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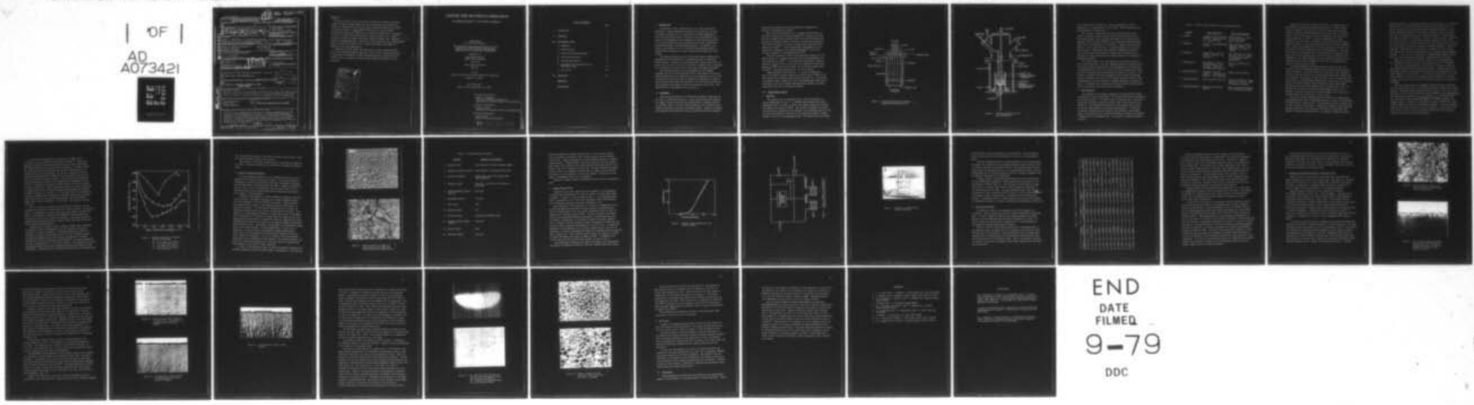

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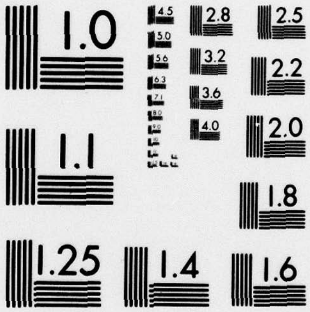

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This report summarizes the results of a two-year investigation of the viability of electrodeposition as a means of preparing indium phosphide, ultimately for electronic device applications. InP proved to be a difficult material to prepare by this technique, mainly because of the restrictions imposed on the maximum temperature of deposition by decomposition of InP and volatilization of In_2O_3 solute.

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A major portion of the total effort was spent on finding an optimum solvent to meet the requirement that the maximum deposition temperature should not exceed 600°C, and the Na,K/PO$_3$,F quaternary eutectic was found to give best results. Reproducible InP deposits of fairly uniform thickness were made onto {0001} single crystal CdS substrates at potentials of -0.90 to 1.00V (versus graphite) with current densities of 1-3mA/cm^{-2}. Sq cm In spite of these low current densities, deposits thicker than 1 [illegible] were micron found to be polycrystalline. The purity of the deposits was not sufficiently high for device applications, but a marked improvement with length of deposition time was demonstrated.

Deposits of InP on (111) InP substrates were also polycrystalline and of less uniform thickness. The most likely cause of polycrystallinity is believed to be imperfect surface preparation prior to deposition, but further study is required to determine the ultimate limitations of this technique.

CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY ◆ STANFORD, CALIFORNIA

Final Report
on a Research Program on

THE PREPARATION AND CHARACTERIZATION OF InP AND RELATED III-V SINGLE CRYSTALS AND EPITAXIAL LAYERS PRODUCED BY MOLTEN SALT ELECTROLYSIS

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I. INTRODUCTION

The purpose of this investigation was to study the electrodeposition of indium phosphide from molten salt solutions in order to develop techniques for the preparation of indium phosphide as thin films and bulk crystals. The core of the investigation was a study of the dependence of the properties of the material deposited on the electrocrystallization parameters such as melt composition, electrode materials, and deposition potential. In addition, the purity of the deposits was to be studied and measurements made to characterize the deposits in terms of physical and electrical properties.

The original proposal was for a three-year period leading to an assessment of the feasibility of preparing material of electronic device quality. Support has been conditionally discontinued after the second year so that it will not be possible to complete this assessment, but a continuation of this work at some stage does appear desirable.

The main achievement of the investigation is that indium phosphide can now be electrodeposited with a good degree of reproducibility provided that the conductivity of the substrates is not too low. The potential and current density required for deposition of uniform layers has been determined for deposition onto InP and CdS substrates, and large grain size deposits were also made onto nickel sheet. The conductivity of the deposits was 0.5-5 ohm cm.

II. BACKGROUND

Electrocrystallization is a little-used technique, especially in the field of electronic materials. Large crystals have been produced of tungsten bronzes, which may find applications in display devices, and of LaB_6, which is used for electron emission, but studies of semiconductor materials have been particularly sparse. Reports of silicon and germanium electrodeposition in the literature have been primarily concerned with demonstrating the feasibility of deposition of material of metallurgical quality.

The first electrodeposition of a compound semiconductor was reported a decade ago by Cuomo and Gambino(1), who made GaP films and also claimed to have deposited ZnSe, ZnTe and InP although the details are extremely sparse in the case of these other materials. After several years of inactivity in this field, ZnSe films were prepared in Japan(2). It was subsequently found possible in our laboratory to synthesize GaAs electrochemically(3) and we have recently succeeded in electrodepositing SiC(4).

The first systematic study of the conditions required for the stable growth of a compound semiconductor by electrodeposition is that reported for GaP(5). It was concluded that smooth, coherent, epitaxial layers of GaP on n-type (111) GaP substrates could be deposited at 800°C only if the current density did not exceed about 20 mA/cm^2. The corresponding growth rate was 23 μm/hr.

Indium phosphide was chosen for the present investigation since it presents a greater challenge than GaP, and is likely to be more widely used in high frequency solid state devices. In addition, its bandgap is near optimum for solar cell applications where purity requirements are less stringent and techniques capable of yielding large area films are of particular interest.

III. EXPERIMENTAL DETAILS

A. Apparatus

The simplest type of apparatus used in this investigation is shown schematically in Fig. 1. A Kanthal-wound furnace surrounds an atmosphere tube of inconel or silica, the maximum temperature attainable being in the region of 900°C. The crucible containing the molten salt solution is located near the bottom of the atmosphere tube, and two or three electrodes are inserted into the solutions through a flange bolted to the top of the atmosphere tube. The flange also has fittings

