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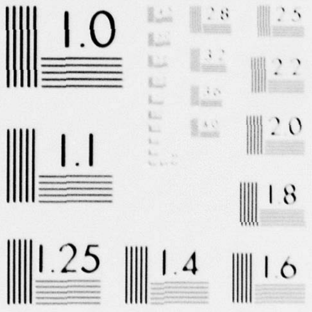
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19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Indium phosphide
Single crystal
High purity
Polycrystalline
Low defect density

10 to the 14th power

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Extremely high purity polycrystalline InP was prepared from solution, having background carrier concentration of 4×10^{14}/cc and mobility at 77°K greater than 90,000. When this material is used for the growth of undoped single crystal it results in $N_{(D)}-N_{(A)} = 1 \times 10^{15}$/cc and mobility = 53,000. Low temperature PL also indicate both materials to be of extremely high purity. Preliminary results indicate that doping of single crystal InP by Sn, Fe and particulary Zn results in improved defect density.

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10 to the 15th power

SUMMARY

Growth of polycrystalline InP from solution can be reproducibly prepared in 450-g ingots. The material is of extremely high purity, based on van der Pauw and low temperature photoluminescence measurements. The growth process is capable of growing InP at a 2 cm/day rate. Increase of the growth rate to greater than 2 cm/day results in undesirable nonstoichiometry levels, detrimental in the growth of single-crystal InP by liquid encapsulation Czochralski (LEC). LEC-grown InP crystals when undoped exhibit extrmely low background carrier concentration $<1 \times 10^{15}$/cc and mobilities at 77°K greater than 53,000 cm^2/V-sec. This represents the highest purity single-crystal InP reported. The effect of doping on structural imperfections of single crystals has been investigated for Sn, Fe, and Zn; in every case a decrease was observed in dislocation density compared with the undoped crystals, and particularly the Zn-doped crystals were practically dislocation-free for doping levels of 2×10^{18}/cc.

1. INTRODUCTION

This program was originally aimed at investigating the growth properties of polycrystalline and single crystal InP. The InP growth technology is very similar to that of GaP which, at the time this program was initiated was fairly well developed. There were a number of distinct differences originating from the device applicability of each material. GaP is exclusively used for visible light emitting diode (LED) fabrication, while InP is used for a wide variety of optoelectronic and microwave applications. The requirements for crystal perfection and electrical properties are far more demanding for InP compared to GaP, therefore; the growth processes from polycrystalline synthesis to single crystal growth was investigated bearing in mind device application requirements.

This research effort resulted in the development of processes for the growth of high purity polycrystalline InP from In solution, growth of high resistivity Cr doped and Fe doped single crystals InP and growth of practically zero dislocation p^+ Zn doped single crystal InP.

Characterization of the bulk crystals included:
a) Van der Pauw, b) photoconductivity, c) photocapacitance, d) optical microscopy, x-ray transmission topography, and photolumincise measurements.

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2. DISCUSSION

Under this program the growth parameters have been established for the preparation of polycrystalline InP from In solutions. The system is a horizontal Bridgman reactor consisting of two 36 inch resistance heated furnaces each controlled separately to produce the profile shown in Fig. 1. The low temperature furnace controls the partial pressure of P during the reaction. The temperature dependence of the partial pressure of commercial red P has been determined by Bachmann and Buehler[1] and is given by

$$\mathrm{InP(atm)} = (10.8 \pm 0.4) \times \frac{10^3}{T} + 16.5 \pm 0.6 \qquad (1)$$

They have experimentally determined the P-T relationship for commercial red P procured from various vendors. It is believed that the error limits of equation 1 represent the processing differences among suppliers rather than the irreproducibility of the P-T relationship based on the product of a single supplier. Experimenting with P from different suppliers we found that the best quality with respect to purity and density is from MCP Ltd. The original system was capable of synthesizing approximately 500 gm per run -- typically the travel rate of the reactor was limited 1 cm/day so that the ingot shown in Fig. 2 required 30 days for complete growth. Attempts to increase the charge size failed; however increase of the travel rate to 2 cm/day resulted in material slightly more nonstoichiometric compared to ingots grown at 1 cm/day rate.

