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AFML-TR-72-131

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SINGLE CRYSTAL CADMIUM TELLURIDE
HIGH ENERGY IR LASER WINDOWS

A. R. Hilton

Texas Instruments Incorporated

TECHNICAL REPORT AFML-TR-72-131

August 1972

Distribution Statement

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by Texas Instruments Incorporated, Dallas, Texas, under Air Force Contract F33615-71-C-1762. The work was administered under the direction of the Air Force Materials Laboratory, with Dr. G. Edward Kuhl (AFML/LP) as project engineer. Dr. A. R. Hilton was project manager for the work at Texas Instruments.

Major contributions to the work described in this report were made by Mr. James Frank, who was responsible for most of the experimental efforts, and by Drs. G. R. Cronin and L. G. Bailey, who participated in many helpful discussions concerning the program.

This is the Final Technical Report for this contract. It covers the period from 1 June 1971 to 29 February 1972. It was submitted by the author in April 1972.

Texas Instruments report number is 08-72-19.

This technical report has been reviewed and is approved.

WILLIAM GOLDBERG, Major, USAF
Laser Window Program Manager
Materials Physics Division
Air Force Materials Laboratory

ABSTRACT

The goal of this program was to grow thick, large-area plates of CdTe using a solution epitaxy method. Solution epitaxy was chosen as the method for growth in the belief that fast reaction rates could be obtained at lower temperatures than those used for vapor growth. Operating at a temperature well below the wide existence region found for CdTe would reduce the trouble with impurities and lead to greater control of stoichiometry.

Generally, solution epitaxy is a batch process used to grow thin layers. The process as used is rate-limited by diffusion of one constituent through the solution. Mechanical motion of the solution was used in an effort to overcome the batch-type nature of the process. Motion of the solution in the vicinity of the substrate led to extremely irregular layer growth along with spontaneous nucleation and growth of CdTe dendrites and platelets. Solution entrainment was observed for all deposits. Solution epitaxy is not a good method of forming thick pieces of CdTe. For the finished process, the large-area substrate would be a mosaic made up of pieces of single crystal CdTe cut from a crystal grown in a conventional manner. Several methods of fabricating the substrate are discussed, along with efforts to alloy the mosaic pieces together.

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INTRODUCTION

The purpose of this program was to develop the technology required to prepare large plates of single (or near-single) crystal CdTe suitable for application as optical elements in systems based on high intensity CO_2 lasers emitting at 10.6 μm. The method chosen for preparing the plates is based on solution epitaxy growth on a mosaic CdTe substrate. The substrate was to be formed from pieces cut from single crystal CdTe grown in a conventional manner. Solution growth was chosen over chemical vapor deposition because of the conviction that greater growth rates at lower temperatures could be obtained. Lower operating temperatures would provide higher purity because contamination by the reaction chamber would be less. An additional advantage would be that the stoichiometry of the material could be more easily controlled. The existence region of CdTe (two volatile constituents) is quite wide for temperatures above 900°C. A process operating below this temperature should lead to a better control of resistivity (and thus quality) than that obtained for melt-grown materials.

A general discussion of the solution epitaxy method as applied in the semiconductor industry points out that the process is batch in nature and is used to form relatively thin layers (< 5 mils). Growth on the substrate occurs over a range of temperatures (between two limits), thus leading to a change in quality as the layer grows. Efforts in this program to define a practical, constant temperature, semicontinuous process are described. Solution growth on the CdTe substrates has been confined, for the most part, to the use of small pieces (1 cm in diameter) in an attempt to conserve effort while trying to establish growth conditions. Attempts to use conventional semiconductor batch reactors to define the best growth conditions are described. However, most of the program effort was devoted to the closed system, which utilizes mechanical rocking motion to resaturate (or replenish) the solution.

The conventional method used to prepare single crystal CdTe and the current results are described. Problems associated with the fabrication and use of mosaic substrates are discussed. Attempts to alloy pieces of CdTe together to form a single substrate are described.

SECTION II

THE METHOD - SOLUTION EPITAXY

A. General Discussion

The illustration used to describe the epitaxy process as applied to the CdTe system[1] in our original proposal and in the First Technical Progress Report[2] for this contract is shown in Figure 1. Basically, the process consists of bringing Te solution saturated with CdTe at 900°C into contact with a CdTe substrate placed in a cooler zone (700°C) to bring about epitaxial growth. The conditions shown in the drawing are intended only to illustrate the principles, not to indicate the process operating conditions. The actual temperature differences were an order of magnitude lower. It is important to note that the temperature of the substrates is fixed and not varied.

The use of tellurium-rich solutions to grow CdTe was based on the relative volatility of Cd (boiling point 765°C) as compared to Te (boiling point 989.8°C). High vapor pressure of a constituent represents a practical disadvantage. The decision to grow from dilute solutions (relative to concentration of Cd) is based on the desire for the process to take place at temperatures of 700 to 800°C, where impurity problems will be minimal and where the CdTe produced will be very close to stoichiometric (formed in a narrow existence region). The operation temperature will have to be balanced against lower growth rates at the lower temperature and degradation of crystalline quality.

B. Conventional Process

An excellent analysis of the theoretical considerations governing solution growth is found in an article published by Tiller.[3] In his analysis, Tiller points out that the rate-limiting step in conventional solution epitaxial growth is the diffusion of one constituent through the solution of the other to the crystal surface. That is, in growing compound AB from a solution rich in B, the first step is depletion of A from the solution in the immediate vicinity of the surface as the first layer of AB forms. The depletion produces a concentration gradient for constituent A, resulting in a steady-state diffusion which

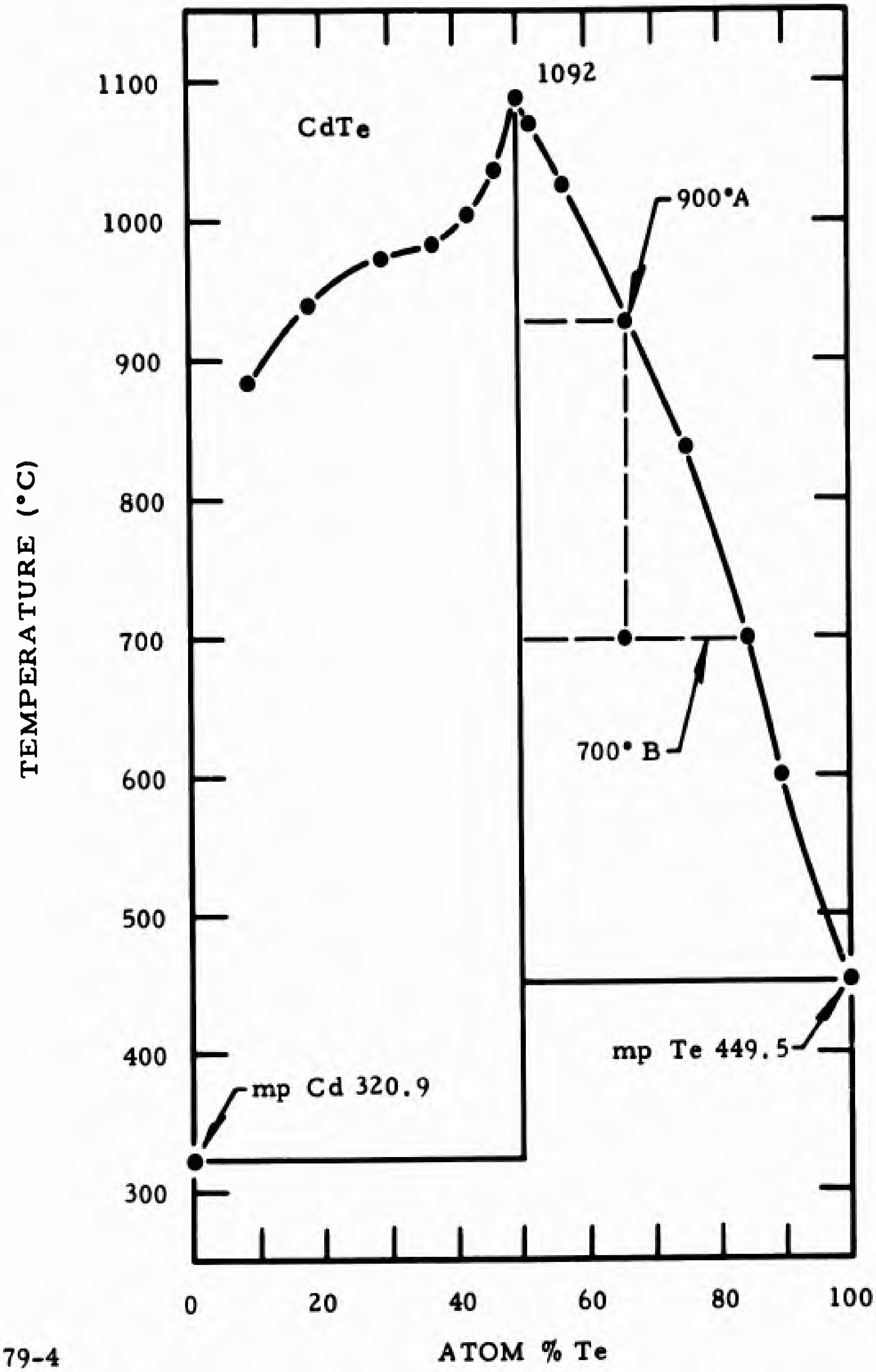

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Figure 1 CdTe Binary System

limits the rate of formation of AB. A diffusion-limited process would be quite slow and would severely handicap our efforts to grow 1/4 to 1/2 inch plates. For this reason, we had to alter the general method of solution epitaxy growth. Our changes may be better understood by first considering a conventional process.

