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Preparation and characterization of $In_{1-x}Ga_xAs_yP_{1-y}$ epilayers by liquid-phase epitaxy

YAN-KUIN SU, JIAN-HONG WANG*, M. P. HUNG*
*Institute of Electrical and Computer Engineering and *Institute of Mineral, Metallurgy and Materials Science, National Cheng Kung University, Tainan, Taiwan*

$In_{1-x}Ga_xAs_yP_{1-y}$ epilayers with three different solid compositions of $In_{0.73}Ga_{0.27}As_{0.60}P_{0.40}$, $In_{0.59}Ga_{0.41}As_{0.87}P_{0.13}$ and $In_{0.53}Ga_{0.47}As$ were grown on (1 0 0) InP substrate at 623° C by the step cooling technique of liquid-phase epitaxy. From the optical transmission measurements, the corresponding wavelengths of the InGaAsP epilayers were 1.30, 1.55 and 1.69 μm, respectively, which are in good agreement with those obtained from the calculations using Vegard's law. The full widths at half maximum of the photoluminescent spectra at 14 K of these layers were as low as 18.6, 22.5 and 7.9 meV, respectively. The electron mobility of the InGaAsP epilayers is a function of the solid composition with the $In_{0.53}Ga_{0.47}As$ epilayer having the highest electron mobility. The mobility and concentration of this layer are 8,873 $cm^2 V^{-1} sec^{-1}$, $9.7 \times 10^{15} cm^{-3}$ and 22,900 $cm^2 V^{-1} sec^{-1}$, $8.5 \times 10^{15} cm^{-3}$ at 300 and 77 K, respectively. The compensation ratio is between 2 and 5.

1. Introduction

The low loss and minimum dispersion characteristics exhibited by optical fibres currently under study has stimulated interest in the 1.0 to 1.55 μm wavelength range for use in long-distance fibre-optic communication systems [1, 2]. When InP is used as a substrate, lattice-matched InGaAsP can be prepared the bandgaps of which span the energy range between 0.75 and 1.35 eV ($\lambda = 0.92$ to 1.65 μm). In addition to the application of the InGaAsP/InP heterojunction devices to fibre-optic technology, band structure and transport studies indicate that these alloys could be used to improve the performance of high-frequency microwave discrete devices and integrated devices [3].

Many papers have described the characterization and devices for InGaAsP epilayer growth by liquid-phase epitaxy (LPE), vapour-phase epitaxy (VPE), metal–organic chemical vapour deposition (MOCVD) and also chemical beam epitaxy (CBE). In this paper, the liquid-phase epitaxial system was used to grow three different solid compositions of $In_{1-x}Ga_xAs_yP_{1-y}$ epilayers on InP substrate. The experimental procedure and characterization of epilayers, including X-ray diffraction, EPMA analysis, FTIR measurement, PL and Hall measurements are presented and the results obtained compared with those of other workers.

2. Experimental procedure

Epitaxial layers of three different compositions of $In_{1-x}Ga_xAs_yP_{1-y}$ were grown on InP substrate by the step-cooling technique of LPE with a multiwell sliding boat and a low thermal mass, gold-plated semi-transparent furnace [4–8]. The furnace temperature was controlled by a programmable controller monitoring the temperature near the bottom of the graphite boat. The substrates were tin-doped n-type or iron-doped semi-insulating (1 0 0) InP with an etch-pit density (EPD) of about $10^4 cm^{-2}$. Before growth, the indium melt was first baked at 800° C in hydrogen gas flowing at a rate of 500 $cm^3 min^{-1}$ for 10 h. This process is very important for obtaining low carrier concentration and high photoluminescent intensity in $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial layers. After indium baking, the melt was again baked by adding the appropriate polycrystalline GaAs, InAs and InP to the indium to form a solution. The liquidus temperatures were determined by visual observation through the gold-coated transparent furnace. The samples were heated at 670° C for 1 h to dissolve the charges and to homogenize the melt completely. In order to suppress the evaporation of phosphorus, the melt was covered with a graphite lid. The surface of the InP substrate was covered with another InP wafer during the saturation process to minimize contamination of the substrate surface by the evaporated phosphorus. The step-cooling technique was used in this system. The growth temperature was 623° C. After a growth period of 3 to 5 min, the melt was wiped off the substrate and the boat was cooled rapidly to avoid damage of the growth layer.

