Bulk growth of polycrystalline indium phosphide

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Abstract. The growth of polycrystalline indium phosphide of different grain sizes varying from 15 μm to 4000 μm has been discussed. The materials have been characterized by a variety of methods including electrical and optical techniques. Device application of the InP prepared was demonstrated by the fabrication of Ag Schottky diodes and p^+–n junction using Zn diffusion. The variation of mobility with varying grain size has been determined experimentally and the results interpreted taking into account the effect of compensation.

Keywords. InP; crystal growth; III V compounds.

1. Introduction

Indium phosphide (InP) is a direct band-gap semiconductor ($E_g = 1.34$ eV at 300 K) which is increasingly being used in optoelectronic and microwave devices e.g. InGaAs/InP double heterostructure lasers, InGaAs/InP FET and InP mm-wave devices. The higher electron-saturation velocity as compared to GaAs is an advantage for TED and MESFET operating above 10 GHz. It is also a promising substrate for MIS devices since the minimum surface state density is 10^{11} cm^{-2} as compared to 2×10^{12} cm^{-2} for GaAs. With respect to its mass manufacture and long term use, the absence of a hazardous component like arsenic in its production, gives InP a distinct edge over GaAs.

The growth of InP is complicated by the high pressure of phosphorus (28 atm) at the melting point of the compound (1070°C). The conventional LEC technique employs high temperature and high pressure to grow InP crystals. This is an expensive method and it is also difficult to grow defect-free crystals by this method. Thus it is desirable to investigate alternative methods for growing InP crystals. In this work, the growth and subsequent characterization of polycrystalline InP of different grain sizes have been discussed.

2. Growth

2.1 *Low temperature growth*

Several approaches have been made to avoid the complications of high pressures and temperatures needed for the growth of InP from a stoichiometric melt. Gradient-freeze (Miller 1962) and synthesis solute diffusion (Kaneko *et al* 1973; Roy *et al* 1983) techniques have been used to avoid the problem of high vapour pressure but the growth temperature required in both these cases is more than 1000°C leading to the possibility of contamination from the container. The low temperature

(500°C) growth of polycrystalline InP has been reported earlier (Roy *et al* 1981) using iodide formation as an intermediate step.

High purity indium (5N), red phosphorus (4N) and AR grade iodine were taken in stoichiometric quantities, mixed well and placed in a thick-walled (2 mm) high-purity silica tube. The tube was vacuum-sealed and then kept in a constant temperature zone horizontal furnace. The furnace was heated at the rate of (20°C/h) to 250°C and kept at this temperature for one hour. The temperature was then raised (at the rate of 20°C/h) to 500°C and kept constant at this level for 44 h. The chemistry involved in this growth procedure may be explained as follows.

During the first stage of heating the reaction

$$2In + 3I_2 \rightarrow 2InI_3 (H_f^\circ = -59\cdot5 \text{ kcal/mole})$$
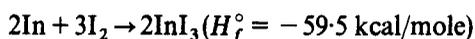
occurs. The red phosphorus initially taken, changes to reactive white phosphorus at 280°C, while the decomposition of InI_3 occurs at approximately 300°C. Therefore during the second stage of heating, the reaction

$$2InI_3 + 2P \rightarrow 2InP + 3I_2 (H_f^\circ = 72\cdot5 \text{ kcal/mole})$$
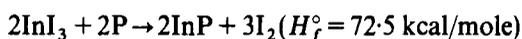
occurs. An alternative path through InI formation by the reaction

$$InI_3 + 2In \rightarrow 3InI \ (H_f = -23\cdot9 \text{ kcal/mole}),$$
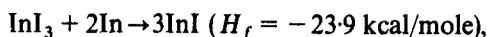
in the presence of indium melt, cannot be ruled out. In that case InI would react with white phosphorus giving InP by the reaction

$$2InI + 2P \rightarrow 2InP + I_2 (H_f^\circ = -41\cdot8 \text{ Kcal/mole}).$$
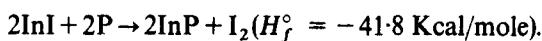
After the growth run the furnace was cooled slowly (at 10°C/h) to room temperature. To remove the iodine formed, high-purity hydrogen gas was passed for 15 min through the tube, which was kept in a furnace while the temperature was slowly raised to 350°C. The iodine sublimed to the cooler part of the container silica tube, where it condensed and was thus recovered.