A solution epitaxy reactor similar to those used in this laboratory to produce layers of III-V compounds 1 to 5 mils thick is shown in Figure 2, In the diagram, the graphite boat used to hold a CdTe substrate is fitted with a graphite slide which contains a solution chamber. The entire apparatus is heated to the saturation temperature, which corresponds to the liquidus temperature for that solution. (See the diagram in the lower part of Figure 2.) After the CdTe-Te solution has had sufficient time to reach equilibrium, controlled cooling is started. The rate of cooling may be some convenient rate, such as 1°C/minute. At the reaction temperature, the slide is moved to position 2 so that the saturated solution can come into contact with the substrate. The reaction may be allowed to proceed over a temperature range of, for example, 50°C for 50 minutes. The slide is then moved back to position 1 so that the solution and the layer will not be stuck together. As shown in the diagram, the apparatus is a H_2 flowing system and is considered dynamic, not static. Equilibrium vapor pressures for volatile constituents are never reached. The system is operated in this manner for several practical reasons, such as ease of fabrication and ease of loading or unloading. A flowing system cannot be used if volatility of constituents at the reaction temperatures is large. This point will be discussed later in more detail.

In the diagram, the solution is slowly cooling while it is in contact with the substrate. As the saturated solution is cooled, it is depleted of CdTe in excess of the equilibrium concentration. In the immediate vicinity of the CdTe substrate, the formation of the CdTe layer depletes the solution of excess Cd. Soon, the concentration of Cd in the surface vicinity is below that found in the bulk of the solution. Further growth of CdTe on the surface requires diffusion of Cd in the direction of the concentration gradient, away from the bulk to the surface of the CdTe layer. The rate of growth of CdTe is thus limited by the diffusion of Cd in Te at the temperature of the reaction. A diffusion-limited process is

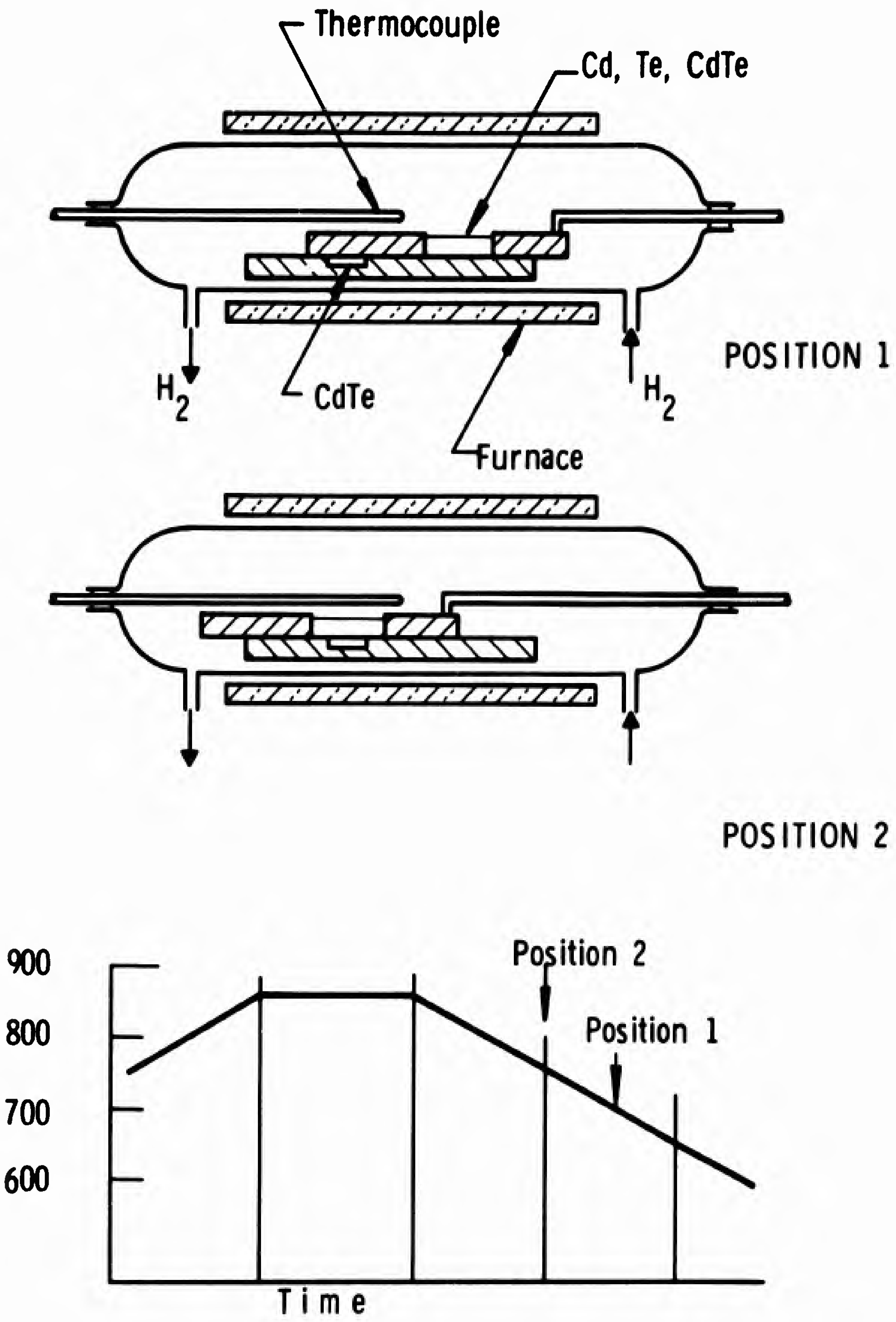

Figure 2 Conventional Solution Epitaxial Process

generally slow, especially at the temperatures we would prefer to use for our process (700 to 800°C).

C. Conventional Process Results for CdTe

Very few references[4] are found in the literature regarding solution growth of CdTe. Generally, the discussions center on layers grown for device fabrication,[4] and no details are given. Statements made regarding solution growth from Te or Cd solutions seem to indicate crystal growth at high temperatures where the solution (or melt) is in reality close to stoichiometric (± a few percent). One should keep in mind that the liquidus curve determines the concentration of the solutions. Once the growth temperature is selected, the concentrations in the solution are fixed. In this investigation the upper growth temperature of 800°C corresponds to a Cd concentration of about 23%, while the lower temperature of 700°C corresponds to about 15 atom % Cd. A desire to operate out of this concentration range requires the selection of a different growth temperature. In actual practice, care is exercised always to exceed the concentration indicated by the liquidus curve so that there is no doubt concerning the saturation of the solution at the specified temperature.

The drawing in Figure 3 illustrates modification of a conventional reactor for mosaic substrate solution epitaxy CdTe experiments. The bottom of the graphite boat was machined so that the two 1-cm circular slices of CdTe could be closely fitted together after a flat surface had been handground on both slices. The reactors were unchanged otherwise from their normal construction or operation.

