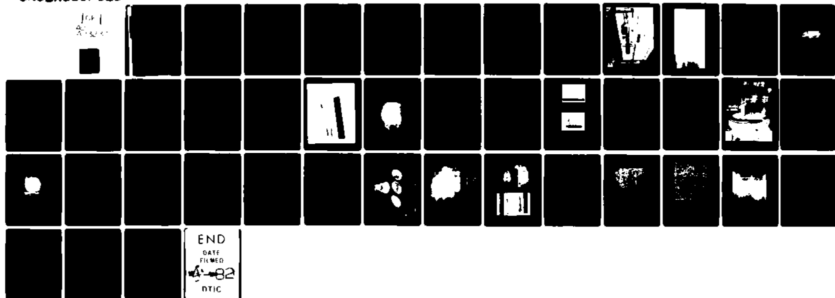
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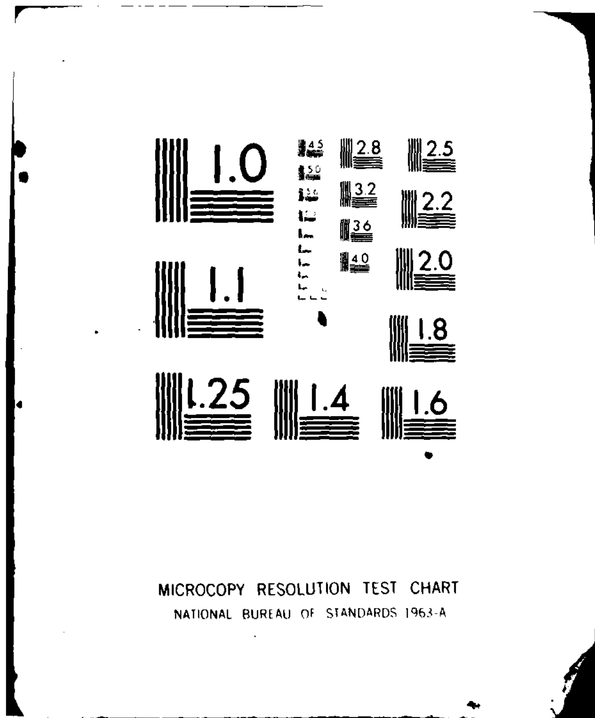
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BASIC IMPROVEMENTS IN SUBSTRATE InP MATERIAL

S. B. Hyder

Varian Associates, Inc.
Solid State Laboratory
611 Hansen Way
Palo Alto, CA 94303

15 January 1982

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Different methods for the synthesis of Indium Phosphide were devised and growths evaluated for photoluminescence, mobility, carrier concentration, and resistivity. Single crystals of InP were grown doped with Fe, Cr, Zn, and S and evaluated by photoluminescence, van der Pauw analysis and X-ray topography.

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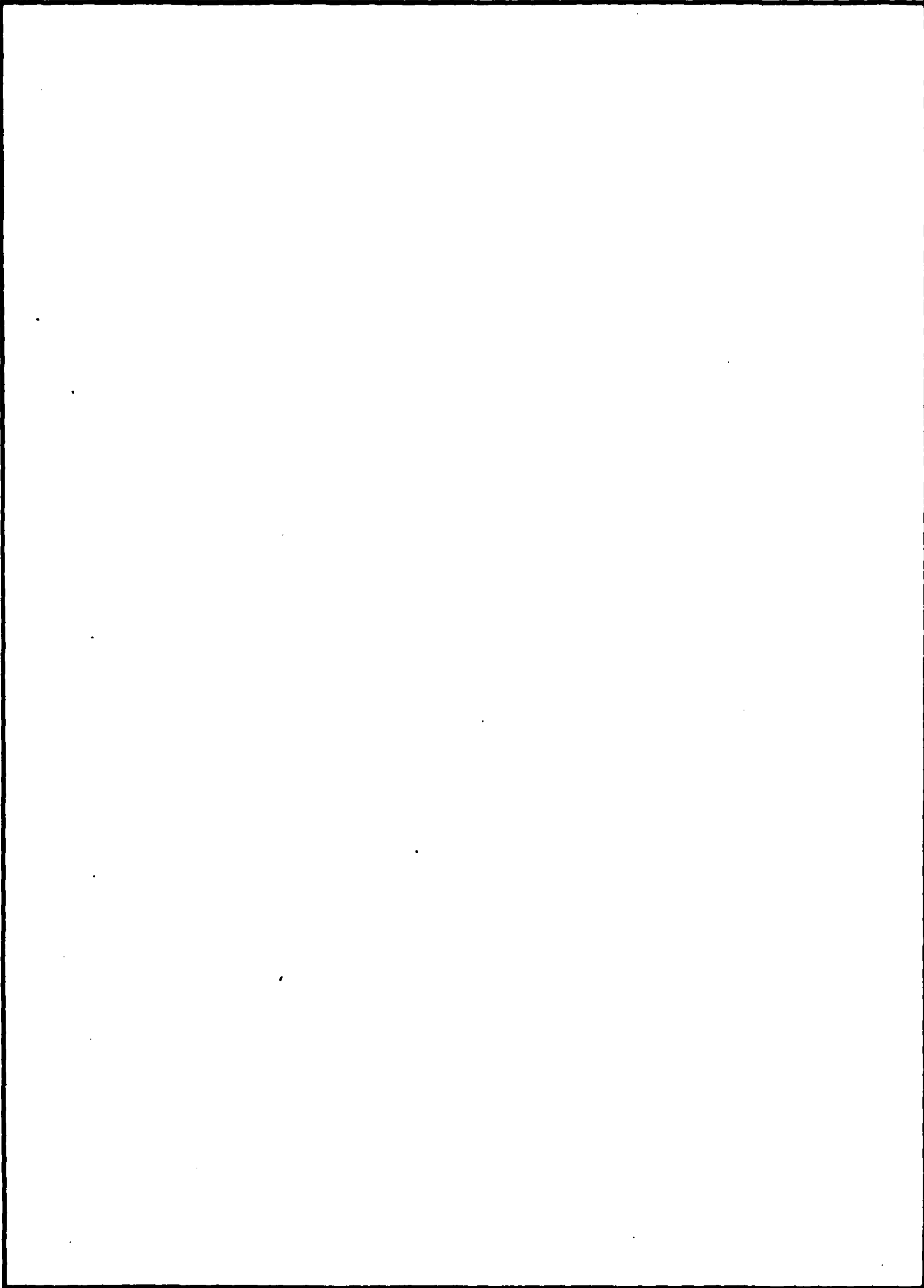

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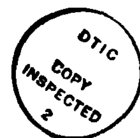

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I. INTRODUCTION

A. Purpose of Research

Among all the III-V compounds, GaAs and InP stand out as the most important for microwave and opto-electronic applications. Synthesis and growth of GaAs is at present well established and is far simpler than that of InP, whose column V component has a high enough partial pressure at the stoichiometric melting point of InP to complicate synthesis. Certain material properties of InP, however, appear to be superior to those of GaAs. InP was found to have a large current peak-to-valley ratio[1] that degrades less with increasing temperature than GaAs.[2] Its high effective transit velocity and fast intervalley scattering also should allow higher-frequency operation in millimeter-wave applications.[3] Current research in microwave devices has confirmed these advantages of InP devices. InP transferred-electron devices have been operated in the 110-GHz range with low noise and high gain[4] and can potentially be operated to 150 GHz. Field-effect transistors can also be made with InP[5] and have a potential of operating in the 60-GHz range without excessive degradation of operating characteristics. The advent of optical fiber communication and with the development of low-loss fibers with optimum properties in the 1.0-1.6 μm region has also increased interest in InP. In this region, AlGaAs/GaAs and silicon devices are not usable, but InGaAsP/InP sources and detectors are admirably suited since they can be grown lattice matched to InP substrates with any desired bandgap. With these varied applications, InP has attracted much attention in recent years and, with research in InP at the threshold of digital and integrated devices, considerably increased demand is envisaged in the near future. A need therefore exists for the study of methods to improve the availability and quality of the material to meet the demand.

B. Background of Problems

Horizontal Bridgman-type gradient freeze method is the commonly-used method for InP synthesis,[6-8] although other methods such as a synthesis solute diffusion (SSD)[9] and an injection synthesis method[10] have also been reported recently. However, the cost of production still remains high, mainly because of the labor costs involved in separate synthesis and single-crystal growth and also the equipment needed to take into account the vapor pressure of phosphorus at the growth temperature, about 27.5 Atm.[11] The lower stacking fault energy of InP also contributes to lower single-crystal yields as the material twins readily during growth. For InP to achieve its highest potential and to meet future demands, it is important to not only improve the quality, but also to improve the availability of this material at moderate cost. This can be done by developing techniques for cost-effective production methods in synthesis and growth of InP. The primary consideration of the present project, therefore, was to investigate new methods of synthesis and growth to achieve this aim.

C. Scope of Work

In this report are described some of the methods investigated for the synthesis of InP with an eye towards a low-cost, commercially-feasible process. Growth of single-crystal InP by the liquid encapsulated Czochralski technique is also described and some material characteristics investigated by means of the van der Pauw analysis and photoluminescence. X-ray topographs of some single crystals are also presented.

Metallic indium from three sources -- namely MCP, Indium Corporation of America, and Mitsubishi -- was used in this work; however, no attempt was made to evaluate the advantage of one over the other, as all were nominally 6-9's pure. However, phosphurus from MCP alone was used as commercial red phosphorus from different sources has been shown by Backman and Buehler[12] to tend to have a wide range of vapor pressures at the growth temperature.

II. BRIEF REVIEW OF SYNTHESIS METHODS IN LITERATURE

Solution growth of InP was suggested as early as 1959 by Wolf, Keck and Broder,[13] and Harman et al.[14] reported synthesis and Bridgeman single-crystal growth of InP in 1958. Richman[15] and Bachman and Buehler[11] later grew InP by the horizontal gradient freeze technique using thick-wall, small-bore fused silica tubing. Antypas,[6] Isler,[7] Barthruff and Benz,[16] and Henry and Swiggard[17] using conventional gradient freeze method and two-zone furnaces produced practical amounts of InP polycrystalline material. However, synthesis near the decomposition vapor pressure was avoided to reduce the danger of explosion and low linear rates of crystallization were used, necessitating increasing the time of synthesis to days and weeks. The problem of high vapor pressure and low yield was solved by the development of the high-pressure synthesis reactor by Metals Research, and Rumsby et al.[8] have reported growth of 1.3-Kgm polycrystalline InP in about 6 hours. Single-crystal growth after a gradient freeze synthesis at high pressure was also attempted by Alred et al.[18] using a high-pressure vessel and quartz bellows attached to the reactor tube so that the differential pressure inside and outside the reactor could be monitored by a transducer and automatically controlled to stay near zero.

Polycrystalline InP was also grown by synthesis solute diffusion method by Marshall and Gillessen[19] and Sugii et al.[9] A sealed vertical arrangement was typically used with the melt held in a conical tube in the top region typically at the temperature of 900°C and P at about 200°C. Synthesis occurred by P dissolution in indium with growth rates of about 1-2 mm per day. However, growth of large amounts of material by the SSD method have not been reported. Between 1 and 1.5 Kgm of InP polycrystalline material was reported to have been grown by Wardell et al.[10] using injection synthesis method described by Fischer[20] for growth of GaP. A vertically-aligned silica system inside an autoclave was used with argon pressure of up to 40 Atm. Phosphorus kept in an ampoule held vertically was vaporized and bubbled through molten indium kept in a crucible and covered with boric oxide.

