_{1-x}P$ alloy with a composition of $x\sim0.5$ and direct band gap of 1.9 eV at room temperature is the most studied ternary in this family of alloys. This ternary alloy grown on GaAs had first appeared[2] to be an attractive alternative to the AlGaAs/GaAs system for the heterostructure bipolar transistor because of the larger valence-band-gap discontinuity. However, it now seems[3] that this discontinuity is less than previously believed. Nevertheless enhanced properties have been shown[4] for the (Ga,In)P grown on AlGaAs with high-Al composition. Recent interest has developed in the effect of spontaneous long-range ordering in (Ga,In)P alloys grown lattice matched on GaAs substrates.[5,6]

Advances in epitaxial growth techniques, for example molecular-beam epitaxy (MBE) and metal organic chemical-vapor deposition (MOCVD), have allowed (Ga,In)P to be grown even though there has been[7] speculation of a miscibility gap near the $x\sim0.5$ composition. Growth of (Ga,In)P across the whole x composition range shows[8,9] a direct- to indirect-energy band-gap transition between $x=0.6$ and 0.7.

Pressure is often used as a tool to examine the band structures of semiconductors. In most III–V semiconductors, increasing pressure primarily causes an increase in the Γ- and L-conduction bands while inducing a small lowering in the X band. These effects are large enough to be observed by optical and electrical measurements. In (Ga,In)P one expects that with pressure a Γ-X transition would precede a Γ-L transition from known[10] pressure variations of the Γ, L, and the X bands in the constitutive III–V binaries. However, it is speculated[11] that the Γ-L transition could precede the Γ-X transition at low temperature.

In the present work results of the first room-temperature Hall and photoluminescence (PL) measurements at high pressure in a diamond-anvil cell are reported for (Ga,In)P grown on GaAs by gas-source MBE. Analysis of the results in terms of a simple two-band model has been carried out.

EXPERIMENT

The (Ga,In)P sample consisted of a $Ga_{0.49}In_{0.51}P$ film of 7300 Å thickness grown on (100) GaAs by MBE using a P_2 molecular beam produced by thermal cracking of PH_3 gas. The growth rate was 0.5 μm/h at a substrate temperature of 490 °C and the film was doped with Si at a free carrier concentration of 8×10^{17} cm^{-3}. Double-crystal x-ray diffraction was used to determine the alloy composition.

For PL measurements the sample was thinned to 30 μm total thickness. A sample with typical dimensions of $150\times150\times30$ μm^3 was loaded into a diamond anvil (high quasihydrostatic pressure) cell (DAC) with a small ruby chip to measure *in situ* the ruby fluorescence and from it determine the pressure. Silicone oil was used as the pressure-transmitting medium.

PL was excited by the 514.5-nm Ar-ion laser line. Typical power reading at the DAC was less than 2 mW. A $\frac{1}{4}$ m Jarrell-Ash spectrometer and a cooled GaAs photomultiplier tube were used to detect the signal. For calibration, known Ne lines were recorded simultaneously and were superimposed on the PL spectra.

The experimental procedure for the electrical measurements in a DAC has been described in detail elsewhere.[12,13] Au-Sn contact pads were vacuum evaporated and alloyed at a temperature of 280 °C in an Ar atmosphere. Typical sample dimensions were $80\times80\times20$ μm^3. Electrical leads were attached to the Ohmic contact pads with 20-μm gold wires and conducting silver epoxy. Room-temperature Hall measurements were performed by placing the DAC in a low magnetic field (<0.5 T). At $P=0$ the electron Hall mobility (μ_e) and PL peak width were similar to those reported by Hsu *et al.*[14] after correction for sample geometry.