Several runs were carried out using borrowed equipment while our own equipment was being constructed. In the preliminary experiments, several important facts became clear. First, when Cd, Te, and CdTe were placed in the solution chamber separately, examination of the reactants after the experiment revealed that a homogeneous solution was not formed. Moreover, loss of Te during the heating process occurred before the Cd and the CdTe were dissolved in the solution, reducing the volatility. The resultant solution

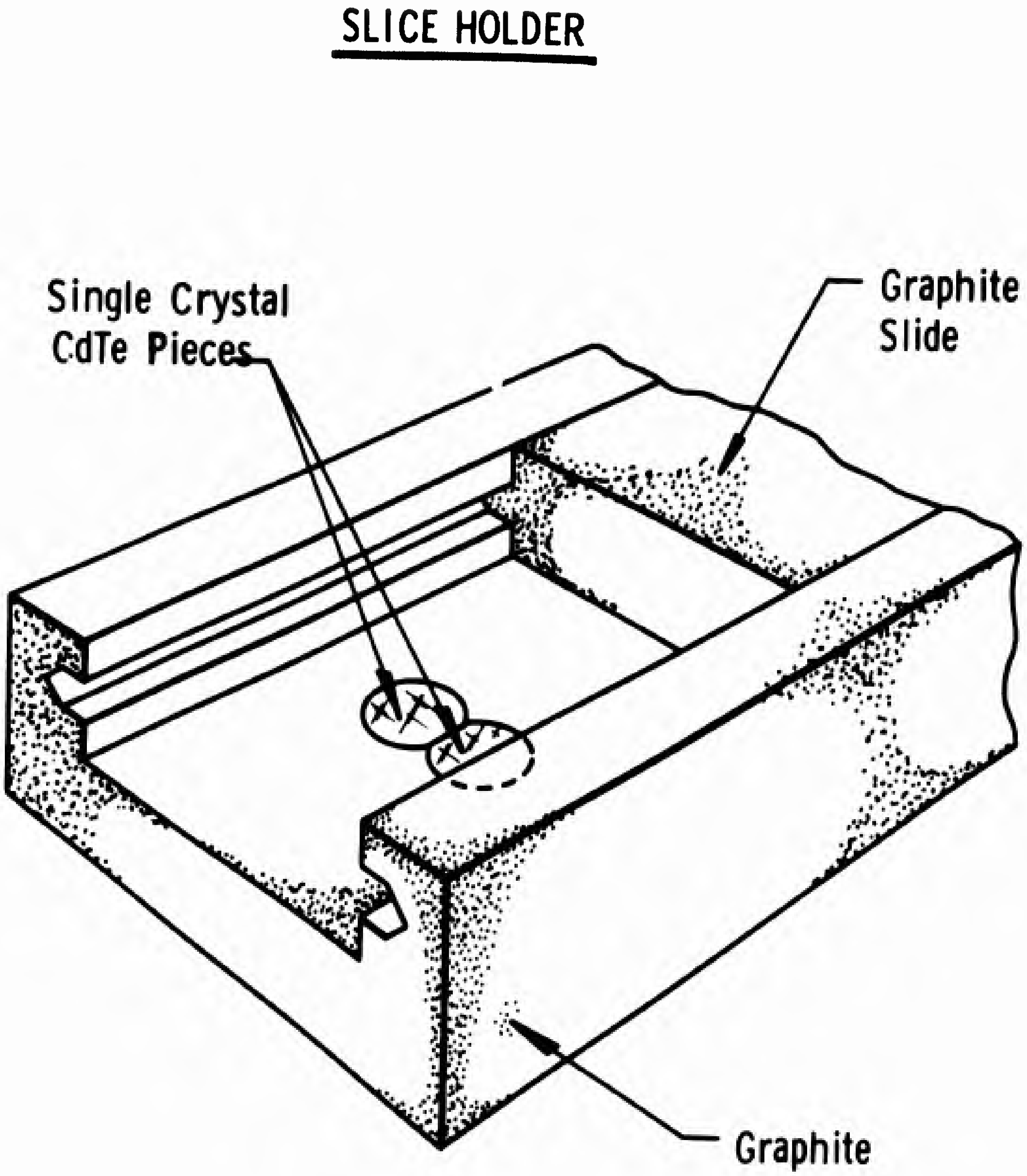

Figure 3 A Conventional Solution Epitaxy Reactor Modified for Mosaic Substrate Growth Experiments

had a higher percentage of crystalline CdTe than originally planned. At the end of a run, the solution had become a sponge-like mass which adhered strongly to the substrate. As a result, the graphite slide could not be moved to displace the solution (mass, in this case) from the samples. In all cases the system was operated as a flowing system using a protective atmosphere of hydrogen.

The decision was made to try to establish reaction conditions for layer growth at around 750 to 700°C. This temperature was chosen, as mentioned before, because of the narrow existence region and because contamination problems would be minimized. The results obtained from a series of reactions are summarized in Table I. The run numbers listed in column 1 refer to the notebook page on which the description of the experiment begins. Such a procedure is generally followed in this laboratory and was used for all results listed in this report. Run number 9 was perhaps the most successful experiment, producing a high resistivity layer of CdTe 5 mils thick in 74 minutes. A photograph of the resulting layers on the substrate is shown in the right-hand portion of Figure 4. Note that the two pieces of CdTe substrate appear to be joined together. However, close examination indicates the region between the slices is filled with solution rather than CdTe. Close examination of the layer also indicates the adherence of a Te-rich deposit on top of the CdTe layer. This fact indicates the solution was not entirely fluid at the end reaction temperature, 700°C. The source was precompounded using 20 atom % Cd and 80 atom % Te, the correct concentration range for this temperature growth range.

Additional results listed in Table I represent attempts to prepare a nonviscous Te solution of the proper concentration. The Cd concentration was lowered to the 8 to 10% range on the assumption that Te loss during the heat-up cycle would bring the final concentration up to the proper concentration as the solution was brought into contact with the substrates. The results are found for runs listed in Table I after number 11. Results obtained from run number 12 are shown in the left-hand side of Figure 4. The layer has a Te-rich appearance and is not a CdTe deposit. Attempts to vaporize the Te so that the CdTe layer found underneath could be examined were not successful. (See run number 15.) Examination of the results in Table I shows that the Te

Table I

Conventional Reactor Liquid Epitaxy Results

Run No.	Reaction Conditions	Remarks
8	Reacted from 750 to 700°C @ 1°C/min. Beveled edges on substrates.	Could not move slide.
9	20 atom % Cd, 80 atom % Te precompounded at 850°C. Reaction from 750 to 700°C. Source was not homogeneous. Used the center or Te-rich portion.	Layer 5 mils thick in 74 minutes; resistivity of layer comparable to that of substrate. Substrate pieces appear grown together. Weight loss of Te ∿ 6%.
10	Repeat of No. 9, but solution was precompounded at 900°C and quenched to make homogeneous source.	Solution wet slices but layer growth was not good. Solution was found between slices, but no evidence of CdTe formation between pieces was found. Te loss was ∿ 6%.
11	Same as No. 10.	Substrate pieces floated out of position and were so strongly attached to the reactant mass that no results could be obtained. Graphite slide would not move.
12	10% Cd, 90% Te. Solution precompounded. Reaction run from 750 to 709°C.	Slices were stuck together. Layer was very Te-rich, not CdTe. Te loss ∿ 26% by weight.
13	8% Cd, 92% Te precompounded at 900°C. Reaction run at 750 to 700°C.	Samples floated out of compartments and could not be examined. Te loss excessive, ∿ 26%.
14	Same as No. 13.	Mechanical failure occurred, but slices were wet by solution. Layer appeared to be Te-rich solution.
15	Same as No. 13.	About same results. Attempts to drive Te solution off substrates to examine CdTe layers were not successful.

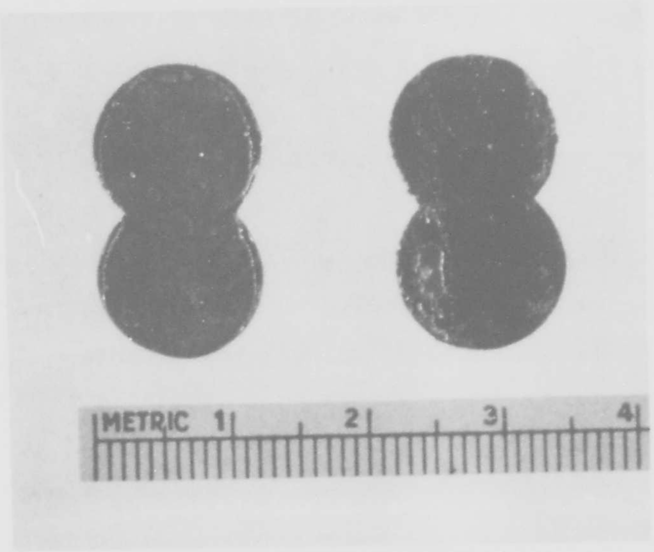

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Figure 4 Layers Produced on CdTe Substrates Using a Conventional Solution Epitaxial Reactor and Te-Rich Solutions loss increased to about 25% by weight when the lower concentrations of Cd were used. In addition, the CdTe layers did not grow from the dilute solutions.

All results indicate that a flowing or dynamic system cannot be used because of the volatility of the constituent elements. (The conditions would have undoubtedly been worse had we chosen to grow from high Cd concentration solutions.) Loss of Te leads to excess concentrations of Cd, which in turn lead to spontaneous nucleation and growth of CdTe in the solution. Such growth forms a porous structure which traps the remaining solution, preventing proper solution contact with the substrates. Therefore, no further attempts at solution growth were made using open or flowing systems.