The (6 0 0) symmetric planes of X-ray diffraction measurements were used to determine the degree of lattice mismatch, $\Delta a_\perp / a_0$, where $\Delta a_\perp = a_{epi} - a_0$, and a_{epi}, a_0 are lattice constants of the epilayer and substrate, respectively. Cleaved planes and surfaces of InGaAsP wafers were examined with a scanning electron microscope to determine the growth thickness and to evaluate the surface morphology. The compositions of the epilayers were determined from the emitted X-ray intensities of the In$K\alpha_1$ Ga$K\alpha_1$, As$K\alpha_1$

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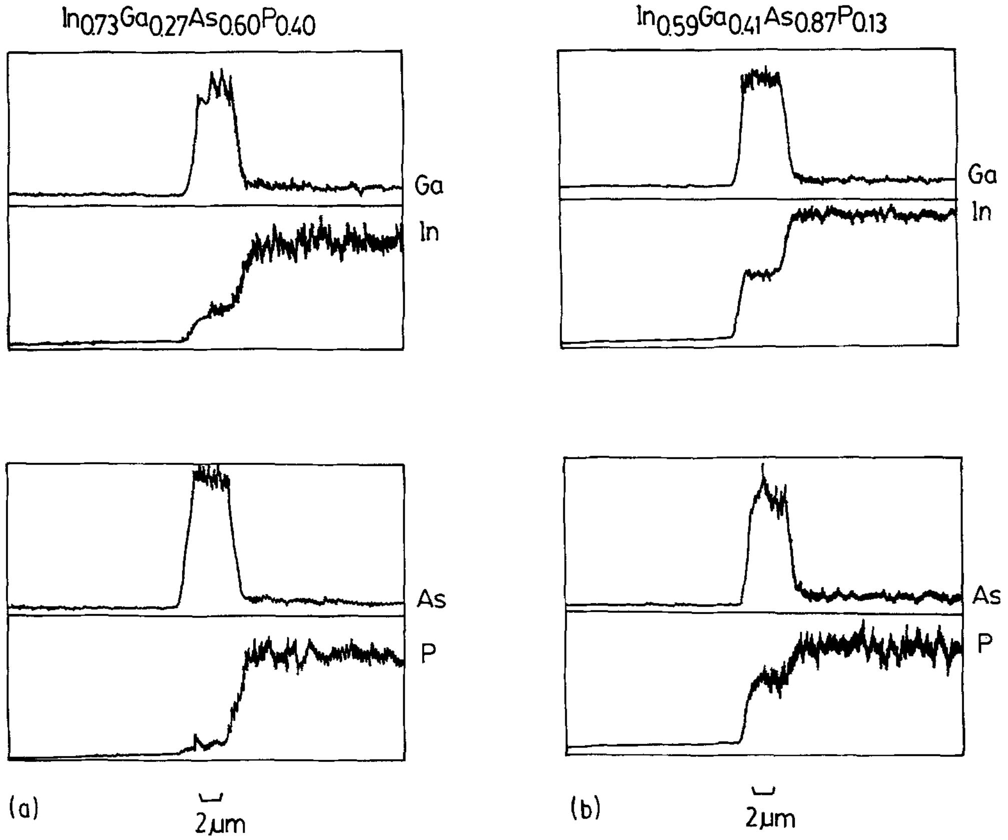