Single crystal growth was carried out by the standard LEC process. Typical ingots weighed 350 gm, with diameters 1.2 - 1.4 inches. N, p and insulating crystals have been prepared. There exists an apparent correlation between doping species and density on the dislocation density of InP. Fig. 3 shows a comparison of the representative defect

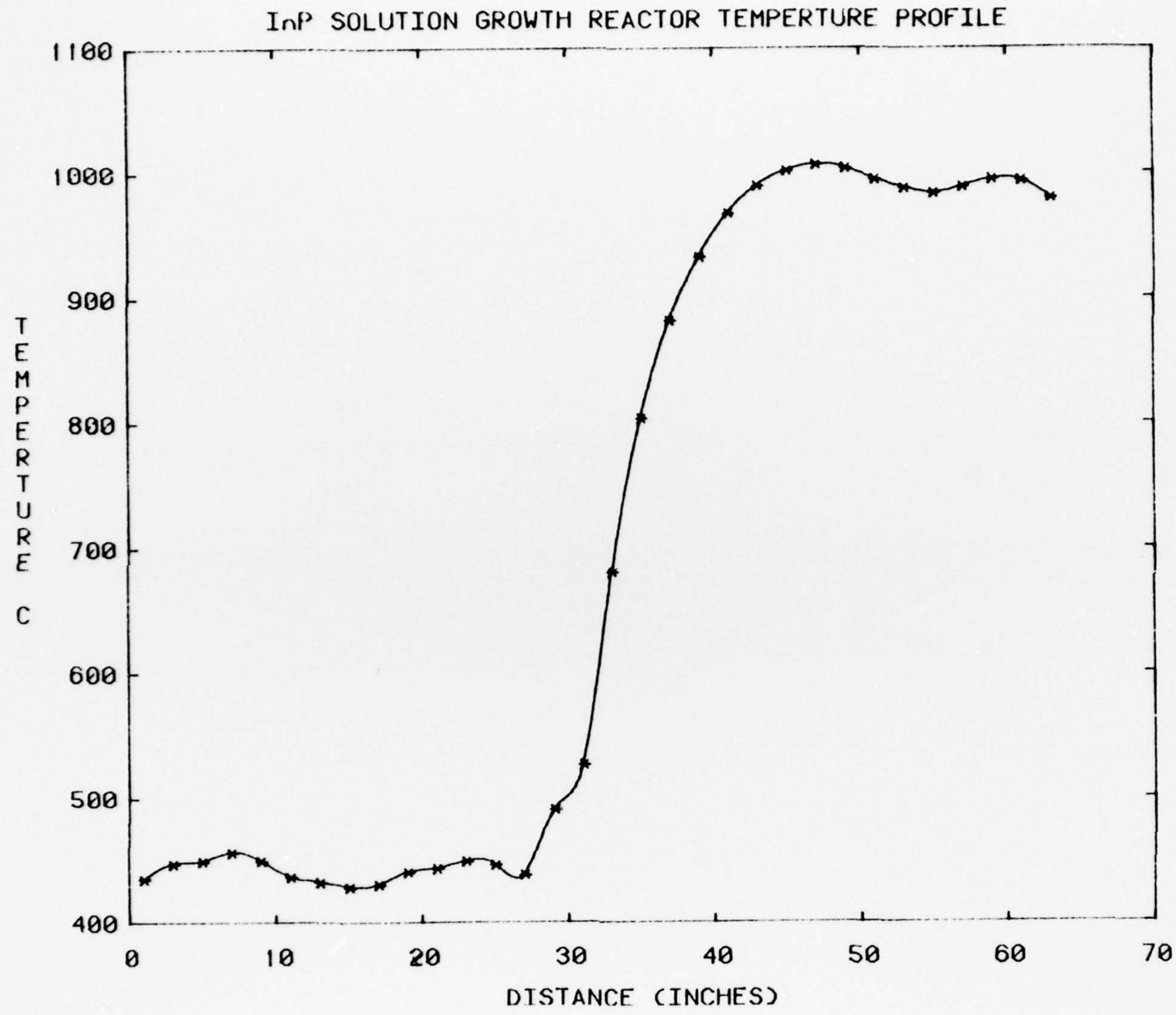
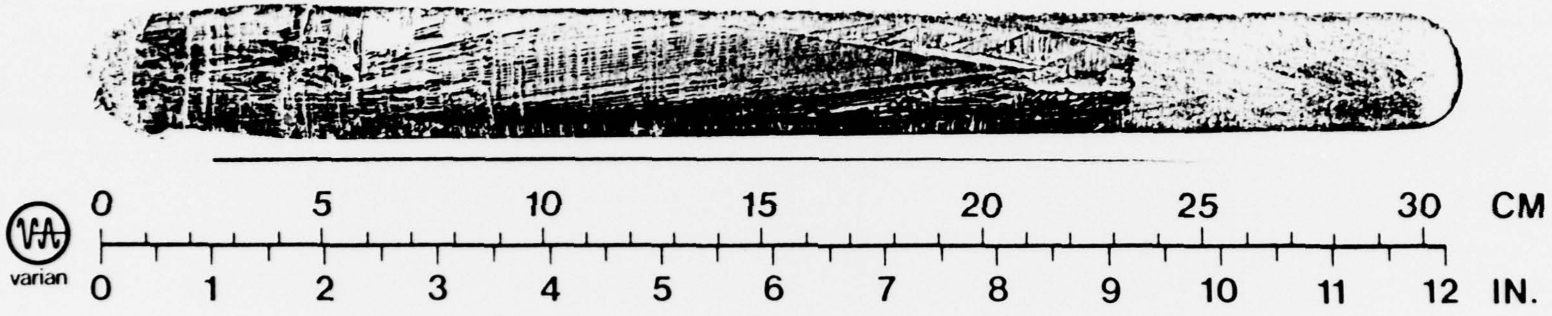
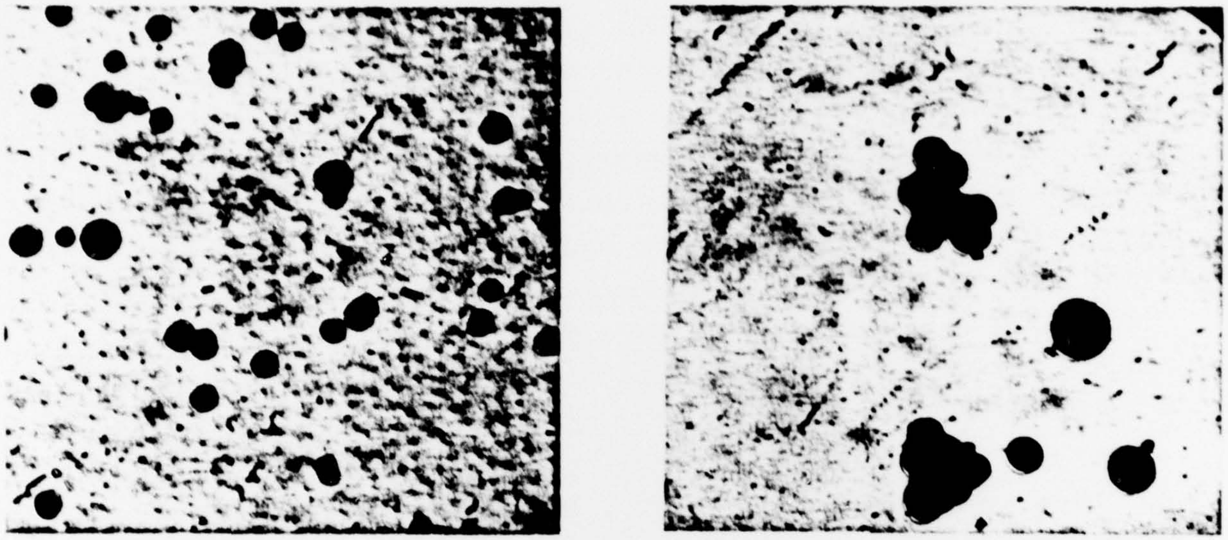


Fig. 1. Typical temperature profile in the horizontal reactor for the solution growth of polycrystalline InP.