D. Semicontinuous Process - Mechanical Motion of the Solution

Efforts to design, build, and operate a semicontinuous reactor were carried out concurrently with the conventional epitaxy experiments. As pointed out earlier, the decision to keep the substrates in contact with the solution in a constant temperature chamber was made in order to control the quality of the thick layer. The remaining problem was to provide for the movement of fresh solution across the CdTe substrate surface (thus decreasing the diffusion limitation). Our first approach was to utilize thermal convection currents in the system shown in Figure 5. In the diagram, a "thermal loop" or "thermal pump" is provided which moves the solution in a loop as a result of the density gradients which exist when the solution is heated in the source chamber. A cool solution return brings Te-rich material back to the bottom of the source chamber for resaturation. Although this system was built, it was never operated because of its impracticality. Each reactor would have to be individually fabricated from quartz, and wired and insulated separately; thus, good reproducibility or heating uniformity would be very unlikely. In addition, knowledge of the CdTe solutions' densities and viscosities, and temperature dependencies of these quantities, was not sufficient to allow reasonable estimates of pump performance. Therefore, mechanical motion was used as the basis for providing fresh saturated solution.

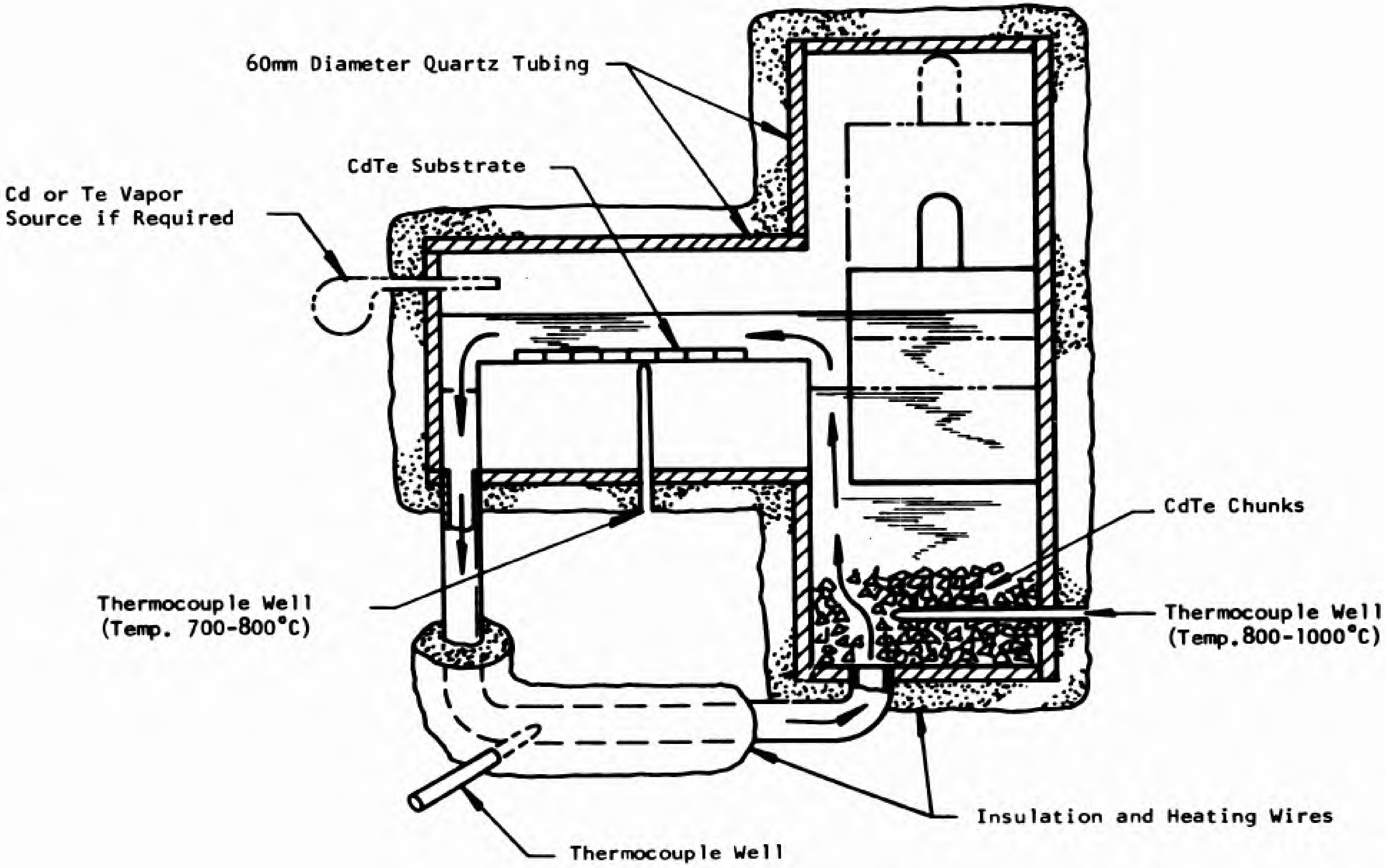

Figure 5 Continuous Liquid Epitaxy Reactor

The first design which used mechanical motion for movement of the solution is shown in Figure 6. The reactor has two source chambers, one at each end of the substrate reactor chamber. The two end chambers are placed in the outer furnaces of a three-furnace system. Each of the three furnaces is of commercial origin and thus requires no additional winding or insulation. The reactor chamber is made entirely of quartz and was assembled in TI's glass shop for installation in the furnaces, which are split to facilitate insertion of the reactor vessel. The two source furnaces are controlled at a temperature above the center reaction zone. The two chambers which serve as sources are constructed so that solution is taken from the bottom to avoid the solid CdTe which forms on the top of the saturated solution. The entire apparatus, furnaces and reaction chamber, is placed on a rocking platform and rocked so that liquid leaves the source chamber, it cools and is depleted of CdTe, forming (hopefully) a layer of CdTe on the substrate. Repeated twice a minute over a period of hours, this process led to the rapid transport (relative to thermal movement and concentration diffusion) of CdTe from the source chambers to the plate and the growth of a thick plate. The system as described is a sealed system which can be easily fabricated in a reproducible manner.

E. Rock Process Results

Only two reactions were carried out using the reactor depicted in Figure 6. In the first, an implosion occurred before the reaction could be run. In the second, a reaction was run for 18 hours with the source chambers at 900°C and the reaction chamber at 700°C. The results were very disappointing. The strips of single crystal CdTe used to make up the substrate (discussed in detail in a later section of this report) did not grow together into a plate, and, in fact, disappeared to a great extent. It was concluded that the temperature differences were much too great and the rocking speed was probably too fast. In addition, the tubes leading from the source chambers to the substrate chambers were too long, and plugging occurred as the solution cooled in passing between the chambers. Because of the amount of effort required for one reaction run, the decision was made to resort to small laboratory runs involving small pieces of CdTe (1 cm in diameter and 60 mils thick) as used in the conventional reactor described earlier. The object of the experiments