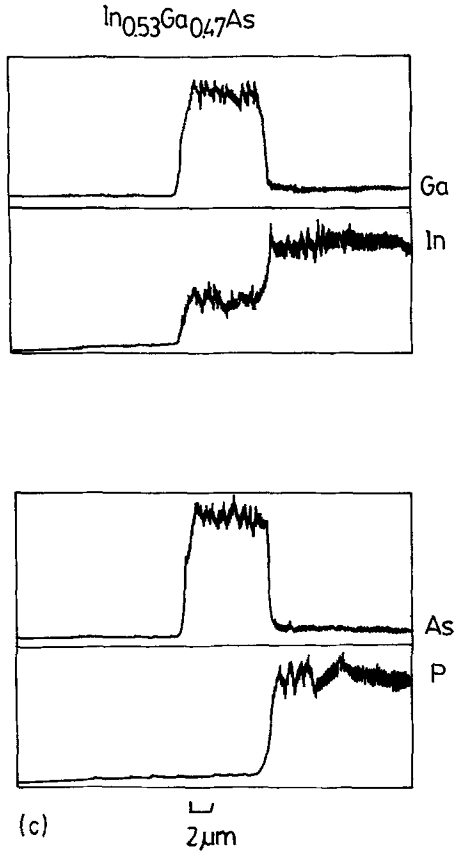

Figure 1 The distribution of the elements gallium, indium, arsenic and phosphorus of $In_{1-x}Ga_xAs_yP_{1-y}$ by EPMA. (a) $In_{0.73}Ga_{0.27}$-$As_{0.6}P_{0.4}$ (λ = 1.30 µm), (b) $In_{0.59}Ga_{0.41}As_{0.87}P_{0.13}$ (λ = 1.56 µm), (c) $In_{0.53}Ga_{0.47}As$ (λ = 1.69 µm).

and P$K\alpha_1$ lines of the sample excited with a 25 keV electron beam. The measured intensities were then converted to compositions by comparing with the intensities of the standard InP and GaAs samples.

A Fourier transform infrared (FTIR) spectrometer was also used to measure the transmission spectrum of the epilayer and then to obtain the bandgap of the epilayer. The 50% maximum transmission photon energy was used as the bandgap of the material [9]. Photoluminescence was measured at 14 K in order to determine the bandgap and to check the quality of epitaxial layers. The excitation source was supplied with a 40-mW argon laser (488 nm) through an interface filter. The conduction type, carrier concentration and Hall mobility were measured using van der Pauw measurements.

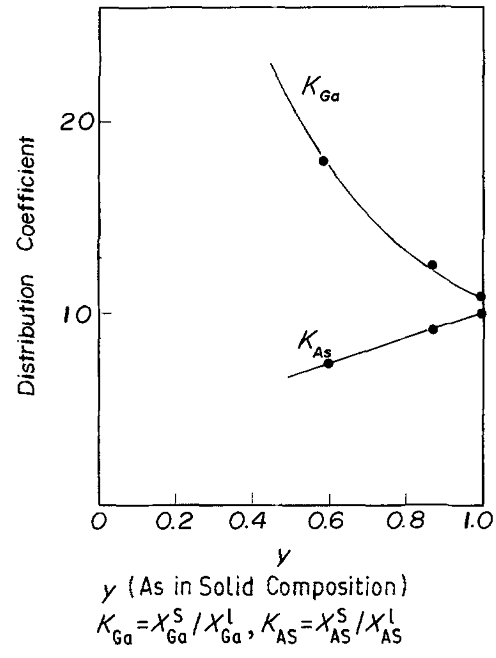

Figure 2 The distribution coefficient of Ga (K_{Ga}) and As (K_{As}) plotted against y (arsenic in solid composition).

