Crystal Growth of InP by VGF Method using Quartz Ampoule Characterization

E.S.Choi, C.H. Jung, J.J. myung, J.Y. Hong and M.K. Kim.

Institute of ceramic Technology, Seoul 153-023, Korea.

Abstract InP, III-V binary compound semiconductor, single crystal 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 changed 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. In metal in the quartz crucible was melted at 1070℃ and phosphorous sublimated at 450℃, there after it was diffused in In melt and so InP composition was formed. By cooling the InP composition melt(2℃~5℃/hr of cooling rate) in range of 1070℃~900℃, InP crystal was grown.

The grown InP single crystals were investigated by X-ray analysis and polarized optical microscopy. Electrical properties of them were measured by Van der Pauw method.

At the cooling rate of 2℃/hr, its direction was (111), quality of the ingot was better upper side of the ingot than lower. It was found that the InP crystals were n-type semiconductor and the carrier concentration, electron mobility and relative resistivity were $10^{15} \sim 10^{16}/\text{cm}^3$, $2\times10^3 \sim 3\times10^4 \text{cm}^2/\text{Vsec}$ and $2\times10^{-1} \sim 2\times10^{-3} \Omega\text{cm}$ in the range of 150K~300K, respectively.

1. Introduction

InP single crystal III-V compound semiconductor have a zincblende structure, bandgap of 1.35eV and electron mobility of 4600cm²/Vsec. InP use for substrate materials of LED(light emitting diode) and LD as light source for low loss attenuation in range of 1.1~1.6㎛ wavelength[1,2] also 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 must be necessary InP single crystal which have homogeneous and low dislocation density and resident impurity concentration. Growth of InP single crystal have difficulty in growth because of high evaporation pressure of 27.5bar at melting point of 1067℃. Generally InP crystal grown by HB(horizontal bridegman), LEC(liquid wncapsulated czochralsky) and VGF(vertical gradient freeze) method[7,8], In HB method, crystal growth was able to move horizontally transverse boat and sealed reactor containing phosphorous in two zone furnace[9,10]. But it is difficult maintenance of stable temperature to move reactor tube or furnace. InP crystal grown by LEC method have a defect as twin crystal to be caused pore between B_2O_3 and InP crystal[11]. Relatively advantage of VGF method is that it is simple appratures and can be kept temperature constantly[12].

In this study, InP single crystal was grown by VGF method and investigate characterization and electrical properties for grown crystal.

2. Experimental method

2.1 Forming of InP melt and crystal growth

It is schematic diagram for crystal growing apparatus as shown in Fig. 1. Furnace was seperated into upper and lower heating zone. Crucible and quartz ampoule for crystal growth was dipped in cleaning solution(H_2SO_4+$K_2Cr_2O_7$) and rinsed with deionization water and impurity was removed in 10vol% of HF aqueous solution and heated to about 1000℃. Because it is affected to quality of crystal by impurity in crystal, In order to remove impurites and oxides in crystal, In was dried and rinsed with distilled water after HNO_3 treatment and heated for 3h at 900℃ in vacuum of 10^{-5}torr. Mole ratio of In to P is 1:1 and add excess 5% of P. The sample must be placed 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℃ and 20~40℃/cm, respectively. InP crystal growth condition is melted at 1100℃, grown temperature range of 1070℃ to 900℃ and cooling rate of 2℃/h under condition that pressure and temperature of lower zone are 2.3atm and 450℃.

Flow chart for crystal growth process is represented in Fig. 2.

2.2 Characterization

Obtained crystal was characterized and identified by X-ray diffraction, lattice parameter was calculated by least square method using 2θ value of X-ray diffraction analysis. Orientation of grown crystal was studied to Laue analysis for transverse plane of growing direction. Microstructure of crystal was observed by polarized optical microscope. The crystal sample was etched for 15 sec in Bromic-Nitric acid solution($HBr:HNO_3(3:1)$) and etch pit density was calculated using polarized 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 Tricholroethylene, Aceton, and Methanol, and etched for 60 sec in Bromic acid (1%Br)-Methanol solution. For electrical properties measurement, InP wafer is prepared to precision treating Hall effect was measured to investigate electrical property of InP crystal. It was heated sample for 2min · at 200℃, made In electrode to weld Ohmic contact under Ar conditions and attached on Al_2O_3 substrate. Current and voltage in range of 150~300K were measured by electrometer. Resistance was calculated from obtained current and voltage. Resistivity, mobility and carrier concentration of InP were got by Van der Pauw method.