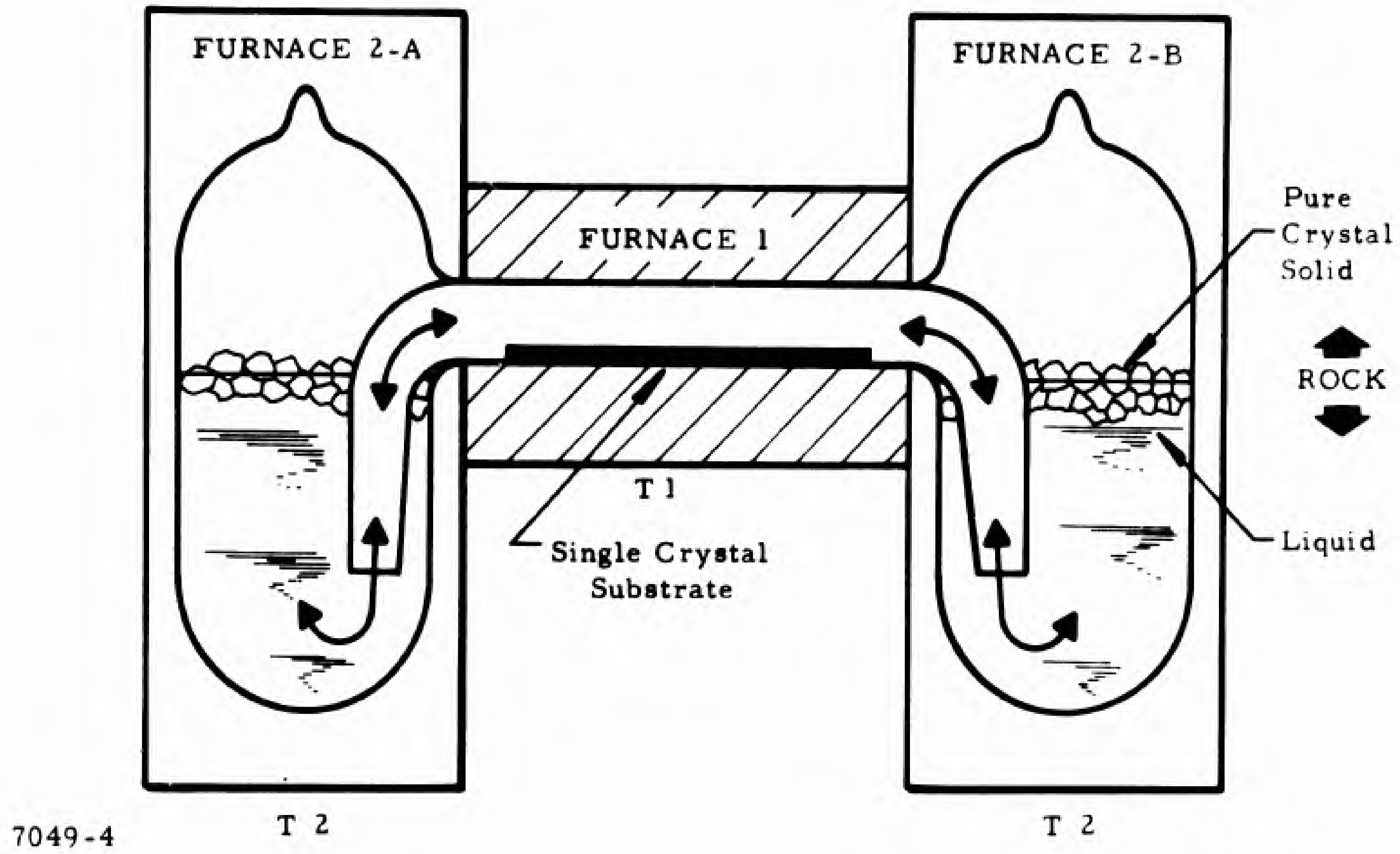

Figure 6 Liquid Epitaxy Reactor Design

was twofold: to establish the proper growth conditions and to demonstrate that layer growth across the mosaic pieces would occur. After these conditions had been established, we planned to return to the larger reactor and form the 2 inch x 2 inch plates.

A diagram of the system is shown in Figure 7. The furnace is the same split furnace used for the central zone in the large reactor. However, three separate sets of heater windings were purchased so that three temperature zones (as in the large reactor) could be provided. Each zone was fitted with its own thermocouple and controller. "Digi-Set" or proportional controllers were used to provide regulation to 1°C. A long graphite boat served as the reactor chamber. The boat was machined in the same manner depicted in Figure 3 to provide recesses for the 1 cm CdTe substrates. For each run, flats were hand-ground and polished on the two substrate pieces. The faces were hand-polished and acid-etched before the pieces were placed in the graphite boat recesses. Reactants were added to the graphite boat as precompounded material or as unreacted elements. Finally, the boat, substrates, and reactants were sealed into a 60 mm quartz tube while the tube was being evacuated (~ 1 μm). This last step was accomplished using a glass lathe in the glass shop. After the sealed tube is placed in the three-zone furnace, the rocking mechanism is turned on so that the reactants are in the down position. The furnaces are then turned on and raised to a temperature (all three zones) slightly above the source temperature. Time is allowed for the solution to form and mix. The temperatures of the zones are lowered to the desired value, and the rocking mechanism is turned on. The reaction is allowed to proceed for the predetermined time. The final step before cool-down is to leave the source end in the down position so that the solution will not be left on the substrates. The overall procedure is comparatively simple and very reproducible.

Results obtained using this system are found in Table II. The results reported in this table represent the best controlled experiments of the program and are therefore the best indication of the feasibility of the approach. The most significant experiments are discussed on the following pages.

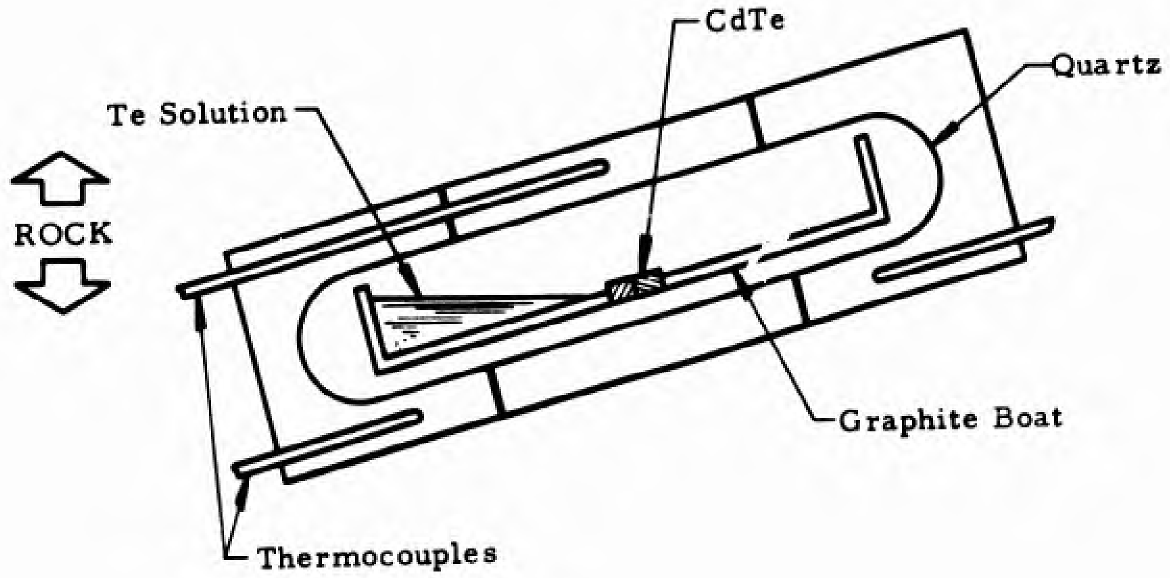

Figure 7 Schematic drawing of present rocking reactor

Table II

Semicontinuous Reactor Results

Run Number	Source Temperature	Substrate Temperature	ΔT	Cycle	Solution	Results
17*	740	700	40	Continuous 2/min., 2 hours	Pre-Compounded	Entrained solution
19	720	700	20	"	"	Substrate washed away
20	720	700	20	"	"	Substrate washed away
21	750	740	10	"	"	Substrates partially lost
22	755	740	15	"	"	Mass of substrate holder too large
25	750	740	10	"	"	Potentiometer failed
26*	750	745	5	"	"	Growth, platelets, solution entrained
28*	750	748	2	"	"	Growth, platelets, solution entrained
31*	800	795	5	"	"	Solution saturated at 825°C
32*	800	795	5	Continuous 10 min/cycle	"	Some substrate loss, substrate entrainment
34	800	790	10	"	"	One substrate lost entirely
36	800	790	10	"	Formed in boat	Both substrates lost
40*	710	700	10	20 min/ cycle	"	Solution entrainment
42*	Cooled from 725 - 675°C at 0.5°C/minute					Dendritic and platelets

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* Microscope photographs of results shown in this report.

Figures 8(a) and 8(b) are diagrams showing the general appearance of finished samples. Figure 8(a) shows a bottom view of the substrates and CdTe-Te solution deposit. The substrates emerge from the graphite boat recesses stuck together (by solution) and at the bottom of the deposit, as shown by the side view in Figure 8(b). The bottom of the boat and the single crystal CdTe substrates serve as a reference so that the deposit can be easily identified. The sample is sawed as depicted in the upper illustration by the dashed line. Half of the sample for each run was polished and examined using a microscope for a side view presentation. Bromine-methanol etch was also used to bring out the differences between deposit and substrate.

Figure 9(a) shows an 88X photograph for a polished sample obtained for run number 17. The substrate temperature was 700°C, and the temperature difference between substrate and source was 40°C. The solution was rocked back and forth for two hours using the two-cycle/minute movement. The substrates were in the center of the graphite boat. The approximate location of the original substrate - solution interface is marked. In addition, a 10-mil scale is shown on the side for reference (the original substrate is 60 mils thick). The photograph shows the sample as it appeared when it was removed from the boat, with the substrates at the bottom and the solution in the top portion of the photograph. The dark regions are identified as crystalline CdTe because their appearance is the same as that of the substrate. The high Te-content solution appears lighter in the photograph.

Figure 9(a) shows the union between two substrates in the center of the photograph. The substrates give the appearance of being grown together, even though Te solution is entrapped below. Layer growth does not appear to have taken place. Probably, spontaneous nucleation and growth of CdTe dendrites occurred in the solution as soon as the first pass across the substrates occurred. The temperature difference, 40°C, was far too large. The decision to reduce the temperature difference was made while the substrates were kept at 700°C.