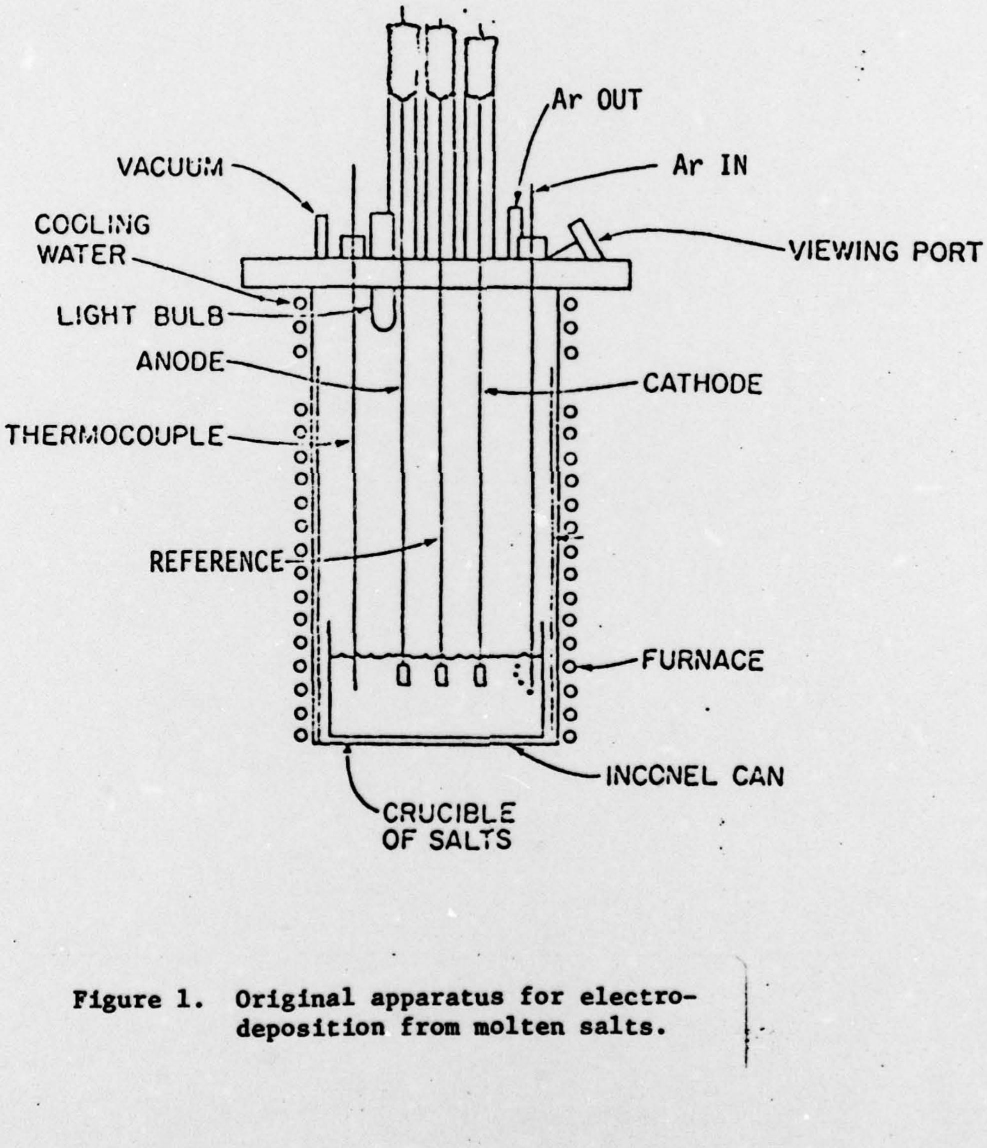

Figure 1. Original apparatus for electrodeposition from molten salts.

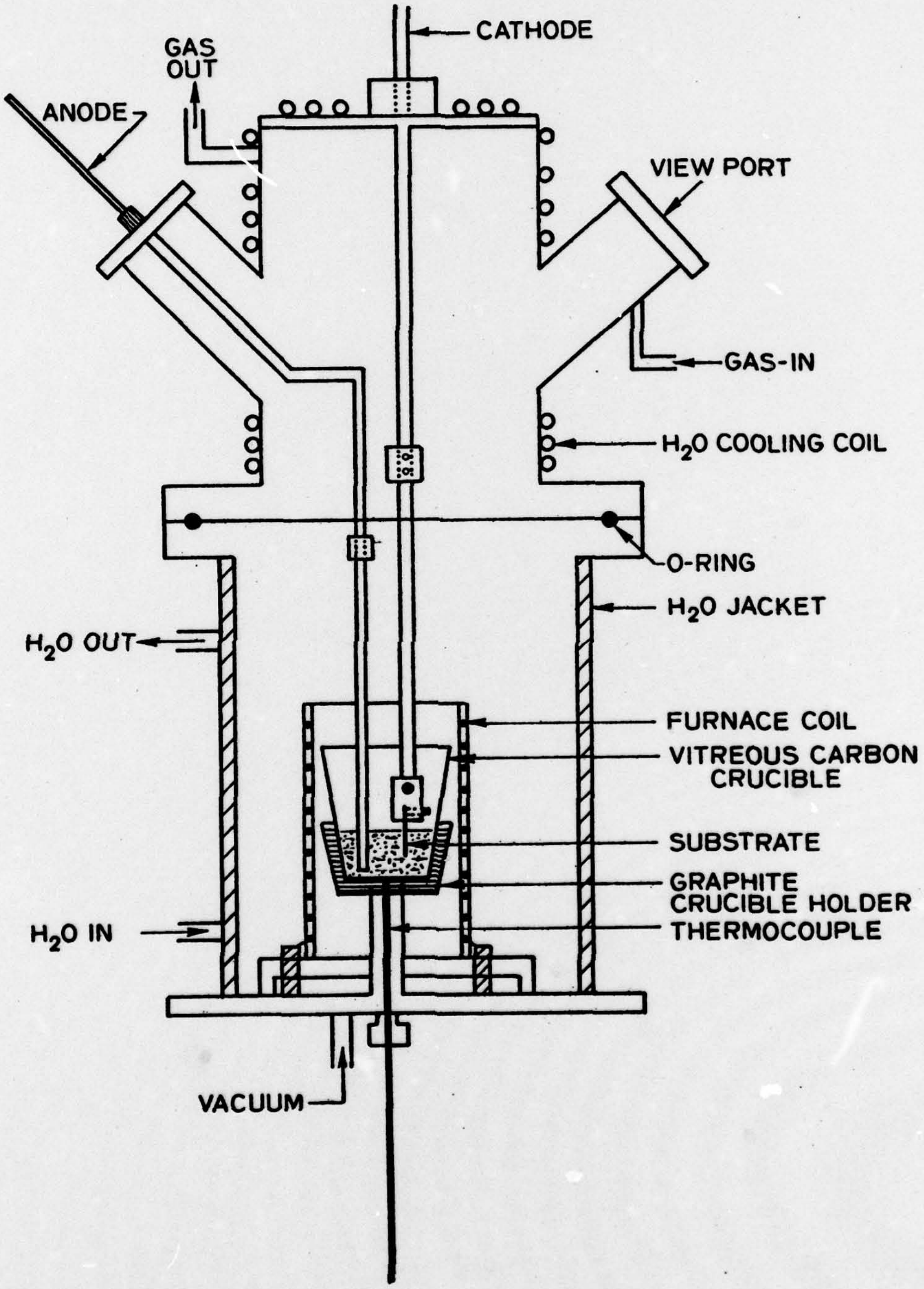

Figure 2. Improved apparatus for InP electrodeposition.

for a light source, viewing port, control thermocouple, and for connections to a vacuum pump or argon supply. Most experiments have been performed in flowing argon.

The crucible is normally of vitreous carbon which has been found to be stable against attack by all the salt mixtures used in this investigation. The additional advantage of this material over graphite is that graphite flakes off and introduces carbon particles which float on the surface of the solution. Graphite has been used, however, for the anode which has a relatively small area in contact with the melt. Flaking has been reduced by rubbing the surface to remove loose material and produce a shiny, more oriented surface. The choice of melt composition and cathode material are discussed in subsequent sections.

At a later stage in the investigation, the apparatus shown in Fig. 2 was mainly used. This was originally built for pulling silicon from the melt and was converted to electrodeposition by introducing a rotating mercury contact to the pull rod and by replacing one viewport by an insulated disc through which the anode was inserted. The furnace is internal and this arrangement offers the great advantage that the stainless steel walls of the vessel are water-cooled so that contamination of the melt from the container materials is greatly reduced. In addition, the visibility of the melt surface during deposition is much better than in the earlier apparatus.

B. Bath Selection

The selection of a suitable composition for the solution formed a major part of this investigation. The systems which were investigated are listed in Table 1. An ideal solvent is one which has a high solubility for the solute which acts as the source of the material to be deposited. The decomposition potential of the solvent must be high so that it remains stable at the operating potential. In addition, the solvent should have low viscosity, low volatility, low melting point, low reactivity with container materials, and should be available in high purity at reasonable cost. Low toxicity is another desirable property.

Table 1: Solvent Systems Studied for InP Electrodeposition

Solvent	Major Advantages	Major Disadvantages
1. LiCl/KCl	Low melting point eutectic (328°C). High solubility for In_2O_3 and InF_3.	High volatility. Reactivity with nickel. No InP deposits.
2. $NaPO_3$/NaF	Used for electrodeposition of GaP.	High viscosity. Rather high M.P. (490°C). Low solubility of In_2O_3 at ~600°C.
3. LiF/NaF/KF	Oxygen-free. Low M.P. eutectic (454°C). Low viscosity.	Low solubility for In_2O_3 and InF_3. KPF_6 as source of phosphorus is very hygroscopic.
4. Li_2O/B_2O_3/LiF	Used widely in electrocrystallization, e.g., for LaB_6. Quite low viscosity and volatility.	Very low solubility for In_2O_3.
5. $NaPO_3/NaF/KPO_3$/KF	Lower M.P. eutectic (~439°C). Gives good InP deposits. Low volatility.	Rather high viscosity.
6. $LiPO_3/LiF/KPO_3$/KF	Lower viscosity than (5).	Lower solubility for In_2O_3 than (5) - ($\lesssim$ 1m/o). LiF is insoluble in water.
7. $LiPO_3/LiF/NaPO_3$/NaF	Very low melting point (300°C).	Has not given InP deposits. LiF is insoluble in water.