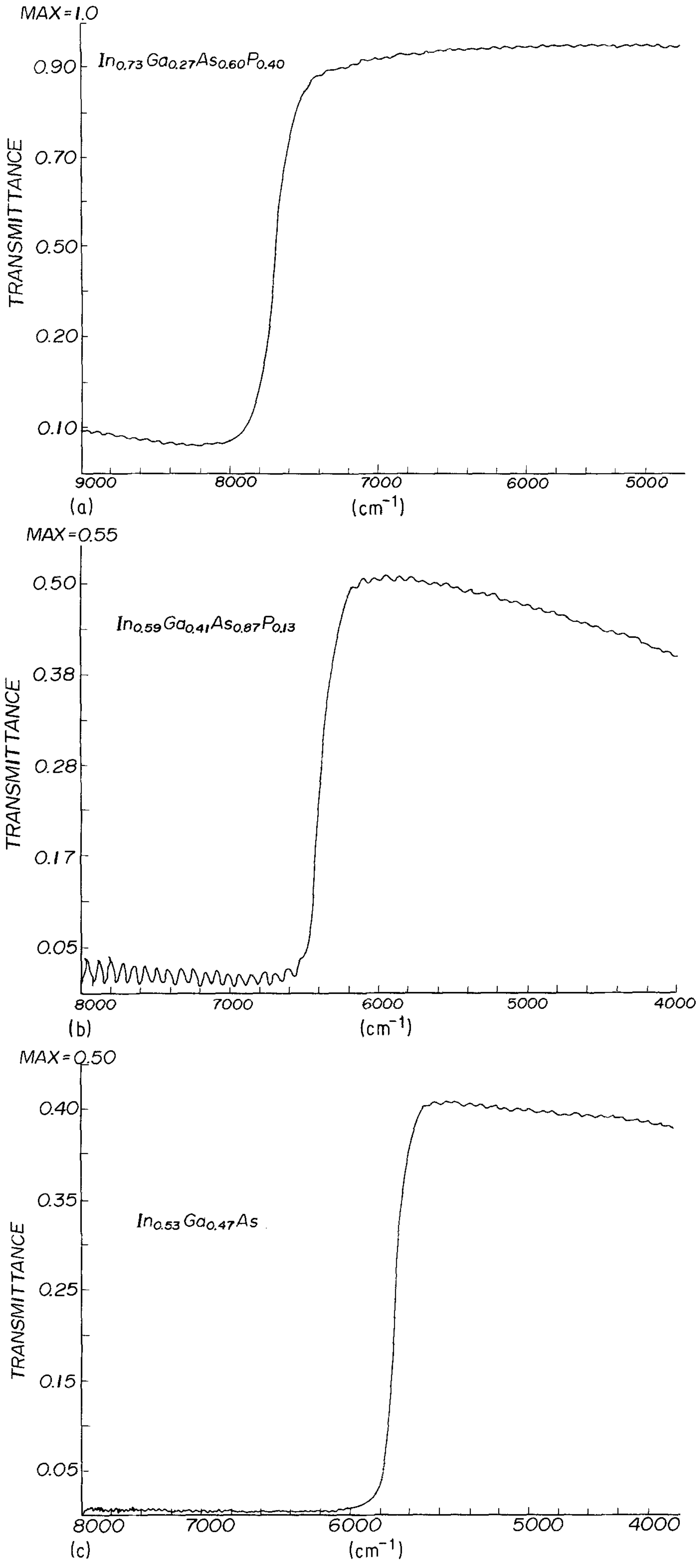

Figure 3 The transmission spectra for (a) $x = 0.27$, $y = 0.60$, (b) $x = 0.41$, $y = 0.87$ and (c) $x = 0.47$, $y = 1.0$.

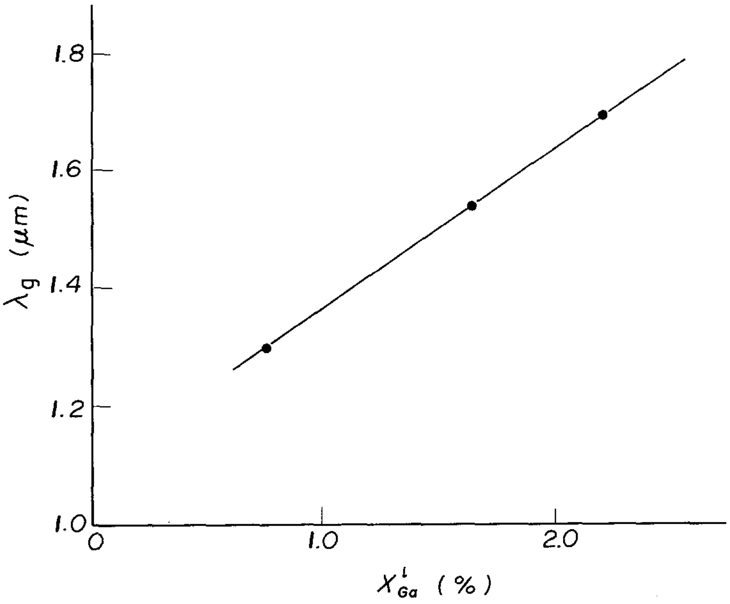

Figure 4 The effect of X^{l}_{Ga} (gallium content in liquid solution) on the wavelength of the $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}_y\mathrm{P}_{1-y}$ system.