3. Result and Discussion

3.1 Characterization

Fig. 3 shows 20mm sized InP ingot that was grown by heat treatment of range from 1070℃ to 900℃ under slow cooling rate of 2℃/h and rotating speed of 5rpm. Fig. 4 and 5 show X-ray diffraction pattern for powder and transverse position parts to the growth direction. It could be shown that from X-ray diffraction data, substance was identified InP crystal what it synthesized. Lattice parameter, a_o of grown InP crystal is valued in range of

5.8655~5.8697Å and it could be consider because composition is change a small quantity. 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). Fig. 6 show back Laue pattern and stereo projection for (111) plane of crystal, It was ceritificated that transverse plane to the growth direction is (111).

Fig. 7 shows optical microscope photographs of InP wafer which were cut to upper 2cm and 7cm position of crystal and polished as mirror plane. In Fig. 8, crystal surface of cutting at upper position of 7cm show more low pore and smart shape than that of lower position(3cm). It tend to crystal quality increase to rise upper position from bottom to top.

3.2 Electrical properties

Generally, it is bridge style sample shape for Hall effect measurement but if its thickness is constant Van der Pauw method[13] can be test of for any shape. Therefore electrical property of grown InP crystal was investigated by Van der Pauw method. When Hall effect is electric field, E=-Bv, Hall voltage of V_H which have one directional electric field is considered

$$V_H = f \frac{BI}{qwtp} d_y = \frac{BI}{qtp} \text{ ------------(1)}$$

If Hall coefficient R_H is defined as follow

$$R_H = \frac{tV_H}{BI} \ (m^3/C) \text{ ------------------(2)}$$

electron and hole concentration are

$$p = \frac{1}{qR_H} \qquad n = \frac{1}{qR_H} \text{ ------------(3)}$$

respectively. also Hall movility

$$\mu H = \frac{|RH|}{\rho} = |RH| \sigma \text{ ----------(4)}$$

Therefore, semiconductor type, resistivity, conductivity, carrier concentration and Hall mobility could be obtained from given thickness(t) and measured Hall coefficient(R_H). From this results, grown InP crystal was n-type semiconductor and it is caused by donor carrier which formed from impurity in crystal. This could be consider formation of impurity as 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 3000~2000cm^2/Vsec depend on carrier concentration, according as carrier concentration was increased to 10^{15}~10^{16}cm^{-3}. This is caused collision dispersion of carriers in lattice by impurity which was formed by concentration increment. Fig. 8, 9 and 10 show the results for electron mobility, conductivity and resistivity in range of 150~300K respectively. In Fig. 8, value of electron mobility was decreased from 3×10^4cm^2/Vsec to 2×10^3cm^2/Vsec with temperature increment. This may be caused that lattice scatter was intensed depend on temperature rising. Fig. 10 show change of resistivity and carrier concentration as a function of temperature, respectively. The value of resistivity increase from 2×10^{-1}cm to 2×10^{-3}cm as to increase temperature and this may be caused that carrier concentration increase with temperature increment.

4. Conclusions

Results for growing experiment of InP single crystal which is important as substrate materials for semiconductor device as follow.

1. Growing conditions of InP single crystal were that melting and vaporizing temperatures are 1100℃ and 450℃ cooling rate is 2℃/hr in range of 1070~900℃ and rotation speed is 5 rpm.
2. Growth characterization of InP single crystal are that transverse section to the growth direction is (111) plane and crystal quality is more better that of upper zone than lower zone.
3. From the result of Hall effect measurement, grown InP crystal shown n-type semiconductor, and carrier concentration, electron mobility and relative resistivity were 10^{17}~10^{19}cm^{-3}, 2×10^3~3×10^4cm^2/Vsec and 2×10^{-1}~$2\times10^{-3}\Omega$cm in range of 150~300K, respectively.