In general no solvent system is ideal and a compromise must be made between desirable and undesirable properties. Alkali halides are very frequently used since they meet the viscosity and electrochemical stability requirements, and the eutectics have low melting points. The LiCl/KCl eutectic has been frequently used and has the low melting point of 348°C. Its major disadvantage is a high volatility, and the vapor was found to be very reactive with nickel which was used as an electrode holder and with the inconel atmosphere tube. Nickel was transported via the vapor phase into the melt, and was present in high concentration in the electrodeposits. The LiCl/KCl system has the advantage of a high solubility for In_2O_3 and InF_3, which are the most obvious choices of solute to give indium in the InP deposit, but indium phosphide was not successfully deposited from LiCl/KCl using an alkali phosphate as the source of phosphorus and In_2O_3 or InF_3 to give the indium.

The system $NaPO_3$/NaF was chosen because it had been used with success for the electrocrystallization of GaP films, with Ga_2O_3 as the source of gallium. The main problem with this solvent for the growth of InP is that the eutectic has a rather high melting point (490°C) and the solubility of the In_2O_3 or InF_3 at 600°C is very low, probably less than 1% molar. Slightly higher temperatures can be used, but volatilization of the indium compound becomes appreciable above about 650°C. The major practical handicap posed by this volatilization is that the window used to observe the crucible becomes fogged and it is not possible to adjust the location of the electrodes so that they are not touching either the crucible wall or each other.

The ternary alkali fluoride eutectic "Flinak" has a significantly lower melting point than the $NaPO_3$/NaF eutectic, but has a low solubility at 600°C both for In_2O_3 and InF_3. The solubility of InF_3 is about 1 m/o but that of In_2O_3 is even lower. Flinak was considered a very desirable solvent because of its low viscosity and fairly low volatility, and because it offered the possibility of a completely oxygen-free system.

Oxygen is normally an undesirable impurity in semiconductors and, although the presence of fluorides in phosphate-based solvents should act as a getter to retard oxygen incorporation into the growing crystals, a completely oxygen-free system was considered preferable. KPF_6 was used as the source of phosphorus and an InP layer was produced on one occasion with InF_3 as the source of indium. It was not found possible to reproduce this result, however, the main problem being that KPF_6 and InF_3 react in the fluoride melt, with the evolution of a volatile species in the form of a white smoke, which makes visibility extremely difficult. $NaPF_6$ and $LiPF_6$ were investigated as alternatives to the KPF_6 but both are even more hygroscopic than the potassium salt, and presented serious handling problems. In no case of a Flinak/alkali fluorophosphate/indium fluoride bath was it found possible to produce a chemically stable solution.

$NaPO_3$ was introduced into Flinak in place of the fluorophosphate but, although the melt was stable, InP deposits could not be obtained.

The system $Li_2O/B_2O_3/LiF$ was tried since this had been used to produce various materials by electrocrystallization. Although these were frequently borides, the boron does not necessarily electrodeposit so that other compounds can be obtained. In the case of InP, however, it was not found possible to deposit the phosphide and the solubility in the bath of In_2O_3 was found to be too low for the solvent system to be considered promising.

Since the problem with the $NaPO_3/NaF$ system was mainly associated with its high melting point, the quaternary system Na, K/PO_3, F was investigated. The lowest melting composition was reported (6) to have a melting point of 424°C and this value has been confirmed at least approximately. This low-melting composition $Na_{.814}K_{.186}(PO_3)_{.75}F_{.25}$ (called "Pofnak") has been found to give reproducible deposits of indium phosphide with In_2O_3 as source of indium. The solubility of In_2O_3 is rather low, about 3 m/o at 600°C, but this was considered acceptable. The other disadvantages of this solvent system are that the viscosity is rather high, and an increase in the F^- to PO_3^- ratio (which should lower the viscosity) leads to a rapid increase in melting point.

In view of these limitations, the systems Li, K/PO_3, F and Li, Na/PO_3, F were studied as alternatives to Pofnak(7). These were expected to have lower melting-point eutectics and lower viscosities, but similar chemical and electrochemical properties. In order to find the composition of lowest melting point in these systems, melts containing equal molar concentrations of the four constituents in each case were unidirectionally solidified by slow horizontal traverse of a 15 cm long crucible through a furnace. The fraction which solidified last was analyzed and a melt of the composition so determined was subjected to a further unidirectional solidification to test the accuracy of the first analysis. Atomic absorption analysis was used to determine the alkali metal ratios in these low-melting compositions but electron microprobe analysis for the PO_3^- to F^- ratio was found to be unreliable. A section through the phase diagram was therefore taken with the alkali metal ratios fixed at the values determined for the lowest melting composition, but with the $PO_3^-:F^-$ ratio varied. The results are shown in Fig. 3.

The Li, Na and Li, K systems were both found to give rise to compositions of much lower melting points than the Na, K system. The melting point of a composition $Li_{.496}Na_{.504}(PO_3)_{.8}F_{.2}$ was found to be 300 ±10°C which is substantially lower than the alternative systems considered. Both the Li, Na and Li, K systems form glasses in the region around the lowest-melting composition and the minima in Fig. 3(a) and (b) are very broad rather than eutectic-like.

Although the Li, K/PO_3, F and Li, Na/PO_3, F appear very attractive as solvents for the electrodeposition of InP, they have not been so successful as Pofnak in practice. The major limitation is that the solubility of In_2O_3 in both systems is low ($\lesssim$ 1 m/o at 600°C) and does not increase substantially if the fluoride concentration is raised. Although InP films have been deposited from the Li, K solvent, deposition was not so reproducible as in the case of Pofnak. The viscosities of melts containing lithium ions were not substantially lower than Pofnak, as had been hoped. In addition, melts containing LiF suffer from the disadvantage

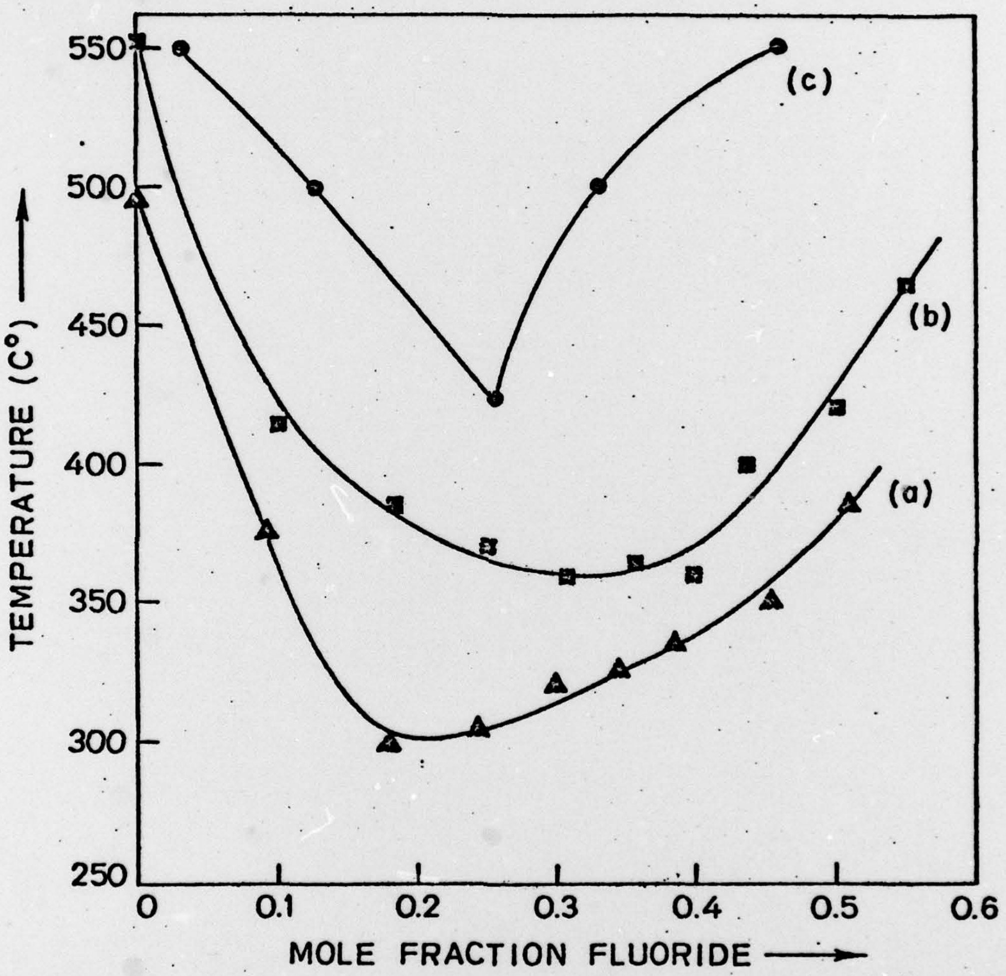

Figure 3. Melting temperature of compositions in the systems

(a) $(Li_{0.496}Na_{0.504})(PO_3,F)$

(b) $(Li_{0.538}K_{0.462})(PO_3,F)$

(c) $(Na_{0.814}K_{0.186})(PO_3,F)$.

that solvent which adheres to the films on removal from the melt cannot be readily removed by dissolution in water.