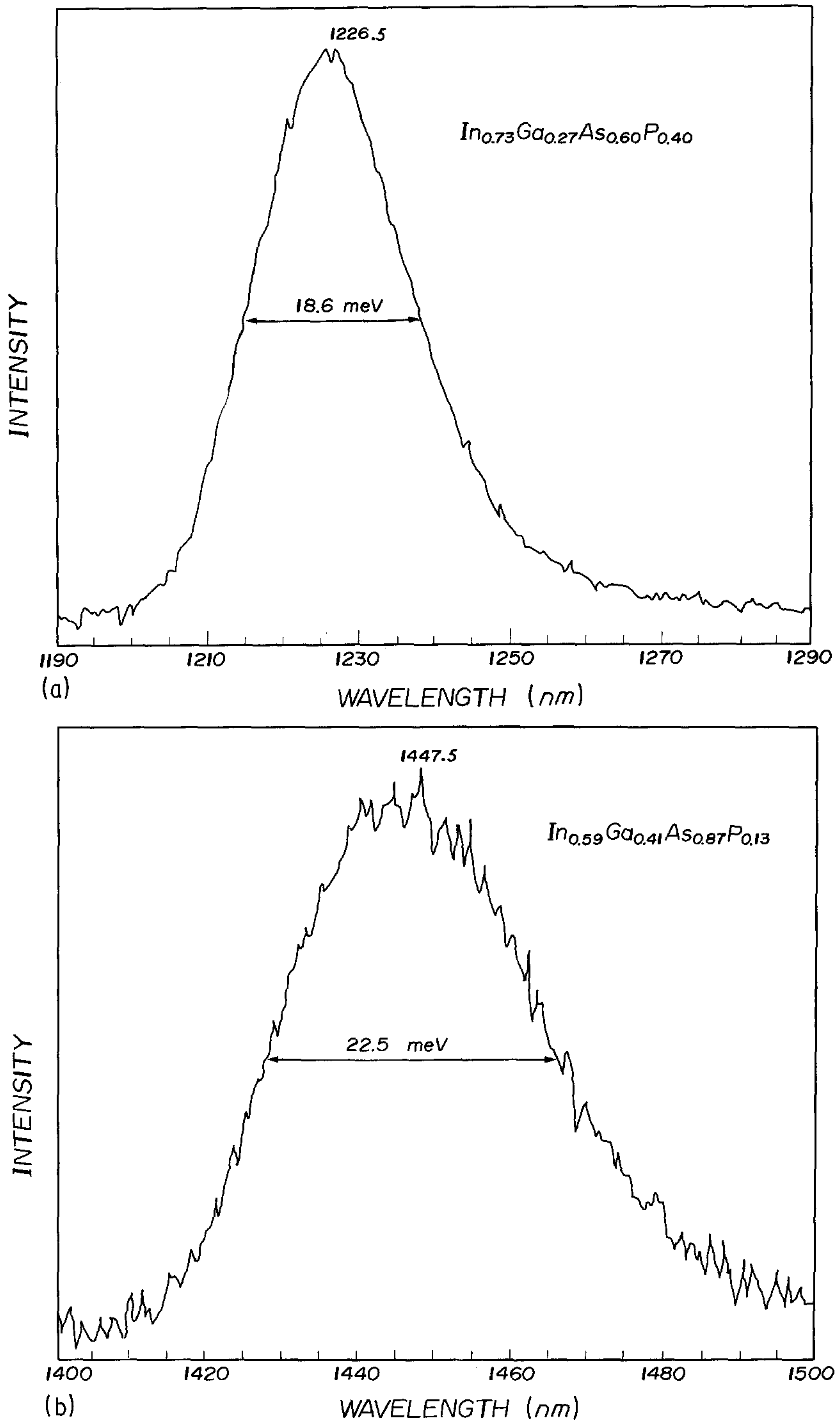

Figure 5 Photoluminescent spectra at 14 K of (a) $x = 0.27$, $y = 0.60$, (b) $x = 0.41$, $y = 0.87$ and (c) $x = 0.47$, $y = 1.0$.