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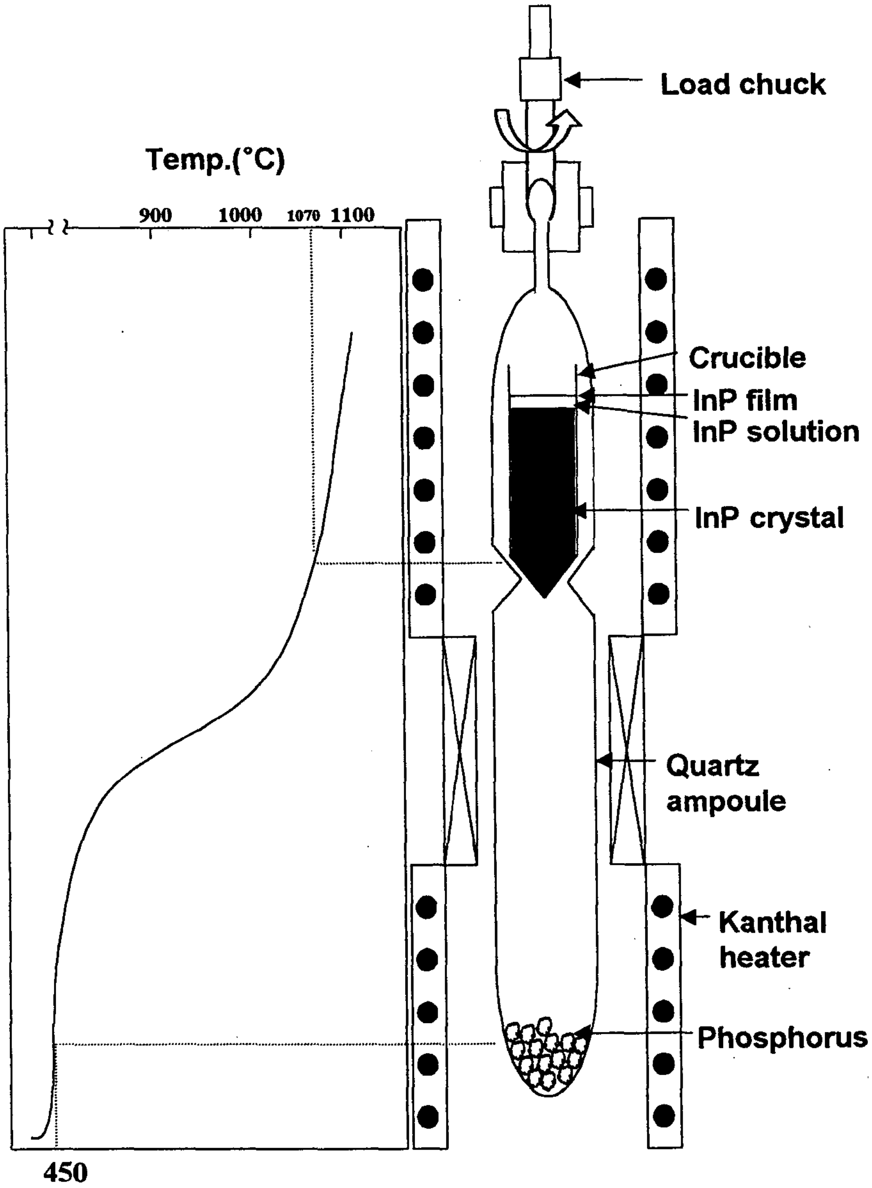