Several growth runs were performed with two different growth times (44 and 114 h). It was found that the quality of the crystals improved significantly when the reaction time was increased from 44 to 114 h. This may be due to the annealing effect after growth. Single crystal formation by this technique is unlikely because of random nucleation during growth. The grain size can be increased by prolonged annealing at high temperature. Growth and annealing can be performed simultaneously by increasing the growth time.

2.2 *Synthesis solute diffusion growth*

In the low temperature growth technique the phosphorus vapour pressure problem and the possible incorporation of impurities from the quartz crucible were minimized but the quality of the crystal with respect to grain size, mobility etc was poor.

The synthesis solute diffusion (SSD) technique permits the growth of InP crystals at low temperature (700–900°C) from an indium melt containing a certain amount of phosphorus. This technique was first developed by Kaneko *et al* (1973) for the growth of GaP and was subsequently modified for the growth of InP (Kaneko *et al* 1973; Kubato and Sugii 1981; Engh *et al* 1981).

In this method the melt was held in a temperature gradient; phosphorus reacted with indium melt at the surface to form InP which was transported by diffusion to the cooler end and solidified due to lower solubility. A quartz crucible containing In was placed in a larger diameter quartz tube containing phosphorus. After evacuation and sealing, the system was placed in a vertical two-zone resistance furnace. The temperature of phosphorus, T_p, was 450°C, corresponding to a vapour pressure of about 2 atm. The growth rate is dependent on the temperature difference between the top of the solution (T_2) and the temperature of the growing interface (T_1) and is limited by the diffusion process of the solute. The quality of the crystal also depends upon the temperature gradient. Since the diffusion coefficient of phosphorus in the indium melt is low, a large temperature gradient is normally required to increase the growth rate. On the other hand, a large temperature gradient produces poor quality crystals. Hence, optimization is necessary to obtain the best results. The following temperatures may be used:

$$T_1 = 710°C, \qquad T_2 = 910°C, \qquad T_p = 450°C$$

and temperature gradient $\dfrac{\mathrm{d}T}{\mathrm{d}x} = 20°C/cm.$

The above conditions were maintained for 114 h with the help of a programmable temperature controller. After the growth run was completed, the furnace was cooled slowly (3°C/h) up to $T_2 = 850°C$ and $T_1 = 650°C$ and then to room temperature at a rate of nearly 20°C/h.

The kinetics of InP growth by the SSD technique was studied to determine the growth rate taking into account the law of conservation of mass. The diffusion coefficient of phosphorus in indium melt thus was found to be

$$D = 1·695 \times 10^{-3} \exp(-0·23/kT).$$

The experimental data required for this analysis have been taken from the literature (Sugii *et al* 1979).

2.3 *Gradient-freeze growth*

The low growth rate with the SSD technique is a distinct disadvantage which apparently cannot be easily overcome. The gradient-freeze technique is analogous to the horizontal Bridgman (HB) method. The two methods differ only in that solidification by the gradient-freeze technique takes place by the movement of a temperature gradient along the ingot, making the entire system stationary. The main advantages of the gradient-freeze technique are, then, simplicity and no relative motion between the furnace and the crucible.

The growth was carried out in a horizontal two-zone resistance furnace with In (5N) kept at 1070°C and P (5N) at 450°C. The temperature of the hot zone was programmed to decrease by 1·6°C/h after the synthesis. The growth run occurred for 114 h.

P-type InP was also grown by this technique by Zn-doping during growth. The effect of phosphorus pressure during growth was investigated by varying the temperature on the phosphorus side. The growth run was performed at three different temperatures i.e. 450, 460 and 475°C. An improvement in the quality of the

crystals was observed with increasing phosphorus pressure directly through an increase in electron mobility.

3. Characterization

X-ray diffraction showed crystalline character of all the samples. No other peaks were observed within the sensitivity (0·1%) of the instrument used. The *d*-values agreed fairly well with the standard value for pure InP.

The grain size of the material grown by iodine reaction was measured from SEM photographs and found to be approximately 15 μm for 44 h growth time and approximately 200 μm for 114 h growth. The grain size was estimated by the methods described by Jain *et al* (1981). The grain size of the SSD and gradient-freeze grown InP determined by optical micrography was found to be approximately 3–4 mm.

The stoichiometry of both SSD and gradient-freeze grown InP were determined by electron microprobe analysis taking single-crystal InP obtained from Metals Research, UK as the reference. The results are given below as percentages.

