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LARGE PLATE CdTe SYNTHESIS BY SEALED VESSEL TRANSPORT

A. R. HILTON, PRINCIPAL INVESTIGATOR
(214) 494-5624

QUARTERLY TECHNICAL REPORT NO. 4

REPORT PERIOD: SEPTEMBER 1 - DECEMBER 31, 1982

SPONSORED BY:

Defense Advanced Research Projects Agency (DOD) ARPA Order No. 4383. Under Contract No. MDA903-82-C-0159 issued by: Department of Army, Defense Supply Service - Washington, Washington, D. C. 20310

AMTIR

AMORPHOUS MATERIALS, INC.
3130 BENTON • GARLAND, TEXAS 75042

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

The fourth quarterly Technical Report for the program to grow large plates of high purity CdTe in a sealed system covers the period Sept.1-Dec.31,1982. Previously, in Technical Report 3,the decision to change to a vapor-melt process involving a three chambered system was reported. Results of 10 attempts to grow 6" (6-in.) plates from Stoichiometric melts are reported. In all cases, a void region occurs between the faces of the plate. To solve this problem, solution growth was selected over stoichiometric growth. A solid whole grain structure was obtained. The method was applied to growth of 8" (8-in.) plates but some difficulty

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was experienced. Analytical results of material grown in the vapor-melt process have demonstrated purity improvement. The AMTIR approach as applied promises to meet all program goals. Continuation of the effort to grow 8" and 10" diameter plates is recommended.

8-in 10-in

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SUMMARY

The goal of this program is to use vapor growth to form polycrystalline plates of cadmium telluride (CdTe) 6", 8" and 10" in diameter. The resultant material will be evaluated as substrates for mercury-cadmium-telluride (HgCdTe) growth and as an infrared optical material. Late in the program, mercury vapor will be used in an attempt to grow HgCdTe layers on the large area CdTe plates.

Previous workers have grown large plates of CdTe 6" in diameter transporting the vapor using an inert gas. The starting material was pre-compounded. The method to be used in this program was to compound the material and transport the vapor through a filter into the casting chamber for growth in one operation under vacuum. Solid state recrystallization carried out at high temperatures over a long period of time will produce the desired large grain structure.

Results reported in the first three quarters demonstrated the initial process concept was impractical. Vapor transport of compounded CdTe in a sealed evacuated system was too unpredictable. High temperatures coupled with the presence of cadmium oxide caused a high percentage of quartz failures. Program goals could not be reached with the original process approach. The decision was made to convert to a three chamber quartz system in which the cadmium and tellurium vapors entered the plate chamber from separate tubes.

The new process approach was used ten times to produce 6" diameter plates from a stoichiometric melt. Plates weighing almost 2Kgms and possessing the required large grain structure

resulted. However, a void region was found to occur between the faces of the plate each time. Growth from solution was used to eliminate this problem. A plate was grown with grains running from the bottom face to the top face from a solution of approximately Cd45 Te55. Total process time was about 72 hours.

Analytical results demonstrate the purity of the CdTe produced using the full AMTIR method with the 3 chambered system was improved over the beginning reactants. The process promises to meet all the program goals. Results from the 6" attempts are used as a basis for recommending continuation of the effort to produce 8" and 10" diameter plates. A special report is contained in Appendix 1.

Application of the method to 8" plates has thus far not been as successful as expected. Plugging of the filters in the Cd side has become a problem. Changes in process variables and changes in filter construction should eliminate the problems.

Efforts next quarter will concentrate on improving the process variables relative to grain size, grain quality and purity. New process control equipment will be applied to obtain better growth rates.

I INTRODUCTION

A crucial problem in the volume production of U. S. Government FLIR systems is the availability of mercury-cadmium-telluride (HgCdTe) detector arrays. Certainly fabrication of the arrays is difficult but the major problem is the availability of high quality detector material. The production of bulk HgCdTe alloy is a slow, difficult low yield process. The preferred method to produce detector materials is to grow HgCdTe layers epitaxially on a high quality cadmium telluride (CdTe) substrate. However, the availability of high quality Cd Te is also limited. Part of the reason for the shortage is that the conventional method for preparing CdTe crystals is to slowly (0.1"/hour) zone refine small diameter (1") crystals using the Stockbarger technique. The purpose of this program will be to develop an alternative approach.

Large plates of high purity large grain cadmium telluride will be grown from the vapor in a sealed system. Cadmium telluride will be compounded from the elements and sublimed through a filter into a separate growth chamber 6", 8" or 10" in diameter. Grain size will be increased by solid state recrystallization. Material thus produced will be evaluated regarding purity, optical homogeneity and suitability as substrates for HgCdTe growth. Attempts will be made to grow HgCdTe layers by mercury vapor deposited on large area plates insitu.

II. VAPOR GROWTH OF CADMIUM TELLURIDE

A. General

Cadmium telluride is formed from the group II element

cadmium and the group VI element tellurium. All II-VI compounds, as they are called, are difficult to grow because of their high melting points and the fact that both constituent elements are volatile. An appreciable vapor pressure exists for each element at the solid melting point which leads to complications for melt growth. For the same reason, vapor growth of the solid becomes attractive.

Solid CdTe may be grown from the vapor at temperatures considerably below its melting point, 1097°C, according to the following equation:

$$Cd\ (g) + \tfrac{1}{2}\ Te_2(g) \rightleftharpoons CdTe\ (s)$$

Where: g signifies gas or vapor
s signifies solid

The reaction as written is reversible which indicates that solid CdTe will sublime or vaporize into its constituent elements. Thus, the source of Cd or Te_2 gas may be either the pure heated elements or a heated source of pre-compounded CdTe solid.

The quality of the CdTe grown from the vapor (or melt) depends upon maintaining the exact ratio of 1:1 between the cadmium and tellurium atoms. The pressure of cadmium vapor (pCd) and the pressure of tellurium vapor (pTe_2) in equilibrium over solid CdTe at the growth temperature is very critical and a function of temperature. Deviations from stoichiometry will occur if the ratios are not closely controlled. Supplying the vapors from pure elemental sources heated separately and mixed together at the reaction sight is not too accurate. Even the use of inert carrier gasses does not improve the situation to any great extent. Sublimation of precompounded CdTe followed by removal of the vapor to the reaction sight is far more accurate. The compounded material may

be weighed to an accuracy of 0.1% or better. The accuracy of the ratios may be maintained through direct sublimation in a closed system or through use of an inert carrier gas in a flowing system.

One quality criteria not mentioned thus far is crystallinity. In melt growth, crystals of one single grain may be grown provided that a seed is used and growth rates are very slow. Such restrictions are also the prime limitation relative to diameter of the crystal. In vapor growth, crystals are grown on other crystal surfaces of the same or similar structure, or they grow on an amorphous substrate with spontaneous nucleation and growth occuring over the entire surface. The first case may produce single crystals provided that growth conditions are carefully controlled. The latter method may produce large grain material provided high growth temperatures are maintained over long periods of time.

B. Previous Work

The first extensive investigation of the preparation of CdTe was carried out by D. de Nobel [1] of Phillips. The results published in 1959 details the thermodynamic properties, optical, electrical and semiconducting properties of the materials. The liquidus-solidus curve and related pressure-temperature studies have served as the basis for melt growth of CdTe over the years. Discussions related to melt growth will not be repeated here only as they are relative to vapor growth.

L. R. Shiozawa and co workers at Gould (now Cleveland Crystal Laboratories) carried out an extensive investigation

beginning in the late 1960's concerning the vapor growth of II-VI compounds generally [2] and cadmium telluride [3] specifically. Diagrams from their papers will be used to discuss the problems involved in vapor growth of cadmium telluride.

Figure 1 shows the simple binary phase diagram of the Cd-Te system [2]. The diagram indicates a single compound is formed, CdTe, which has a congruent melting point of 1092°C. The term "congruent melting point" indicates that except at perfect stoichiometry, below the 1092°C melting point, both Cd rich and Te rich liquids exist in equilibrium with pure CdTe. The point is better illustrated in the diagram [4] shown in figure 2. Only in a vary narrow range of stoichiometric ratios does the pure CdTe and its equilibrium vapor pressure exist. The range is less than one part per hundred thousand or 0.001 percent. Minimum vapor pressure at all temperature exist along this line. Equilibrium vapor pressure would be exactly in the right ratio. However, considering the accuracy required, it is more likely that the solid cadmium telluride would be either Cd rich or Te rich. Vapors above the solid would reflect this fact and be larger than those above exactly stoichiometric material.

