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CHARACTERIZATION OF EPITAXIAL $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ LAYERS ON InP GROWN BY LIQUID PHASE EPITAXY

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The step cooling technique for liquid phase epitaxy was used to grow $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ thin films on InP substrates. The optimum growth temperature is 635 °C with a supercooling temperature (ΔT) of 10 °C. Under these conditions, the lattice mismatches between epilayers and substrates were less than 0.03% as determined by X-ray diffraction measurements. The solid composition was studied. From optical transmission measurement, the corresponding wavelength of the quaternary layer was 1.28 μm. The quality of the $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ epitaxial layers was studied by using the diffraction patterns from transmission electron microscopy. The measured room temperature mobility and carrier concentration of undoped InGaAsP epilayers were 3200 $cm^2/V \cdot s$ and 1.76×10^{16} cm^{-3}, respectively.

1. Introduction

The $In_{1-x}Ga_xAs_yP_{1-y}$ quaternary system lattice-matched to an InP substrate is very important in optical fiber communication applications [1–4]. The bandgap energies correspond to the wavelength range where attenuation and dispersion are minimum in glass fibers [5,6]. Liquid phase epitaxy (LPE) with supercooling is a common method to fabricate InGaAsP emitters and detectors [7–10]. However, the composition of elements along the growth direction is not constant [11]. On the other hand, a step cooling LPE method always gives a constant composition even in thick layers [11,12].

In this paper, the step cooling technique of transient LPE growth method was used to grow InGaAsP thin films on InP substrates. The physical properties of the growth layers were evaluated by X-ray diffraction, electron-probe microanalysis (EPMA), scanning electron microscopy (SEM), and optical transmission measurements. To assure the high crystal quality of the epitaxial layers, we also present the data of diffraction patterns using transmission electron microscopy (TEM). To our knowledge, this is the first publication about the TEM diffraction data for these epilayers. The electrical properties were studied by Van der Pauw measurements.

2. Experimental procedures

A horizontal sliding LPE system was used in this experiment. The melts used to grow InGaAsP quaternary layers were composed of 69's high purity In shots and undoped polycrystalline GaAs, InAs, and InP. The required amounts of these solutes were weighed to an accuracy of ± 0.1 mg.

The (100)-oriented InP substrates were 0.8×0.8 cm^2 in size and had an etch pit density of 10^4–$10^5/cm^2$. They were prepared for growth by degreasing with toluene, acetone, methanol and followed by a chemical polish with a 1% bromine–methanol solution. Good surface quality has been obtained with a 5 min Caros etch (5 : 1 : 1, $H_2SO_4 : H_2O_2 : H_2O$), rinse in deionized water and then blow-dry with N_2.

The In, InAs, and GaAs source materials were first loaded into the graphite boat and positioned

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in the growth system. The system was evacuated to 10^{-3} Torr using a rotary pump, and then backfilled with Pd-purified H_2. This process was repeated several times, and a flow of H_2 was established at the rate of approximately 0.5 liter/min. The melt was first baked at 750 °C in flowing H_2 for at least 6 h. Otherwise, a very high donor concentration would result in the epitaxial layers due to Si contamination [13]. After cooling, the polycrystalline InP was loaded into the ternary melt to form an $In_{0.95}Ga_{0.0075}As_{0.04}P_{0.0025}$ solution with a liquidus temperature of 645 °C. This liquidus temperature, T_L, was determined by direct visual inspection of the solution [14]. In order to remove the surface damage of the InP substrate during the pregrowth heating cycle, an undersaturated In–InP "etch" melt was also prepared [15].

After a cleaned InP substrate was loaded into the graphite boat, the system was evacuated and the H_2 flow was re-established. Then, the furnace temperature was raised to 670 °C in 15 min and held constant for 1 h or more to completely dissolve the solutes in the growth solution. During the preheating period, the InP substrate was covered under the sliding plate of the graphite boat. Next, the temperature was lowered at a rate of 0.8 °C/min to 639 °C, at which temperature the cooling rate was changed to 0.3 °C/min. Before growth, the substrate was contacted with the undersaturated In–InP "etch" melt for 3–5 s to remove the thermal damage on the InP substrate. An InP buffer layer was first grown with 5 °C supercooling. Then the InGaAsP epitaxial layer was grown by step cooling with a desired growth period. After the growth, the furnace was slid away and the furnace was rapidly cooled by using a fan.