RESULTS AND DISCUSSION

Room-temperature PL spectra at three pressures are shown in Fig. 1. Ne lines have been superimposed for calibration. The spectra in Fig. 1 have not been normalized with excitation intensity nor have they been corrected for the detector response. A polynomial fit was used, without the Ne lines, to determine the PL peak energy E_m for each pressure. No significant change in the PL intensity was noticed for pressures up to 2.0 GPa, while an order of magnitude decrease in the intensity was observed for greater pressures near 3.0 GPa due to the Γ-X transition. A peak energy of 1.88±0.011 eV was obtained at zero pressure. The PL signal was quenched at 3.4 GPa pressure. No impurity band PL was observed at longer wavelengths. On depressurization the PL peak position returned to the original zero-pressure value. The shift in the PL peak energy with increasing pressure is shown in Fig. 2. A least-squares fit to the data shows a quadratic dependence

$$E_m = E_m^0 + \alpha P + \beta P^2 , \quad (1)$$

where $\alpha = 0.096 \pm 0.005$ eV/GPa and $\beta = -(7.76 \pm 0.04) \times 10^{-3}$ eV/GPa^2. The fit was obtained with emphasis on pressures below the Γ-X transition.

Doping of $\sim 10^{18}$ cm^{-3} was sufficiently high for possible[15] PL from the X band; however, no PL peak was detected at 3.1 GPa for the X minimum even though Γ-X crossover had been achieved. Higher bowing in E_m near the Γ-X transition (Fig. 2) is a possible indication of simultaneous transitions from the Γ and X band.

Pressure dependence of μ_e in the Γ band is shown in Fig. 3. The uncertainty in the Hall mobility is ±5%. These data have not been corrected for the sample geometry. An initial decrease of ~10% is due to the increase in the electron effective mass. The dependence of the mobility on the effective mass is expected to be $\mu \propto m_e^{*-3/2}$ since polar optical-phonon scattering is dominant at low pressure and at room temperature in the III–V semiconductors.[16] A small fraction (i.e., ~3%) of the mobility reduction is due to the presence[16] of alloy scattering because of the random distribution of the elemental constituents of the (Ga,In)P alloy. The mobility due to alloy scattering has an effective mass dependence of $m_e^{*-5/2}$.

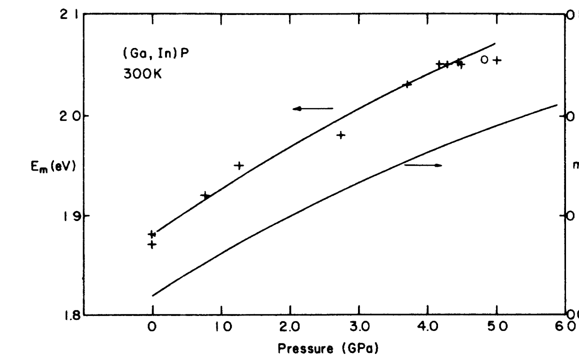

FIG. 2. The shift in the PL peak energy E_m in eV against pressure. + and ○ are data points with increasing and decreasing pressure, respectively. The solid line through the data is a second-order least-squares fit. Also shown is the pressure dependence of the electron effective mass in the Γ-conduction band as deduced from **k·p** theory.

The Γ- and the X-conduction bands move in the opposite directions under pressure resulting in an eventual Γ-X crossover. Γ-X crossover is clearly seen in Fig. 3 with a sharp drop off in μ_e. Parameters governing this transition are the difference in their energies ($E_X - E_\Gamma$), their relative pressure coefficients, $d(E_X - E_\Gamma)/dP$, and their effective mass dependence on pressure.

A two-band model[17] can be used to explain quantitatively the pressure dependence of μ_e up to the Γ-X transition shown in Fig. 3. The pressure dependence of μ_e can

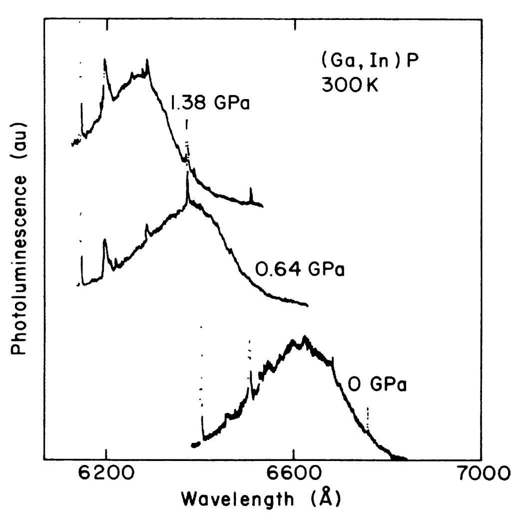

FIG. 1. Pressure-induced shift in the photoluminescence spectrum of (Ga,In)P at three different pressures. Sharp spikes in the spectra are neon-calibration lines.