The pressure of cadmium at the cadmium rich boundry stability field as a function of temperature [2] is shown in figure 3. The tellurium rich [2] is shown in figure 4. In both diagrams, the data is compared to the pressure for the pure element, P Cd (l) and P Te2 (l). For the low temperature, the measured values are very close to those for the pure liquid or close to those corrected according to RAOULT's Law. RAOULT'S law states the vapor pressure of a component is lowered by its atomic fraction in a liquid mixture:

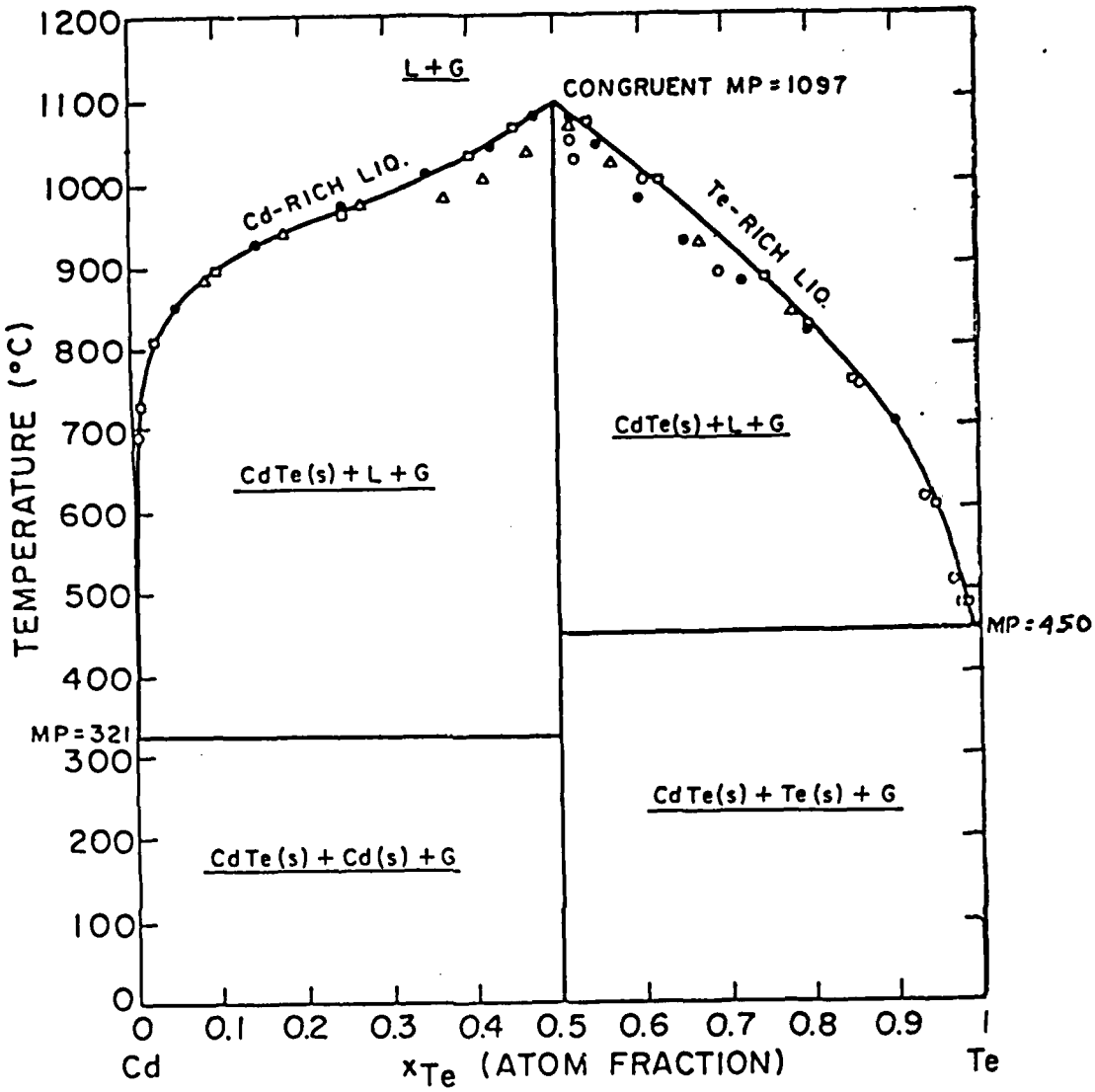


FIG. 1. PHASE DIAGRAM OF THE Cd-Te SYSTEM.

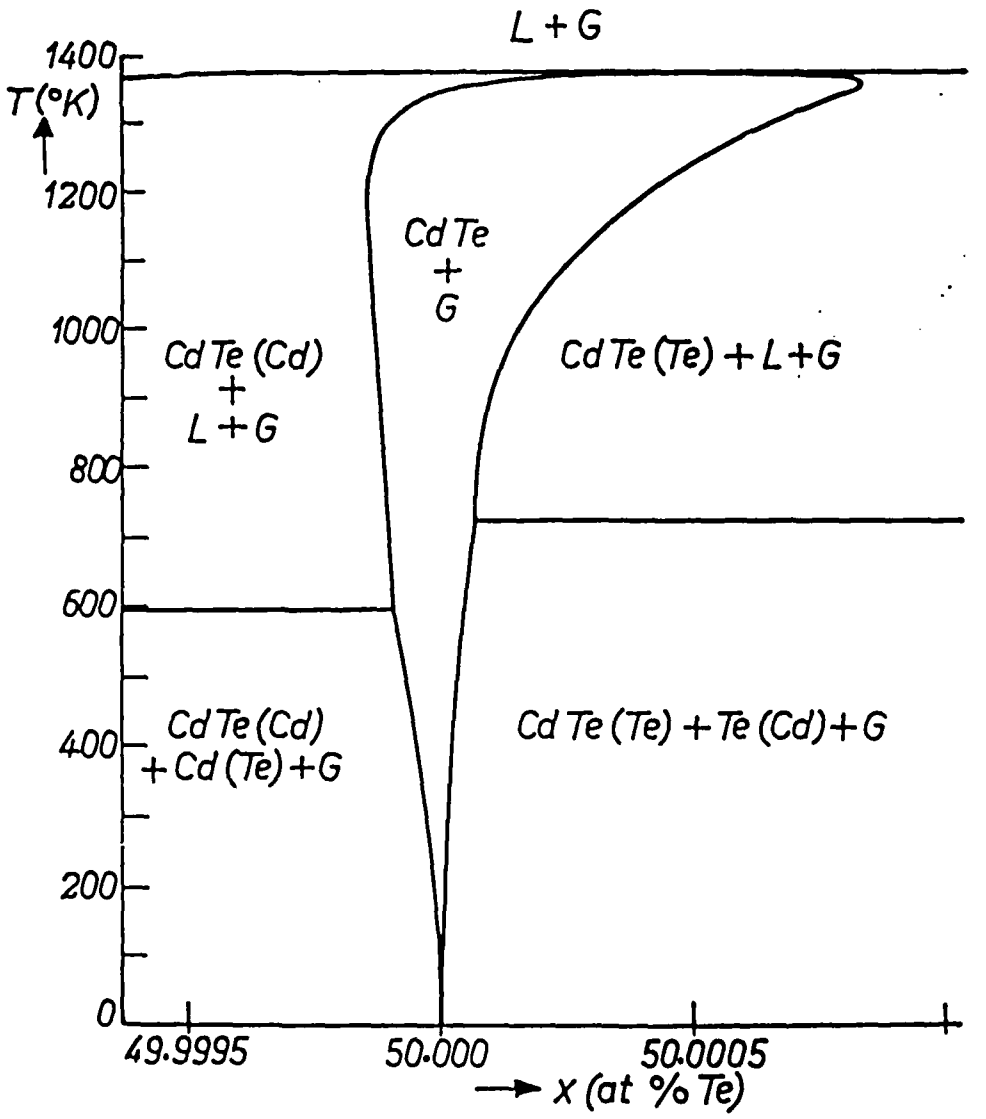


FIG. 2. SOLID STABILITY FIELD OF CdTe.