3. Measurements, results, and discussions

3.1. X-ray diffraction pattern

The (600) symmetric planes of single-crystal X-ray diffraction measurements were used to determine the degree of lattice mismatch, $\Delta a/a_{InP}$, between the InGaAsP epitaxial layer and the InP substrate, where $\Delta a = a_q - a_{InP}$ and a_q and a_{InP} are lattice constants of the quaternary compound and InP, respectively. Fig. 1 illustrates the lattice matching conditions of three quaternary samples grown at different temperatures. Curve (b) indicates good lattice match when the growth temperature $T_G = 635$ °C, while curve (a) shows negative mismatch -0.05% (which means $a_q < a_{InP}$) for $T_G = 636$ °C and curve (c) indicates positive mismatch $+0.19\%$ (which means $a_q > a_{InP}$) for $T_G = 632$ °C. In curve (c), the difference of diffraction angles, $\Delta 2\theta$, between Q-Kα_1 and InP-Kα_1 is 0.27°. According to these results, we found that the best growth condition is $\Delta T = 10$ °C for the step cooling technique.

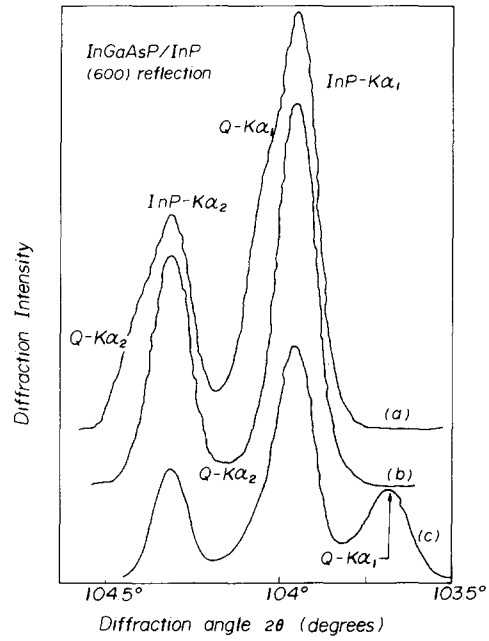

Fig. 1. (600) rocking curves for three InGaAsP quaternary epitaxial layers grown at different temperatures. The growth temperatures and corresponding lattice mismatches are: (a) 636 °C, −0.05%; (b) 635 °C, ≲ 0.03%; (c) 632 °C, +0.19%.

3.2. Electron-probe microanalysis (EPMA)

An electron-probe microanalyzer attached to a scanning electron microscope (SEM), employing wavelength dispersive X-ray detection, was used to measure layer compositions. They were determined from the emitted X-ray intensities of the

In-Kα_1, Ga-Kα_1, As-Kα_1, and P-Kα_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.

The measured composition of the $In_{1-x}Ga_xAs_yP_{1-y}$ quaternary layer can be represented as $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$. The energy bandgap [16] can be expressed as

$$E_g = 2.75 - 1.33y - 1.4(1-x) + 0.33(1-x)y - (0.758 - 0.28y)x(1-x) - [0.21 - 0.109(1-x)]y(1-y)\ \text{eV}. \quad (1)$$

This gives the energy gap of the grown layer to be 0.96 eV, which corresponds to a wavelength of 1.3 μm. The cleaved facet was stained with KOH–$K_3Fe(CN)_6$ solution and the uniform thickness of the epitaxial layers was obtained by means of SEM.

3.3. Optical transmission measurement

The energy gap for the epitaxial layer is estimated from optical transmission measurements. The band gap of the quaternary layer is determined from the wavelength corresponding to the 50% point between the zero and maximum optical transmission. As shown in fig. 2, the band gap of the InGaAsP epitaxial layer corresponds to a wavelength of 1.28 μm, which agrees closely with the data derived from the EPMA measurements. The spectrum at long wavelength (~ 1.37 μm) may be due to water absorption.

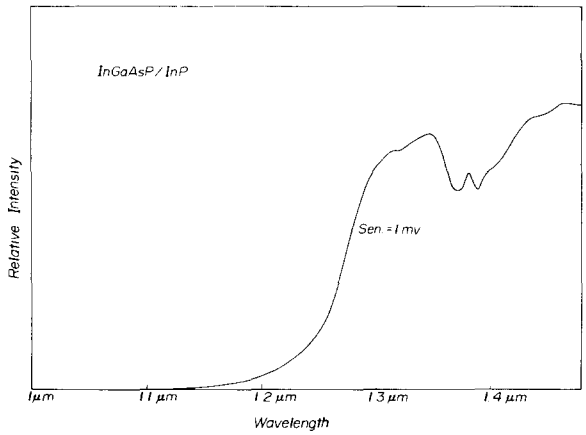

Fig. 2. Optical transmission spectrum of $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ epitaxial layer grown on InP substrate.