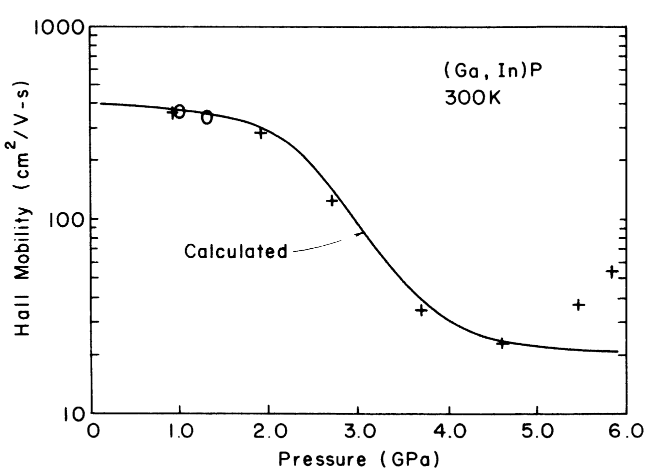

FIG. 3. Pressure dependence of the Hall mobility to ~6 GPa. The drop off in the mobility is due to transfer of carriers from a direct band to an indirect band with higher effective mass and smaller mobility.

be written as

$$\mu_e = \frac{\mu_\Gamma[(\mu_X/\mu_\Gamma)^2 + n_\Gamma/n_X]}{(\mu_X/\mu_\Gamma + n_\Gamma/n_X)} . \quad (2)$$

n_Γ/n_X can be estimated from the density of states functions N_Γ and N_X as

$$n_\Gamma/n_X = (N_\Gamma/N_X)\exp[(E_X - E_\Gamma)/kT] . \quad (3)$$

Assuming that the increase in the PL peak energy E_m tracks E_0, the pressure dependence of m_Γ^* can be deduced from a simple $\mathbf{k}\cdot\mathbf{p}$ relation

$$m_\Gamma^* = \{1 + M[2/E_m + 1/(E_m + \Delta)]\}^{-1} , \quad (4)$$

where M includes the momentum matrix term and Δ is the spin-orbit splitting. The value of Δ was interpolated between values for InP and GaP as given in Table I. This pressure dependence of m_Γ^* has been included in Fig. 2. The pressure variation of $E_X - E_\Gamma$ was determined from the PL results and the interpolated value of dE_X/dP is given in Table I. The remaining unknown parameter in Eq. (2) is the pressure dependence of μ_Γ/μ_X. At $P=0$, $\mu_\Gamma = 400$ cm^2/V s, and $\mu_X = 30$ cm^2/V s. These two values have not been corrected for the sample geometry. The rate of change of μ_Γ with pressure, due mainly to the increase in the effective mass, was estimated to be 30 cm^2/V s GPa from the measured decrease in μ_e up to 2.0 GPa. The pressure dependence of the mobility in the X band is assumed to be zero.

The solid line in Fig. 3 is a representation of the two-band model given in Eq. (2) for the Γ-X transition in (Ga,In)P. A good fit was obtained with $E_X - E_\Gamma = 0.21$ eV at $P=0$ pressure. Other parameters have been summarized in Table I. Well above the Γ-X crossover pressure at 5 GPa there appears to be an increase in the mobility. This may perhaps be due to impurity bands; however, no firm conclusion can be made until a separate experiment, such as deep-level transient spectroscopy has been made at these pressures.

TABLE I. Energy band gap E, effective mass m, and mobility values employed in evaluating a two-band model for (Ga,In)P.