III. EXPERIMENTAL STUDY & RESULTS OF POLYCRYSTALLINE InP SYNTHESIS

A. Gradient-Freeze, High-Pressure Autoclave Synthesis

At present, the state-of-the-art for polycrystalline InP growth is some form of gradient-freeze synthesis technique with the high-pressure vessel either surrounding the furnace or inside the furnace, and the heating system being either RF or resistance heating. This is necessary because of the high dissociation pressure of phosphorus at the stoichiometric melting point of InP. Use of high pressure reduces the synthesis time significantly. The autoclave synthesis system used at Varian for the synthesis of InP is shown in Fig. 1. A 3-inch diameter, 0.25-inch wall Inconel tube sealed at one end and capped at the other with a nitrogen pressurizing inlet is inserted in a double furnace. The elements In and P are placed in a 36-inch long 42-mm diameter fused quartz reaction tube, In being placed in a fused silica boat (Fig. 2). The In boat can be lined with graphite, if desired, to give a nonstick surface. The reaction tube is evacuated to less than 10^{-6} torr, sealed and placed inside the Inconel tube such that the In boat remains in the high-temperature zone and P in the low-temperature zone of the furnace. The temperature profile at the In end is such that there is a gradient of about 10°C over the 12-inch In boat, sloping toward the P end. The Inconel tube is capped and the autoclave purged with N_2. The In furnace is heated first; when the temperature at the In end reaches about 700°C, the phosphorus furnace is also turned on. The In furnace temperature is stabilized near 1070°C, the melting point of InP; while the P temperature is rising, the autoclave chamber pressure is adjusted to closely match the vapor pressure of P using a "Setra" pressure transducer. The P temperature is stabilized around 540-550°C. Synthesis occurs by the evaporated phosphorus mixing with In, low vapor pressure impurities in P being left behind. The synthesis is allowed to continue for about 5 hours. On cool-down, the In temperature is lowered at a rate of about 10°C per hour until the temperature drops to 20-30° below the melting

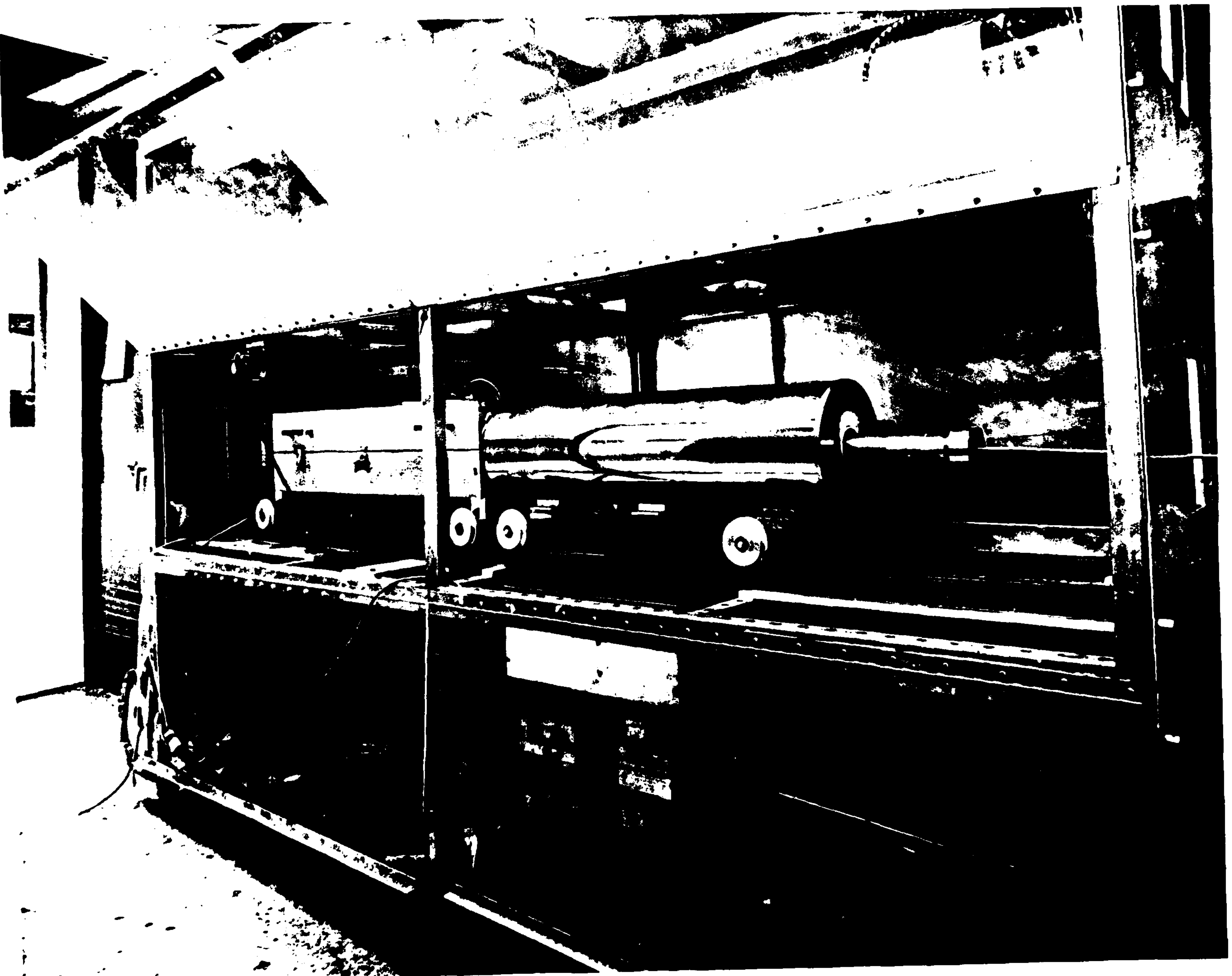


Fig. 1 The high-pressure autoclave synthesis system.

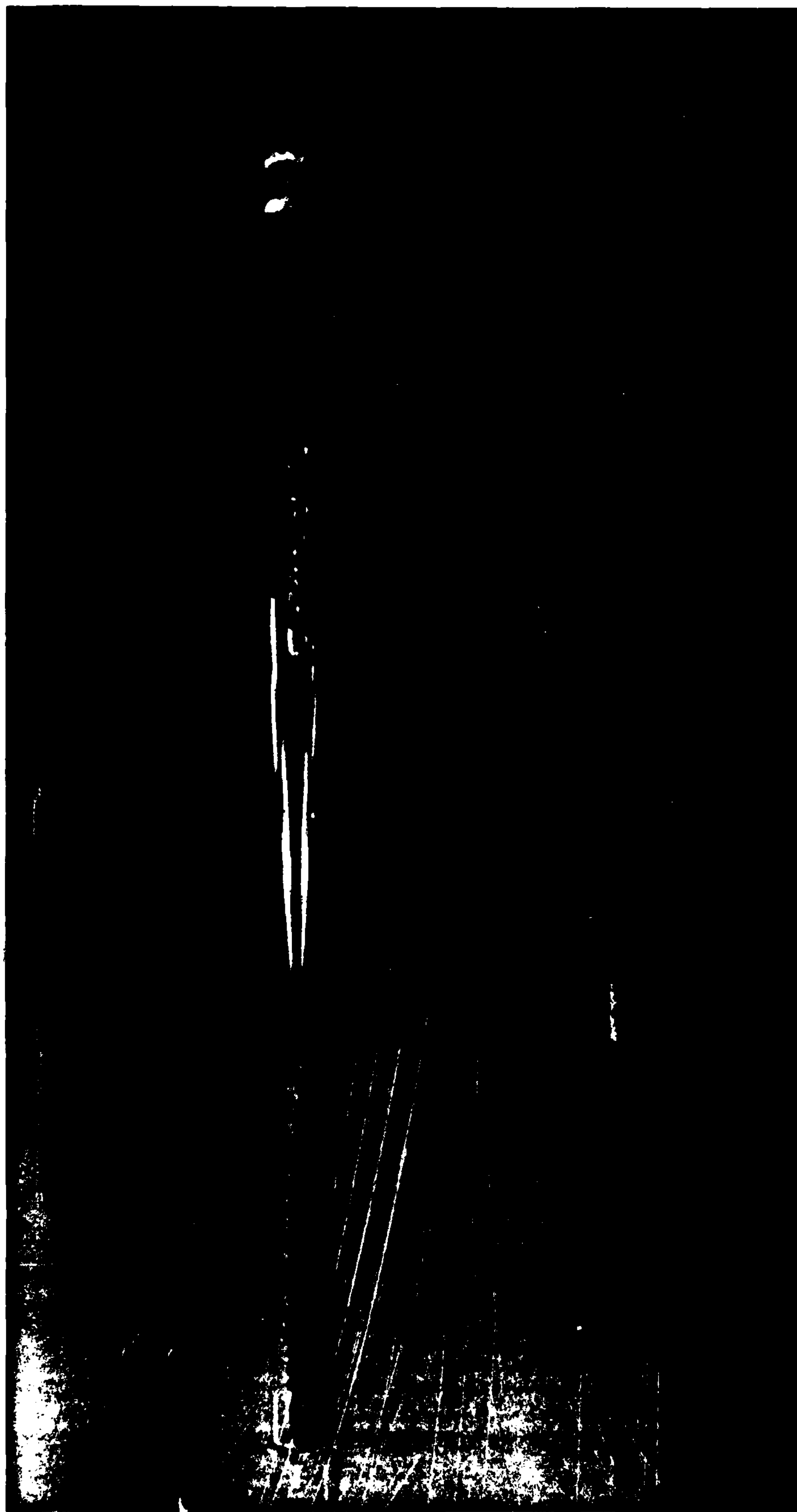


Fig. 2 Reaction tube with In and P used in the autoclave synthesis system.

point of InP. The P temperature during this time is maintained at the synthesis temperature. At the end of this period, both the P furnace and the In furnace are turned off. The decreasing P temperature is again closely monitored and the pressure in the autoclave reduced accordingly, until the P temperature reaches about 450°C with a pressure in the chamber of about 100 PSIA. The system is then left to cool to room temperature. 472 grams to 600 grams of InP poly have been obtained by this method. The material is consistently of good quality with large grains and low background impurity level. The temperature gradient used in the In boat adds to further purification. There is also nearly complete conversion to InP from its constituents.

A section of a typical poly ingot is shown in Fig. 3. The stoichiometry of the charge can be easily adjusted. Stoichiometric amounts (or slight excess) of P are used, as this material gives better mobility than material grown with a deficiency of P, as shown in Table I. In these experiments, In was not baked but was only etched with dilute HCl to remove surface oxides. P was used as received without any purification. Vacuum baking of In can further increase the mobility in this material and reduce its background carrier concentration.

Figure 4 shows a typical photoluminescence spectrum of a InP poly charge formed by the autoclave synthesis method. The sharp bandgap peak and a smaller acceptor peak is seen. Figure 5 shows a P spectrum of an undoped crystal of InP grown from the material obtained by autoclave synthesis for comparison. Only very slight improvement in the acceptor peak shows that this peak is typical of InP material and is usually present even in VPE-grown material whose PL is shown in Fig. 6a. Use of prolonged bakeouts in VPE systems and use of the more expensive and purer AIA indium from Johnson Mathey Co. is the only case when this peak is seen to reduce nearly to background, as shown in Fig. 6b.