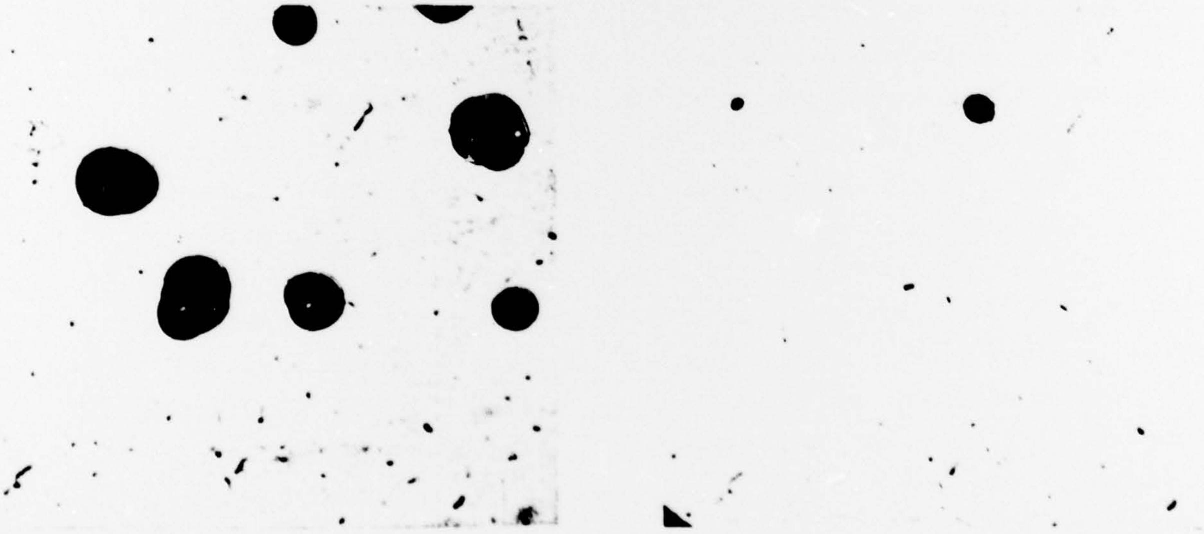


<u>Fig. 2</u>. Photograph of a 430-g polycrystalline solution-grown InP ingot.



(a) Undoped (IPC#50).

(b) Tin-doped (IPC#51).



(c) Iron-doped (IPC#55).

(d) Zinc-doped InP crystals (IPC#56).

Fig. 3. Low magnification (300x) photomicrographs of dislocation etch pits in representative areas of wafers.

densities of four crystals. The undoped crystal had the highest dislocation density, followed by the Sn doped crystal which exhibited, in addition to individual dislocations, appreciable dislocation clustering. Fe doped material exhibited even lower dislocation density with practically no clustering. Since, however the distribution coefficient of Fe is very low in InP, continuous enrichment of the melt during growth results in the precipitation of a second phase identified as FeP[2]. Zn incorporation has the most pronounced effect on dislocation density. Crystals doped to levels in excess of 1×10^{18} had extremely low dislocation densities. In some instances the dislocation density was effectively zero, including the region close to the crystal surface.