Parameter	
E_m (eV)	1.9
Δ (eV)	0.11
$\Delta(E_X - E_\Gamma)$ (eV)	0.20
m_Γ^*	0.096
m_X^*	0.38
μ_0^Γ (cm^2/V s)	400
μ_0^X (cm^2/V s)	30
$E_m(P)$ ($P \le 2$ GPa) (eV/GPa)+(eV/GPa^2)	$0.096P - 7.76\times10^{-3}P^2$
$E_X(P)$ (eV/GPa)	$-0.01P$
$m_\Gamma^*(P)$ (/GPa)+(/GPa^2)	$0.004P - 3.6\times10^{-4}P^2$
$m_X^*(P)$ (/GPa)	0
$\mu_\Gamma(P)$ (cm^2/V s GPa)	-30
$\mu_X(P)$ (cm^2/V s GPa)	0

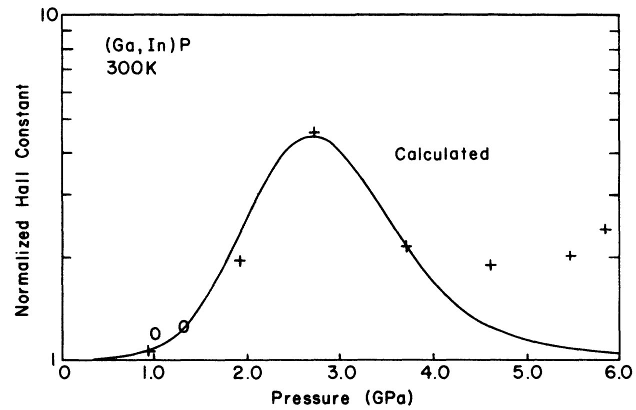

FIG. 4. Hall constant maximum in (Ga,In)P from a direct-indirect energy-band transition induced by high pressure. Trap-out of carriers is observed at pressures greater than 4 GPa.

The pressure dependence of the Hall constant R_H is shown in Fig. 4. In the two-band model R_H can be written[13] as

$$\frac{R_H(P)}{R_H(0)} = \frac{[1 + (n_X/n_\Gamma)(\mu_X/\mu_\Gamma)^2](1 + n_X/n_\Gamma)}{[1 + (n_X/n_\Gamma)(\mu_X/\mu_\Gamma)]^2} . \quad (5)$$

R_H shows a maximum at ~ 2.7 GPa where the conductivity of the two carrier types involved are equal, $n_\Gamma\mu_\Gamma = n_X\mu_X$. The maximum in the $R_H(P)/R_H(0)$ is estimated to be $\mu_\Gamma(0)/4\mu_X$ which is consistent with the maximum height in Fig. 4. The full width at half maximum corresponds to a change of $\Delta E/kT$ equal to 4. From the PL analysis, $d(E_X - E_\Gamma)/dP \sim -0.107$ eV/GPa. Therefore the width at half maximum, in pressure, should be ~ 1 GPa. Experimentally, from Fig. 4 the width at half maximum is ~ 1.5 GPa. This discrepancy may be due to impurity trap-out of carriers resulting in broadening of the peak.

From the mobility model N_X/N_Γ can be estimated to be 25 which is in contrast to 100 for GaAs.[17] The difference in energy $E_X - E_\Gamma$ at the peak in R_H is then found to be 0.2 kT. The peak in the Hall constant in Fig. 4 is found to be at 2.7 GPa. Therefore, the Γ-X transition, $\Delta E = 0$, occurs at ~ 2.8 GPa. Trap-out of carriers has been observed here in (Ga,In)P similar to that found[17] in GaAs for pressures above the Γ-X transition since R_H remains higher than that at $P=0$ pressure.

CONCLUSION

Hall effect and photoluminescence measurements have been carried out on (Ga,In)P to pressures above the Γ-X band crossover in a diamond-anvil cell. The shift in the PL peak energy with pressure was used to estimate the band-gap pressure coefficient. A reasonable correlation between the Hall measurements and PL measurements has been obtained. The **k**·**p** theory was used to determine the pressure dependence of the effective mass in the Γ band. A two-band model was used to explain quantitatively the Γ-X transition observed in the Hall mobility and the Hall constant.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the National Science Foundation (ERC Grant No. CDR-8622236), the Colorado Advanced Technology Institute, and the Naval Research Laboratory (Contract No. N00014-87-K-2044).

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