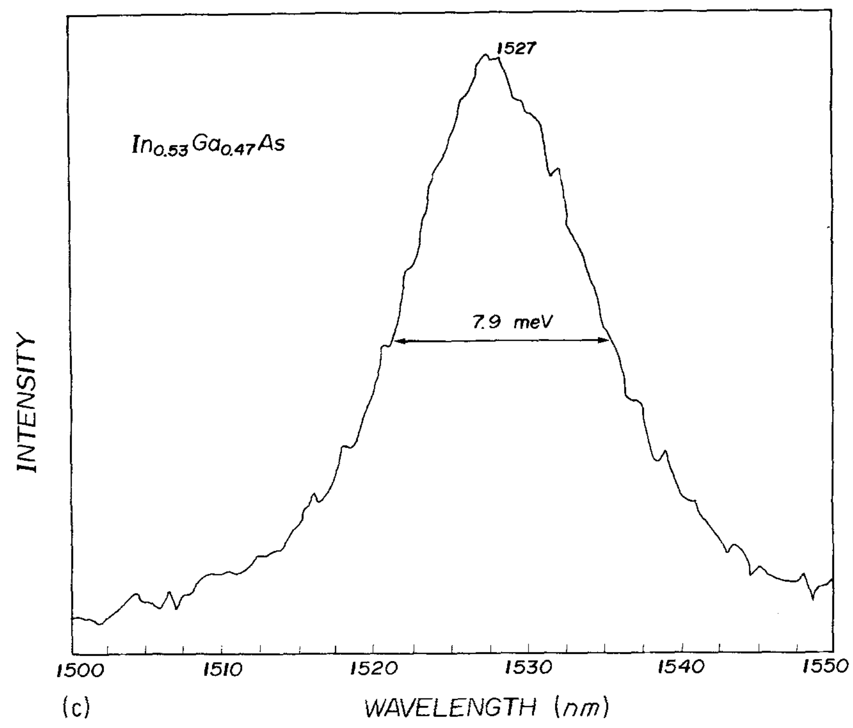

Figure 5 Continued.

3. Results and discussion

Table I gives the lattice mismatch obtained by X-ray diffraction for three different solid compositions of $In_{1-x}Ga_xAs_yP_{1-y}$, where the composition is determined by EPMA. The lattice mismatch for three different materials is smaller than 0.03% in the limit of resolution [10]. Figs 1a to (c) show the distribution of the elements indium, gallium, arsenic and phosphorus in $In_{0.73}Ga_{0.27}As_{0.60}P_{0.40}$, $In_{0.59}Ga_{0.41}As_{0.87}P_{0.13}$ and $In_{0.53}Ga_{0.47}As$ by EPMA. The distribution coefficients of Ga (K_{Ga}) and As (K_{As}) plotted against arsenic in the solid composition is shown in Fig. 2. The energy gap of the epitaxial layer can be estimated from optical transmission measurements. The transmission spectra for three samples are shown in Figs 3a to c. The 50% maximum transmission photon energy was used as the bandgap of the materials [9]. They were 0.955, 0.795 and 0.735 eV, respectively. As seen from Fig. 4, the corresponding wavelengths of three different compositions are in linear relationship with the gallium content in the solution X^l_{Ga}. This linear result is similar to that obtained by Kazarinov *et al.* [9]. If Vegard's law is applied to the material system $In_{1-x}Ga_xAs_yP_{1-y}$, the energy gap will be [11]

$$\begin{aligned} E_g &= 0.35 + 1.07x + y + 0.33xy \\ &\quad - (0.460 + 0.298y)x(1 - x) \\ &\quad - (0.101 + 0.109x)y(1 - y) \end{aligned}$$

From the above formula, the energy gaps were found to be 0.945, 0.797 and 0.738 eV for $In_{0.73}Ga_{0.27}As_{0.60}P_{0.40}$, $In_{0.59}Ga_{0.41}As_{0.60}P_{0.40}$ and $In_{0.53}Ga_{0.47}As$, respectively. The corresponding wavelengths were 1.33, 1.55 and 1.68 μm, respectively, which are in good agreement with the experimental results from FTIR measurements.