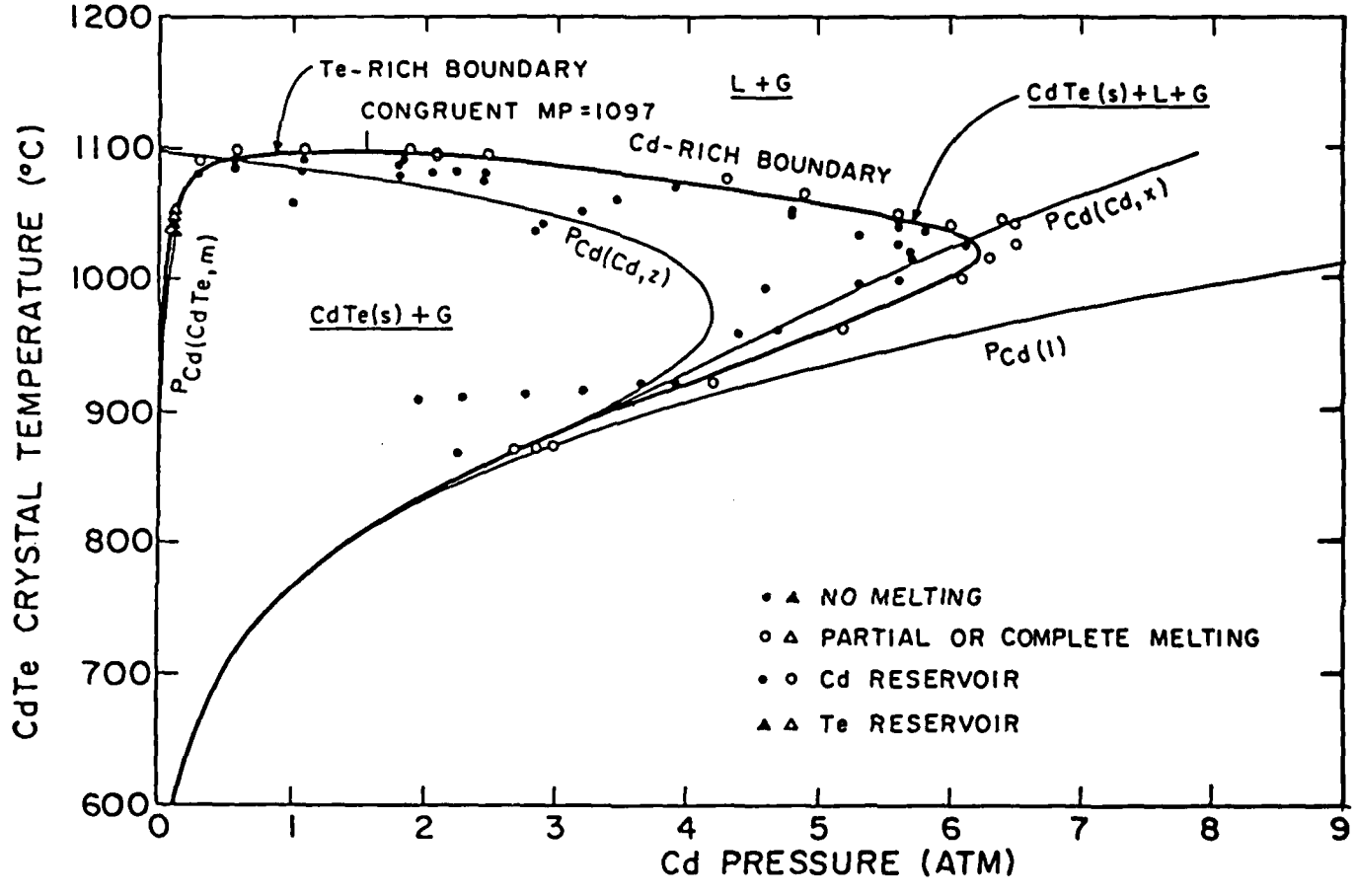


FIG. 3. Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

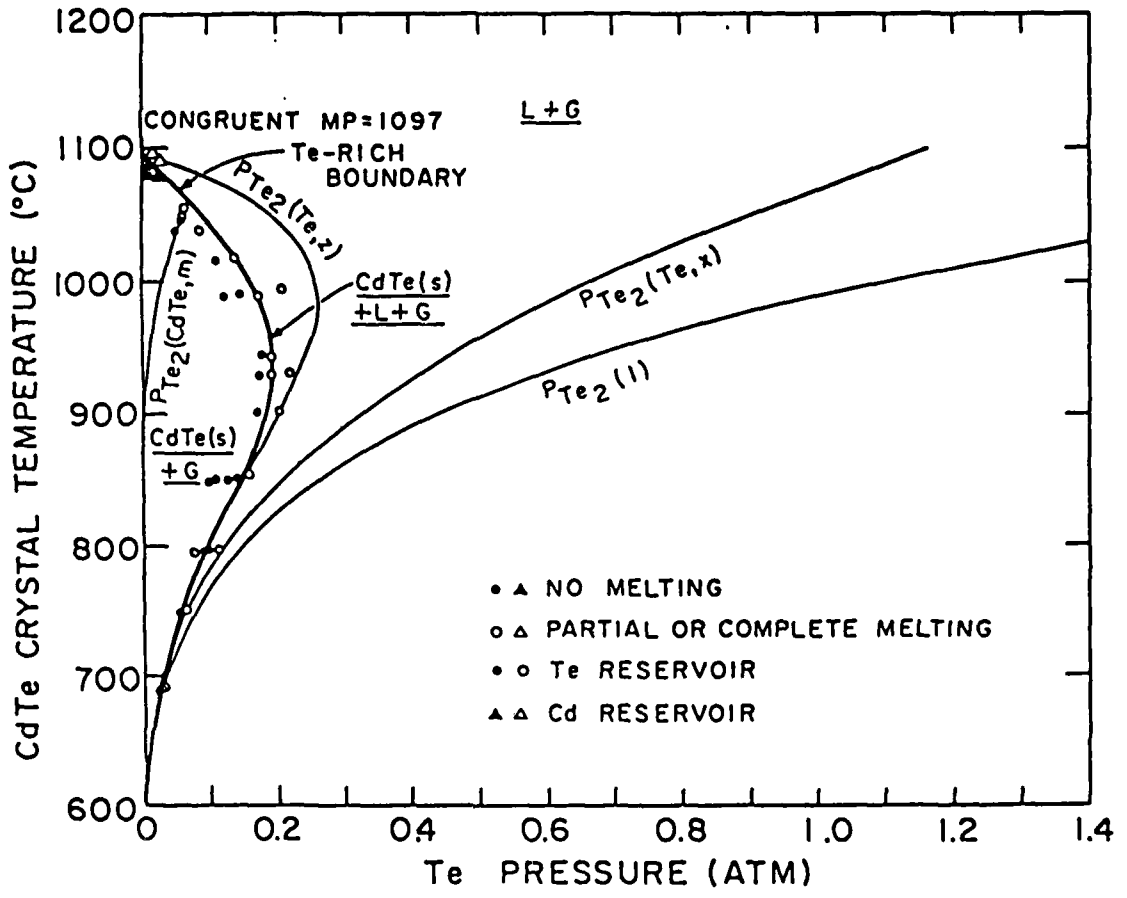


FIG. 4. Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

$$P_{Cd} = x \; P_{Cd}(l)$$

Where P_{Cd} is the pressure of cadmium above the melt

$P_{Cd}(l)$ is the pressure of pure cadmium at the temperature of measurement

X is the atomic fraction of cadmium in the melt.

A similar statement may be made for the pressure of tellurium. The calculated curves using X are a simple application of RAOULT'S law. Those using the Z subscript indicates that association between the atoms in the liquid are taken into account. The curves labeled with the M subscript correspond to the minimum pressure conditions which exist with only pure Cd Te solid present.

The diagrams indicate that the pressure of cadmium may become very large, 4-6 atmospheres, around 1000°C when compounding cadmium telluride. The pressure at the congruent melting point, 1092 °C, is about 0.65 atmospheres. The vapor pressure of tellurium is quite low throughout the compounding range. The trick to compounding without an explosion is to stay close to the perfect stoichiometry point and allow time for the liquid phases to become small in quantity. The trick in vapor growth is to be sure that the subliming material is near the stoichiometric ratio so that the resulting vapors are close to the proper ratio. Maintenance of the proper ratio during vapor growth is complicated by the fact that tellurium exists as a diatomic gas, Te2. The effusion rate for a gas is inversly proportional to the square root of its molecular weight and directly proportional to its pressure. Therefore, for CdTe sublimation, we find the effusion ratios to be [2]

$$R\ Cd/R\ Te_2 = (PCd/PTe_2)\ (MW\ Te_2/MW\ Cd)^{\frac{1}{2}}$$

Where R is effusion rate
P is pressure
MW is molecular weight

Even though the vapor starts out at the perfect 2/1 ratio, the cadmium atoms move faster changing the effusing gas mixture ratio. For Cd Te, the ratio becomes 1.33 instead of 2. Build up of the excess component may limit the deposition rate in a sealed system where equilibrium type conditions may be established. The equilibrium constant is given by:

$$K\ Cd\ Te(s) = (PCd)\ (P\ Te_2)^{\frac{1}{2}}$$

The build up of one component over the other shifts the equilibrium and suppresses further sublimation. Some have used capillary tubes to allow the excess component build up in the vicinity of the source to be pumped away or eliminated. Others have used a carrier gas to carry the subliming vapors, with perfect ratios, to the deposition surface.

C. Vapor Growth of CdTe Plates

Shiozawa [3] and co-workers at Gould used physical vapor deposition (PVD) to grow CdTe plates up to 6" in diameter. Figure 5 illustrates the type of systems used. Pre-compounded CdTe was sublimed from the hot zone of a furnace to a slightly cooler zone. Best results were obtained when growth temperatures of 1000-1050^{o}C were used. Recrystallization was allowed to occur over periods up to 400 hours (17 days).

Figure 6 illustrates the type of grain sizes which were obtained. Growth and recrystallization at 950^{o}C produced small grains. Fast deposition and short growth periods even at the high temperatures produced plates with samll grains and voids.