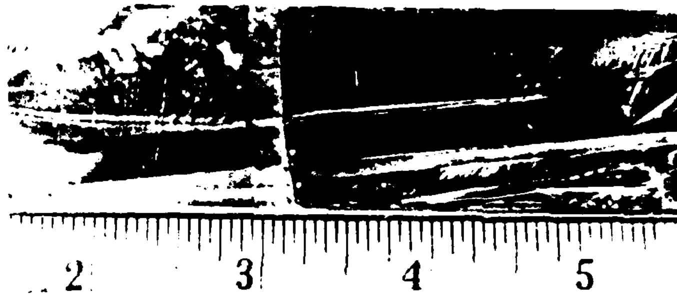


Fig. 3 A section of polycrystalline InP boule produced by the autoclave synthesis method.

TABLE I

Mobility and carrier concentration of InP poly material obtained by the autoclave synthesis method with phosphorus deficiency, stoichiometric amount and excess of phosphorus.

Sample No.	Excess P_4 (gms)	Carrier Concentration (cm^{-3})	Mobility (300°K) $cm^2/V\text{-}sec$	Carrier Concentration (cm^{-3})	Mobility (77°K) $cm^2/V\text{-}sec$
32	- 3.4	1.1×10^{16}	3828	5.5×10^{15}	28150
34	0	3.5×10^{15}	4140	2.9×10^{15}	33000
36	+ 5.97	6.9×10^{15}	4160	5.5×10^{15}	39820

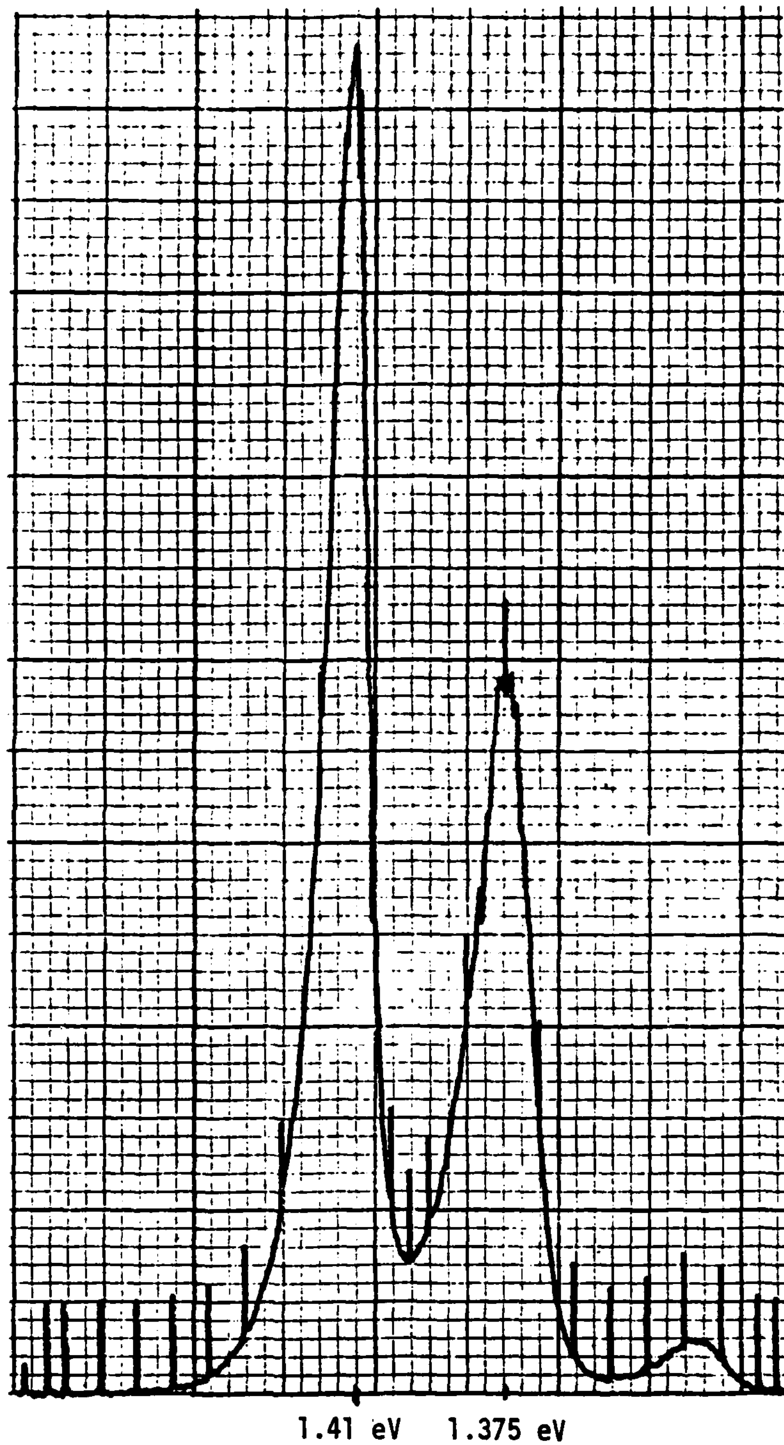


Fig. 4 77°K photoluminescence spectrum of InP poly material produced by the autoclave synthesis.

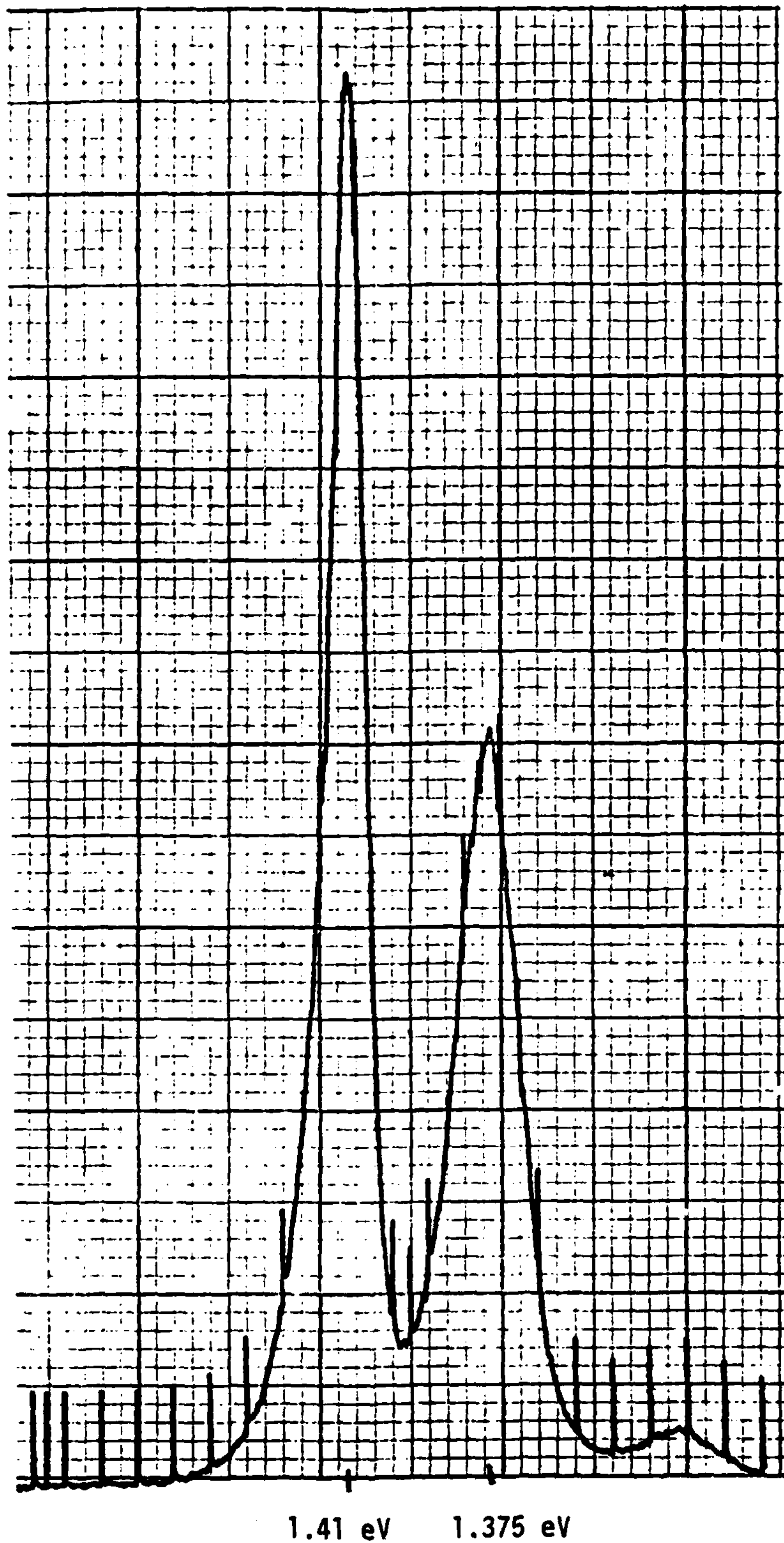


Fig. 5 77°K photoluminescence spectrum of undoped single crystal grown from the poly material produced by autoclave synthesis.

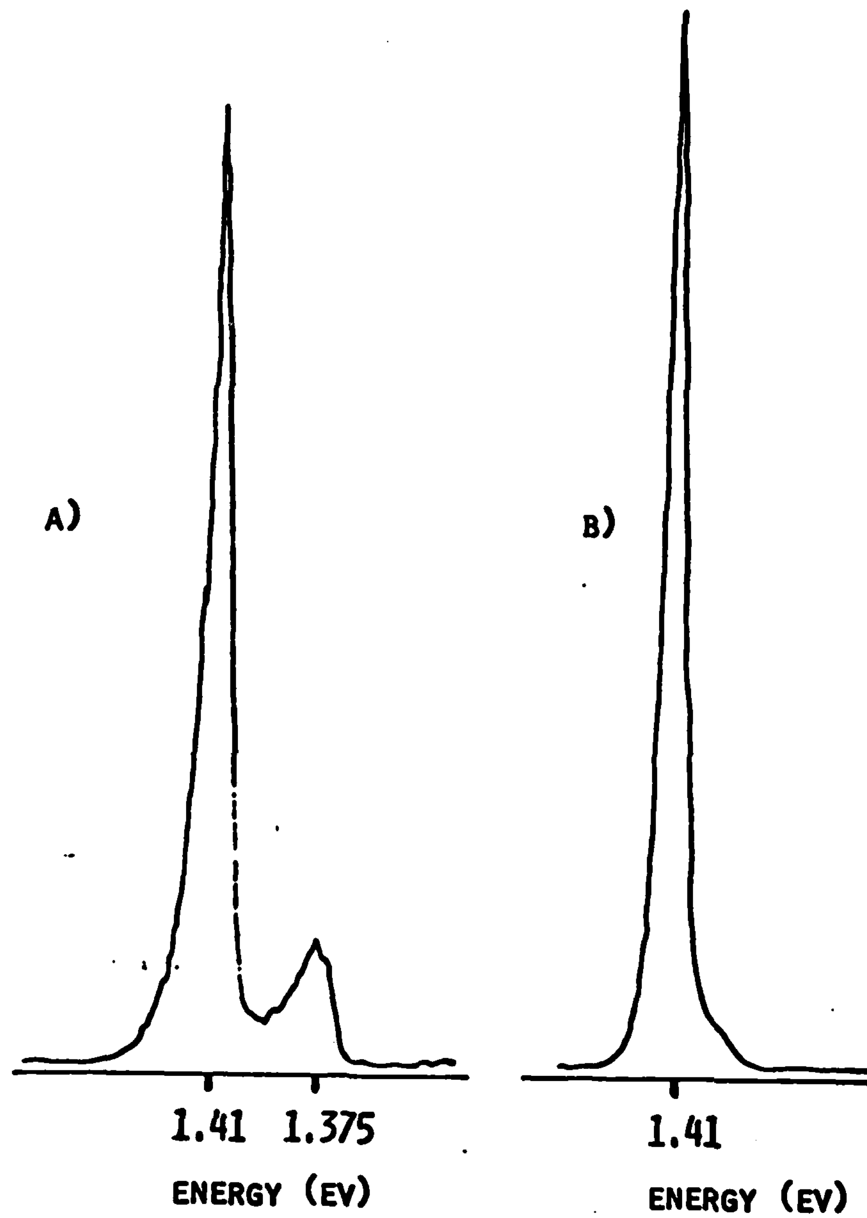


Fig. 6 77°K photoluminescence spectra of InP epitaxially grown layers a) without and b) with extensive bake out.