Fig. 1 Temperature profile and schematic diagra of the crystal growth aparatus

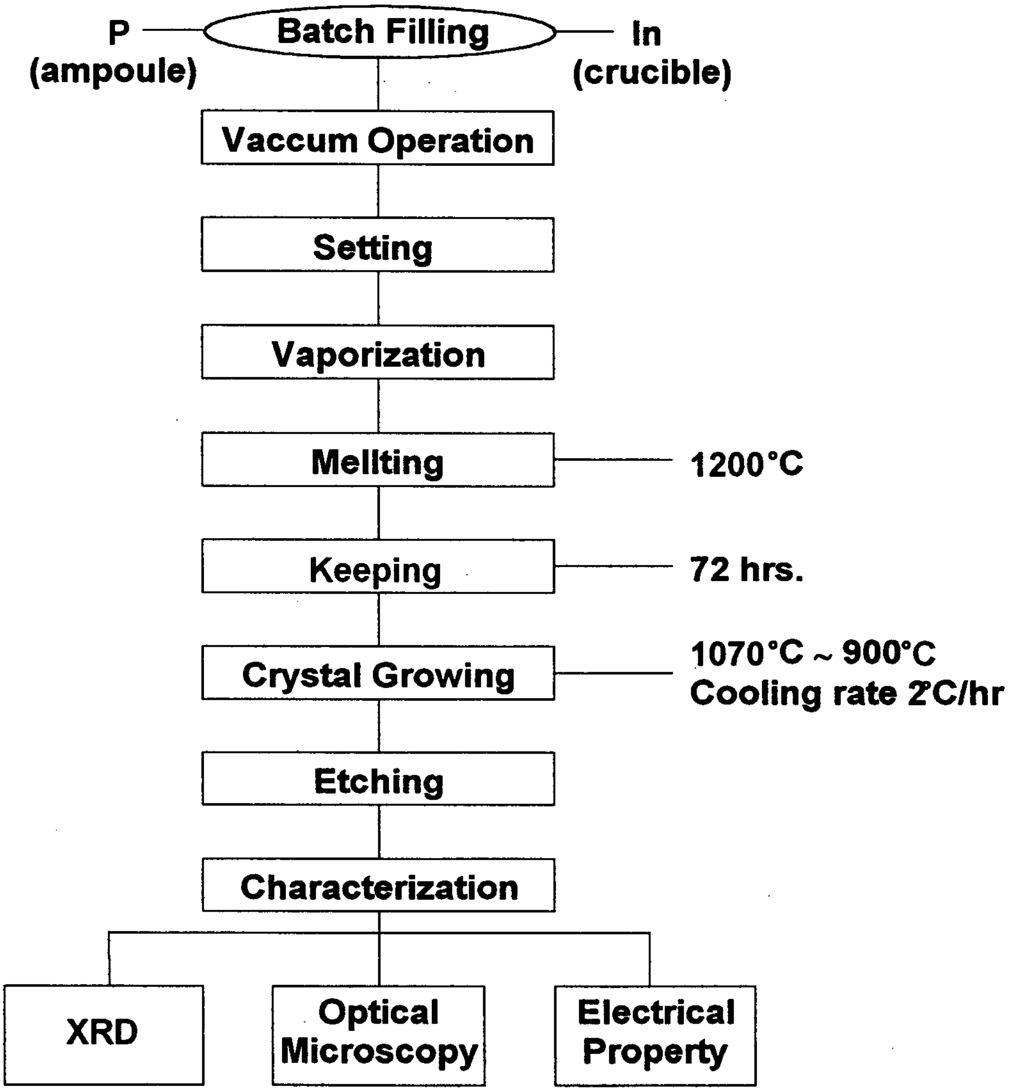


Fig. 2 Procedure for InP crystal growth

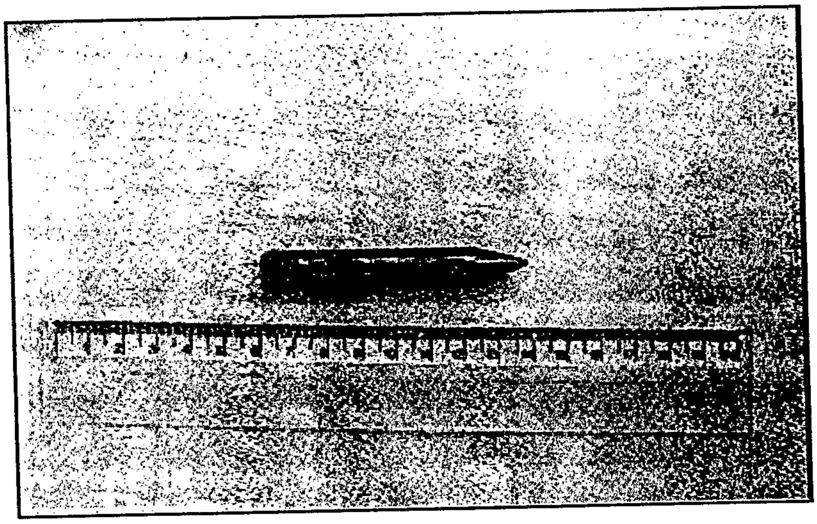


Fig. 3 Crystal ingot grown by VGF method

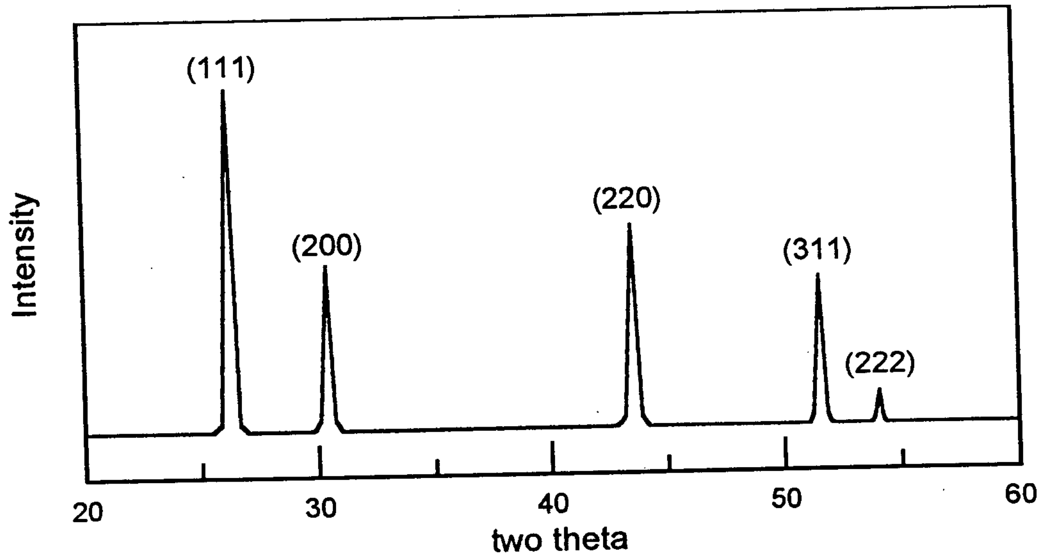