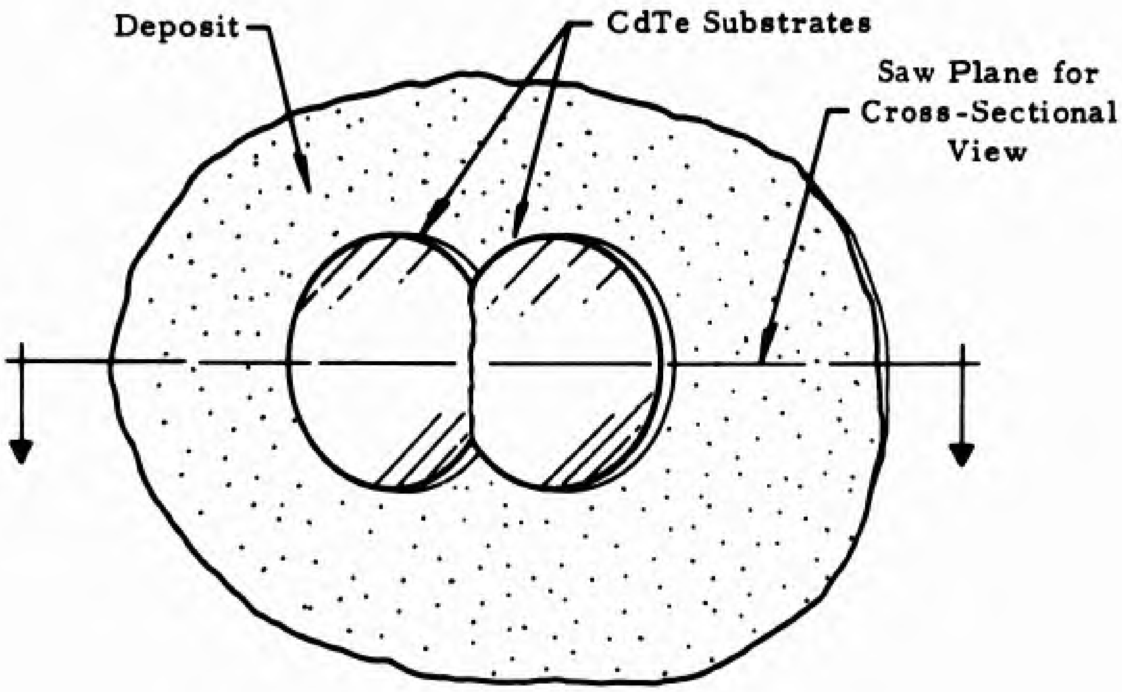

Figure 8(a) Bottom View of Samples After Removal From the Reactor

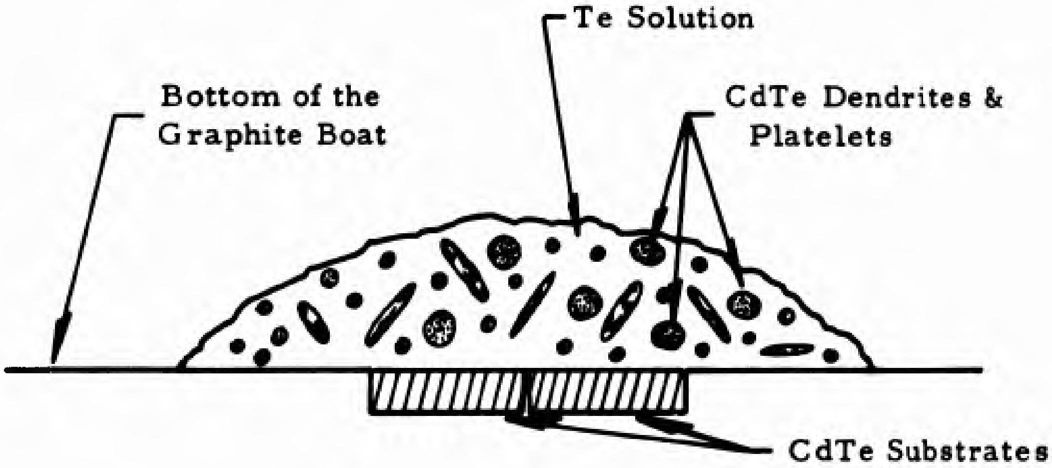

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Figure 8(b) Side Cross-Sectional Appearance of Samples After Removal From the Reactor

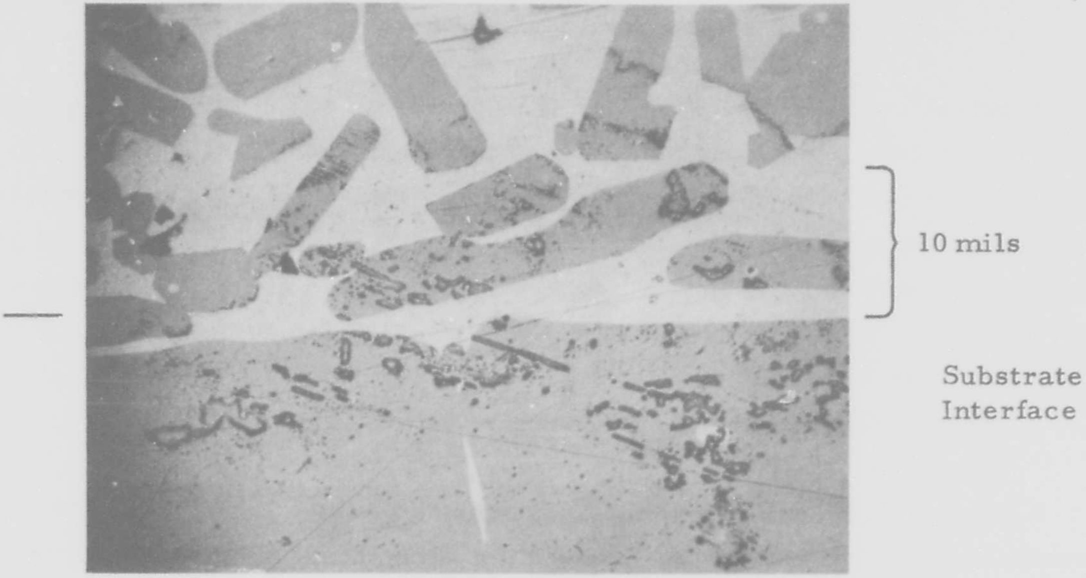

Figure 9(a) Microscopic Photograph of Cross Section for Run Number 17 (88 X). Dark is CdTe; light is Te-rich solution. Substrate Temperature 700°C, $\Delta T = 40°C$.

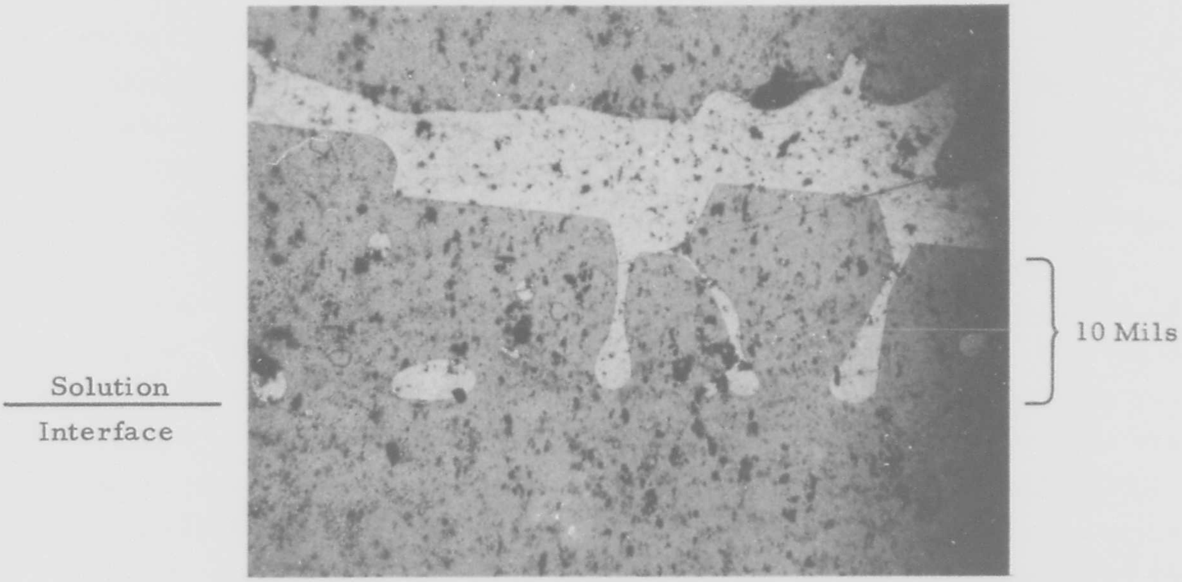

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Figure 9(b) Microscopic Photograph of Cross Section for Run Number 26 (88 X). Dark is CdTe; light is Te-rich solution. Substrate temperature 745°C, $\Delta T = 5°C$.

Examination of Table II reveals that growth at 700°C was attempted two additional times. Both runs were ruined because the washing action of the solution dislodged the substrates from their graphite recesses. A graphite piece was designed and built which wedged into the boat from the top and placed pressure on the outside edges of the two substrates so that they could not wash away. The mass of the graphite piece was relieved so that it would not serve as a cold spot for the solution. Growth of layers was achieved using this graphite piece and a higher substrate temperature.

