Journal of Korean Association of Crystal Growth
Vol. 9, No. 6 (1999) 542-546

Characterization and crystal growth of InP by VGF method using quartz ampoule

E.S. Choi, C.H. Jung, J.J. Myung, J.Y. Hong and M.K. Kim
Institute of ceramic Technology, Seoul 153-023, Korea
(Received June 9, 1999)

Abstract InP single crystal, III-V binary compound semiconductor, was grown by VGF (vertical gradient freeze) method using quartz ampoule and its electrical optical properties were investigated. Phosphorous powders were put in the bottom of quartz ampoule and Indium metal charged in conical quartz crucible what was attached at the upper side position inside the quartz ampoule. It was vacuous under the pressure of 10^5 Torr and sealed up. Indium metal was melted at 1070°C and InP composition was formed by diffusion of phosphorous sublimated at 450°C into Indium melt. By cooling the InP composition melt (2°C~5°C/hr of cooling rate) in range of 1070°C~900°C, InP crystal was grown. The grown InP single crystals were investigated by X-ray analysis and polarized optical microscopy. Electrical properties were measured by Van der Pauw method. At the cooling rate of 2°C/hr, growth direction of ingot was [111] and the quality of ingot was better at the upper side of ingot than the lower side. It was found that the InP crystals were n-type semiconductor and the carrier concentration, electron mobility and relative resistivity were 10^{15}~$10^{16}/cm^3$, 2×10^3~3×10^4 $cm^2/Vsec$ and 2×10^{-1}~2×10^{-3} Wcm in the range of 150 K~300 K, respectively.

1. Introduction

InP III-V compound semiconductor has a zincblende structure, bandgap of 1.35eV and electron mobility of 4600 $cm^2/Vsec$. InP is used for the substrate materials of LED(light emitting diode) and LD(laser diode) as light source for low loss attenuation in the range of 1.1~1.6 μm wavelength [1, 2] and also for FET(field effect transistor), MISFET (metal insulator semiconductor field effect transistor) etc as high logical circuit and photo-switching device which work to high speed for short wavelength light [3-6]. To make these device, it needs InP single crystal which has homogeneous and low dislocation density and resident impurity concentration. Growth of InP single crystal is difficult due to its high evaporation pressure of 27.5bar at the melting point of 1067°C. Generally InP crystal was grown by HB (horizontal bridgman), LEC (liquid encapsulated Czochralsky) and VGF (vertical gradient freeze) method [7, 8], In HB method, crystal growth was able to be move horizontally transverse boat and sealed reactor containing phosphorous in two zone furnace [9, 10]. It is difficult to maintain stable temperature to move reactor tube or furnace. InP crystal grown by LEC method has a defect as like twin crystal between B_2O_3 and InP crystal [11]. Relative advantage of VGF method is that it is simple and can be kept under constant temperature [12].

In this study, InP single crystal was grown by VGF method and investigated to characterize electrical properties of grown crystal.

2. Experimental method

2.1. *Forming of InP melt and crystal growth*

Figure 1 is the schematic diagram for crystal grow-

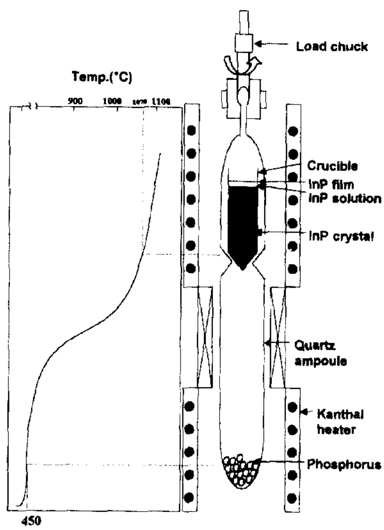

Fig. 1. Temperature profile and schematic diagram of the crystal growth apparatus.

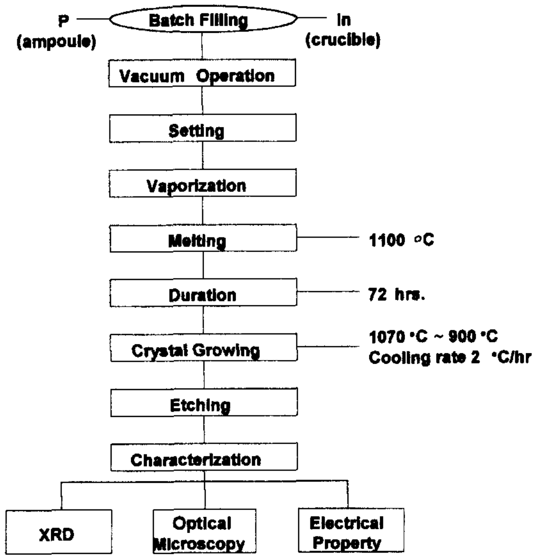

Fig. 2. Procedure for InP crystal growth.