TABLE I Bandgap and lattice mismatch for three different compositions

Solid composition				Band gap (300 K)	Wavelength (300 K)	Lattice mismatch,
In_{1-x}	Ga_x	As_y	P_{1-y}	E_g (eV)	λ_g (μm)	$\Delta a_\perp/a_0$ (%)
0.73	0.27	0.60	0.40	0.95	1.30	< ±0.03
0.59	0.41	0.87	0.13	0.79	1.56	< ±0.03
0.53	0.47	1.00	0.00	0.73	1.69	< ±0.03

Optical properties of the lattice-matched InGaAsP system were studied by photoluminescence (PL). Typical PL spectra at 14 K of three different materials are shown in Figs 5a, to c. The peak wavelengths are 1.23, 1.45 and 1.53 μm, and the full widths at half maximum (FWHM) are 18.6, 22.5 and 7.9 meV, respectively. These values are better than those obtained by Temkin *et al.* [12] at 6 K PL spectra.

Measurements using the Hall method were carried out at 300 and 77 K using the van der Pauw technique. The mobility was found to be slightly decreased from $y = 0$ to $y = 0.3$ to 0.4, and then reached a maximum

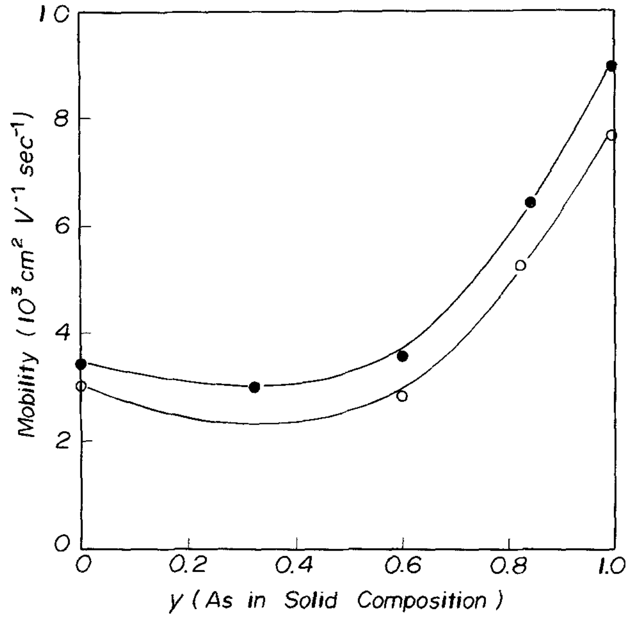

Figure 6 Mobility plotted against y (arsenic in solid composition at room temperature). (●) Pearsall [13], $N_D + N_A = 10^{17}\,cm^{-3}$; (○) present work, $N_D - N_A = (7\ to\ 8) \times 10^{16}\,cm^{-3}$.