3.4. Electron diffraction measurements

The specimen for diffraction studies was prepared by etching in 1 HF/10 HBr [17], which attacks the InP substrate and not the InGaAsP layer. The diffraction measurements were performed in a JEOL-100U TEM operated at 80 keV. The quaternary layer has the zinc-blende structure and its electron diffraction patterns are shown in figs. 3–5. In fig. 3a, the regular spots show that the epitaxial layer is a very good single crystal. fig. 3b displays the identified reciprocal lattice spots of fig. 3a. Each point represents one plane and its index is calculated and shown in this figure. The corresponding beam direction is [001]. Fig. 4a shows the diffraction pattern from the [$\bar{1}$23] zone axis for the quaternary single crystal. Kikuchi contrast patterns are shown as streaks along specific spots. Fig. 4b is the corresponding indexed diffraction pattern of fig. 4a.

In fig. 5a, the diffraction pattern in the [001] orientation was enhanced by a strong Kikuchi pattern, which consists of pairs of parallel bright and dark lines. In order to show such contrast patterns, the sample has to have a low defect density ($\lesssim 10^5$ cm^{-2}) and a suitable thickness ($\lesssim 0.1$ μm) [18]. Fig. 5b is the indexing of fig. 5a together with a scale factor.

3.5. Electrical properties

Unintentionally doped InGaAsP layers always give n-type conduction. Silicon is believed to be the main dopant due to its high segregation coefficient ($K_{Si} \sim 30$) in InP grown by LPE techniques [13]. Baking the melt at 750 °C for 8 h usually produces background carrier concentration below 1×10^{17} cm^{-3}. Van der Pauw measurements at both room temperature and liquid nitrogen temperature were performed on InP and InGaAsP epitaxial layers grown lattice-matched on a (100) surface of Fe-doped semi-insulating InP substrates. For quaternary layers, the measured mobility and concentration at room temperature are

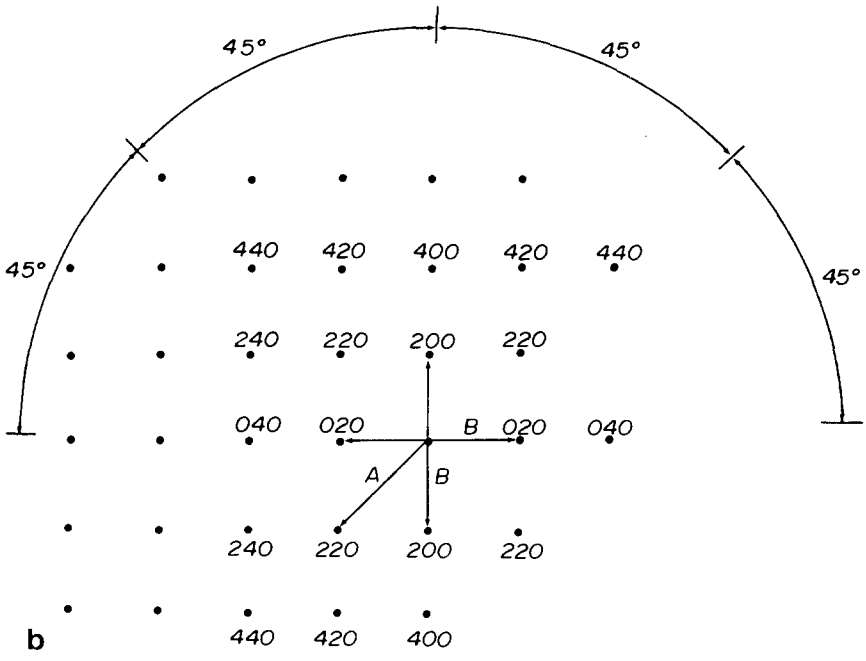

Fig. 3. (a) Diffraction pattern of $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ epitaxial layer in [001] orientation. (b) Reciprocal lattice section relevant to (a), $A/B = \sqrt{2}/1 = 1.414$, $B = z = [001]$.