The results of this study therefore led to a decision to adopt the Na, K/PO_3, F eutectic (Pofnak) as the solvent for subsequent investigations.

C. Study of Substrate Materials

It was originally planned to use an inexpensive substrate such as graphite for the initial evaluation of melts. A study was therefore undertaken of various polycrystalline materials as possible substrates for the deposition of polycrystalline InP films. Graphite appeared the obvious choice since it is chemically inert in molten salts, can be fabricated easily into suitable shapes and has been used successfully for a number of other materials.

In practice the adhesion of indium phosphide to graphite was found to be very poor, the deposit adhering only in small isolated patches with the remainder of the InP floating in the melt. Similar behavior was observed with a range of other possible substrate materials, as indicated in Table 2. Of the metallic materials, only on nickel was adhesion relatively good, with little InP detectable in the melt. The deposit on a nickel cathode cleaned by a light etch in acid is irregular, with the formation of "craters" of various sizes, as shown in Fig. 4(a). These craters are believed to be associated with the liberation of excess phosphorus which rests on the surface in the form of bubbles around which the deposition occurs. This effect could probably be eliminated by adjustment of the current density, the bath composition, or by the use of agitation. As can be seen in a photograph at higher magnification (Fig. 4(b)), the InP crystallites are quite well formed but there are holes visible in the deposit. It is not certain at this stage whether these holes may be eliminated by some change in the etching procedure, but nickel or a nickel alloy appears to be the best choice for applications which require an InP film on a metal substrate.

In view of the unfavorable nature of metal and graphite substrates for detailed comparisons between different melts, the majority of the deposits

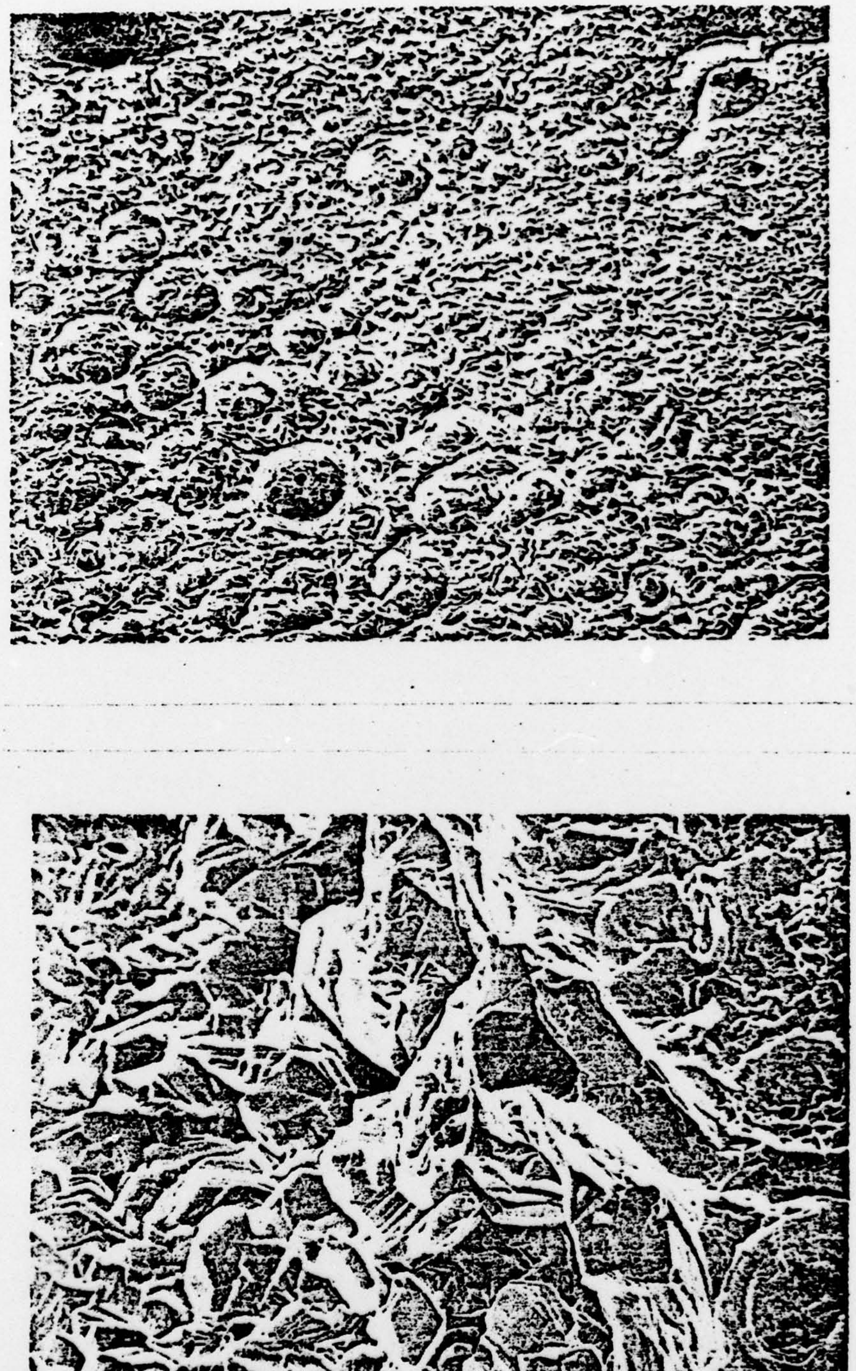

Figure 4. Polycrystalline InP deposit on nickel substrate (a) 160X magnification (b) 400X magnification.

Table 2: Cathode Materials Studied

	Material	Adhesion of InP Deposit
1.	Graphite (rod)	Poor; adheres in small, isolated regions
2.	Germanium (single crystal)	Poor; adheres in isolated patches only.
3.	Pyrolytic graphite	Fairly poor; only little better than normal graphite
4.	Tungsten (sheet)	Very poor. No trace of InP shown by microscope
5.	Indium phosphide (single crystal)	Very good
6.	Molybdenum (sheet)	Very poor
7.	Gold (foil)	Fair
8.	Niobium (sheet)	Poor
9.	Platinum (foil)	Attacked by phosphate melts
10.	Cadmium sulfide (single crystal)	Very good
11.	Nickel (sheet)	Good
12.	Tantalum (sheet)	Very poor

have been performed on cadmium sulfide wafers. This material appears to be an excellent substrate in most respects except cost and possibly conductivity. Indium phosphide forms a good adherent deposit on randomly oriented wafers, although {0001} CdS slices should be the best choice since there is an epitaxial relationship between this plane and the {111} plane of InP with a mismatch of only 0.3%. The major handicap presented by CdS is that it is normally available only in single crystal form and the boules are very expensive, so that cost imposes a limitation on the number of experiments which can be performed.

Deposits on single crystal InP substrates have also been successfully made.

D. Current-Voltage Plots

Pofnak melts are well behaved from the viewpoint of the dependence of current upon voltage when the latter is swept in a quasi-static mode. A typical I versus V plot is shown in Fig. 5. The deposition potential is consistently 0.85 ± 0.05 volts and varies little with different source materials, the age of the bath, temperature, etc.

One limitation in the usefulness of I-V plots in studying the melts is that the deposition potential for the evolution of phosphorus gas from the Pofnak alone is the same within experimental error as that for deposition of InP when In_2O_3 is added. In order to improve the usefulness of this potentially valuable measurement, attempts have been made to develop a differential I-V technique in which the current through a cell is compared with that through a similar "standard" cell when the same potential sweep is applied simultaneously to the two cells. A signal proportional to the difference in the current through the two cells can be amplified, so greatly increasing the sensitivity compared with that possible with a single cell. This technique could be used, for example, to detect the small difference when In_2O_3 is added to Pofnak. A diagram of the circuit which has been used in these studies is shown in Fig. 6.