ing apparatus. Furnace was seperated into upper and lower heating zone. Crucible and quartz ampoule for crystal growth were dipped in cleaning solution (H_2SO_4 + $K_2Cr_2O_7$) and rinsed with deionization water and impurity was removed in 10 vol% of HF aqueous solution and heated to about 1000°C. Because impurity in crystal affects to quality of crystal, Indium was dried and rinsed with distilled water after HNO_3 treatment and heated for 3 h at 900°C in vacuum of 10^{-5} torr. Mole ratio of In to P is 1 : 1 and excess 5 % of P was added to balance stoichiometry. The sample was placed at the position of conical crucible chip end between hot and low zone in furnace and crystal was grown by VGF method. Surface temperature of molten In and temperature gradient were 1070°C and 20~40°C/cm, respectively. Indium (hot zone) was melted at 1100°C and Phosphorus (low zone) was vaporized at 450°C to diffuse into In melt, it was cooled to 900°C with cooling rate of 2 K/h and rotation rate of 5 rpm. Flow chart for crystal growing process is represented in Fig. 2.

2.2. Characterization

Obtained crystal was characterized and identified by X-ray diffraction and lattice parameter was calculated by least square method using 2θ value of X-ray diffraction analysis. Orientation of grown crystal was studied by Laue analysis for transverse plane of growing direction. Microstructure of crystal was observed by polarized optical microscope. Crystal sample was etched for 15 sec in Bromic-Nitric Acid[HBr : HNO_3(3 : 1)] solution and etch pit density was calculated using optical microscope.

2.3. Electrical properties

Carrier concentration and electron mobility of InP crystal were measured by Van der Pauw method. InP wafer was rinsed in order of Trichloroethylene, Aceton, and Methanol, and etched for 60 sec in Bromine water (1 %Br)-Methanol solution. Hall effect was measured to investigate electrical property of InP crystal. Sample was heated for 2 min. at 200°C and In electrode was attached on Al_2O_3 substrate to weld Ohmic contact under Ar conditions. Current and voltage in range of 150~300 K were measured by electrometer. Resistance was calculated from obtained current and voltage. Resistivity, mobility and carrier concentration of InP were measured by Van der Pauw method.

3. Result and discussion

3.1. Characterization

Figure 3 shows 20 mm sized InP ingot that was grown by the heat treatment in the range from 1070°C to 900°C under slow cooling rate of 2°C/hr and rotating speed of 5 rpm. Figures 4 and 5 show X-ray diffraction patterns for powder and grown crystals with transverse position parts to the growth direction. Grown ingot was identified InP crystal from X-ray diffraction data. Lattice parameter, ao, of grown InP crystal is valued in range of 5.8655~5.8697 Å. X-ray pattern of plane characterization of crystal growth direction were shown initially with (111), (220) and (311), gradually remained (111) and (220) and later with (111). The result of the back Laue reflection pattern and stereo projection for (111) plane of crystal, it

Fig. 3. Crystal ingot grown by VGF method.

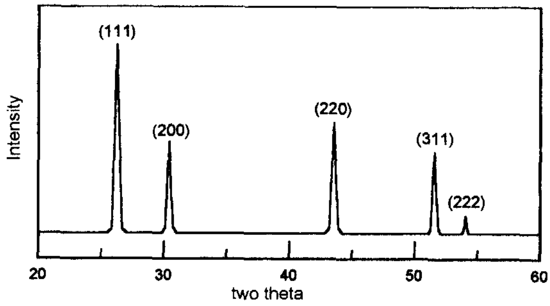

Fig. 4. XRD pattern of InP crystal powder.

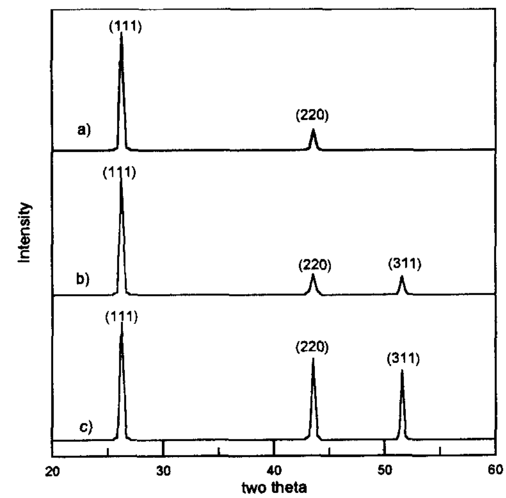

Fig. 5. XRD patterns of vertical section of crystal grown at 1070°C when cooling rate is 2°C/hr and rotation speed is 5 rpm a) 7 cm, b) 4 cm and c) 2 cm from first solidified position.