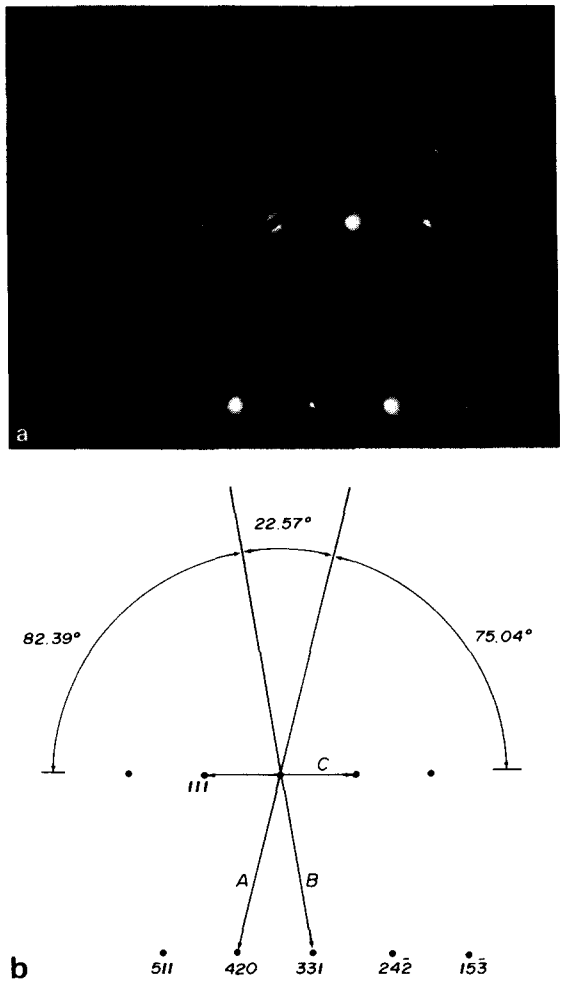

Fig. 4. (a) Diffraction pattern of $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ epitaxial layer in [$\bar{1}$23] orientation. (b) Reciprocal lattice section relevant to (a), $A/C = \sqrt{20}/3 = 2.582$, $B/C = \sqrt{19}/3 = 2.519$, $B = z = [\bar{1}23]$.

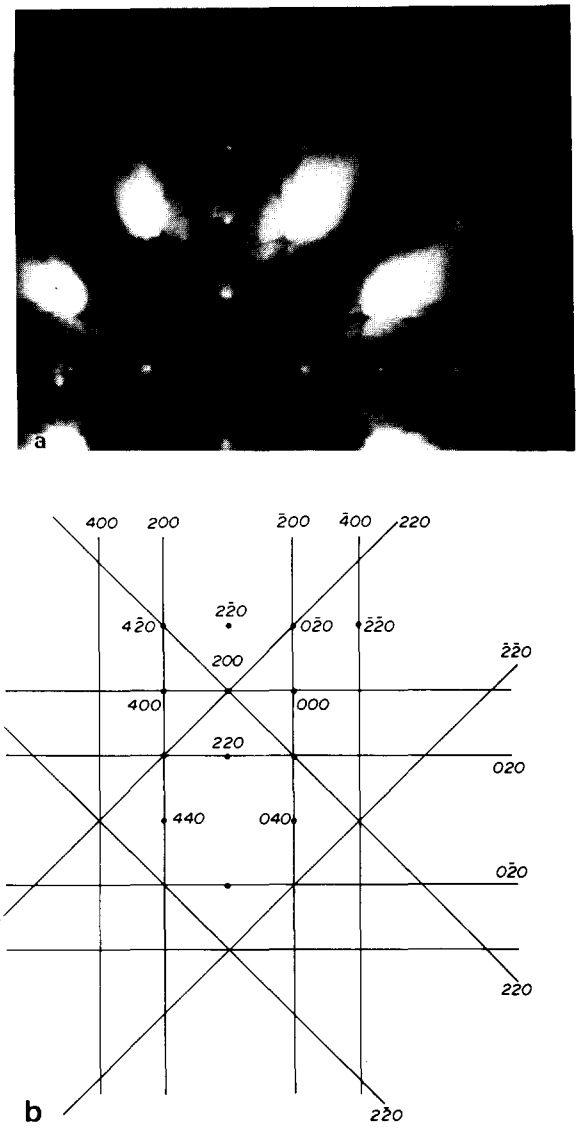

Fig. 5. (a) Kikuchi contrast pattern enhanced diffraction pattern in $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ sample. (b) The indexing of (a) together with scale factors.

3200 $cm^2/V \cdot s$ and 1.76×10^{16} cm^{-3}, respectively; while those at liquid nitrogen temperature are 5800 $cm^2/V \cdot s$ and 1.67×10^{16} cm^{-3}, respectively. These results at room temperature are comparable to those of Yamazoe et al. [19] (1800 $cm^2/V \cdot s$ and 10^{17} cm^{-3}) and of Leheny et al. [20] (3300 $cm^2/V \cdot s$ and 4×10^{16} cm^{-3}). For InP layers, the measured mobility and concentration at room temperature are 2330 $cm^2/V \cdot s$ and 8.94×10^{16} cm^{-3}, respectively; while those for liquid nitrogen temperature are 4340 $cm^2/V \cdot s$ and 5.76×10^{16} cm^{-3}, respectively.

4. Conclusions

$In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ thin films were grown on InP substrates by LPE using the step cooling method. The optimum growth conditions to give lattice matching between the epilayer and the substrate are $T_G = 635\,°C$ and $\Delta T = 10\,°C$, and were

confirmed by X-ray diffraction measurements. The solid composition and band gap of the quaternary epilayers were determined by EPMA and optical transmission measurements. The diffraction patterns were used to check the crystal quality of the grown layers. Strong Kikuchi patterns were obtained in these high quality quaternary epitaxial layers. The mobilities and carrier concentrations of undoped $In_{0.75}Ga_{0.25}As_{0.56}P_{0.44}$ and InP epilayers were comparable to or better than those reported earlier [19,20].

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