The differential technique also offers the prospect of investigating the effects of impurities present in the melt, and may permit the deposi-

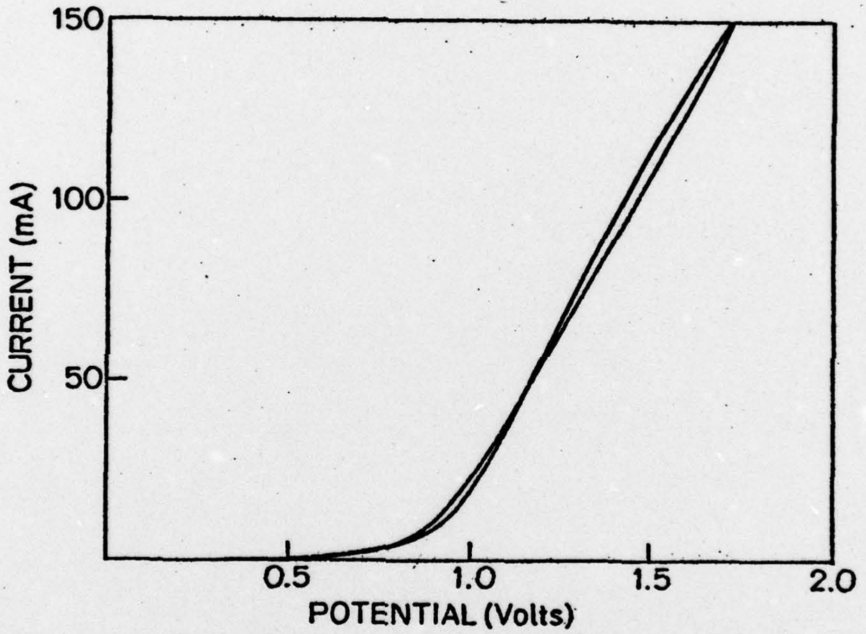

Figure 5. Current versus voltage plot for Pofnak at 600°C.

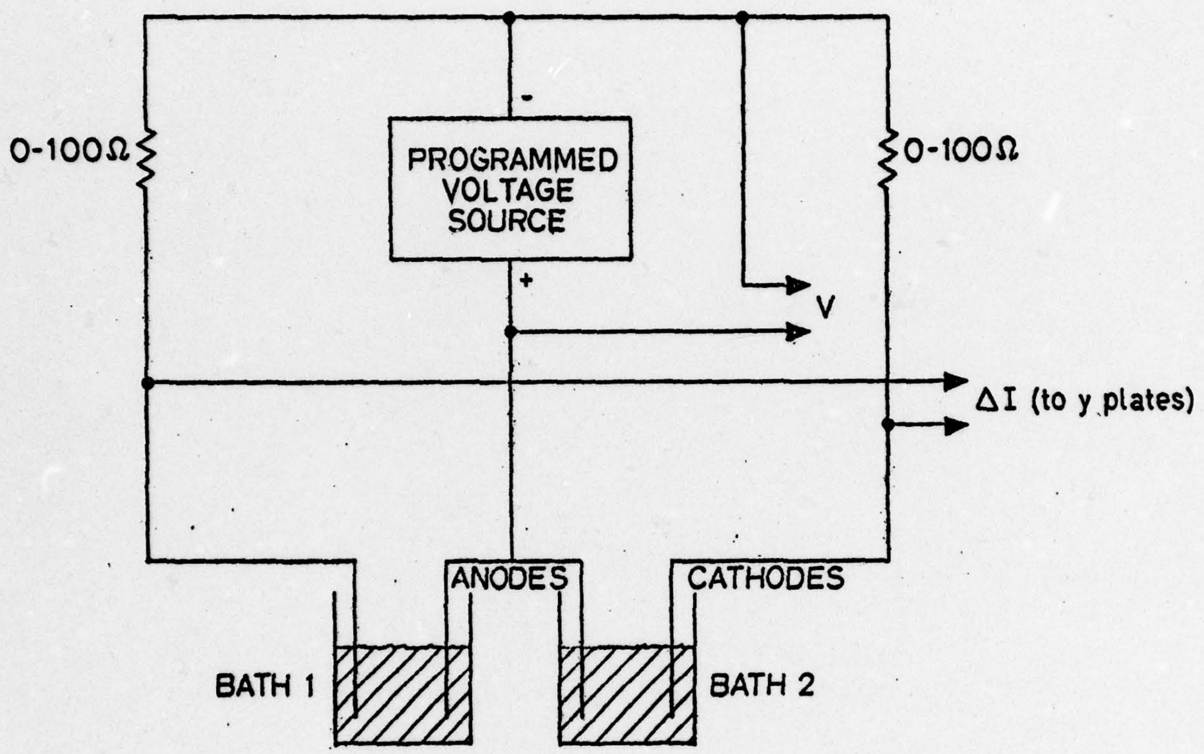

Figure 6. Circuit diagram of apparatus for differential current technique.

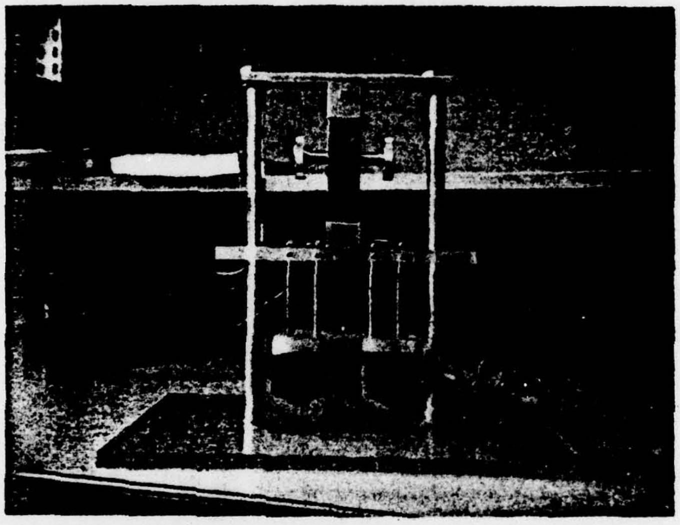

Figure 7. Apparatus for differential current technique.

tion potentials of trace impurities to be determined. This information would be very useful in the purification of the bath by electrochemical means.

In initial measurements with a simple apparatus it was found possible to balance the currents in two nominally identical Pofnak-containing cells to within 1-2 percent of the total current. The resulting gain in sensitivity should be extremely useful, but a simple apparatus suffers from the disadvantage that the current through each cell is strongly dependent upon the depth of immersion of the electrodes.

In order to gain a more thorough understanding of the applicability of this differential technique, a model apparatus has been built for use with aqueous solutions (Fig. 7). The two pairs of electrodes move simultaneously on a vertical screw thread so that the depth of immersion in the two solutions is the same. Initial measurements have shown that it is possible to detect about 0·02% of Cu^{2+} ions in a silver nitrate solution, the impurity giving a characteristic contribution to the differential current. The construction of a similar apparatus for molten salt studies is considered desirable as a means of studying electrochemical purification.

E. Purification Studies

The materials used for the deposition of InP from Pofnak were as follows: 98% pure $NaPO_3$ from Stauffer Chemical Corporation; KPO_3 made from J. T. Baker KH_2PO_4 of 98% purity by vacuum dehydration at 300°C; 99% pure KF and 99.9^{+}% pure NaF from Hudson Laboratories. Column 1 of Table 3 shows the concentration of impurities in a new Pofnak melt as determined by emission spectrographic analysis.

Column 2 of Table 3 shows the concentration of these impurities in the same melt after the deposition of 15 successive InP layers of 1-5 µm thickness onto CdS substrates. Several impurities such as aluminum and magnesium show a marked decrease in concentration, suggesting that these are incorporated into the deposited films. This is confirmed by the data of column 4, which shows an analysis of InP films scraped from a CdS wafer after deposition.

Table 3: Results of Emission Spectrographic Analysis

Element	PoFNak before elect.	PoFNak after 15 deposits	PoFNak Melt 13	InP 1.2	InP 1.11
Al	0.002	0.0005	0.0002	0.05	N.D. < 0.0005
B	N.D. < 0.0001	0.0003	0.0002	N.D. < 0.005	N.D. < 0.005
Cd	< 0.001	0.0002	0.0003	Major	Maj. to Base
Ca	0.001	0.0004	0.0004	0.0005	0.0002
Cr	0.0003	0.0003	0.0002	N.D. < 0.005	N.D. < 0.005
Cu	0.0002	0.00005	0.00002	0.03	N.D. < 0.005
Fe	0.0005	0.0002	0.0002	0.01	0.003
Pb	0.00009	0.00005	0.00001	0.0001	N.D. < 0.0001
Mg	0.0003	0.0001	0.00004	0.0003	N.D. < 0.0001
Ni	0.0007	0.0003	0.0002	N.D. < 0.01	N.D. < 0.01
K	Major	Major	Major	N.D. < 0.02	N.D. < 0.05
Si	0.01	0.001	0.0007	0.5	N.D. < 0.01
Na	Major	Major	Major	N.D. < 0.05	N.D. < 0.05

The most encouraging feature of these results is the observation of column 5 that all impurities are undetectable in the 11th film deposited in this series, with the exception of Ca and Fe. The high Fe concentration (0.03%) in this film is disturbing especially since it is higher than in the second film. The furnace used for these depositions has a water-cooled stainless steel wall and a stainless steel cathode support rod, and it may be that the production of high purity films will require modification to the apparatus. An alternative version of the furnace of Fig. 1 which has been used in these investigations has a silica atmosphere tube, and a melt prepared in this furnace and used for five deposits (column 3 of Table 3) does have a slightly lower Fe content than the initial concentration in the melt prepared in the stainless steel furnace.