Fig. 4 XRD pattern of InP crystal powder

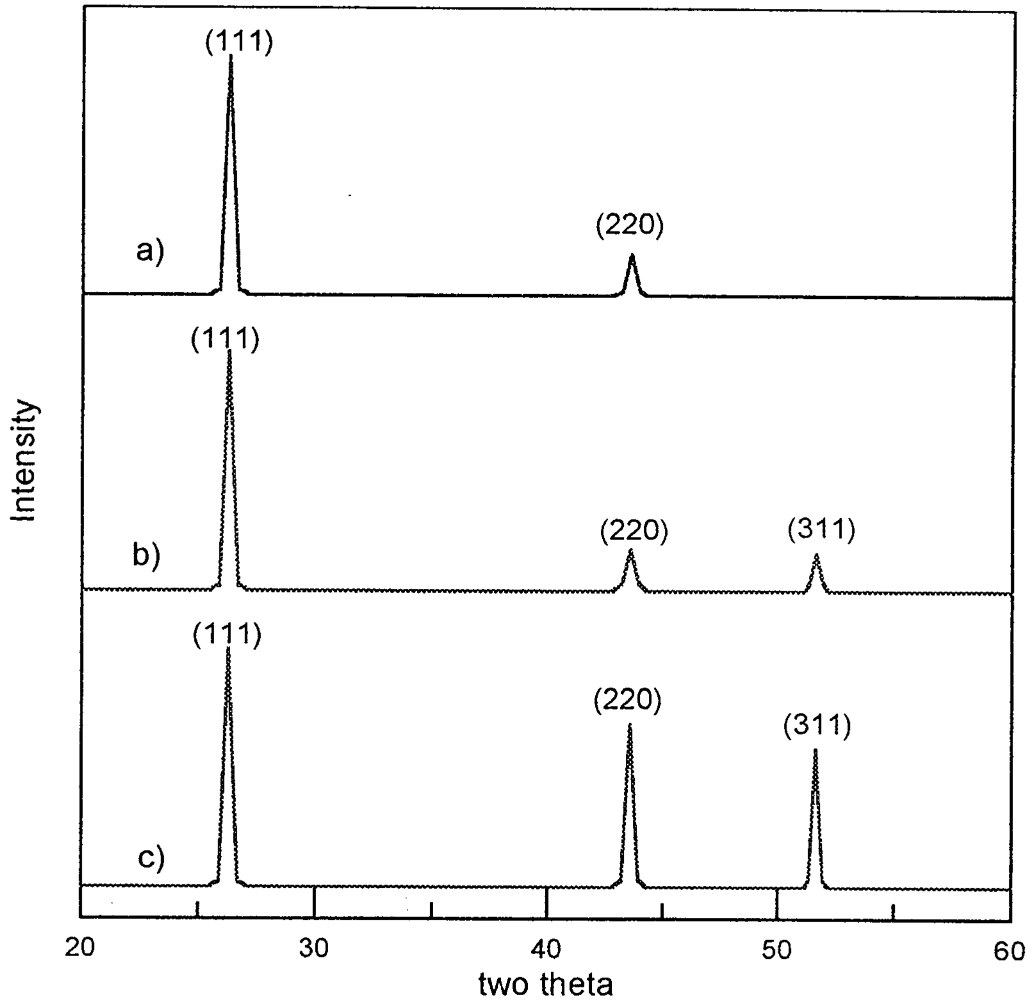


Fig. 5 XRD patterns of transverse section of crystal grown at 1070℃ when cooling rate is 2℃/hr and rotation speed is 5rpm a) 6cm, b) 4cm and c) 2cm from first solidified position