	In content	P content
Standard InP (obtained from Metals Research, UK)	78·74	21·26
SSD-grown InP	77·976	21·477
Gradient-freeze grown InP	79·246	21·326

The results show that the stoichiometry is very close to that of the standard sample and that there is no phosphorus deficiency in the grown crystals since the observed differences are within the limit of the accuracy of the instrument.

The electrochemical technique described by Faktor *et al* (1981), which is fairly accurate, was adopted to determine the energy band gap of the materials prepared. The specimens were used as anodes and platinum as the cathode in 1M potassium hydroxide solution (pH = 11·5) electrolyte. The anodes were illuminated, the wavelength of the incident light was varied between 0·4 and 0·89 micron using a Jarrell-Ash monochromator and the resultant photovoltages measured. A photovoltage vs wavelength plot was obtained and from the cut-off wavelength the band gap was determined using the relation $E_g = 1·24/\lambda$ (eV). The band gap was found to be 1·28 eV for low temperature grown (both 44 h and 114 h reaction time), gradient-freeze grown and SSD grown InP, and 1·29 eV for the standard single crystal of InP obtained from Metals Research, UK.

The band gap of gradient-freeze, SSD and standard single-crystal InP was also measured by optical absorption and photoluminescence (PL). The measured band-gap by this technique agreed fairly well (1·30 eV) with the band-gap measured by the electrochemical technique.

Thermopower experiments were carried out to determine the type of conductivity. The Van der Pauw technique was adopted to measure the resistivity of the grown samples. The carrier concentrations and Hall mobilities were determined from Hall effect measurements using the Van der Pauw technique. Table 1 shows the summarized results of growth conditions and properties of InP.

Low temperature resistivity and Hall-effect measurements were carried out between 160 and 300 K. The activation energies and temperature variations of

Table 1. Growth conditions and properties of InP.

Method	Conditions	Type	Band gap (eV)	Grain size	Resistivity (ohm-cm)	Mobility (cm²/ V-s)	Carrier concentration (cm⁻³) (× 10¹⁸)
Iodine reaction (44 h)	$T = 500°C$ $P_p = 7.5$ atms	n	1.29 (PEC)	10–20 μm	11.2	27.9	200
Iodine reaction (114 h)	$T = 500°C$ $P_p = 7.5$ atms	n	1.29 (PEC)	200 μm	0.349	224	800
SSD (114 h)	$T_{In} = 710–910°C$						
	$dT/dx = 20°C/cm$ $T_p = 450°C$ $P_p = 2$ atm	n	1.32 (optical absorption and PL)	2–3 mm	3.46×10^{-2}	691	30
Gradient -freeze (114 h)	$T_{In} = 1070°C$ $T_p = 450°C$ $P_p = 2$ atms	n	1.31 (optical absorption and PL)	3–4 mm	3.2×10^{-2}	610	32
	$T_p = 460°C$ $P_p = 3$ atm	n		3–4 mm	2.5×10^{-2}	724	34
	$T_p = 475°C$ $P_p = 4.2$ atm	n		3–4 mm	2.26×10^{-2}	890	31
	$T_p = 450°C$ $P_p = 2$ atm Dopant – Zn	p		3–4 mm	3.2×10^{-2}	93	2.1
LEC (Metals research)	––	n	1.29 (PEC)	Single crystal (Sn-doped)	2×10^{-2}	1300	2

Table 2. Temperature dependence of carrier concentration and mobility.

Sample	Mobility at 160 K (cm²/V-s)	Carrier activation energy (E_n) obtained from 1/T vs ln n plot (meV)	Conductivity activation energy (E) obtained from 1/T vs ln plot (meV)	X where $\mu \times T^{-x}$
Iodine reaction (114 h)	900	19.4	11.5	3.24
SSD	2700	13.9	9.09	2.24
Single crystal	5248	8.1	8.3	2.25

mobility were determined from these measurements. The results are summarized in table 2.

Since there is no grain boundary scattering for single crystals, E_n is expected to be equal to E. In the presence of grain boundary scattering the activation energies are given by

$$E_n \alpha - \frac{\partial \ln n}{\partial (1/T)} \tag{1}$$

$$E_n \alpha - \frac{\partial \ln \sigma}{\partial (1/T)} \tag{2}$$

Since grain boundary scattering is observed to increase the temperature dependence of mobility, the mobility thus decreases with increasing temperature while n increases with temperature. So it is obvious that

$$\left| \frac{\partial \ln n}{\partial (1/T)} \right| > \frac{\partial \ln \sigma}{\partial (1/T)} \quad \text{i.e. } E_n > E_\sigma$$

The magnitude of difference between E_n and E_σ depends upon grain boundary scattering which increases with decrease of grain size. Our measured value of $x = 2.25$ for single crystal is in good agreement with the reported (Kubato and Sugii 1981) results, $x = 2.0$–2.4.