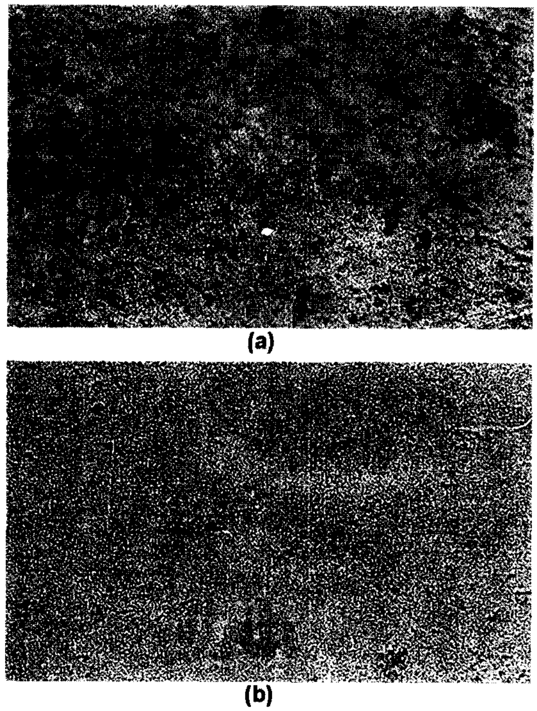

Fig. 6. Photographs for InP ingot slice cut perpendicularly to the grown axis at 2 cm (a) and 7 cm (b) from crucible tip.

was certificated that vertical plane to the growth direction is (111). Figure 6 shows the optical microscope photographs of InP wafer which was cut at upper 2 cm and 7 cm position of crystal. In Fig. 7, crystal surface cut at upper position of 7 cm shows lower pore and smarter shape than those of lower position (3 cm). It tends to increase crystal quality to rise upper position. Average dislocation density was 9×10^4.

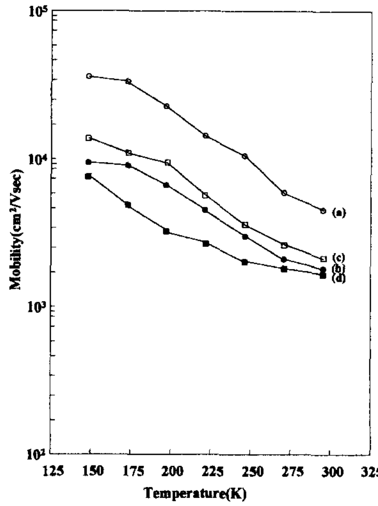

Fig. 7. The relationship between electron mobility and temperature. (a) 7 cm and (c) 2 cm from first solidified position (at 1070°C, cooling rate of 2°C/h and 5 rpm) (b) 7 cm and (d) 2 cm from first solidified position (at 1070°C and cooling rate of 2°C/h).

3.2. Electrical properties

Generally, bridge style sample shape was used for Hall effect measurement but if its thickness is constant, Van der Pauw method [13] can be used for any shape. Therefore, electrical property of grown InP crystal was investigated by Van der Pauw method. Semiconductor type, resistivity, conductivity, carrier concentration and Hall mobility could be obtained from the given thickness(t) and the measured Hall coefficient (RH) by Van der Pauw equation. From these results, grown InP crystal was n-type semiconductor due to influence of donor carrier which was formed from impurity in crystal. This could be considered as the formation of impurity by In substitution of P site or penetration of Si into crystal due to high diffusion coefficient [14].

Electron mobility at room temperature was decreased to 3000~2000 $cm^2/Vsec$ according to the carrier concentration was increased to 10^{15}~10^{16} cm^{-3}. This is caused by the collision dispersion of carriers in lattice by impurity which was formed by concentration increment. Figures 7, 8 and 9 show the results for electron mobility, conductivity and resistivity in range of 150~300 K respectively. In Fig. 7, value of electron mobility was decreased from 3×10^4 $cm^2/Vsec$ to 2×10^3 $cm^2/Vsec$ with temperature increment. This may be caused by the lattice scatter which was intense depending on temperature increase. Figure 8 and Fig. 9 show change of resistivity and carrier concentration as a function of temperature, respectively. The value of re- sistivity increased from 2×10^{-1} cm to 2×10^{-3} cm with temperature increase and this may be caused that carrier concentration increase with temperature increase.