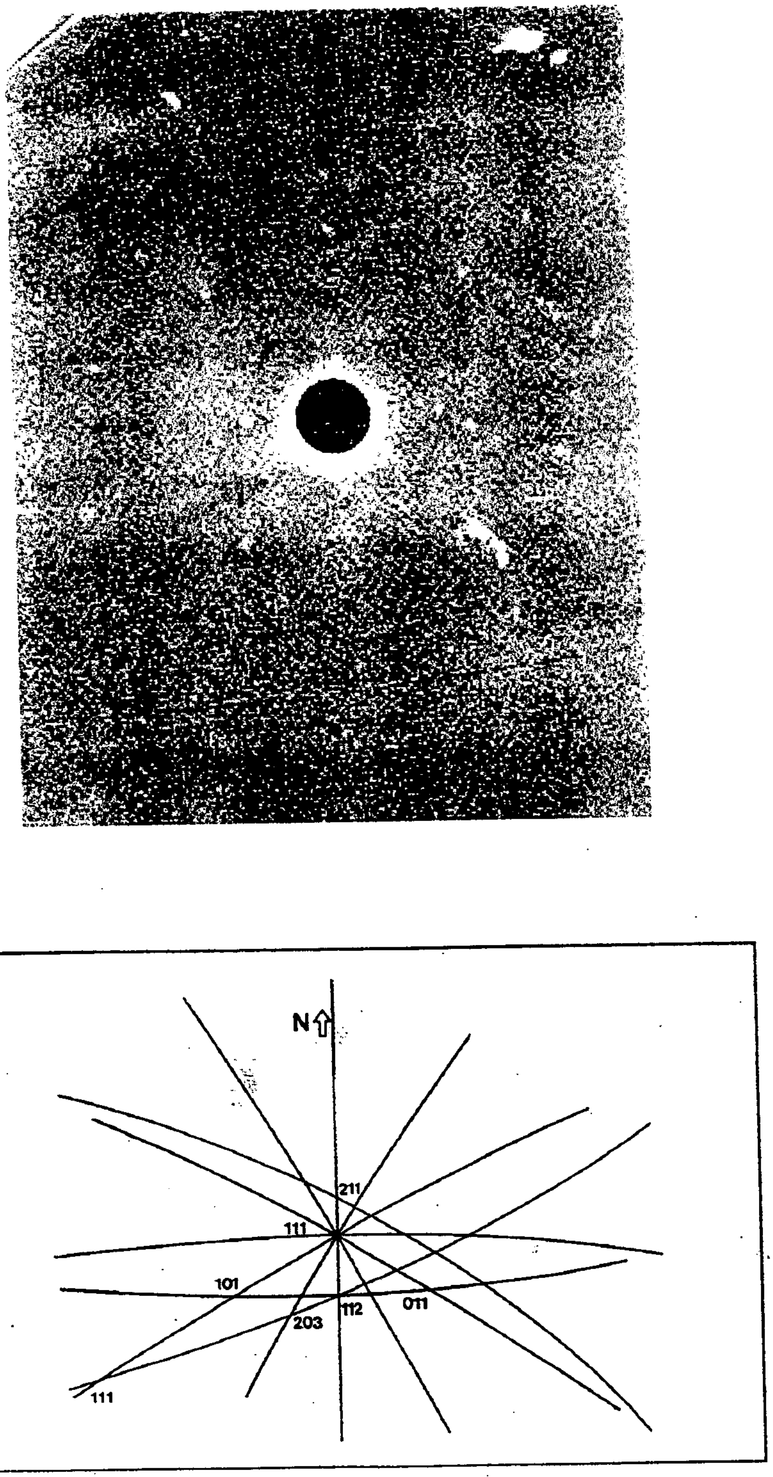
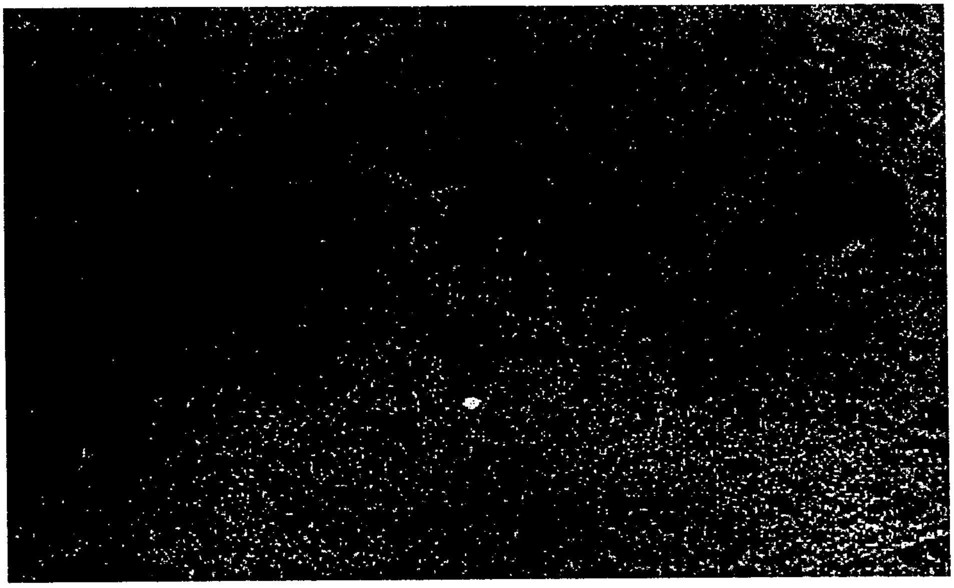