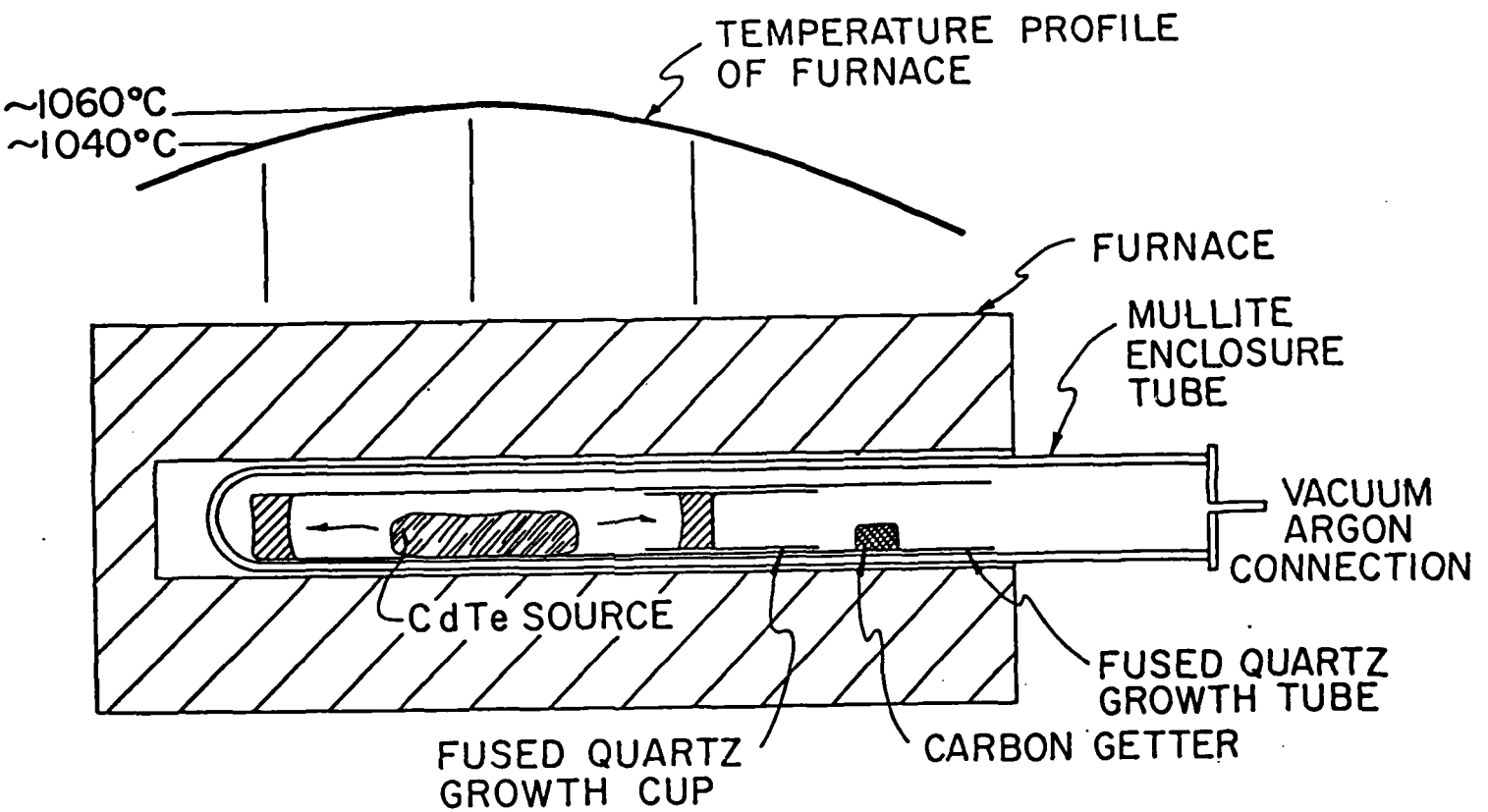


FIG. 5. HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH

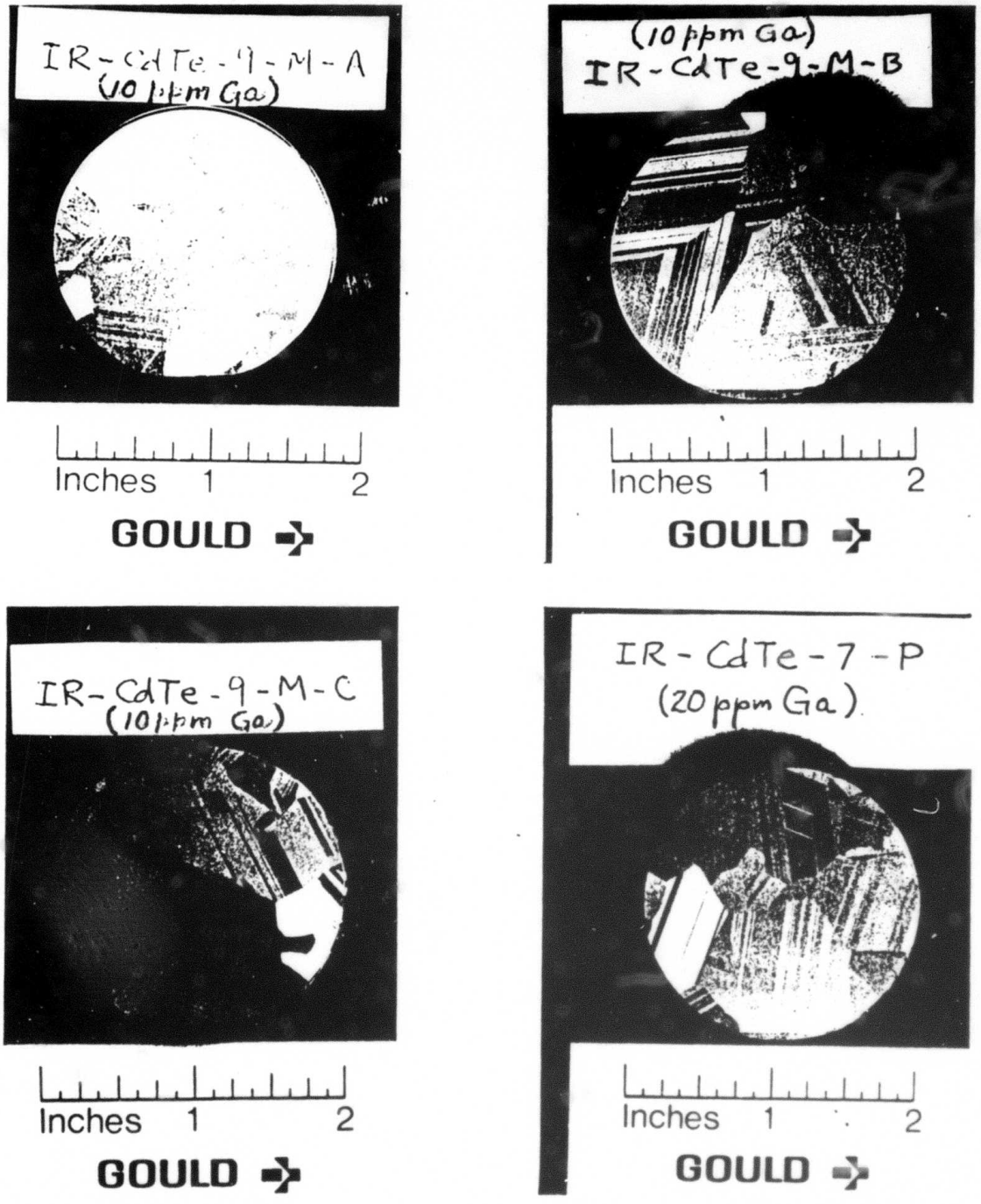


FIG. 6. Lapped Surfaces of CdTe Window Blanks Highlighting Grain and Twin Patterns.

The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures up to 1 atmosphere was used but 180 mm, the vapor pressure of stoichiometric Cd Te at 1050°C, was the preferred pressure. Later versions of the system used graphite parts to minimize the effects of air leaks. Also, inert gas was flowed through the furnace to protect the graphite components.

Plates thus produced were heat treated with both Te_2 and Cd vapors at temperatures of 700-800°C. Treatments were alternated and lasted 1-5 days. Measured absorption at 10.6μm was 0.001-0.002 cm^{-1}. The effect of heat treating on the infrared transmission of one of their CdTe plates is shown in figure 7. From the transmission for Cd treatment alone, one can see that dual treatment is necessary. After treating with Te_2 vapor, almost theoretical transmission was obtained.

III APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

A. Preparation of AMTIR-1 glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-1, is shown in figure 8. A high purity quartz container is placed in a dual zone resistive heated furnace. Zone 1 contains the round empty chamber which will serve later in the process as the casting mold. Zone 2 contains the glass compounding chamber. The process employed at Amorphous Materials combines all three glass processes (element purifications, compounding the glass and casting the plate) into a single continuous process.