Cadmium sulfide is etched slowly by the Pofnak melt, as is confirmed by a progressive increase in the Cd concentration in the melt. The cadmium is probably not incorporated into the layers because of its large atomic radius, and the etching has the useful effect of cleaning the surface of the wafer prior to deposition.

In view of the low purity of the phosphate starting materials, purification of these materials prior to electrodeposition has been attempted using recrystallization. The $NaPO_3$ and KPO_3 have low solubility in water but the corresponding monobasic salts NaH_2PO_4 and KH_2PO_4 are water-soluble and form well-developed and extremely clear crystals on slowly cooling an aqueous solution. The metaphosphates are then prepared by dehydration of of the first batch of crystals, but the results of analysis of these materials does not indicate an appreciable improvement in purity as a result of recrystallization. The concentration of iron in the starting sodium metaphosphate (the main constituent of the melt) was measured by emission spectrographic analysis as 3ppm by weight. The lowest level detected in samples of recrystallized material was 1ppm, but one sample contained 100ppm presumably as a result of some flaw in the handling procedure rather than because of local segregation. The level of chromium also remained at 3±1ppm after recrystallization, and the level of copper in the recrystallized material was also 3±2ppm, higher than in the starting material.

Electrochemical purification of the solutions seems to offer the most convenient method for the purification of melts used to deposit InP. Essential requirements for this method to be effective are long-term stability of the melt and a clean furnace so that contamination from constructional materials is avoided. These requirements were only partially met at the conclusion of the present study.

F. Morphology and Characteristics of InP Films on CdS

Several series of InP films have been deposited on polished CdS wafers oriented on or close to the {0001} plane. The wafers are typically about $1cm^2$ in total area, of which roughly 50% is immersed in the melt. The wafer is supported on a graphite holder, either by a graphite set screw or simply by frictional support in a wedge-shaped groove.

The CdS crystals were grown in our laboratory or obtained either from Cleveland Crystals Inc. or the 3M Company. Although most of the crystals were undoped, the in-house material has a room-temperature resistivity ~10Ω-cm falling to ~3Ωcm at 600°. The Cleveland and 3M crystals are nominally of 10^4Ωcm resistivity at room temperature and values up to 10^7Ωcm have been measured. These relatively high resistivity materials were heated in cadmium vapor at 800°C where the Cd vapor pressure is around 2 atmospheres. Heating slices for four hours was found to lower the resistivity by a factor of 2-10 but prolonged annealing (~24 hrs.) resulted in a resistivity of ~10Ω cm at room temperature and 1-2Ωcm at 600°C.

Even with low bulk resistivity, problems were encountered during early stages of the project in producing deposits of uniform thickness. The first InP deposits were often dendritic as in the example of Fig. 8. This problem was attributed to inadequate surface preparation, with growth occurring preferentially on protuberences on the CdS. Subsequent difficulties in reproducing the current density with polished, low resistivity CdS wafers were believed to be mainly due to changes in the contact resistance either between the wafer and the holder on the wafer and the melt. Attempts

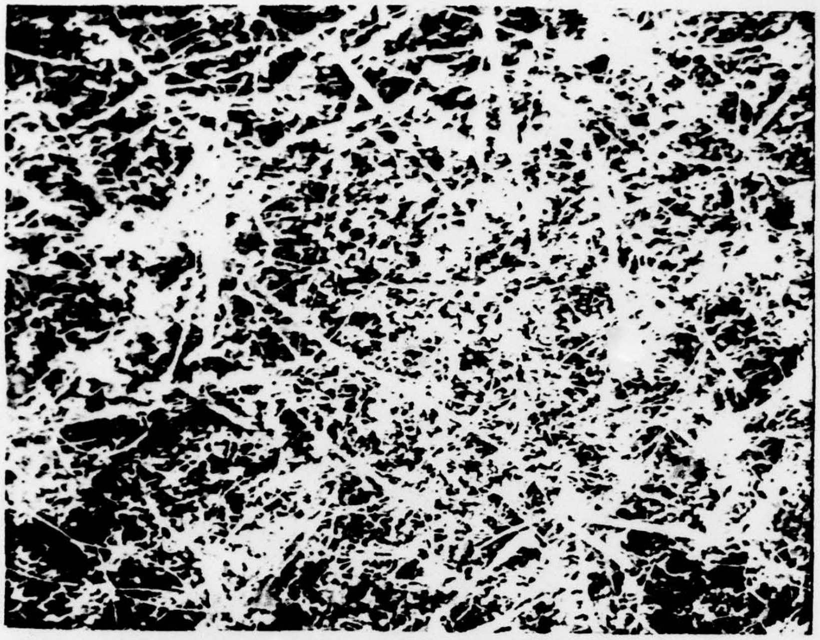

Figure 8. Typical dendritic deposit produced during the earliest stage of the investigation.

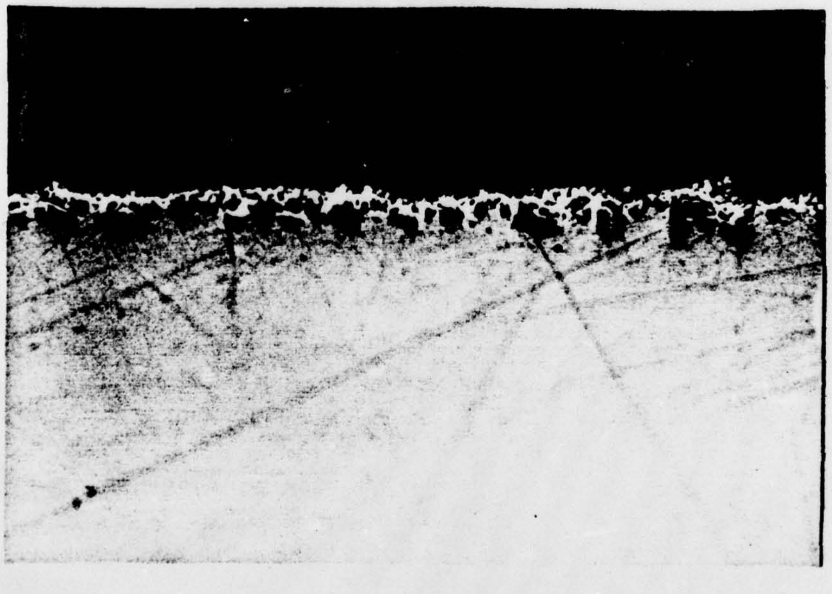

Figure 9. Cross section showing irregular InP deposit on CdS at very low current densities. The deposit appears bright and the dark regions are voids.

were made to minimize this problem by coating the wafer either in the region which contacts the holder or over the entire surface facing away from the anode. Various metals were tried for these coatings, which were normally applied by vacuum evaporation, and gold was found to give the best deposits. However, the uniformity and morphology of the deposit on gold-coated substrates previously heated in Cd vapor were inferior to those obtained on uncoated but high conductivity CdS.

Systematic studies of the variation of growth rate with electrodeposition parameters were therefore made using the low resistivity in-house material or wafers given a prolonged heating in cadmium vapor. The {0001} oriented wafers were cut to about 1mm thickness, polished on both sides and were cleaned in acetone and methanol. Immediately prior to use the wafers were given a 30 second etch in 10% hydrochloric acid and were rinsed ultrasonically in distilled water. The final cleaning was performed in the melt used for electrodeposition; no potential was applied for five minutes after immersion in the Pofnak melt, and the slight solubility of CdS in this melt will result in light etching prior to application of a potential to deposit InP.

An additional problem leading to lack of reproducibility of the current density was traced to the formation of an insulating deposit on the anode. This deposit gives a complex x-ray diffraction pattern and it has not been identified, but its effects have been substantially eliminated by cleaning the anode after each experiment.

The dependence of the morphology of the cathodic deposit on the deposition potential has been studied in the potential range 0·80-1·30V (versus graphite). At potentials below 0·85V, InP films are absent or extremely thin indicating that the deposition rate is very low and probably comparable with the rate of diffusion into the CdS(8). Prolonged deposition at 0·85V results in a smooth, opaque film but sectioning shows that the substrate surface becomes very irregular due to etching by the melt, and the film is very nonuniform. (Fig. 9).