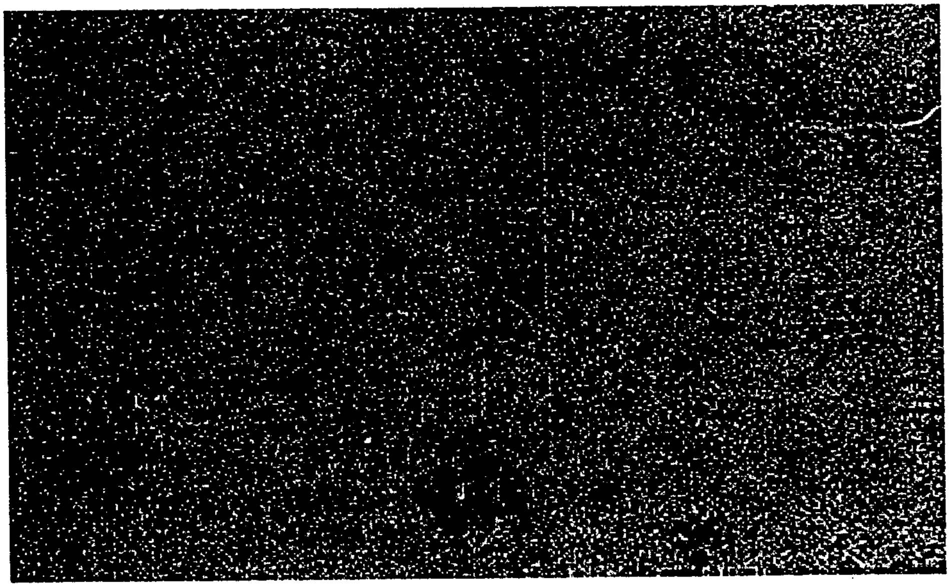