B. Two-Bulb In-Puller Solute-Diffusion Synthesis

The two-bulb sealed-ampoule in-puller synthesis consists of two bulbs about 3 inches in diameter, connected by a length of smaller diameter tubing. The total length of the ampoule was about 9 inches. The lower bulb contains indium, and this bulb is divided by two tiers of indium trays. The top bulb contains red phosphorus. The ampoule is evacuated to $\sim 10^{-6}$ torr and sealed and placed in the hot zone of the high-pressure crystal puller. The temperature gradient along the vertical geometry of the ampoule can be adjusted by either positioning the ampoule with respect to the picket-fence heater or by use of thermal shielding. Thermocouples are attached close to the phosphorus ampoule and the indium chamber so that the temperatures can be monitored and the chamber pressure adjusted to track the P vapor pressure in the ampoule at different temperatures. In this way the differential pressure is maintained as close to zero as possible. Phosphorus temperatures of 350-450°C with In at ~1070°C were successfully used. At P temperatures near 540°C, frequent explosions occurred as the pressure tracking could not be accurately timed and adjusted. As expected, the growth rate at lower P temperatures was small but fairly good yield, and large crystals were obtained by this synthesis method at a P temperature of 450°C in about 4 hours of synthesis time. Figure 7 shows a two-tier, two-bulb ampoule used in those experiments. Figure 8 is a photograph of the InP poly ingot discs grown by this method using a P temperature of 450°C. The best background doping achieved by this method, as determined by van der Pauw analysis, was $5 \times 10^{15} cm^{-3}$, with a room-temperature mobility of 2950 cm^2/V-sec. Photoluminescence spectra obtained on grains of poly material from the lower tray, however, shows a substantial acceptor peak, as shown in Fig. 9a compared to that from the larger grain on the upper tier in Fig. 9b, indicating some purification on crystallization by segregation of acceptor impurities in large grains.

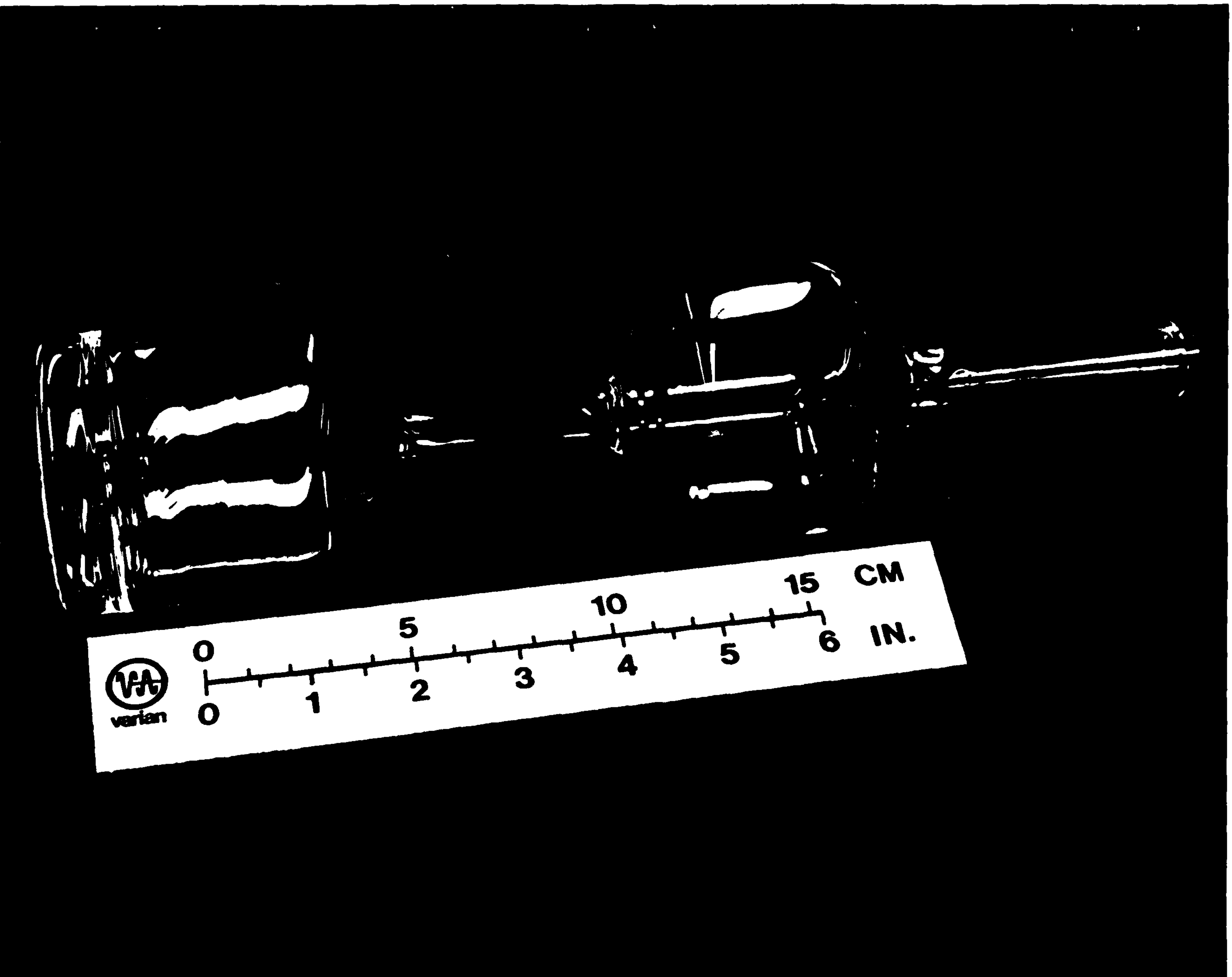
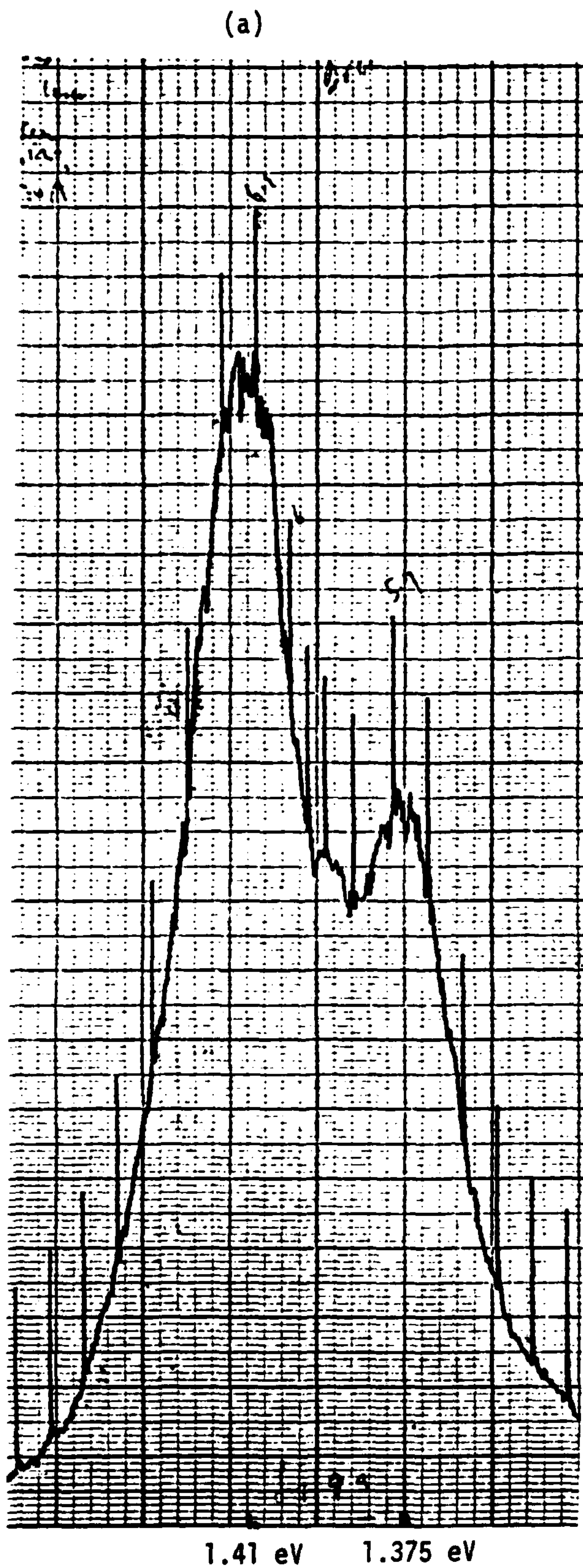


Fig. 7 Two-bulb quartz ampoule used for synthesis by solute diffusion.

Fig. 8 InP polycrystalline ingots grown in the two-bulb ampoule synthesis.