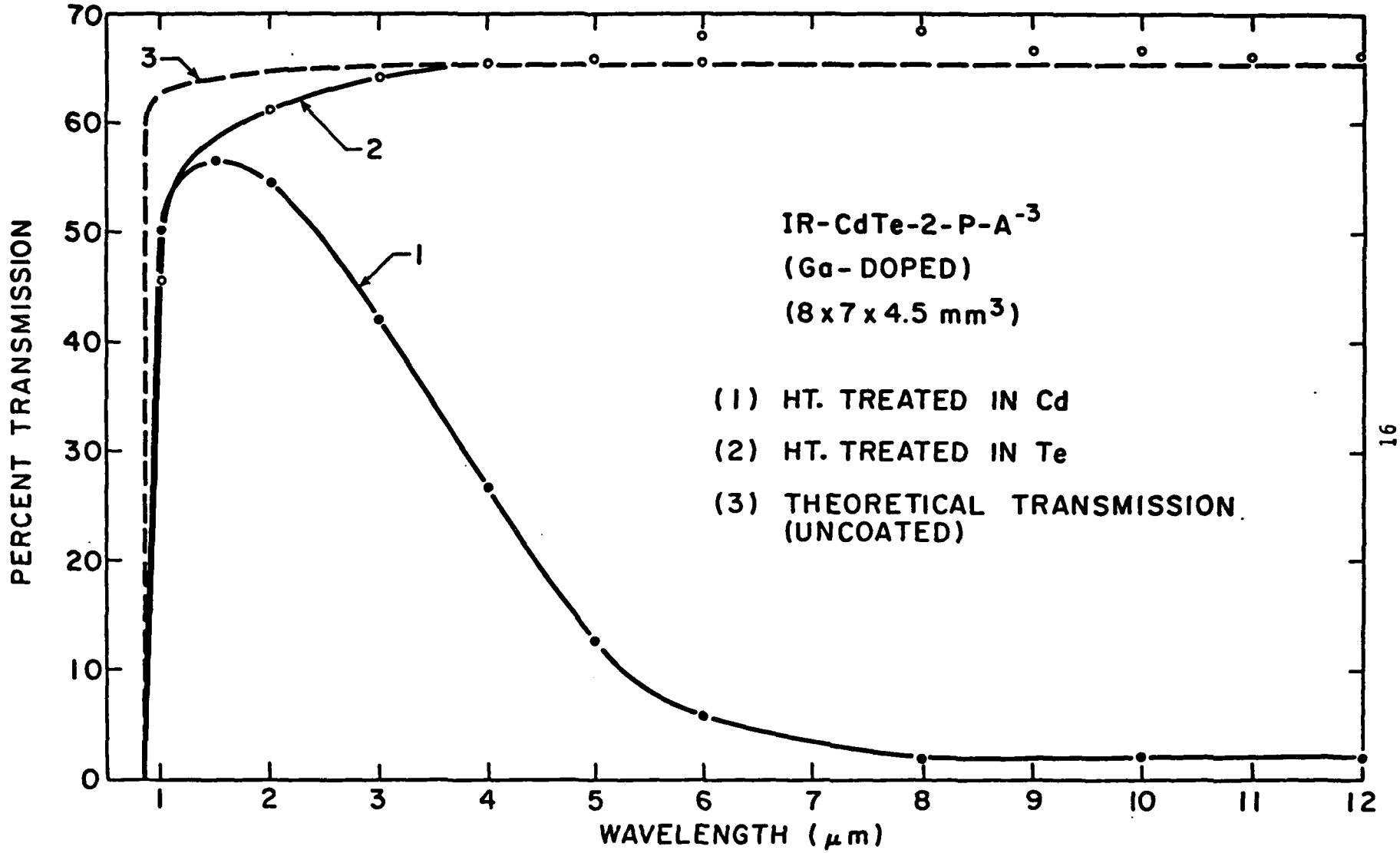
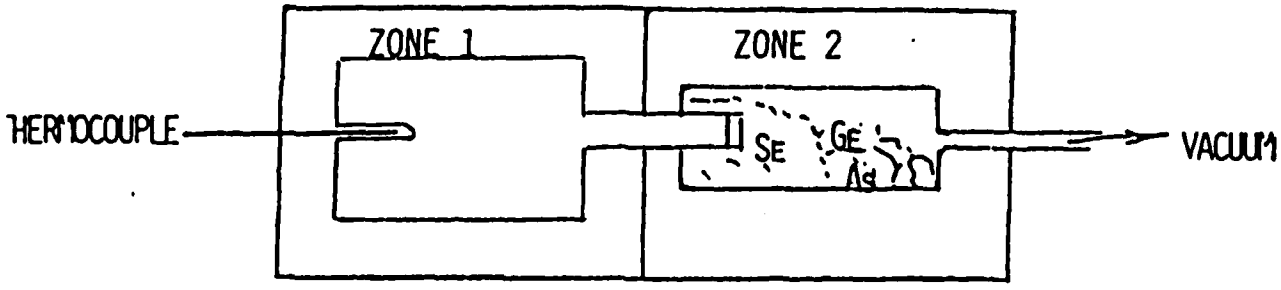
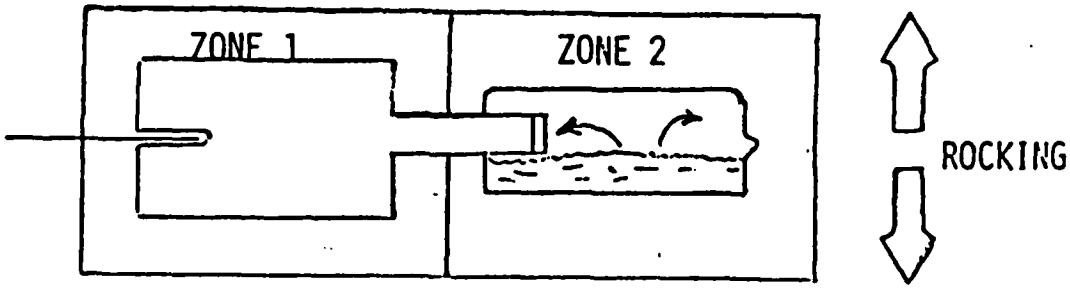


FIG. 7. OPTICAL TRANSMISSION OF Ga-DOPED CdTe

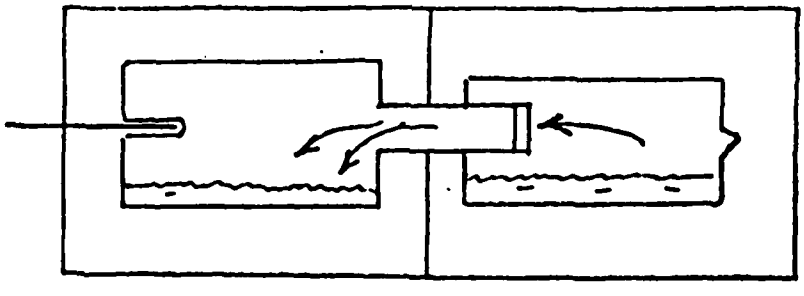
FIGURE 8. GLASS PROCESS DIAGRAM



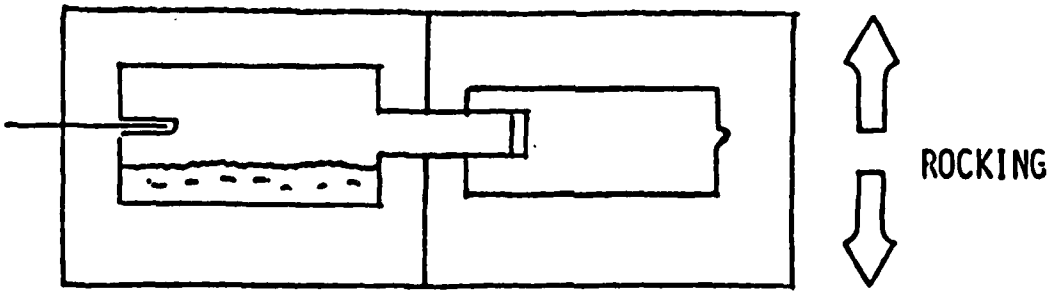
PURIFICATION



COMPOUNDING



DISTILLATION



CASTING

In the first step, both chambers are evacuated and heated to remove moisture. A small amount of aluminum wire is added to the elements to act as a getter of oxides in the molten glass. After several hours, the chamber is sealed off while still under vacuum by heating and collapsing the pumping tube. The furnace is closed and need not be opened again until the glass is quenched.

The temperature is raised in both chambers while rocking the furnace. The casting chamber is heated to prevent premature transfer of the elements from the compounding chamber. The furnace is rocked for several hours to insure that all the elements have reacted properly and are uniformly mixed.

Rocking is stopped and the glass casting chamber cooled to allow transfer of the compounded glass into the casting chamber. Distillation occurs through a porous quartz filter which removes all particulate matter. The distillation generally takes 12-15 hours. The amount of material passed through the frit varies depending upon diameter and thickness. A 6" diameter plate 2" thick requires about 4Kgms of glass while a 8" diameter plate 2" thick requires 7Kgms of material. It is interesting to note that the purity of the finished material improves with quantity prepared. The total amount of impurities from quartz walls, vacuum system, etc. remains constant while the ending concentration decreases with increase in mass. The distilled glass is mixed by rocking. The glass is then allowed to cool while rocking down to the casting temperature range. Rocking is stopped and the furnace leveled up. The glass is rapidly cooled using compressed air to the anneal range 370^{o}C. The glass is annealed 6-8 hours before being allowed to cool to room temperature.

AMTIR-1 glass is compounded in very unique and valuable high purity quartz containers. Casting chambers 6", 8" and 10" in diameter are routinely prepared. Methods have been worked out to open the chambers with a diamond saw so that the cast plate may be removed without breaking. The chambers are cleaned up and resealed for reuse. The compounding tubes are not saved. The impurities within the high purity beginning reactants are left behind during the distillation. The residues are sometimes quite large indicating the effectiveness of the method in preparing high purity solid materials.