Fig. 6 Back Laue pattern(up) and stereo projection (down) of (111) plane of InP crystal



(a)



(b)

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

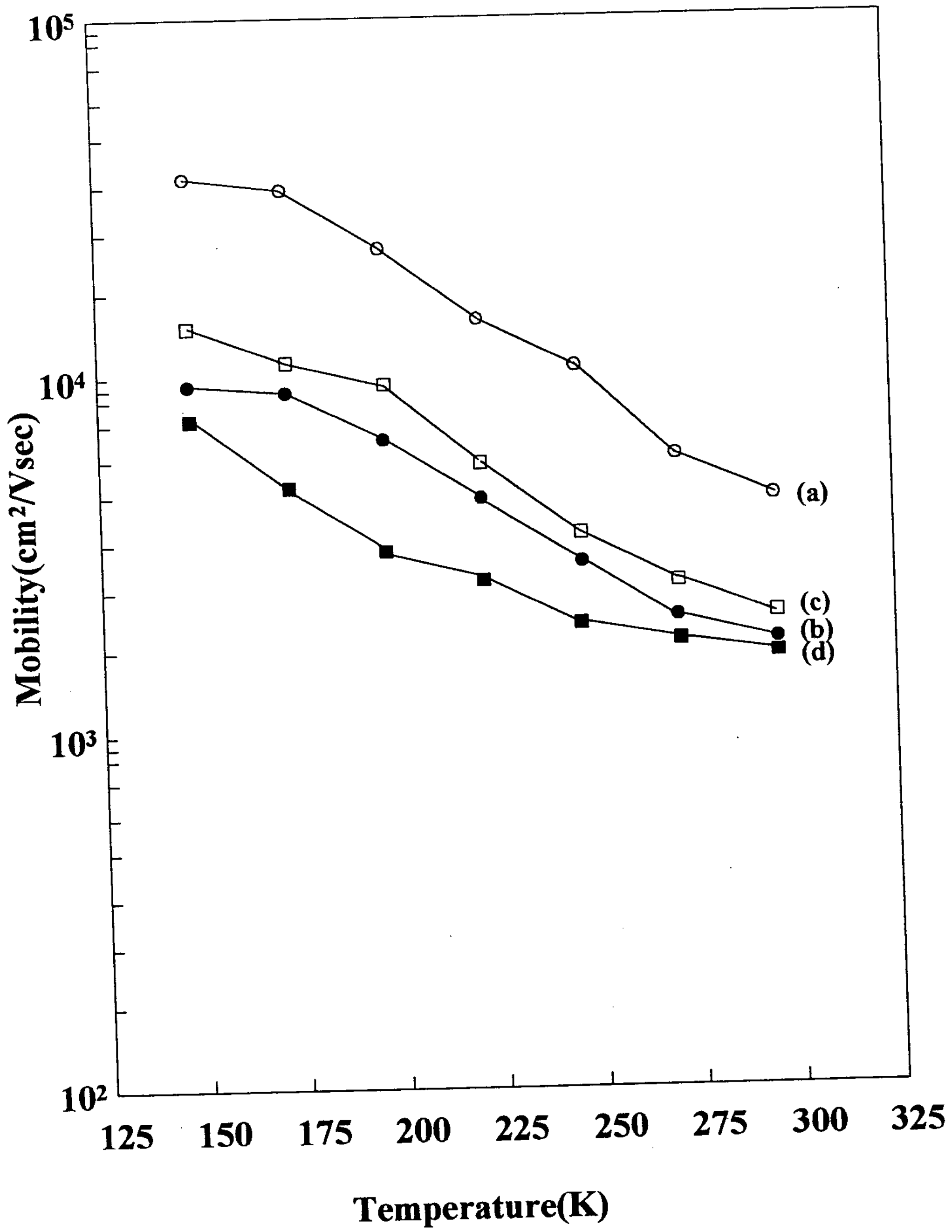


Fig. 8 The relationship between electron mobility and temperature