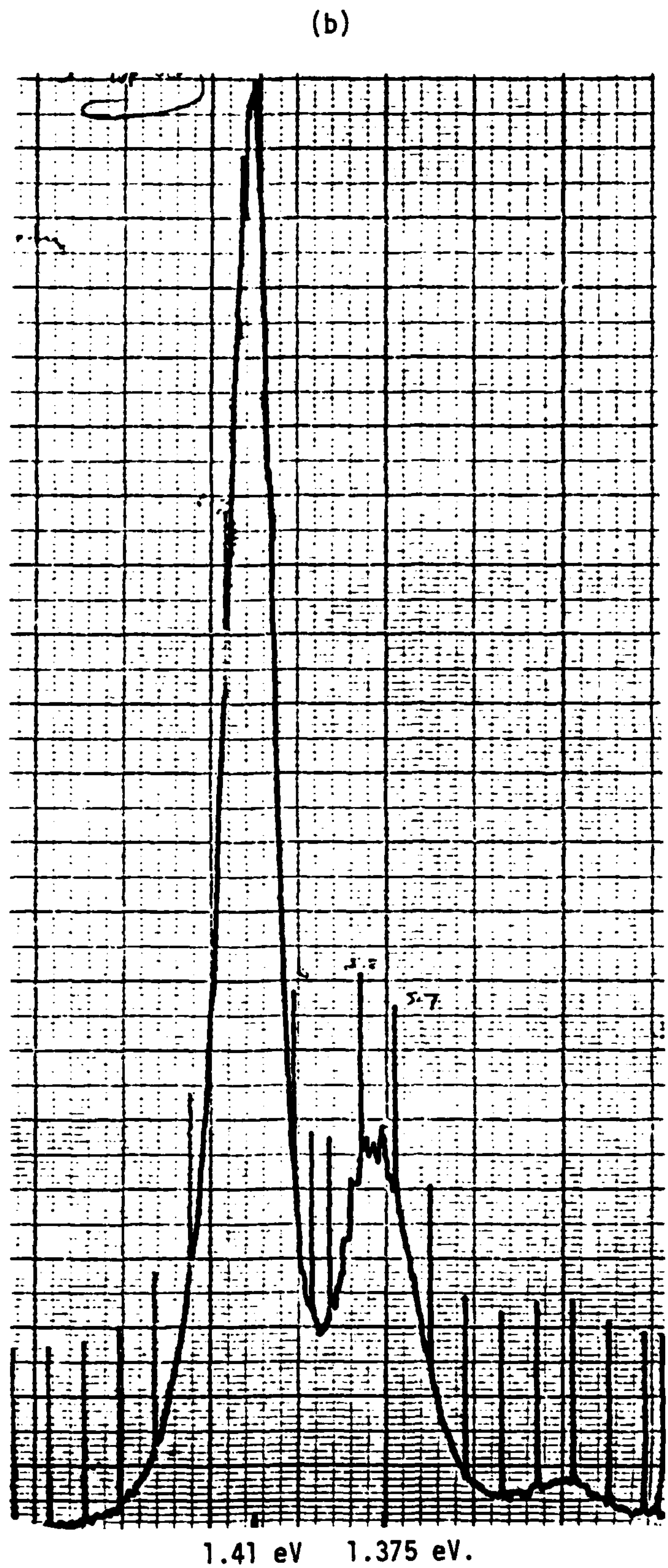


Fig. 9 77°K photoluminescence spectra of poly InP grown by solute diffusion in the (a) upper tray and (b) lower tray.

C. Double-Wall Crucible Insitu Synthesis

Conceptually this synthesis method involves synthesis of the compound by vapor transport of the group V component and allows the growth of single-crystal from the same crucible. GaAs growth was initially made to study the growth behavior with this system. Figure 10 shows the crucible used for synthesis. The open double-wall crucible has two chambers; gallium in chunk form together with B_2O_3 encapsulant material is placed in the lower inside chamber. As_4 chunks are filled in the top chamber through the feed tube. The tube is then sealed and both chambers of Ga and As are at atmospheric pressure as the As chamber is separated from the lower crucible by a skirt about 50-mil smaller than the I.D. of the crucible, to allow passage of As vapors.

The crucible is placed in the high-pressure crystal puller and the chamber pressurized to 200 PSI. The crucible is then heated and the temperature of the Ga and As chambers monitored by two W-W/Rh thermocouples. The upper As chamber is wrapped with fiber-fax to shield As from direct radiation from the heater. The As_4 chamber temperature reaches about 750°C when the Ga temperature is about 1200°C. 300 grams of gallium, 322 grams of As_4 and 110 grams of B_2O_3 encapsulant were used in the first growth run, and the chamber pressure was maintained constant at 200 PSI.

The synthesis was rather rapid and was complete in approximately 1 hour. However, some As_4 was lost to the chamber because of rapid temperature increase of the As_4 chamber and low chamber pressure. After the synthesis, the chamber pressure was lowered to about 50 PSI and the charge cooled to solidification. Some portion of the charge rose up between the two walls because of the 50-PSI left in the chamber; as the As_4 chamber pressure evidently dropped to 1 Atm. as As cooled down. Figure 11 shows the GaAs polycrystalline pellet that synthesized. Single-crystal growth was not attempted because of loss of visibility.

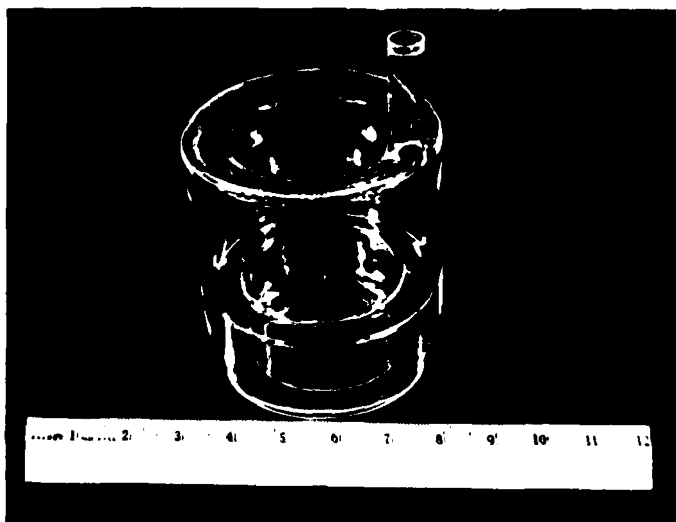


Fig. 10 Double wall injection synthesis crucible.

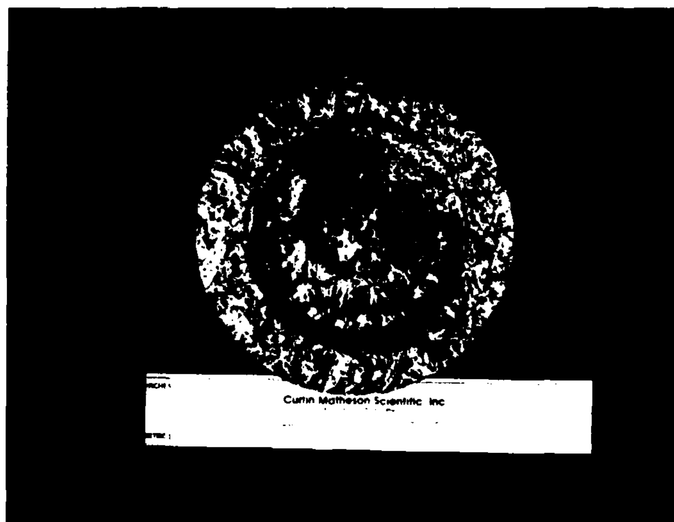


Fig. 11 Polycrystalline GaAs ingot grown in the double wall crucible.

This synthesis method could be fine-tuned to work well with GaAs single-crystal growth by slowing down the synthesis rate to avoid As loss, and has advantage over conventional insitu GaAs synthesis by admixture of Ga and As in that the As vapor transport is used, impurities in the As are eliminated and synthesis takes place at 200 PSI rather than 900 PSI. The major disadvantage for use with InP is that constant high pressure (600 PSI or higher) has to be maintained during growth, but just before cool-down, the pressure in the chamber has to be lowered to near atmospheric pressure. Phosphorus loss in this process can be very large. Therefore, growth of InP is not feasible by this method in its present form.

D. Insitu Injection Synthesis and Growth

The Fischer-Wardill injection synthesis method employs an inverted ampoule of P hung from the seed holder in the high-pressure chamber of a Czochralski crystal puller, with the injection tube from the ampoule dipping in molten In held in a crucible in the hot zone. The P ampoule is lowered into the melt and heated by radiation from the hot zone. A disadvantage of this method is that the mobilities obtained are slightly lower than that observed by the gradient-freeze autoclave method and the charge can be indium rich if stoichiometric amounts of In and P are used, due to some uncontrolled loss of P. The situation, however, can be remedied by using excess P. Another significant disadvantage of the method used by Wardill et al.[10] is that for single-crystal growth the P ampoule that is hung from the seed pull rod has to be removed and a seed has to be introduced. Also, the pressure of 40 atm (~600 psi) used by Wardill appears to be on the high side and requires higher temperature at the P end; consequently, the possibility of conversion to liquid phosphorus increases, causing excessive bubbling and decreased reaction with the indium.

The method of injection synthesis initiated at Varian has a number of advantages over the Wardill synthesis method. It operates at a lower pressure and lower phosphorus temperature, the P ampoule temperature can be controlled and does not depend on radiation heating from the main heat zone and, most important, it has the advantage of allowing single-crystal growth immediately following synthesis without the necessity of opening up the high-pressure chamber of the crystal puller, thus making it a true insitu synthesis and growth system.

This system consists, in essence, of a phosphorus evaporation ampoule with a feeder/injection tube bent at two right angles leading the P vapors from the ampoule to the molten indium held in a crucible in the hot zone of the a high-pressure Czochralski crystal puller. The phosphorus ampoule is procided with an auxiliary heater in the cooler region of the chamber beyond the heat shields surrounding the main heater assembly. The geometry of the arrangement allows easy access of the seed crystal to the molten charge and permits crystal growth immediately after synthesis without any obstruction. A photograph of an early setup is shown in Fig. 12.

Typically stoichiometric amounts of In and P are used, with about 2.5 gm excess P to compensate for the volume of P ampoule; P is sealed in the quartz P ampoule and the In is placed in a crucible within the main heater assembly and covered with a 100-gram B_2O_3 pellet. The crucible lift rod is adjusted to be at its lowest position with the P injection tube above the B_2O_3 (so that at the start of the run the pressure inside the ampoule is the same as the chamber pressure). The chamber is then evacuated and subsequently pressurized with N_2 to above the dissociation pressure (17.5 atm) of InP, before the main heater is turned on. When the temperature of the In approaches close to the melting point of InP (1068°C) and the In and B_2O_3 are molten, the crucible lift mechanism is raised until the stationary injection tube from the P ampoule penetrates the molten B_2O_3 and enters the molten indium. The P