Figure 9(b) shows results obtained from run number 26. The substrate temperature was 745°C and the temperature difference 5°C. Epitaxial growth from the substrate is clearly present, but solution was entrained from the first. Growth of 10 to 15 mils occurred over a two-hour period (half duty cycle). Oriented facets are clearly visible.

The use of proportional current controllers ("Digi-Set" or thermoelectric) enabled us to reduce and maintain the temperature difference between source and substrate at 2°C. The results are shown in Figure 10(a). Substrate temperature was 748°C. Again, the oriented facets from the substrate clearly demonstrate single crystal growth of 10 to 20 mils. However, as before, solution entrainment occurred in isolated areas from the beginning of the run. The actual percentage of volume which is solution entrainment is greatly reduced.

The decision was made to go to higher temperatures so that the Cd concentration in the solution would increase and, hopefully, reduce the tendency toward solution entrainment. Results obtained for run number 31 using a substrate temperature of 795°C and a temperature difference of 5°C are shown in Figure 10(b). Layer growth was no better. Some improvement in the total volume of solution entrained may have occurred, but the characteristic facets disappeared. The void at the union of the two pieces is shown in the center of the photograph. Again, there is evidence that the two pieces were growing together.

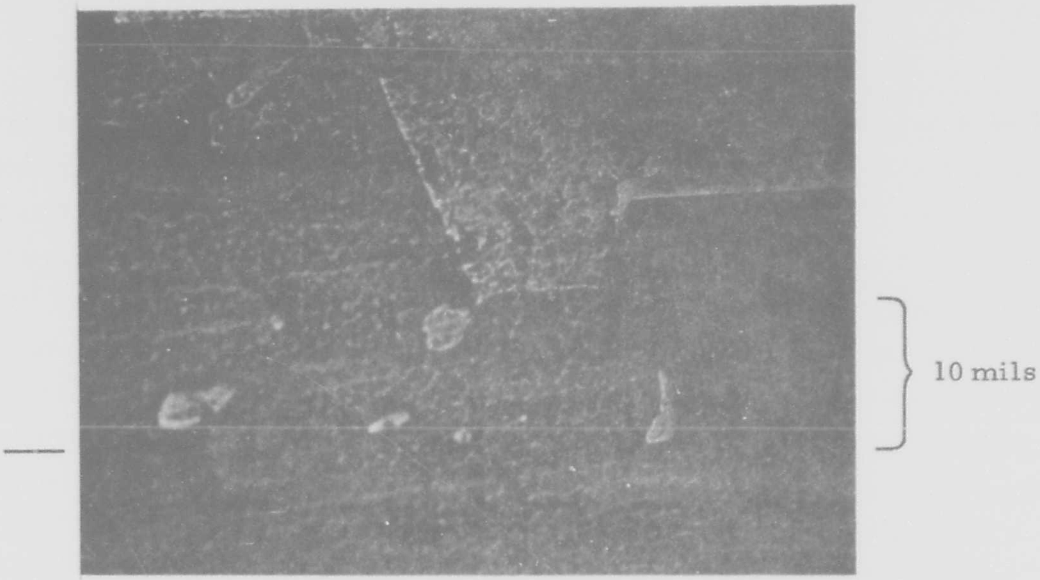

Figure 10(a) Microscopic Photograph of Cross Section for Run Number 28 (88 X). Dark is CdTe; light is Te-rich solution. Substrate temperature 748°C, $\Delta T = 2°C$

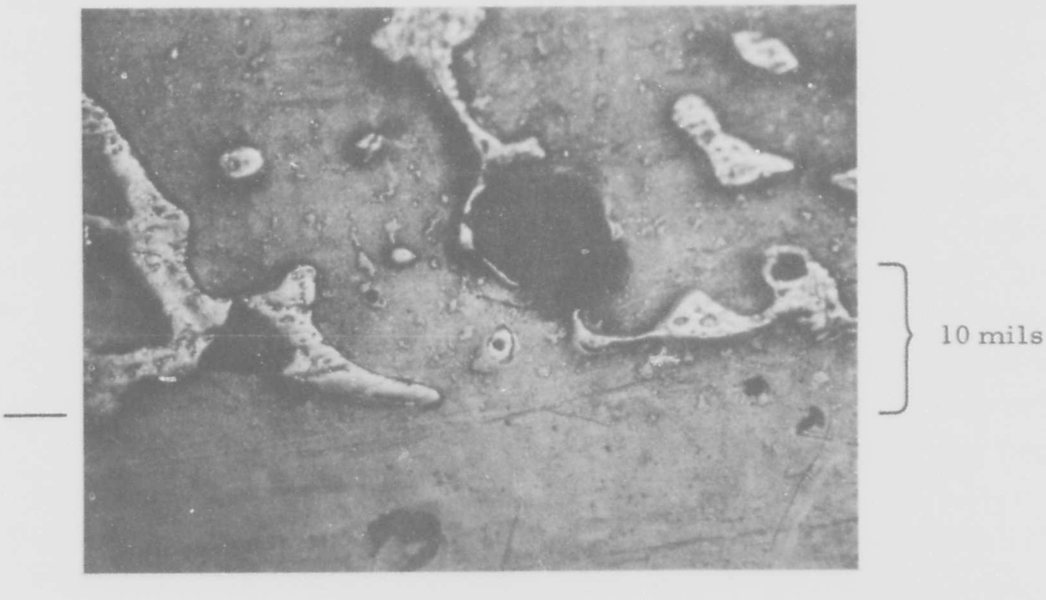

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Figure 10(b) Microscopic Photograph of Cross Section for Run Number 31 (88 X). Dark is CdTe; light is Te-rich solution. Substrate temperature 795°C, $\Delta T = 5°C$.

Some substrate loss was noticed at the higher temperatures. The loss of CdTe was attributed to dissolving by the solution because it was not saturated. It seemed likely that the 30 seconds on,30 seconds off cycle time was too fast for any type of equilibrium to occur; therefore, the decision was made to change the rocking cycle to 10 minutes on and 10 minutes off for resaturation. The graphite boat was changed so that a set of recesses could be placed in one end. In this way, the presaturated solution in a down position was moved to the substrates by turning the rocking motor on until the solution end raised to the high position. The motor was cut off for 10 minutes, then turned on and the solution allowed to return to the hot end for resaturation. In all these experiments, solid CdTe crystals were added to the hot end chamber to provide an adequate supply of CdTe to saturate the solution.

Results for run number 32 are shown in Figure 11(a). The substrate temperature was 795°C, and the temperature difference was 5°C. Layer growth was 10 mils or less using the 10-minute rocking cycle. Facet growth is again visible, with solution entrainment and substrate loss still occurring. We continued to attribute the substrate loss to failure to achieve saturation during the cycling at high temperatures.

Several efforts to run reactions at 800°C while ensuring solution saturation were made. Substrate loss continued to spoil all results. Finally, it became obvious that sublimation of the CdTe substates must be occurring. Long-term experiments (18 hours) were run at 700°C and 800°C using sealed tubes in which substrates and solutions were placed, but not in contact with one another. The 800°C results produced a high percentage loss (> 50%) of substrates, while at 700°C the loss was small ($\sim$ 5%).

An additional growth attempt was made at lower temperatures, but using the long rocking cycle. Figure 11(b) shows the results obtained using a substrate temperature of 700°C, a temperature difference of 10°C, and a 20-minute rocking cycle. In the diagram, growth of less than 5 mils occurred, along with solution entrainment from the substrate. A great deal of spontaneous

Figure 11(a) Microscopic Photograph of Cross Section for Run Number 32 (88 X). Dark is CdTe; light is Te-rich solution. Substrate temperature 795°C, $\Delta T = 5°C$.

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Figure 11(b) Microscopic Photograph of Cross Section for Run Number 40 (88 X). Dark is CdTe; light is Te-rich solution. Substrate temperature 700°C, $\Delta T = 5°C$.

nucleation and growth of CdTe dendrites in the solution were observed, as shown in the photographs. Platelets were also found farther from the substrate area.

A final attempt to grow CdTe from solution was made in run number 42. Solution was compounded in the graphite boat in the down end at 725°C. The furnace was rocked to the other position, covering the substrates, and all three zones were slowly cooled at 0.5°C/minute from 725°C to 675°C. A photograph of the cross-sectioned sample is shown in Figure 12. The region between the pieces can be seen. Some signs of growth between pieces were observed. Layer growth was less than 5 mils, with some faceted regions visible. The layer growth is not good. Again, spontaneous nucleation and growth have occurred. The percentage of deposit attributed to entrained Te-rich solution increased markedly at the lower temperatures.