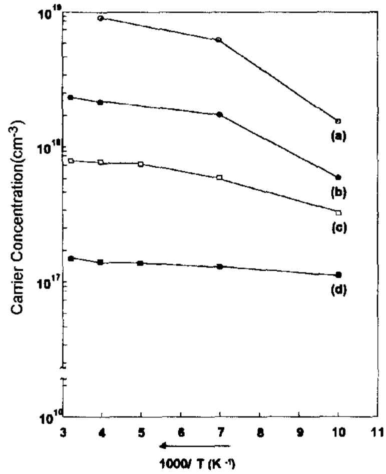

Fig. 8. Carrier concentration as a function of temperature variation. (a) 7 cm and (c) 2 cm from first solidified position (at 1070°C, cooling rate of 2°C/h and 5 rpm), (b) 7 cm and (d) 2 cm from first solidified position (at 1070°C and cooling rate of 2°C/h).

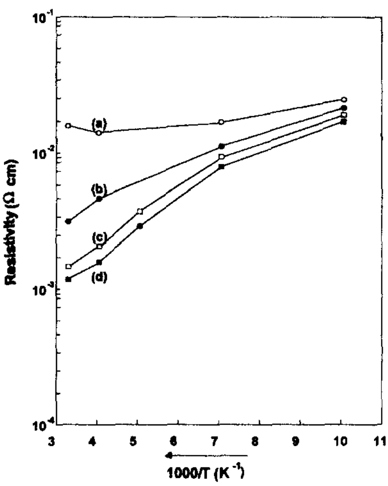

Fig. 9. The relationship between temperature and resistivity (a) 7 cm and (c) 2 cm from first solidified position (at 1070v, cooling rate of 2°C/h and 5 rpm) (b) 7 cm and (d) 2 cm from first solidified position (at 1070°C and cooling rate of 2°C/h).

4. Conclusions

Results for the growing experiment of InP single crystal by VGF method using quartz ampoule follow.

1) Growing conditions of InP single crystal were that melting and vaporizing temperatures are 1100°C and 450°C, respectively, cooling rate is 2°C/hr in range of 1070~900°C and rotation speed is 5 rpm.

2) Characterization of InP single crystal shows that vertical section to the growth direction is (111) plane and crystal quality is better at the upper zone than the lower zone.

3) From the result of Hall effect measurement, grown InP crystal was n-type semiconductor, and carrier concentration, electron mobility and relative resistivity were 10^{17}~10^{19} cm^{-3}, 2×10^3~3×10^4 $cm^2/Vsec$ and 2×10^{-1}~2×10^{-3} Ωcm in range of 150~300 K, respectively.

References

[1] D.B. Keck, R.D. Mauer and P.C. Shutz, Appl. Phys. Lett. 22 (1973) 307.
[2] S. Yamakoshi, M. Abe, O. Wada, S. Komiya and T. Sakurai, IEEE Trans. Quantum Electron, QE-17 (1981) 167.
[3] Y. Imai, T. Ishihashi and Ida, IEEE Electro. Device Lett. EDL-2 (1981) 67.
[4] M. Okamura and T. Kobayashi, Jpn. J. Appl. Phys. 19 (1980) 2143.
[5] A.G. Foyt, F.J. Leonberger and R.C. Williamson, Appl. Phys. Lett. 40 (1982) 447.
[6] R.R. Mandal, Solid State Tech. (1982) 94.

[7] M.E. Weiner, D.T. Lassota and B. Schwartz, J. Electrochem. Soc. 118 (1972) 301.
[8] M. Morioke, T. Toda and S. Akai, Ann. Rev. Mater. Sci. 17 (1987) 75.
[9] Yamamoto, S. Shinoyama and C. Memura, J. Electrochem. Soc. (1981) 586.
[10] T.P. Chen and Y.D. Guo, J. Cryst. Growth (1989) 683.
[11] K.J. Bachmann, E.B. Buehler, J.L. Shay and A.R. Stand, J. Electron Mater. 4 (1975) 389.
[12] W.A. Gault and E.M. Monberg, J. Cryst. Growth (1986) 491.
[13] Van der Pauw, Philips. Res. 13 (1958) 1.
[14] S.N.G. Chu and C.M. Jodlauk, J. Electrochem. Soc. (1982) 352.