Figures 10-12 show cross sections of InP films deposited on CdS at potentials in the range 0·90-1·0V. These films are 2-5μm in thickness depend-

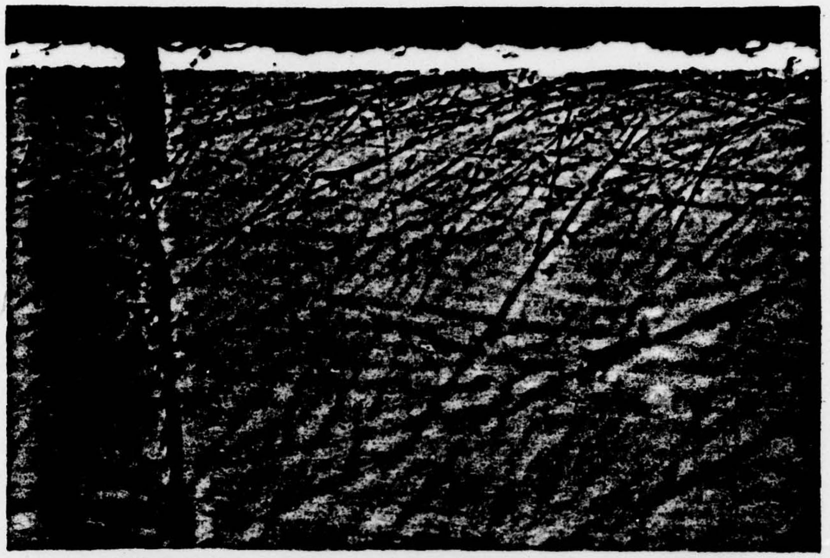

Figure 10. Cross section of InP deposited on CdS at 1·0V. (The crack was introduced during mounting). (1550X)

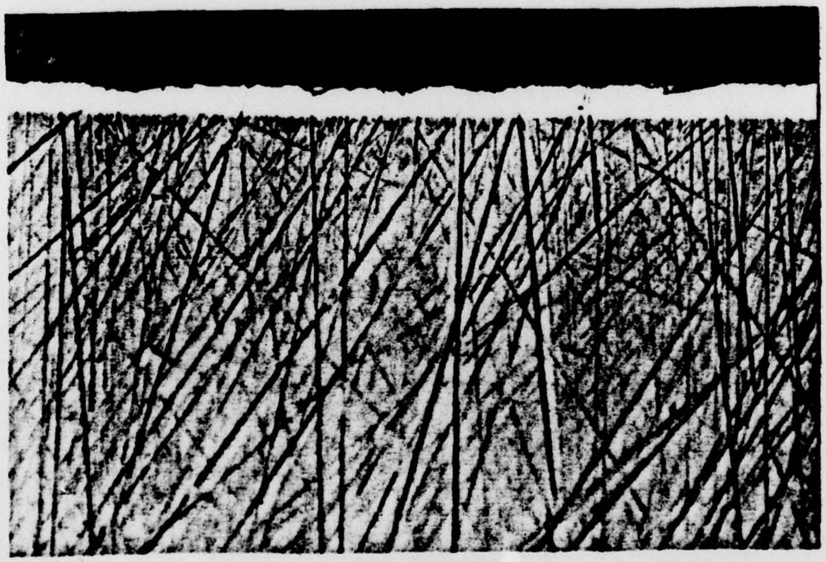

Figure 11. InP deposited on CdS at 0·95V. (Polishing marks are seen on the CdS.) (1550X).

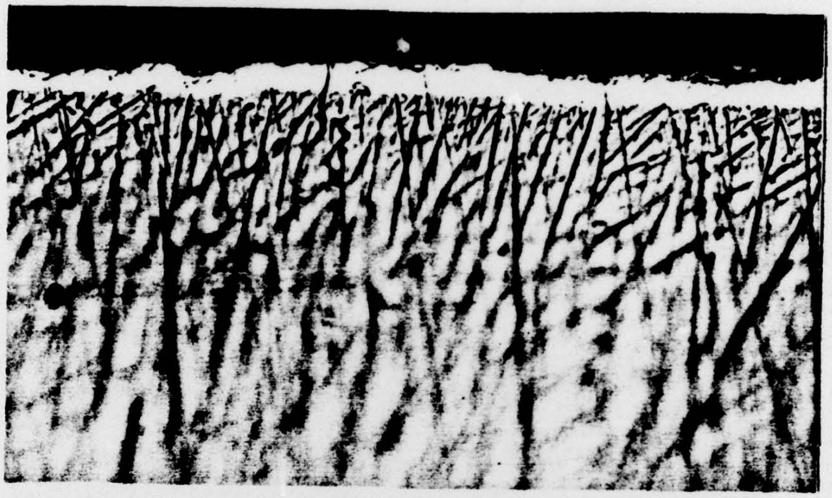

Figure 12. InP deposited on CdS at 0·90V.
(1550X)

ing on the current density and time of deposition, the growth rate being 1-2 μm/hr. Although these deposits do have some areas of nonuniform growth, the uniformity is greatly superior to that of films grown at lower (or higher) potentials so that the potential range from 0·90V to about 1·00V has been identified as the optimum for film uniformity. The corresponding current densities increase from 1 to 1·5 mA/cm^2 at 0·90V to about 3 mA/cm^2 at 1·00V. These values are much lower than the corresponding figures for the stable growth of GaP on (111) n-type GaP, since in that case stable growth was found to be possible at current densities as high as 20 mA/cm^2(5). The reason for this difference in behavior has not been fully established but the relatively low solubility of In_2O_3 at the deposition temperature and the high viscosity of the solution in comparison with that used to deposit GaP at 900°C are factors that will lower the maximum rate of stable growth (9).

The efficiency of deposition, calculated from the thickness of the deposit, has been found to be 50±4% for all the deposits at constant potentials in the range 0·90 - 1·00V. No systematic trend in the deposition efficiency could be observed across this range.

At potentials above 1·0V, deposits become irregular in morphology and dendritic growth is frequently observed. Deposits occur preferentially at the edges of the substrate wafer.

Very thin (~0.5 μm) deposits on (0001) CdS at .90-.95V appear from morphological observations to be epitaxial and additional rings or spots from these films (Fig. 13) have not been detected by x-rays. There is, however, no positive evidence that the InP layers are epitaxial. Thicker deposits such as these shown in Fig. (10-12) appear polycrystalline as is indicated by scanning electron microscope photographs normal to their surfaces (Figs. 14). The grain size is 1 μm or less, but there is evidence in the deposit of Fig. 14b of preferred orientation of the InP crystallites. Since it was found possible to electrodeposit epitaxial films of GaP on both Si and GaP substrates, the origin of the polycrystallinity in the case of InP on CdS cannot be attributed to a universal problem of electrodeposition. The failure of this system to give single crystal films is not understood and studies of the nucleation of InP on CdS have not yet shown why the deposits are polycrystalline.