Compensation arising out of impurities in the starting materials has been theoretically calculated. The effect of compensation on carrier mobility in single crystal InP has already been analysed by Jensen (1979). By extending this analysis to include grain boundary scattering, the dependence of electron mobility on grain size in polycrystalline InP has been determined (Roy *et al* 1983).

The compensation parameter defined as $r = N_i/n_e$ where $N_i = N_d^+ + N_a^+$ and N_d^+ and N_d^- are the charged donors and acceptors respectively and $n_e = N_d^+ - N_a$, $C = N_d^- / N_d^+$.

Compensation and related parameters are given in table 3. The plot between grain size and mobility can be used to find the mobility of any polycrystalline n-InP sample where grain size and compensation ratio are known.

From steady-state photoconductivity experiments the majority carriers life-time of gradient-freeze sample was estimated and compared with that of the standard single crystal. The value of p (photo-generated charge carriers) was measured from the I–V characteristics in dark and under illumination. To estimate the life-time steady-state photo-conductivity was measured using chopped monochromatic radiation. From the intensity of illumination measured using an Si pin diode including the loss due to reflection from the sample, the life-time was determined as given in table 4.

Dislocation densities were estimated from the etch pits revealed by Abrahams and Buiocchi (1965) and Huber and Lint (1975) etchants. The etch pit densities as determined from SEM are given in table 4.

The improvement of the quality of crystals grown with higher phosphorus pressure is evident from the above table. The increase of life-time with the increase of phosphorus pressure is mainly due to the decrease of dislocation density. The dislocation density is considerably lower for Zn-doped InP. This is due to the low misfit factor and lattice strain due to Zn atom in InP.

Device application of the InP prepared was demonstrated by the fabrication of Ag Schottky diodes and p^+–n junction using Zn diffusion. The height of a typical Schottky barrier was found to be 0.59 eV. The ideality factor n was found to be 2.07

Table 3. Compensation ratio in n-InP.

Sample	n_e (cm^{-3}) ($\times 10^{16}$)	μ_e (cm^2/V-s)	N_d^+ (cm^{-3}) ($\times 10^{17}$)	N_a (cm^{-3}) ($\times 10^{17}$)	C	r
Iodine reaction (44 h)	2	29	2.1	1.9	0.905	20
Iodine reaction (114 h)	8	224	2.4	1.6	0.667	5
SSD	30	691	3.5	0.5	0.143	1.333

Table 4. Etch pit densities of InP grown by different techniques.

Growth technique	Etch pit densities (cm^{-2})	Life-time (s) ($\times 10^{-8}$)
SSD grown n-InP $T_p = 450°C$	1.2×10^4	—
Gradient-freeze grown p-InP (Zn-doped)	3×10^1	—
Gradient-freeze grown n-InP $T_p = 450°C$	1.8×10^4	2.25
Gradient-freeze grown n-InP $T_p = 460°C$	9×10^3	3.62
Gradient-freeze grown n-InP $T_p = 475°C$	7×10^3	5.11
Single crystal n-InP (Metals Research)	—	8.22

at 300°C. A novel method of barrier height enhancement of Schottky diodes was demonstrated by chemical modification of the n-InP surface by the Ru ion (Bose *et al* 1984).

p^+–n junction was fabricated by diffusing Zn in n-InP grown by gradient-freeze technique. The reverse saturation current of 5.3×10^{-9} A and ideality factor of 1.36 were thus obtained. The built-in voltage was found to be 1.29 volts. From the measured value of J_0 current transport was found to be dominated by generation-recombination mechanism with an effective junction hole life-time of 2.36×10^{-9} s.

4. Conclusion

Polycrystalline InP of different grain sizes varying from $15 \mu m$ to $4000 \mu m$ has been grown by iodine transport, SSD and gradient-freeze techniques. The materials have been subsequently characterized by a variety of methods including electrical and optical techniques and used for the fabrication of P^+–n junction and Schottky diodes. The effect of phosphorus vapour pressure on gradient-freeze grown InP has been demonstrated. The electron mobility was determined with varying grain size taking compensation into account. The growth kinetic of SSD technique has been studied to determine the theoretical growth rate.

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