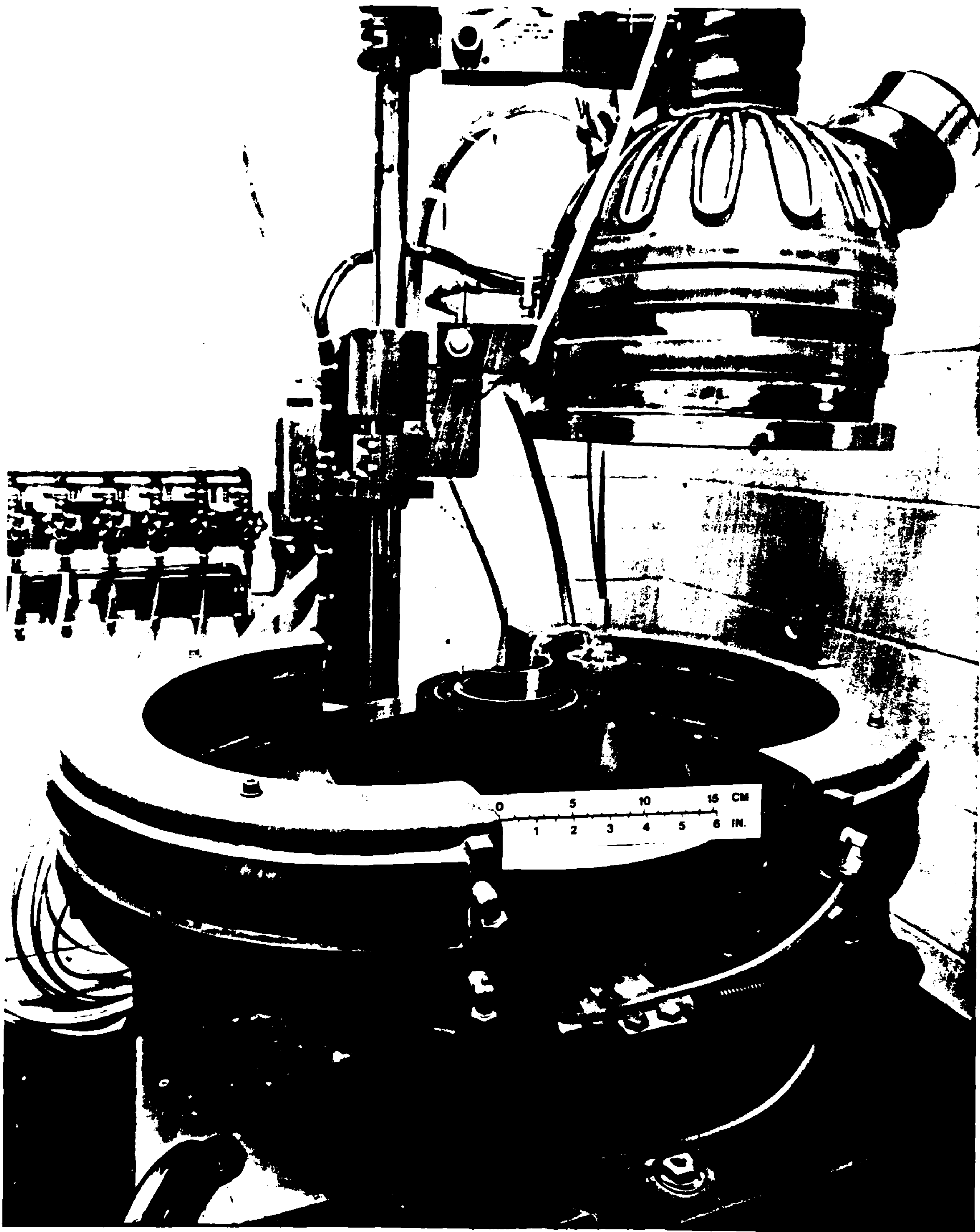


Fig. 12 Setup of insitu puller injection synthesis and growth system.

ampoule heater is then started and the temperature of phosphorus, monitored by thermocouple, is adjusted to between 450 and 500°C, so that after the initial displacement of N_2 from the ampoule, little or no phosphorus bubbling occurs in the indium. It was found experimentally that the phosphorus temperature needs to be kept below its melting point (≈ 570-600°C) so that no liquid phosphorus forms. Formation of any liquid phosphorus causes excessive bubbling in the indium melt, as liquid phosphorus can trickle down the injection tube into In at near 1070°C. At this temperature, the vapor pressure of P is very high. This causes undesirable escape of phosphorus and results in low yield of synthesized InP, and fogging of the puller chamber windows occurs, obscuring the vision necessary for subsequent seeding and single-crystal growth.

Chamber pressure of 450 PSIA (30.6 atm) or lower (as recorded by a "Setra" pressure transducer) has been found to be suitable for synthesis and subsequent seeding. Over 90% conversion of In and P into InP has been obtained at such low pressures, whereas at high pressure the yield dropped dramatically. Figure 13 shows an InP poly ingot synthesized by injection at 600 PSIA; the yield was poor in this case, as seen by excess indium left in the poly.

After synthesis, which typically takes about two hours, seeding for single-crystal growth can be accomplished by lowering the crucible to the growth position and then lowering the seed into the melt. In experiments to date, the injection tube was left inside the melt with the P ampoule at synthesis temperature. Successful seeding was accomplished and small-diameter crystals could be grown. However, because of the asymmetric temperature gradients in the melt caused by the injection tube, control of the crystal expansion to larger diameter ("shoulder") was difficult, as the crystal typically flared out making control of the diameter and further growth impossible.

Fig. 13 InP polycrystalline ingot synthesized by injection at 600 PSIA chamber pressure.

The nonuniform temperature gradients in the melt can possibly be reduced by use of a larger 4" diameter crucible rather than the 3" crucible used at present, and also by increasing the rotation rates of the cup and seed from 4 rpm and 6 rpm used. (111)B seed growth may also be preferable in this case over the (100) growth that was attempted. The injection tube, of course, can also be removed from the melt to beyond the B_2O_3, but this sometimes can cause escape of unreacted P from the ampoule, thus fogging the windows unless the ampoule is cooled rapidly. At present, this is not practical, as the power to the P heater can be shut off only after the injection nozzle is out of the B_2O_3; otherwise, molten B_2O_3 tends to get sucked into the ampoule.

Another solution to these problems that is envisaged is to incorporate a lift and rotation system into the high-pressure chamber. A sketch of such a lift and rotation system is shown in Fig. 14. The P ampoule can be mounted onto this lift and the rotation shaft surrounded by the heater mounted on a heater platform. At the end of the synthesis, the whole ampoule and injection tube can be lifted out of the melt and B_2O_3, the power to the heater can be shut off, and coolant can be passed through the shaft so that the P can be quickly quenched. The ampoule can then be rotated so that the injection tube is moved out completely from the hot zone, if desired. The single-crystal growth can then be made in the normal manner.

Figure 15 shows the photoluminescence spectrum of the material near the seed end of the crystal grown from insitu system material. The acceptor peak is seen to be considerably larger, indicating excessive acceptor impurity contamination. Van der Pauw analysis of this material consequently showed p-type conductivity with a carrier concentration of $1.29 \times 10^{15} cm^{-3}$ and a hole mobility of 530 cm^2/V-sec and a resistivity of 8.39 Ω-cm. Further work in purification of material used in this method and refinement in the system is therefore required.

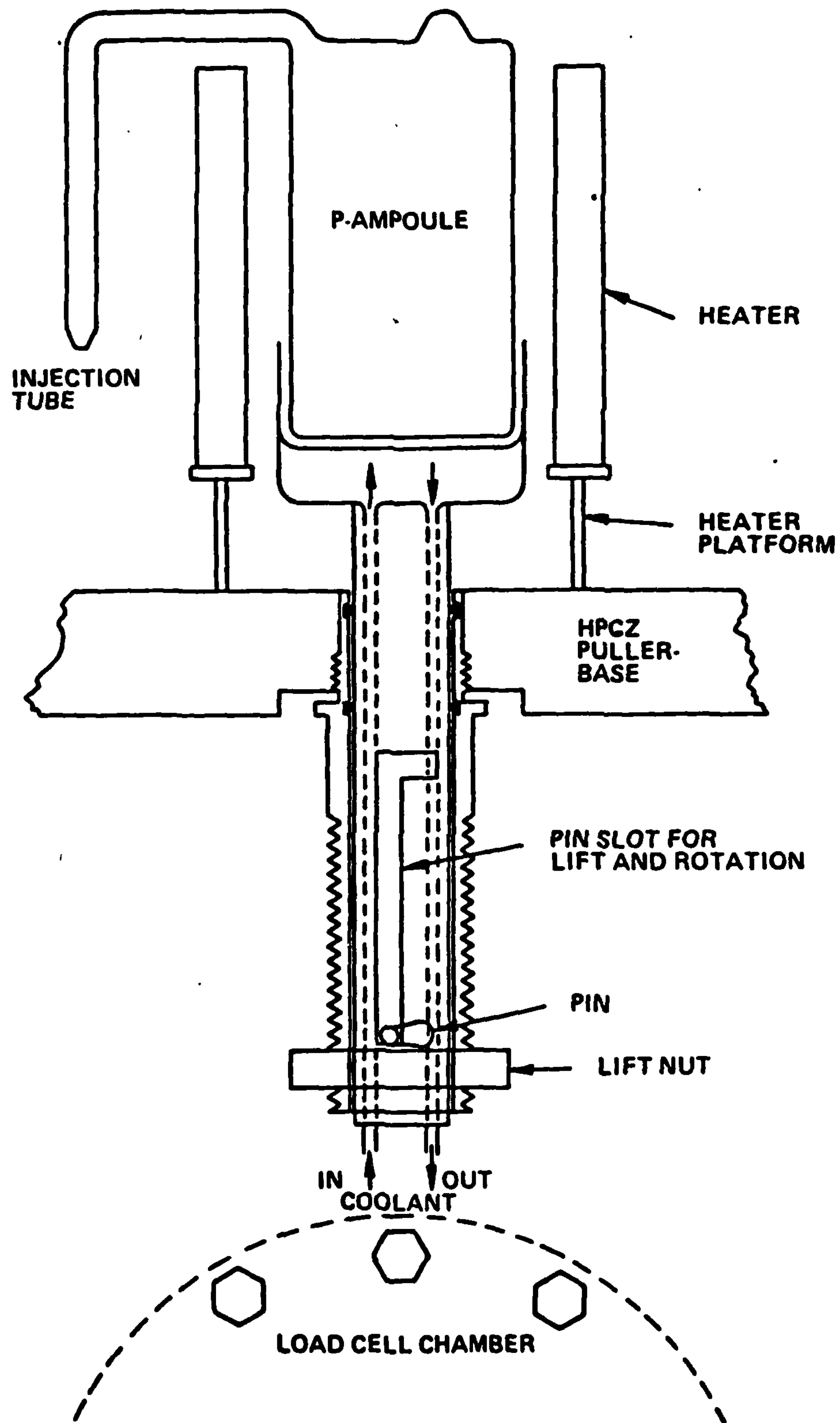


Fig. 14 Lift and rotation system to lift the P ampoule out of the melt in the insitu injection synthesis and growth system.

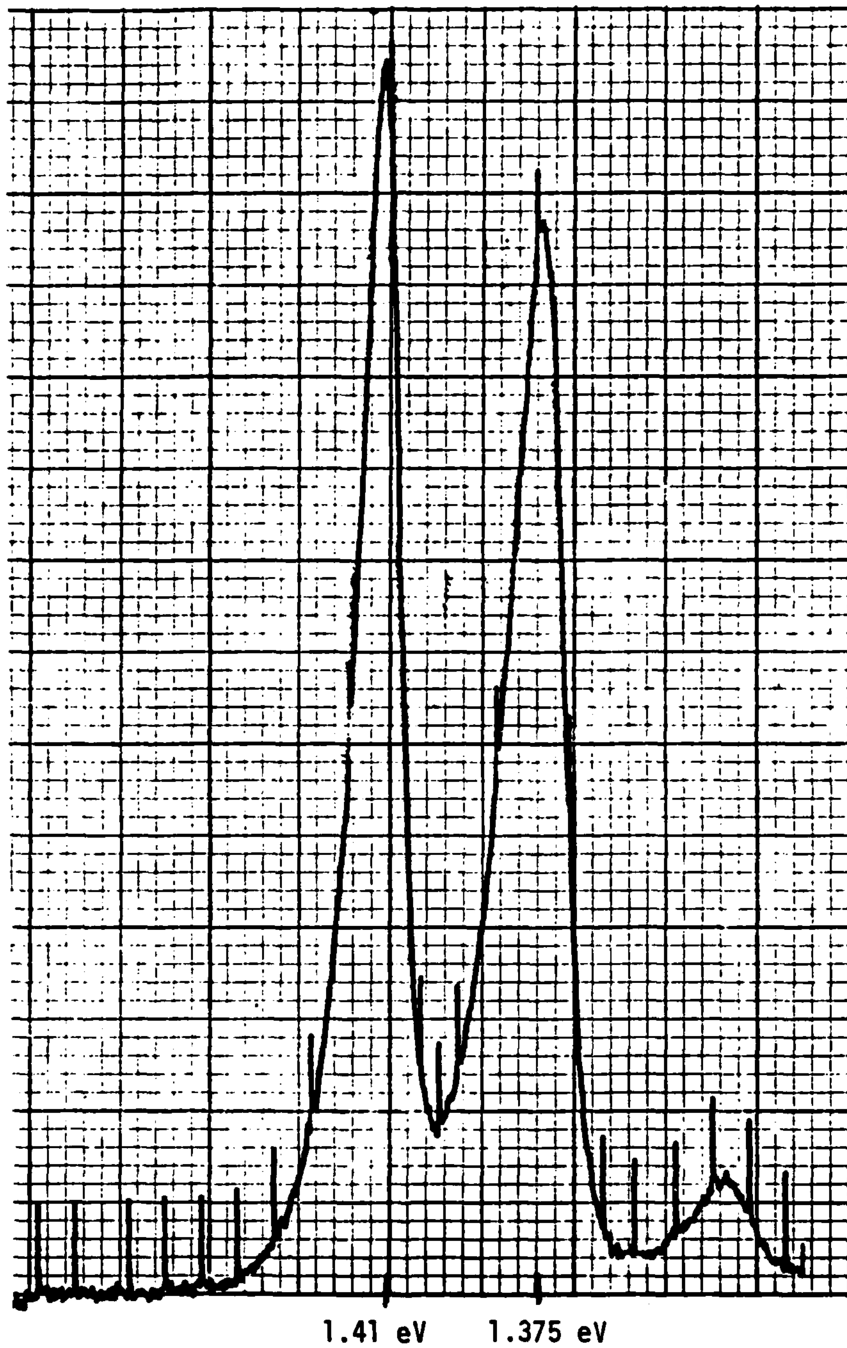


Fig. 15 77°K photoluminescence spectrum of InP material from seed end of the crystal grown from the injection system.