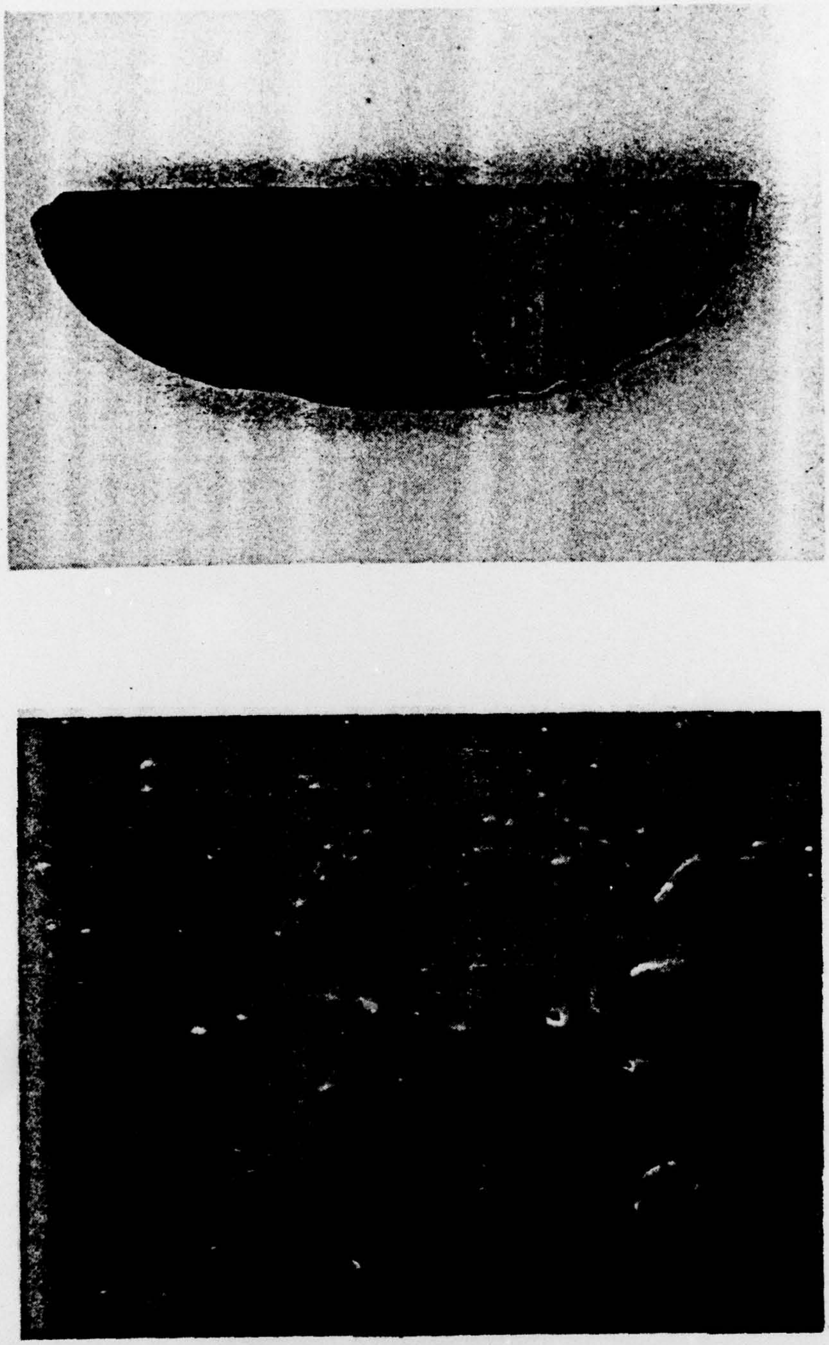

Figure 13. (a) CdS wafer with InP film on lefthand side (the parallel bands for resistance measurement).
(b) Scanning electron micrograph of the InP surface (800X).

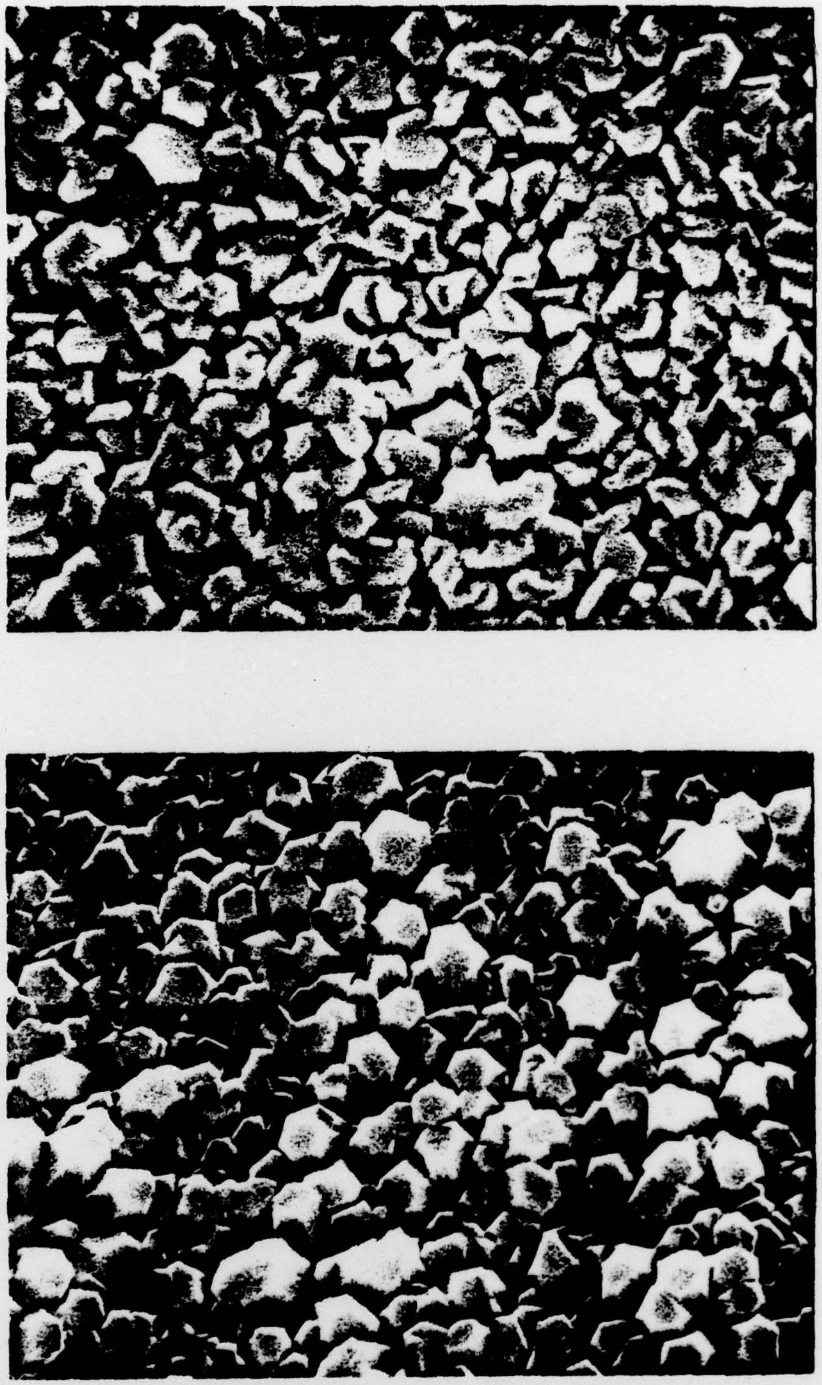

Figure 14. Surface structure of InP deposit on CdS at (a) 0·95V (b) 0·90V. (10,000X)

Characterization of the electrical properties of the deposits is made difficult by the requirement that the substrates should be of fairly high conductivity, and it cannot be assumed that the substrate conductivity is much lower than that of the deposits. Four-contact measurements on representative samples have indicated resistivities in the range from 0·5-5 Ωcm. These values are not untypical for doped InP with $\gtrsim 10^{16}$ carriers/cm^3, but the measured values will be increased by grain boundary effects and it is probable that the carrier concentration is higher than 10^{18}cm^{-3}.

Electroluminscence measurements showed a very broad peak, again indicating an influence of grain boundaries.

G. InP on InP

A number of deposits have been made on {111} and {100} n-type InP substrates grown by Varian Associates. The wafers were polished on one side and cleaned using a similar procedure to that described for CdS.

The quasi-static I-V plot was similar to that for CdS and so it was expected that uniform thickness deposits could be obtained by deposition at constant potentials in the range 0·90 to 1·00V. No problems were encountered with reproducibility of currents in the range 1-3mA, and values of 55-80% were measured for the current efficiency for InP deposition.

In each case the deposits were found to be polycrystalline and nonuniform, with small projections less than 1 μm in separation together with larger features up to 20 μm in diameter. The origin of the nonuniformity in the deposit is not understood at the present time but has been attributed to the cleaning procedure used for the wafers. A follow-up study of this problem is currently in progress and alternative cleaning procedures are under investigation.

IV. CONCLUSIONS

Indium phosphide has proved much more difficult than gallium phosphide to electrodeposit in epitaxial layers of uniform thickness. Severe restrictions on the highest temperature at which deposition is practicable are imposed by the tendency of the material to decompose by evolution of phosphorus and also by the vapor pressure of In_2O_3 which has been found to be the most effective solute to deposit indium. The maximum deposition temperature has been found to be in the region of 600°C.

Of the various candidate solvents investigated, the quaternary $NaPO_3/KPO_3/NaF/KF$ eutectic has proved the best choice and the reproducible deposition of InP from solutions of In_2O_3 has been studied on CdS and InP single crystal substrates. Deposits on CdS are uniform and inclusion-free if the deposition potential is in the range from -0.90V to -1.00V versus graphite. Although very thin (<1 μm) layers may be monocrystalline, thicker layers are polycrystalline even with current densities as low as 1-3 $mAcm^{-2}$. Resistivities of the deposits are in the range 0·5-5Ωcm, but characterization of the material deposited has been handicapped by the problem of making epitaxial films. This same limitation applied to studies of electropurification, but the concentration of most impurities in the layers decreases as successive deposits are made, so that high purity layers could be deposited following a clean-up procedure using a sacrificial cathode.

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