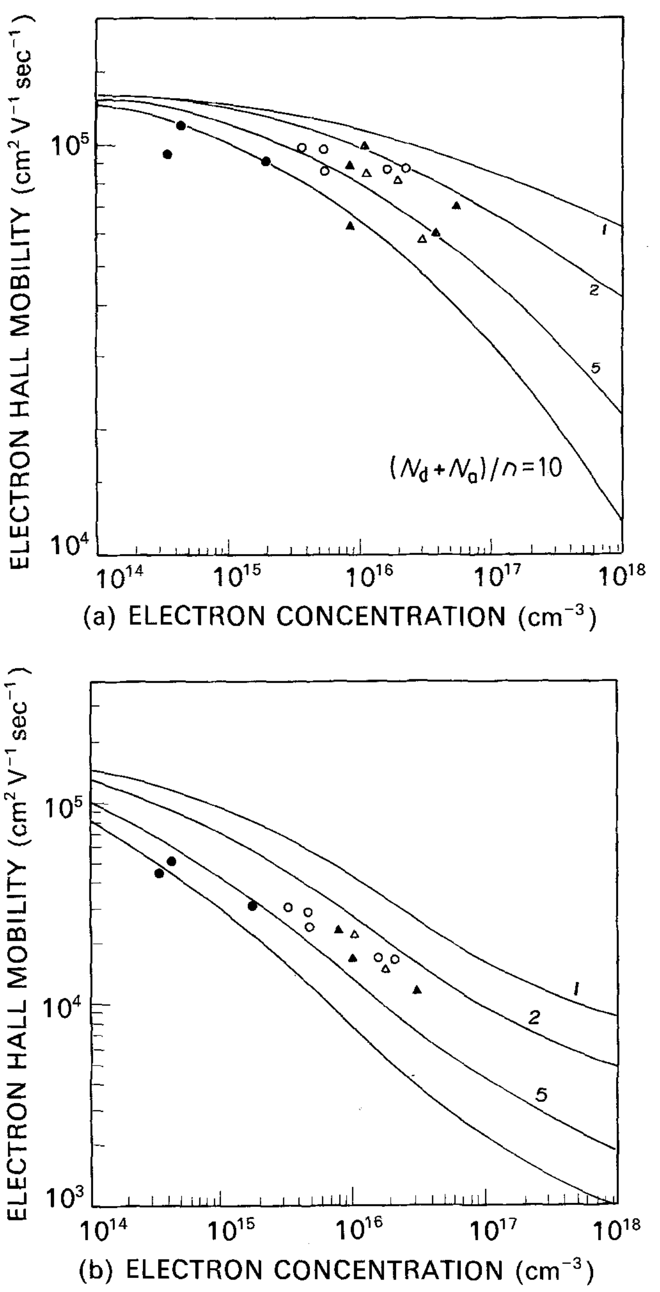

Figure 7 The relationship between mobility and concentration of $In_{0.53}Ga_{0.47}As$ ($x = 0.47, y = 1.0$) at (a) 300 K, (b) 77 K. (○) Leheny and Pollack [14], (●) Amono *et al.* [15], (△) Takeda *et al.* [16], (▲) present work.

at $y = 1.0$ (i.e. $In_{0.53}Ga_{0.47}As$) as shown in Fig. 6 at the same concentration. Pearsall [13] obtained a similar trend for this material, as also shown in this figure. The relationships between mobility and concentration at room temperature and 77 K are shown in Figs 7a and b, respectively. The results obtained by Lehney and Pollack [14], Amono *et al.* [15] and Takeda *et al.* [16] are also shown in these figures for comparison. The figures also show the curve of the theoretical calculations obtained by Takeda [17]. The compensation ratio, i.e. $(N_D + N_A)/n$, in our sample is in the range 2 to 5.

4. Conclusions

Three different compositions of the lattice-matched $In_{1-x}Ga_xAs_yP_{1-y}$ epilayers were grown on (1 0 0) tin-doped and iron-doped InP substrates by the step-cooling technique of LPE. The growth temperature was 623° C. The lattice mismatches for the three different materials were all smaller than $\pm 0.03\%$ in the resolution limit.

From the Fourier transform infrared (FTIR) measurements, the energy gaps for $In_{0.73}Ga_{0.27}As_{0.60}P_{0.40}$, $In_{0.59}Ga_{0.41}As_{0.87}P_{0.13}$ and $In_{0.53}Ga_{0.47}As$ were found to be 0.955, 0.795 and 0.734 eV, respectively. The corresponding wavelengths were 1.30, 1.56 and 1.69 μm, respectively. These results are in good agreement with those calculated using Vegard's law. The full widths at half maximum for the three materials at 14 K were 18.6, 22.5 and 7.9 meV, respectively.

The concentrations can be effectively reduced by long-term baking of indium and charge solution. In our experiments, the optimum electron concentration and mobility were 9.7×10^{15} cm^{-3}, 8,873 cm^2 V^{-1} sec^{-1} at 300 K and 8.5×10^{15} cm^{-3}, 22,900 cm^2 V^{-1} sec^{-1} at 77 K. The mobility decreased slightly from $y = 0$ to $y = 0.3$ to 0.4, then increased sharply and reached a maximum value at $y = 1.0$ (i.e. $In_{0.53}Ga_{0.47}As$). The compensation ratio in our samples was between 2 and 5.

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