The electrical properties of the polycrystalline material were characterized by Van der Pauw, photoluminescence and photoconductivity measurements. Table I shows the results of electrical characterization for a polycrystalline ingot VA-GF #2, a single crystal (IPC #17) prepared with commercially purchased polycrystalline InP and IPC #41 prepared with in-house prepared polycrystalline InP. It is obvious that for both VA-GF #2 and VA IPC #41, there appears to be a tendency for improvement of the electrical properties during the solidification process. This is characteristic in a process where the distribution coefficients of undesirable impurities are greater than unity. Such an impurity, commonly found in InP compounds, is Si, which has a distribution coefficient of 30[3]. Since most undesirable impurities normally have distribution coefficient lower than unity, the background carrier density increases during solidification -- as in the case of IPC #17 which was prepared with commercially purchased polycrystalline InP. In order to determine the purity and compensation ratio of the crystal, the mobility and free

TABLE I

RESULTS OF ELECTRICAL CHARACTERIZATION

	μ (cm^2/V-sec)		(N_D-N_A)/cc		N_D^+/cc	N_A^-/cc
Sample No.	300°K	77°K	300°K	77°K		
VA-GF #2 (first)	5282	76680	$8.5\text{x}10^{14}$	$8.1\text{x}10^{14}$	---	---
" (middle)	5870	85960	$4.4\text{x}10^{14}$	$4.2\text{x}10^{14}$	---	---
IPC #17(top)	4930	23240	$5.7\text{x}10^{15}$	$4.9\text{x}10^{15}$	$7.4\text{x}10^{15}$	$2.5\text{x}10^{15}$
" (bottom)	3410	15620	$5.5\text{x}10^{15}$	$7.0\text{x}10^{15}$	$1.4\text{x}10^{16}$	$7.1\text{x}10^{15}$
IPC #41(top)	4671	42645	$2.3\text{x}10^{15}$	$2.1\text{x}10^{15}$	$2.6\text{x}10^{15}$	$5.3\text{x}10^{14}$
" (bottom)	4664	52793	$1.1\text{x}10^{15}$	$9.7\text{x}10^{14}$	$1.4\text{x}10^{15}$	$3.9\text{x}10^{14}$

electron concentration were compared with the theoretical calculation of Rode[4]. Fig. 4 shows the mobility at 77°K as a function of free electron concentration for various compensation ratios. The highest purity and lowest compensation ratio were exhibited by the polycrystalline material obtained from the middle section of the ingot. For the single crystal growth the lowest compensation material was from the bottom of IPC #41. The electron concentration in this crystal does not vary with temperature (300 to 77°K) within experimental error. This indicates that the donor levels are very shallow, since lower temperature does not cause appreciable donor deionization. The electron mobility varies with a power of the absolute temperature around 2.2 in the temperature range 130-300°K as shown in Fig. 5. Similar variations of mobility with respect to temperature have been reported by Glickman and Weiser[5] for n-type InP single crystals. There the mobility was analyzed in terms of two dominant scattering mechanisms (lattice and ionized impurity scattering), assuming a variation of T^{-2} for the lattice scattering as observed in their purest crystal with LN mobility = 23400 cm^2/V sec.

The quality of the above high purity InP (See Table I.) has also been estimated from high resolution examination of exciton radiative recombination by low temperature (1.8°K) photoluminescence measurements, carried out at Wright-Patterson Air Force Base and at the University of Stuttgart. These indicate that, for the first time, bulk-grown crystals (both pholycrystalline and single crystals) exhibit very sharp PL spectra- hitherto typical only of epitaxial material[6] and distinctly show transitions involving donor and acceptor-bound excitons. The PL spectra observed are characteristic of high purity, low imperfection density, strain-free material. It is also interesting to note that low temperature photoluminescence indicates a sharp emission line centered at 1.3605 eV