B. Modification for Vapor Growth of Cd Te

The temperature range involved in cadmium telluride compounding and solid state recrystallization is 1050-1100^{o}C, well above the compounding temperature used for AMTIR-1. However, the furnaces are of sufficient caliber to reach and maintain these temperatures continuously. Times involved are much longer. From start to finish the AMTIR-1 process requires 48 hours to produce a plate. High quality cadmium telluride grown from the vapor with solid state recrystallization (grain growth method) requires 300-400 hours (12-17 days) to produce good quality material 1" thick[3]. For a 6" diameter plate, 2700gms of cadmium telluride would be grown. Considering all these factors, the procedure carried out would be as follows:

1. The correct amounts of high purity cadmium and tellurium will be weighed out and placed in the compounding chamber as before. For a 6" plate, about 2700 grams will be required. High purity aluminum wire will be added (10-20ppm) to serve as an oxide getter. The casting chamber may need to be carbon coated using graphite formed from the pyrolysis of acetone.

2. The compounding and casting chambers will be heated to 200°C to remove moisture and the chamber will be tipped off.

3. The casting chamber will be heated to 1100°C. The compounding side will be heated to the boiling point of cadmium (765°C) and rocking begun. Over a period of hours, the temperature will be increased to 1100°C while rocking to insure complete compounding of the cadmium telluride.

4. Rocking will cease and material transfer begun. The casting chamber side will be reduced to a temperature of 1000-1050°C to bring about transfer of material to the plate side. The high temperature will be maintained so that grain growth will be a continuous process. Particulate matter and oxide impurities will remain behind in the compounding chamber. The time involved may be as long as 10-15 days.

5. After completion of the run, the cadmium telluride plate will be removed from the chamber using a horizontal glass saw as is done for AMTIR plates.

C. Program Objectives

A large diameter, thick, high purity, large grain plate of cadmium telluride will be formed. Individual large grains 1-4cm^3 in volume will be visible in the surface of the plate after lapping and light etching. Evaluation and treatment of the plate depends upon the desired use.

First emphasis of the program will be to establish the growth parameters using 6" diameter chambers. Purity of resultant material will be verified by chemical analysis. Electrical, mechanical and optical evaluation techniques will be

used where appropriate. After growth parameters are established, scale up for 8" diameter and 10" diameter plates will occur.

Substrates will be cut out of 6", 8" and 10" diameter plates for evaluation for HgCdTe epitaxial growth. Disks 2" in diameter and 0.1" thick will be prepared for evaluation by groups designated by DARPA.

Disks 2"D x 0.25" thick will be prepared for optical homogeneity verification. The disks will be polished flat and paralled in order to carry out MTF based image spoiling tests. Additionally, lenses will be fabricated for evaluation in the U. S. Army small imager FLIR common Module.

The last goal of the program will be to grow large area HgCdTe layers insitu. Mercury vapor will be admitted into the 6", 8" and 10" diameter CdTe growth chambers in an attempt to produce layer growth of the right composition.

D. Vapor Growth Results

The results obtained in 14 attempts to prepare CdTe plates using a stoichiometric vapor approach was discussed in detail in Technical Report No. 2. The major difficulties encountered are summarized below:

1. Numerous quartz failures occured probably due to the attack of cadmium vapor at high temperatures and moderate pressures.

2. Formation of solid CdTe in the filters caused plugging. The use of filters had to be abandoned early to aid attempts to transfer the stoichiometric material from the compounding chamber to plate chamber.

3. Sublimation of stoichiometric material in a vacuum system is difficult to control and unpredictable. Excess of one component relative to another will shift equilibrium conditons.

4. Deposition does not always occur where desired.

5. Analytical results reported in technical Report No. 3 did not demonstrate a purity improvement over the reactants. Filters were not used.

6. Trying to pass Cd and Te vapors through the same entrance at the same time to the plate chamber is the cause of major problems.

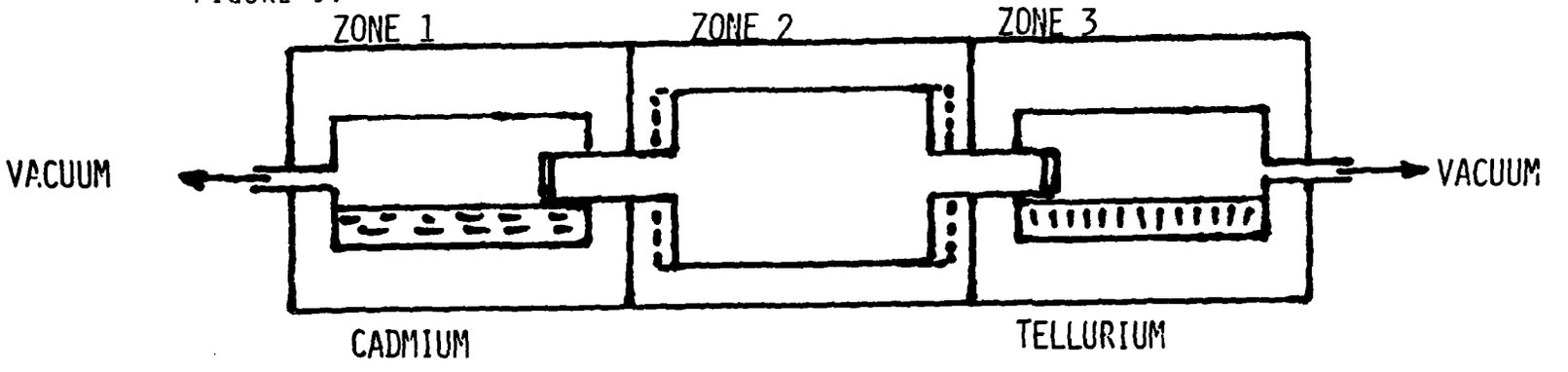
E. Vapor-Melt Growth Method

The conclusion reached from the vapor growth results was that the Cd and Te vapors could not enter the plate chamber through the same entrance. A three chamber zone approach would be required if the program goals were to be met. A diagram depicting the modification of the AMTIR method is shown in figure 9.

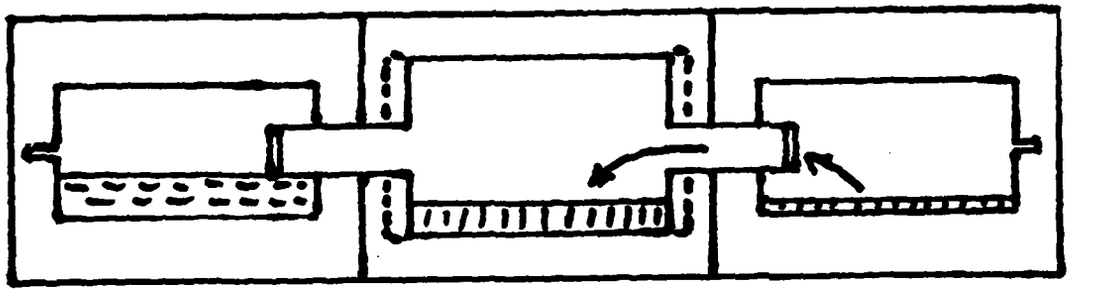
The elements are melted and purified while being pumped from both ends. After this step is completed and the chambers sealed, one element is transferred into the plate chamber and condensed as a liquid. In this case, Te is transferred first. Condensation as a liquid in the bottom of the chamber insures CdTe plate growth will occur where it is most desired. Notice the plate chamber is wrapped with quartz wool insulation to insure uniform temperature.

The second step involves compounding CdTe by transferring Cd vapor into the chamber. After the melt is compounded, air may be blown on the bottom of the chamber to promote crystal growth from the center and the bottom of the melt. The procedure, equipment used and early results were reported in Technical Report No. 3.

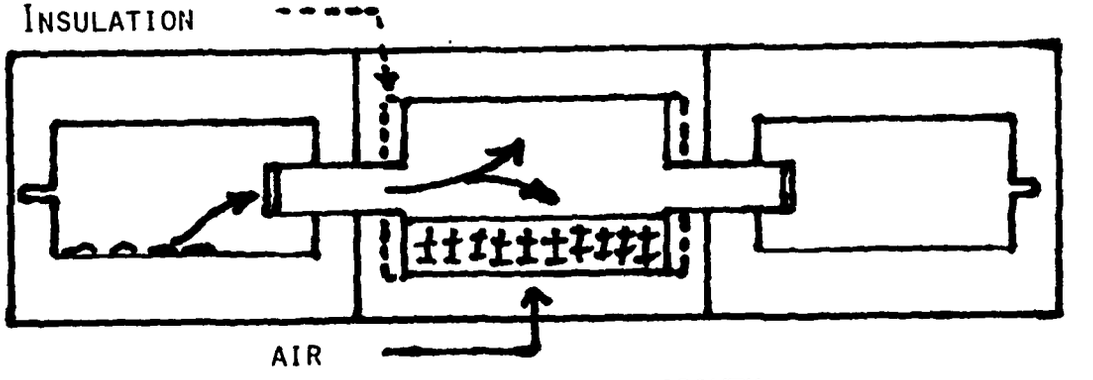
FIGURE 9. THREE ZONE MELT GROWTH PROCESS



REACTANT PURIFICATION



TELLURIUM TRANSFER



CADMIUM TELLURIDE GROWTH

IV. Results for the Quarter

A. General

The conditions and results for all attempts to grow CdTe plates using a three chambered process are listed in table 1. The initial three attempts reported last quarter are included to make the discussion complete .