E. Single-Crystal Growth

Single crystals of InP were grown by the liquid-encapsulated Czochralski method in the Malvern MSR-6 high-pressure puller and the Varian Model HPCZ-II puller. The latter uses resistance heating and the former RF heating to melt the charge. Typically about 400-500 grams of polycrystalline materials was used for crystal growth. The tendency of InP single crystal to twin is due to low stacking fault energy, and this considerably reduces the yield of single crystals. The incidence of twinning can, however, be reduced by increasing the temperature gradients at the interface by adjusting the position of the crucible in the heat zone and by selecting the thickness of B_2O_3 encapsulant. Increasing the chamber pressure also increases the temperature gradient. Isler[21] has indicated that a certain minimum temperature gradient might be necessary for twin-free growth. Excess In in the polycrystalline charge is well known to contribute to twinning, prebaking of B_2O_3 has also been used by many workers in an attempt to reduce twinning by reducing the moisture content in B_2O_3. However, a certain amount of moisture -- between 200-400 PPM -- seems to be necessary for good crystal growth. Boric oxide from JMC and Rasa Industries can now be obtained with specified moisture content. Probably the purity of B_2O_3 rather than dryness is important in reducing twinning. Viscosity effects of B_2O_3 on twinning is also important and additives like Ga_2O_3, PbO, Bi_2O_3 and Na_3AlF_2 have been found to reduce viscosity of B_2O_3. Although the former three oxides may adversely effect the material characteristics, NaAlF has reportedly been successfully used by Ware of Metals Research for the growth of InP.[22]

Seki, Watanabe and Matsui[23] have shown that low dislocation density material can be grown by using Zn to exceed a carrier concentration of 10^{18}. Sulfur doping seems to have a similar effect. K. Sugii, H. Koizumi and E. Kobota[24] have used the impurity-hardening mechanism to

derive reduction in substrate dislocation density. They have shown that addition of Zn and S to InP increases the bond strength, and lattice parameter was found to decrease linearly with impurity concentration. Sn doping, on the other hand, was found to increase the lattice parameter.

We have grown both (111)- and (100)-oriented crystals doped with S, Sn, Zn, Fe and Cr. Figure 16 shows a Cr-doped crystal grown in the (111)B direction and Fig. 17 shows a (100)-oriented growth. Figure 18 shows a montage of Various boules grown with different shapes in the (111)B direction. Although a cone of 19° can typically yield untwinned single crystal,[25] a larger growth angle can also be used to yield single crystals, depending upon the quality of the charge and B_2O_3 encapsulant.[8] 5-9's pure B_2O_3 from Johnson-Mathey Co. is used with a moisture content of between 200-400 PPm. Typically for (111) growth, the crucible is rotated at about 6 rpm and the seed at 12 rpm. Both same-direction and opposite-direction rotations have been used successfully with a pulling rate of about 15 mm per hour for (111) growth and about 10-12 mm per hour for the (100) growth.

In order to obtain usable size of substrate material, especially for (111) growths, we have started growth with a growth angle of 19° or less; after the growth is stabilized, the growth angle is increased to obtain larger diameters, without any problems. For (100) growth, however, larger growth angles have been used and practically flat-top growths have also been grown, as seen in Fig. 18.

The quality of the starting poly material is significant for growth of semi-insulating substrate material. To avoid excessive out-diffusion of Fe dopant, it is important to have low bankground impurities in the material, so that as small an amount of Fe as possible can be used for producing complete compensation. In this respect, Cr is better than Fe, as it seems to diffuse out less than Fe in InP. The segregation coefficient of Fe and Cr, however, are comparable (Fe: 1-4 x 10^{-4} [24] and Cr: 3 x 10^{-4}.[27] Cr-doped InP grown in our laboratory has given a

Fig. 16 Cr-doped InP single-crystal boule and S-doped polished wafers.

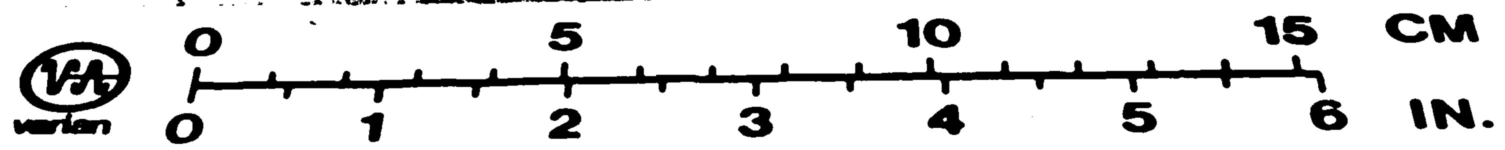
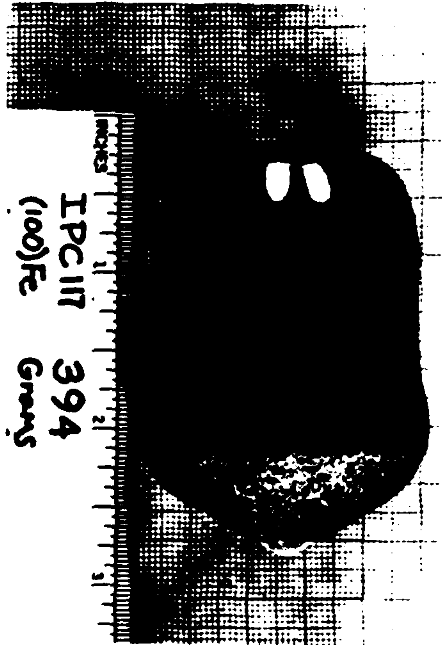
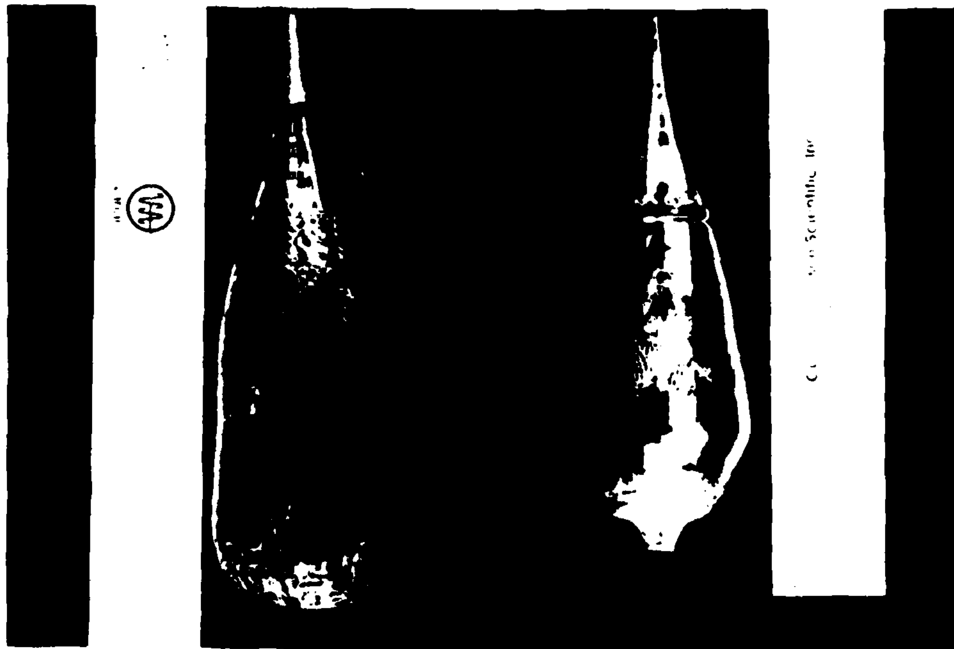


Fig. 17 S-doped InP boule and polished wafers of [illegible] grown in the <100> direction.



350
Grams



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resistivity of $\rho \gtrsim 10^5$ Ω-cm as compared to $\gtrsim 10^7$ Ω-cm for Fe-doped material. For applications where out-diffusion is of more concern than high substrate resistivity, Cr-doped InP substrate can be very useful.

Figures 19 and 20 show (331) transmission X-ray topographs of an Fe-doped (.01 wt % Fe) and S-doped ($n = 1 \times 10^{18} cm^{-3}$) InP wafers using characteristic Mo X-rays. The dislocation density in both those wafers is comparable. Etch pit density data using Huber etch[28] (phosphoric acid: hydrobromic acid, 2:1) indicates an average EPD of $2 \times 10^4\ cm^{-2}$ in Fe and $1.8 \times 10^4\ cm^{-2}$ in S-doped wafers. However, increasing the S doping to above $2 \times 10^{18} cm^{-2}$ dramatically reduces the dislocation density, as shown by the topograph in Fig. 21 for a S-doped wafer with $n = 5 \times 10^{18} cm^{-2}$. Zn doping to a similar high level has given practically dislocation-free material.

Besides growth-related effects, doping effects and effects of temperature gradients at the interface and in B_2O_3 on dislocation density, post-growth annealing of the boule in the plastic state is also of considerable importance. The temperature gradient a growing crystal sees outside the heat zone in a resistance-heated system is considerably smotther than that in RF-heater chamber where the temperature gradient in the nitrogen (because of the high pressure) can be fairly abrupt. Figure 22 shows the dislocation density plot across two Fe-doped wafers and two undoped wafers from boules grown in the Varian HPCZ II resistance-heated puller and the MSR-6 RF-heated puller. The more uniform and lower dislocation density profile in the resistance-heated puller indicates better annealing than that in the RF-heated puller. The crystals grown in the latter also show increased dislocation density near the periphery of the wafers.