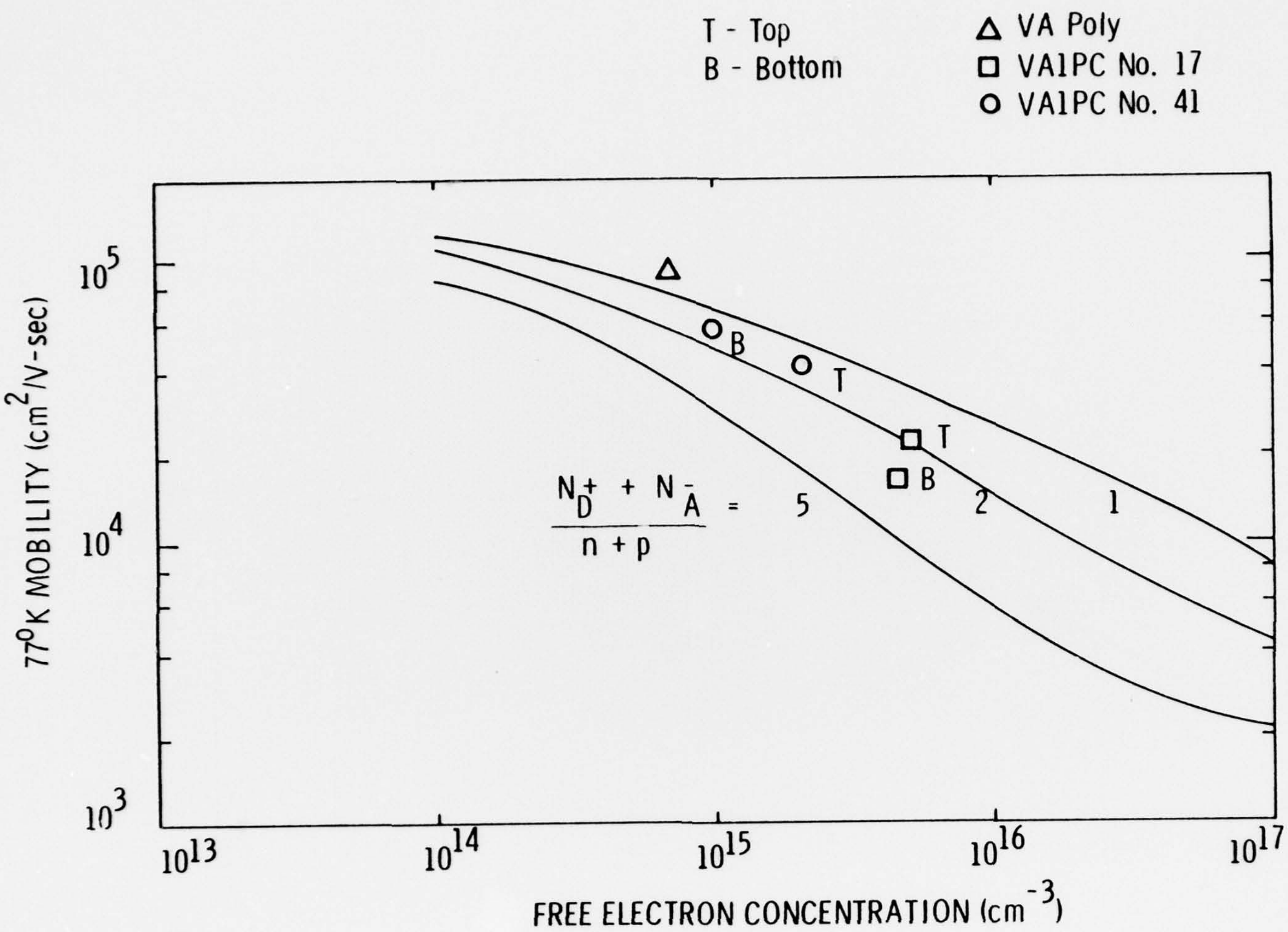


Fig. 4. Variation of LN mobility with free electron density showing a comparison of the experimental data points for different bulk grown n-type InP single crystals with theoretical predictions for three different $N_D^+ + N_A^-/n+p$ ratios (solid curves).