Generally, the CdTe plate may be formed from a stoichiometric melt or grown from solution. First attempts concentrated on stoichiometric melts in 6" diameter chambers. The Te was transferred into the plate chamber first and the temperature in the chamber raised above the boiling point (1100°C) to prevent back transfer of CdTe. Cadmium pressure is then provided by raising the temperature in that chamber to 750°C which is close to the Cd boiling point. The procedure is depicted in figure 10.

The diagram indicates the naturally occuring thermal gradient induces the growth of CdTe on the bottom of the container. However, as the Cd content of the solution increases to the point of stoichiometry, CdTe begins to form on the top of the melt as the temperature is lowered. The result is that the melt is sealed off and the source of Cd vapor eliminated. As the melt is cooled, the thermal gradient reverses itself causing the top layer to grow at the expense of the melt and finally the bottom layer. The final outcome is a plate containing a void space. Such results were found to occur during runs #17-25. No procedure was found to avoid this situaltion.

TABLE 1. THREE CHAMBER MELT GROWTH RESULTS

RUN NO.	TYPE	SIZE	CONDITIONS	
17	STOICH.	2Kgms.6"	1105°C, 5°/15min. 1080 3 Hrs.	Thin Cracks
18	"	" "	EQUIPMENT FAILURE	
19	"	" "	1105,1°/Min, 1080 2 Hrs.	Cracks
20	"	" "	1105, 1°/Min, 1080 4 Hrs.	Layered
21	"	" "	1105, 1°/Min. 1090 4 Hrs.	Layered Dendr.
22	"	" "	1105, 1°/Min. 1090 5 Hrs.	Layered
23	"	" "	1090, 1°/15 Min, 1080 4 Hrs.	Layered
24	"	" "	1090, 45.5 Hrs.	Layered
25	"	" "	1090, 72 Hrs.	Layered
26	Solution	" "	45Cd-55Te,1090-800 Air 24Hrs.	Lg.Grain,1 layer
27	"	6Kgm.8"		Cd Did not Transf.
28	"	" "	" "	" " " "
29	"	4Kgm.8"	45Cd-55Te,1090-800, 24 Hrs. Air	Most of Cd did not transfer
30	"	2.5Kgms.8"	Cd45 Te55, 1050-800, 24 Hrs. Air, Cd transferred first	Smallgrain plate 0.3"Thk.
31	"	2.5Kgms.8"	Cd45 Te55, 1050-800 24 Hrs. Tellurium transferred while Cd cooled	most of Cd did not transfer, thin plate

FIGURE 10.

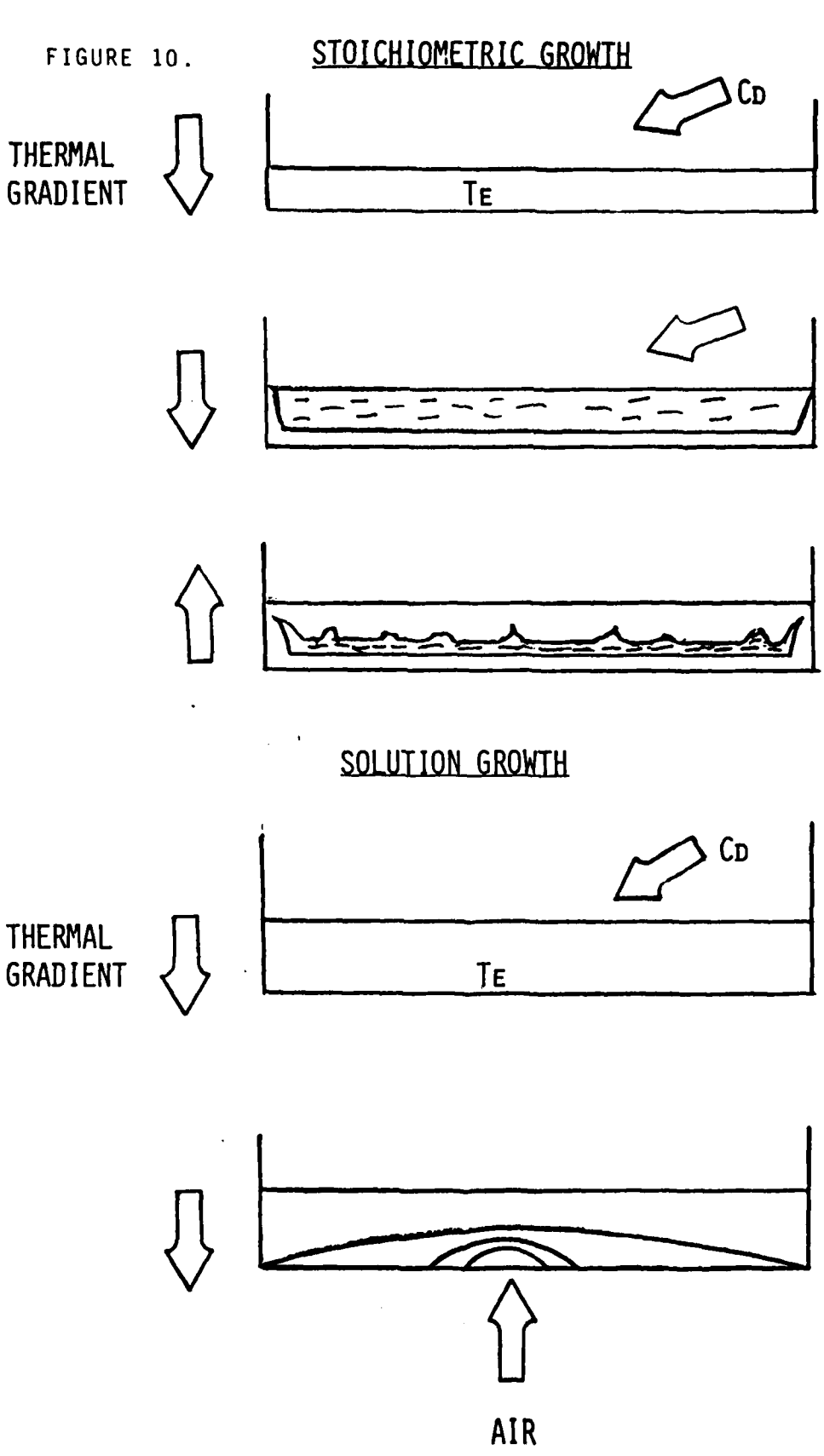


Figure 10. Diagram Depicting Growth of CdTe Plates

Runs #26-31 represent attempts to avoid a layered plate through solution growth as depicted in the bottom of figure 10. In the diagram,the natural thermal gradient is aided by blowing air on the bottom of the chamber to promote crystal growth from the center and bottom of the melt. As the CdTe plate grows, the Cd vapor re-saturates the solution. The plate may be grown at one temperature (isothermal) or the melt may be cooled after saturation.

The first attempt was #26. A solution of $Cd_{45}Te_{55}$ was chosen. The liquidus temperature according to figure 1 is 1075°C. The constituents were weighed such that the composition could be achieved when the Cd and Te were fully transferred. After the temperature had been achieved for 1 hour, an air stream was directed at the bottom of the container. The temperature dropped 20-30°C underneath. Isothermal growth was allowed to occur for one hour. The temperature controlling cam was then turned on to lower the temperaure gradually and anneal the plate.

Examination of the plate revealed the grains extended through the plate. The void between the two plate faces had been eliminated. The grain sizes were large. Some solution entrapment occured in the top surface. However, the general quality was the best we had prepared. The decision was made to move on to the 8" diameter plates. The reasons behind the decision are discussed in Appendix 1 which serves as the "Special Report Recommeding Continuation" promised in the original proposal.

The first attempts to prepare 8" plates are runs #27-31. No scale up problems were anticipated. However, for reasons we have not been able to understand, plugging of the filters

once again became a problem. Very little of the Cd was transferring into the plate chamber to compound the solution. To minimize the problem, the mass of the constituent elements was reduced from 6Kgms for #27 and #28 to 4Kgms for #29 and 2.5Kgms for #30 and #31 which is the same mass transferred for the 6" plates. For run #30, the Cd was tranferred first to avoid the plugging. However, the transfer of the Te was then incomplete. The resulting plate was thin and small grain. Finally, in run #31, the Te was transferred while the Cd was cool. Plugging was less severe but still a problem. The resulting plate was thin, small grained and fractured into many pieces. Poor results for 8" plates relative to 6" cannot be explained at this time. Modification of the filter construction will be necessary to avoid plugging. Changes in the plate chamber construction may help to decrease the problem.