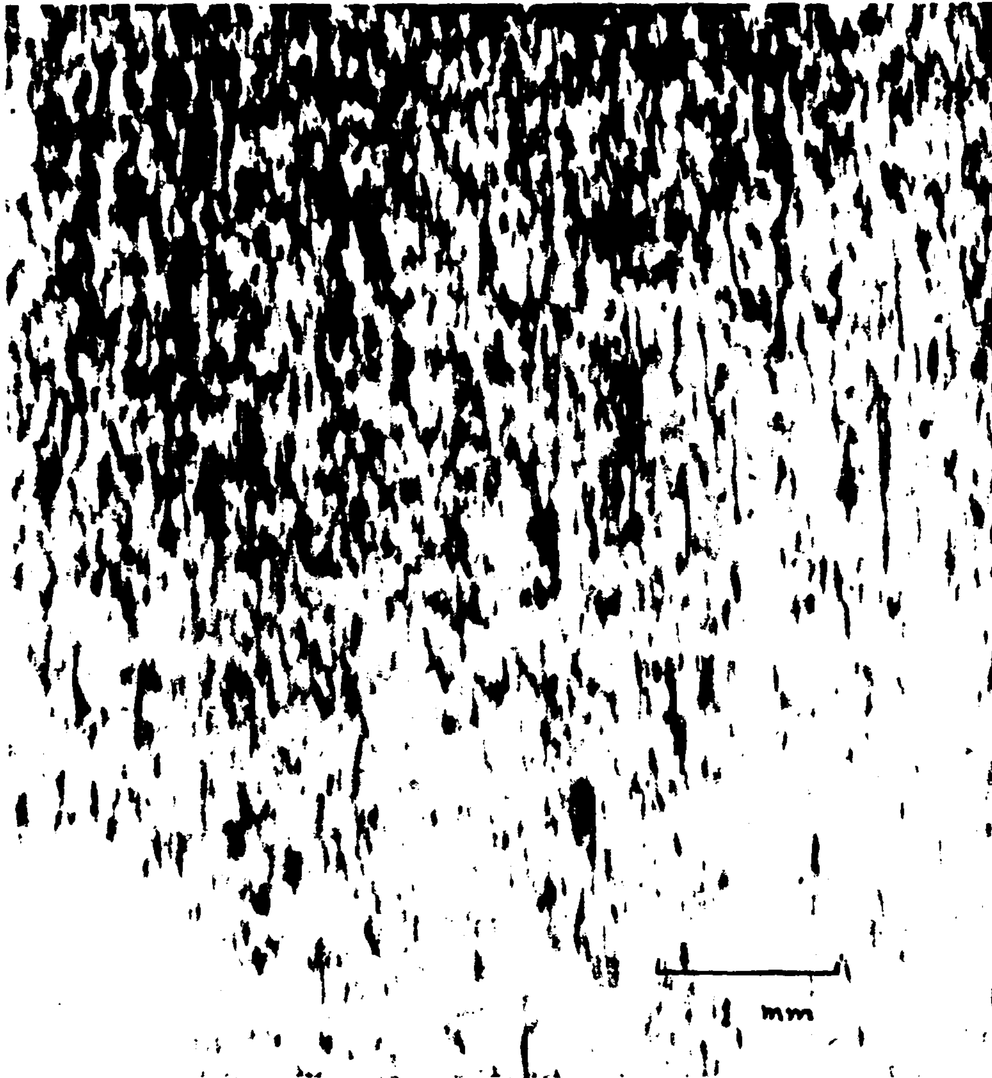

Fig. 19 Transmission X-ray topograph of Fe-doped InP using (331) diffraction and X-rays from a Mo target.

Fig. 20 (331) transmission X-ray topograph of S-doped InP with $n \sim 1 \times 10^{18}$ cm^{-3}.

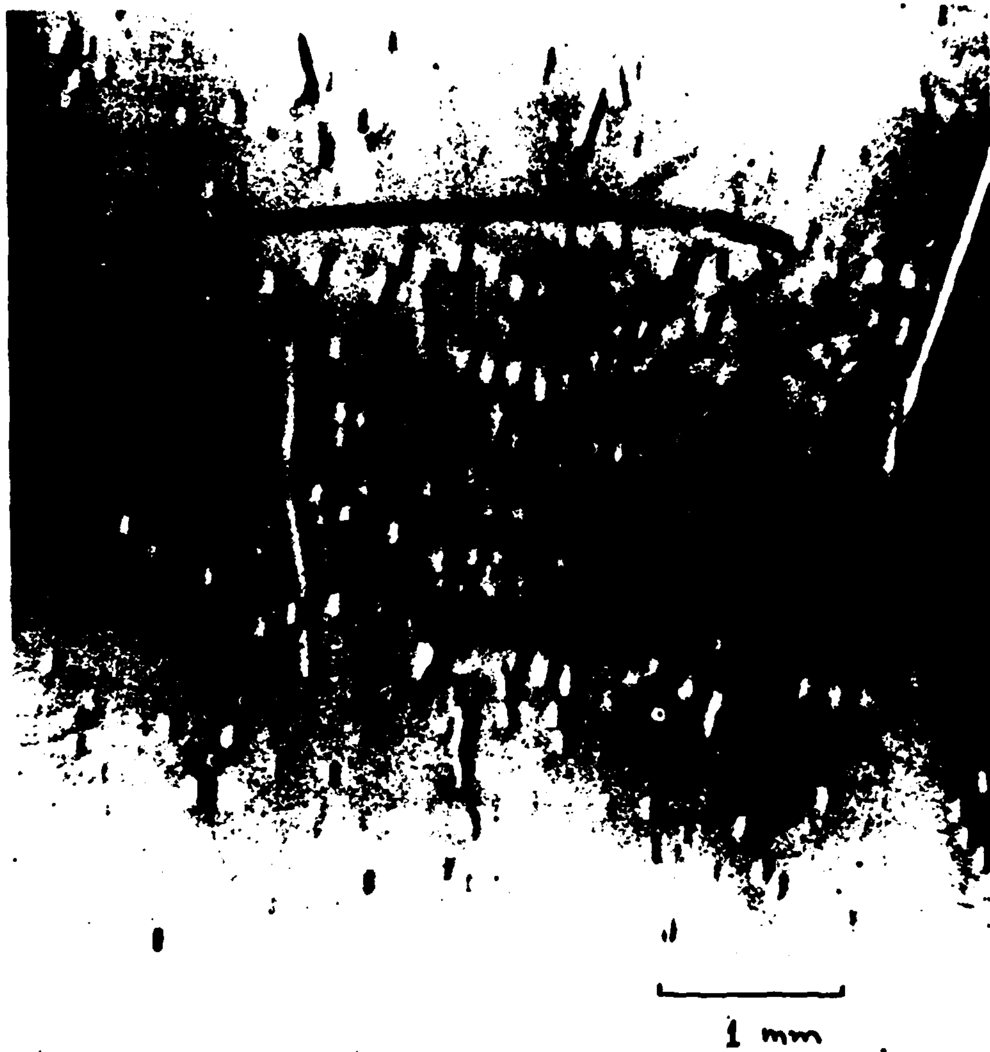

Fig. 21 (331) transmission X-ray topograph of S-doped InP wafer with n ~ 5 x 10^{18} cm^{-3}.

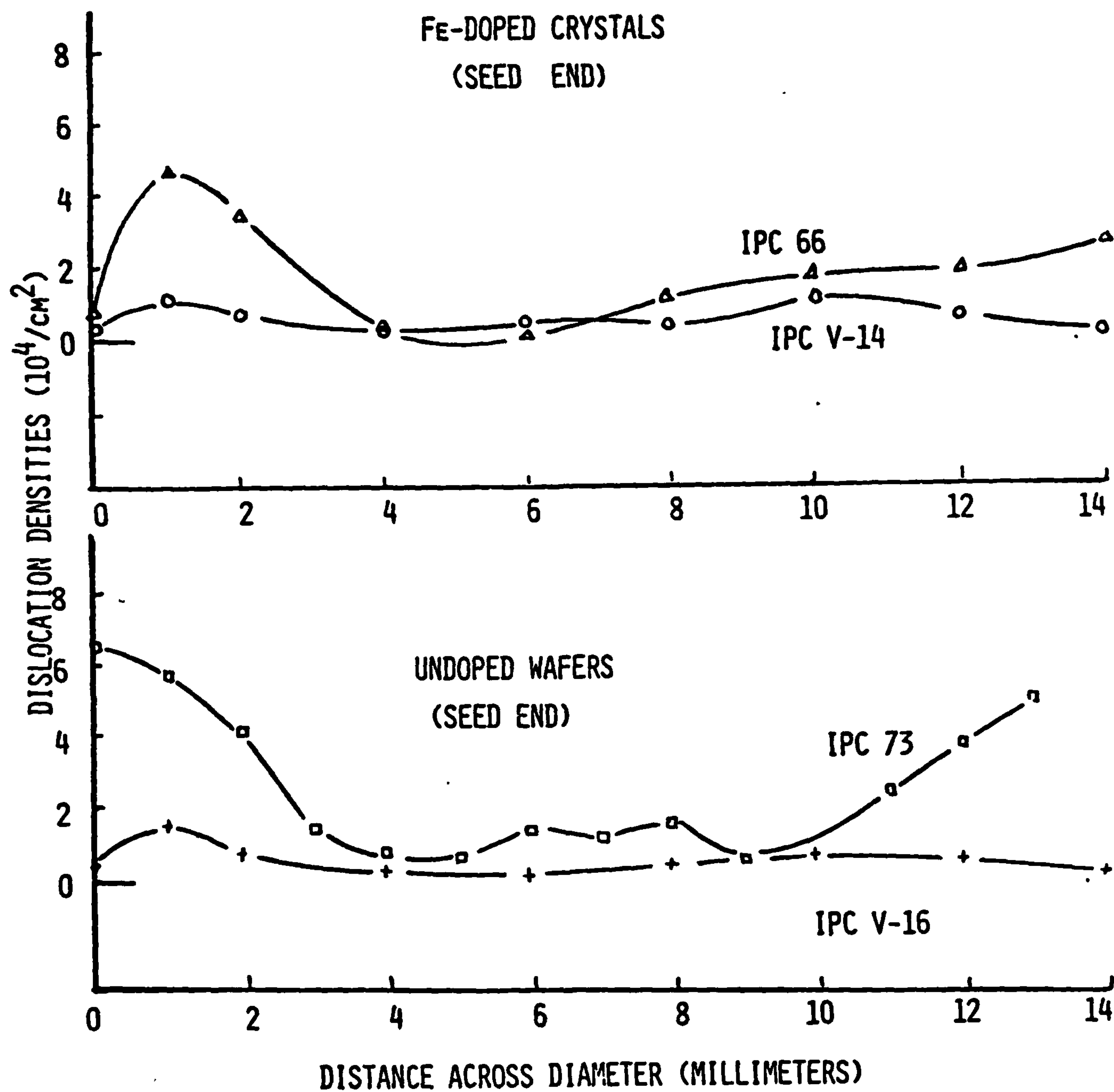

Fig. 22 Dislocation density profiles in Fe-doped and undoped InP crystals grown in the resistance-heated and RF-heated pullers. (IPC in RF-heated and IPC-V in resistance-heated puller.)

IV. CONCLUSION

We have investigated four different InP synthesis methods and found the autoclave synthesis method to yield good-quality material; however, the insitu injection synthesis and growth method initiated in our laboratory was found to be potentially more economical and can be used for a one-step synthesis and growth of InP single crystals. We have also successfully developed growth procedures for single crystals of InP doped with S, Sn, Zn, Fe and Cr in commercially feasible quantities.

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