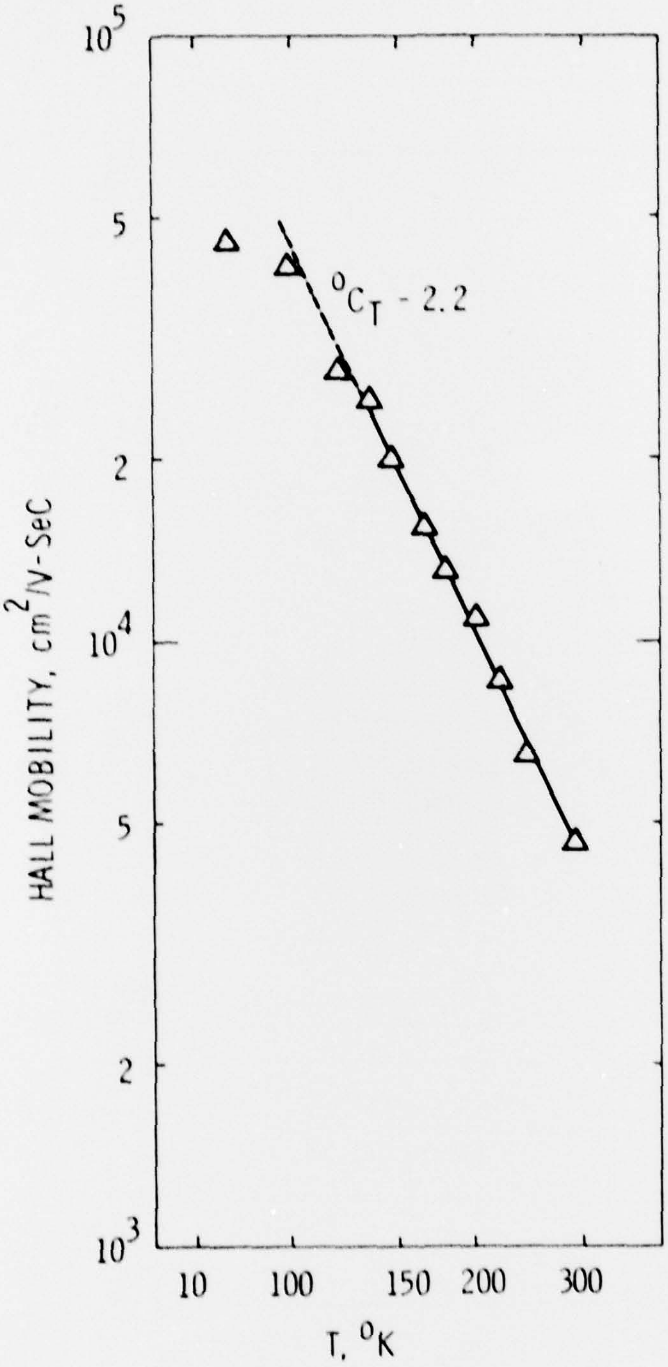


Fig. 5. Dark Hall mobility vs temperature for sample IPC#41.

(E_G = 1.4235 eV) which has not been seen previously and exhibits higher intensity in the first-to-freeze section compared with material from the middle section of the polycrystalline ingot. This could be associated with the Si level, although low temperature photoluminescence of Si doped InP did not reveal such a peak.[1]

3. CONCLUSIONS AND RECOMMENDATIONS

The processes developed under this program for the growth of polycrystalline InP yield high purity material at a slow growth rate. Increase in the growth rate can be accomplished in the present system by increasing the In and P temperatures. This approach should be tried carefully so that the danger of explosions will be minimized. In addition, the effect of the higher reaction temperature on the electrical and photoluminescence properties of the crystals should be investigated.

For single-crystal growth the effect of doping on the defect density of the crystal could potentially become a powerful means to control the defect density. In particular, if isoelectronic impurities such as Ga and/or Al could be incorporated uniformly, low defect density InP crystals of any desired doping level might become available. This development could have important implications in all InP device structures.

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