B. Analytical Results

Samples from run #17 and run #19 were submitted to the Analytical Facility at Texas Instruments for Emission Spectrographic Analysis. The results are given in table 2. Both samples represent CdTe which has been fully treated according to the AMTIR method. That is, reactant purification followed by transfer through a quartz filter into the plate chamber. Very little impurity was found in #17 and practically none in #19. Both samples represent real purity improvements over their beginning reactant purity as reported in Technical Report No. 3. Assuming all less than 1ppm levels are truly 1, the indicated starting pruity given in the last report is about 10ppm. Vapor transported material without filters reported at the same time was about 8-10ppm, no improvement. Results for #17 indicate 6ppm and #19 2ppm, a decided improvement. Impurity improvement using the AMTIR method has been

TABLE 2. MELT GROWTH ANALYSIS

Element	Sample No. 1 (CdTe #17)	Sample No. 2 (CdTe # 19)
B	ND	ND
P	ND	ND
Sb	ND	ND
Ge	ND	ND
Pt	ND	ND
Au	ND	ND
As	ND	ND
Mn	ND	ND
Pb	ND	ND
Cr	ND	ND
Mg	D<0.0001	ND
Si	D<0.0001	ND
Ga	ND	ND
Fe	D<0.0001	ND
Ni	ND	ND
Bi	ND	ND
Al	ND	ND
Be	ND	ND
Mo	ND	ND
Sn	ND	ND
Ca	ND	ND
V	ND	ND
Cu	ND	ND
In	ND	ND
Cd	10-100	10-100
Ag	D<0.0001	ND
Zn	ND	ND
Ti	ND	ND
Zr	ND	ND
Pd	ND	ND
Co	ND	ND
Na	D<0.0001	D<0.0001
K	D<0.0001	D<0.0001
Li	ND	ND
Te	10-100	10-100

Results are in weight percent. D: Detected ND: Not Detected

demonstrated.

C. Optical Results

Table 3 summarizes the optical evaluation results for materials prepared using the Vapor-Melt method. Samples were cut only from plates of reasonable quality. Absorption free transmission 2.5-25μm should be about 65%. The approximate absorption coefficient is calculated using the criteria that a value of 0.01 cm-1 will mean 1% tranmission loss for a 1 cm thick sample. An optical quality material should have a value of about 0.02 cm-1. or less.

Free carrier absorption is an indication that the resistivity of the material is low enough for interaction with the infrared radiation to occur. Absence of free carrier absorption indicated high resistivity and thus high purity. Only in the case of #30 has free carrier absorption been observed. Run #30 was the only one in which the Cd was transferred first. The Te then failed to transfer completely. The result was a Cd rich solution which led to lower resistivity.

Grain size in runs #30 and #31 were relatively small, 3-5mm squared. In the first example, #30, the material was grown from a Cd rich solution. We assumed the small grain size was the result of this change. However, #31 had about the same appearance and the solution was Te rich. Finally, we realized the grain size was the result of the concentration of the solution. When one constituent did not transfer, the resultant solution was very dilute leading to a lower "liquidus" temperature. As the melt was cooled, CdTe growth did not begin until a lower temperature was reached. This factor will be used in the future to control grain size.

TABLE 3. OPTICAL EVALUATION OF VAPOR-MELT GROWN CdTe PLATES

RUN NO.	% TRANS. 2.5-25μm	THICKNESS cm	ABS. Coef.cm^{-1}	FREE CARRIER ABS.
17	55	0.6	0.17	none
26	42	1.5	0.15	none
30	34-10	0.7	0.4-0.8	yes
31	52	0.5	0.26	None

D. Discussion of Results

Growth of the CdTe plates in the round chambers may be may be accomplised meeting all program goals provided the filter plugging problem is solved. Control of the growth process absolutely demands the solution concentration is correct as planned. Quartz filters used for AMTIR are too fine for the CdTe process and must be changed in the manner they are constructed.

Probably, the growth conditions for optical quality material will be different. The small grain structure appears to offer a more suitable material for optics because of better physical strength. Precipitation between grains is lessened.

Growth rate from solution depends upon the rate at which the liquidus point is crossed and the temperature lowered. The present cam controlled systems are not accurate enough. Temperature changes can not be changed conviently. Microprocessor controlled units are meeded to produce the best results.

Substrate material probably will be grown thin. Attempts to core drill and slice substrates from thick plates have thus far not been successful. A large area plate, 8" to 10", that is thin, 0.25", may be sawed into squares using a diamond OD saw. The squares may be used in original thickness. Slicing may be accomplished with an ID saw. A large number of 1" x 1" squares may be produced from a single plate. An 8" plate would yield about 35 and a 10" plate about 60. Considering current prices, the process will be economically attractive even if the squares are used in original thickness.

The process being developed shows great promise of achieving all our original goals. The state of the are for high purity CdTe will be advanced relative to size and capacity.

V. PLANS FOR NEXT QUARTER

1. Solve the filter plugging problem for the 8" Chamber

2. Develop control on the 8" process relative to mass, grain size, grain quality and purity.

3. Develop substrate preparation method and make samples available to the industry for HgCdTe growth.

4. Obtain new microprocessor controlled temperature units for better control of plate growth conditions.

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Appendix 1
Special Report Recommending
Continuation of the Program

A. Introduction

The AMTIR method was developed to prepare large plates of a high purity Ge-As-Se glass some 4-5 years ago. The approach has been very successful. However, when one considers applying the method to the production of high purity crystalline semiconductors, a certain amount of doubt arises with regard to the ultimate success of the approach. To guard against the possibility of being locked into a long two year fruitless program, a suggestion was placed in the original proposal that the potential of the method for preparing CdTe be evaluated in Phase I devoted to 6" diameter plates. The 6" diameter should be less expensive and presumably easier to prepare. At the end of Phase I, if promising results did not occur, we were to recommend in a report that the program not be continued into growth of the larger 8" and 10" diameter variety. After some 9 months of effort, the results obtanined from 6" plates were so encouraging that we began work on the 8" variety. The purpose of this report is to make official that decision. The reasons behind our decision will be stated formally in this report.

B. Program Goals

The main goal of the program is to advance the "state of the art" for the production of high purity CdTe. Advance in this case means the production of larger diameter, heavier mass crystals in shorter periods of time at less cost. No attempt is being made to grow single crystals. Reactants of only moderate purity and cost are to be used with purity

improvement in the CdTe plate expected due to use of the AMTIR method. Diameters of plates will be 8" and 10" since such sizes are readily achievable with AMTIR and have never been attempted with CdTe.

C. Specific Goals

Specific goals to be achieved by application of the AMTIR method are:

1. Purification of reactants by melting and surface sublimation of oxides while under high vacuum.

2. Reduction of residual oxygen concentrations by use of aluminum wire as a getter in the molte reactant

3. Transfer of the reactants through a porous quartz filter into a separate round plate chamber. The filter will remove any particulate matter from the reactants.

4. Prepare large plates 8" and 10" in diameter weighing 2-10Kgms in a period of time which is short relative to conventional processes.

5. Control grain sizes so that areas 1"x1" will be present for HgCdTe growth.

6. Substantially reduce the cost for bulk Cd Te Substrates for Hg Cd Te growth.

D. Results Which Indicate The Goals May Be Achieved

The results for vapor growth and vapor-melt growth were discussed in detail in the present report, Technical Report No. 4. To repeat, some 14 attempts to prepare 6" diameter plates using purely vapor growth techniques indicated the approach would not meet the goals of the program. The change to a three container vapor-melt approach immediately produced better results. Plates 2Kgms. in mass were produced with large grains in a period of 48-72 hours. Improvement in purity almost an order of magnitude was demonstrated when the reactants were transferred into the plate chamber through a filter. A method to grow gains through the thickness of the plate was developed. Control of the grain size through composition selection is possible. All goals may be achieved through use of the present approach. Larger sizes should be readily achievable.

E. Need for Larger Diameter Plates

Growth in the thickness direction of the plate must be controlled relative to rate and temperature to achieve the quality level required for the program. In contrast to glass, the quality of the resulting plate can not be expected to improve with thickness. Probably, a thickness of 0.5-1" will represent the maximum because of quality consideration. Total mass of CdTe produced on one specific run in a period of time will thus be diameter dependent. Heavier plates will be more attractive from an economical viewpoint.

There is some indication that preparation of square substrates from the plates may be difficult to achieve without excessive breakage and surface contamination. The methods used to generate glass lens blanks from thick AMTIR plates

have been found not to apply. For this reason, it is possible that the CdTe plates will have to be sawed in squares and used in original thickness for substrates. If so, it will be impor- that to produce as large an area as possible in a single run so that the substrate cost is economically attractive. The cost per square inch of substrate must be competitive with conventional processes.

Preparation of high purity semiconductors is somewhat mass dependent. The total mass of impurities generated from the quartz container, through handling the reactants or through the atmosphere furnished by the vacuum system is somewhat fixed for each run. If you assume these impurities are picked up by the Cd Te plate, the level or concentration of the impurity will be mass dependent. That is, for the same run, the impurity level for a 2Kgm plate may be twice that of a 4Kgm plate for elements added in the process.

F. RECOMMENDATION

The results achieved during Phase I indicate the original goals of the program may be achieved or exceeded if the present course is followed. A true "state of the art" advance may be achieved. The supply of large grain, high purity Cd Te in large diameter pieces may be substantially increased for Hg Cd Te growth and IR optical application. A substantial reduction in cost may be expected for such material.