F. Discussion of Solution Epitaxy Results

Several conclusions can be drawn from a comparison of the results shown in the series of microscope photographs. First, solution growth for CdTe appears to be better at ~ 750°C than at 800°C or 700°C. The deposit shown in Figure 10(a) was 10 to 20 mils thick, while in Figures 10(b) and 11(a) the deposits were < 10 mils. It may also be inferred from a comparison of Figures 10(b) and 11(a) that the continuous rocking action (1 cycle/half minute) led to greater growth rates. The third point demonstrated is related to quality of the deposit and temperature difference between source chamber and substrate chamber. Comparison of Figures 9(b) and 10(a) shows essentially an improvement in the quality and an increase in the total amount of good material deposited when the temperature difference was cut from 5°C to 2°C. The facets are more distinct, and the volume of entrained solution is smaller in Figure 10(a) than in any other results. However, the area examined is next to the substrate, only about 20 to 30 mils above it. The total thickness of deposits on the substrates was generally 0.5 to 1 cm. The quality of the deposit next to the substrate did not represent the quality of the total deposit. Quite the contrary. The facets demonstrate that epitaxial growth stopped at that point. The rest of the deposit represents solution that was trapped and frozen in a matrix

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Figure 12 Microscopic Photograph of Cross Section for Run Number 42 (88 X). Dark is CdTe; light is Te-rich solution. Conventional run, 725 to 675°C.

of dendrites and platelets during the cool-down process. The same type of appearance was found for large particles of solution left frozen on the graphite structure. In other words, the type of growth we are interested in occurred only in the first 10 to 20 mils of deposit on the substrates. The remainder of the deposit is actually solution which was allowed to cool and freeze in place.

Ideally, growth along the interface between the solution and substrate should proceed smoothly at a rate of 10 to 20 mils/hour. However, the spontaneous nucleation and growth of CdTe dendrites and platelets in the solution immediately above the substrate indicates the existence of a supercooled layer, a condition referred to as constitutional supercooling. According to Tiller,[3] the following inequality leads to the constitutional supercooling condition:

$$\frac{G}{V} < -\frac{M_A(1 - K_A)N_A}{D_A} ,$$

where G is the thermal gradient which exists between the substrate and the solution,

V is the rate of growth of the crystalline phase,

M_A is the slope of the liquidus curve at the point of growth (temperature concentration point for the solution at the substrate),

K_A is the ratio of the concentration of A in the solid phase divided by the concentration of A in the solution (at the temperature of growth),

N_A is the concentration of A in the solution, and

D_A is the diffusion coefficient for A in the solution.

Any factor which tends to decrease the term on the right-hand side, then, should lead to better results. Examination of the terms from the two extremes of solution growth leads to the following general conclusion. In one extreme, growth occurs from solution in which the composition is near stoichiometry. Referring to the diagram for CdTe in Figure 1, we could say the conditions are 50 ± 5% on either the Cd or the Te side. In this range, the slope of the liquidus curve remains about the same for both types of solution; thus, M_A does not change. The value of N_A increases, but the term $(1 - K_A)$ begins to approach zero. Thus, conditions for solution growth are best near the stoichiometric composition.

The other extreme case is represented by very Te-rich or Cd-rich solution growth. In Figure 1, the slope from CdTe solution out to pure Te is almost invariant. However, as the Cd concentration in the solution decreases, the value of K_A becomes quite large. So, ignoring the diffusion coefficient values, the concentration effects, coupled with the slope of the liquidus curve, indicate that Te-rich solution growth is not favored. Similar plots for very rich Cd solutions would be worse, since the melting point of Cd is lower than that of Te.

In Figure 1, an interesting inflection point in the liquidus curve on the Cd-rich side occurs between 900 and 1000°C. The range of 30 to 40 atom percent Te leads to a value for M_A near zero. The value of K_A is also close to one, leading to conditions more favorable for solution growth without constitutional supercooling. Had the purpose of our program been only to grow layers of CdTe from solution, we should have chosen this temperature and composition range.

The loss of CdTe substrates of 800°C while in contact with solution vapors over a long period of time (hours) was described earlier. The loss was probably due to the fact that the Te vapor pressure above the Te solution was below that of p_{min} for Te described in the p Cd (or Te) versus temperature diagram for CdTe.[1] A recent paper by Akutagawa and Zanio[5] described a vapor phase growth process for CdTe in which the rate of growth via sublimation of CdTe was strongly dependent on whether or not the pressure of Cd (or Te) was below that of p_{min}. Sublimation of the substrate might be controlled with overpressure of Te or Cd, but the process would become more complex and impractical. Nevertheless, it is conceivable that a process could be designed in which growth could occur at 900°C to 1000°C using Cd solutions, but the advantage of low temperature growth in a narrow existence region would be sacrificed. Operating conditions would be so close to those of crystal growth from a stoichiometric melt that no practical advantage for solution growth would remain. In other words, a better choice of conditions for CdTe solution growth could have been made, but the conditions would not have been compatible with our program goals.

One final factor contained in the constitutional supercooling expression should be discussed: the temperature gradient G. Comparison of the results obtained for run number 26 [Figure 9(b)] and run number 28 [Figure 10(a)] directly demonstrates the effect of reducing the temperature difference between source chamber and substrate chamber from 5°C to 2°C. Thus, G was almost halved and was beginning to approach zero. The results indicate that G was definitely a factor and affected the quality of the material grown. In addition to this factor, Tiller[3] also points out that movement of the solution, even by convection currents in the vicinity of the substrate, leads to irregular surface growth. This point again emphasizes that the factors which improve the quality of thin layers grown from solution are not compatible with our practical goals. Solution growth of CdTe is not a good method for producing large, thick plates.

SECTION III

THE SUBSTRATE

A. Modified Stockbarger Method of CdTe Growth

Material to be used in the growth of single crystals was precompounded in evacuated quartz vials coated with carbon formed by the decomposition of acetone. The materials were weighed out in stoichiometric amounts of about 150 grams using six-nines pure Cd and six-nines pure Te. Compounding was accomplished at about 1200°C using mild agitation. The molten mass was cooled rapidly to avoid any segregation. A specially shaped carbon coated quartz tube was filled with about 100 grams of the compounded CdTe, then evacuated and sealed off. During the evacuation process, the chamber was heated with a torch until the walls were dull red to drive off excess Cd or Te. The evacuated vial was placed in a Marshall Furnace positioned vertically and adjusted so that a zone about six inches long is maintained slightly above (10 to 15°C) the 1092°C melting point of pure CdTe. The quartz vial was allowed to drop slowly through the furnace at a rate of about 2-1/2 inches (6.5 cm) per day. Currently, best results are obtained using 13 mm I.D. tubing. A photograph of a finished crystal is shown in Figure 13. In the First Technical Progress Report it was pointed out that the results obtained using 13 mm tubes were better than those obtained with 25 mm tubes. Although the crystal shown in Figure 13 is not single over its entire 12 cm length, a large portion of it is single crystal. Crystal material of this kind with large grain sizes is satisfactory for fabricating the mosaic crystal substrate.

B. Crystal Quality

Major emphasis was not placed on improving the quality of the substrate crystal. Instead, the emphasis was on developing a practical solution process. The quality of the substrate material was adequate. However, it is useful to examine some of the evaluation data commonly obtained in a program of this kind.

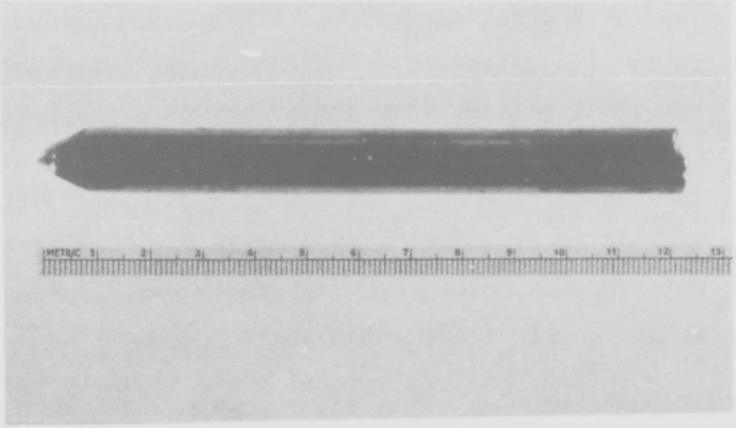

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Figure 13 High Purity Single Crystal of CdTe Produced by Modified Stockbarger Technique

Emission spectrographic analysis results of the reactants and a single slice of CdTe are shown in Table III. The beginning Cd is found to contain Cu, Mg, Si, and Ag in small amounts. The beginning Te contains Bi, Fe, and Si in small amounts. Analysis of the slice of CdTe revealed all of these impurities plus Pb, presumably picked up from the quartz container. For some reason, the Bi was found to be concentrated in the slice that was analyzed (the position in the crystal is not known). The total impurity concentration ranges from an estimated 11 ppm to 110 ppm, or in the 10^{18} range. These analyses are only estimated because calibration curves have not been carefully established for CdTe in our laboratory.

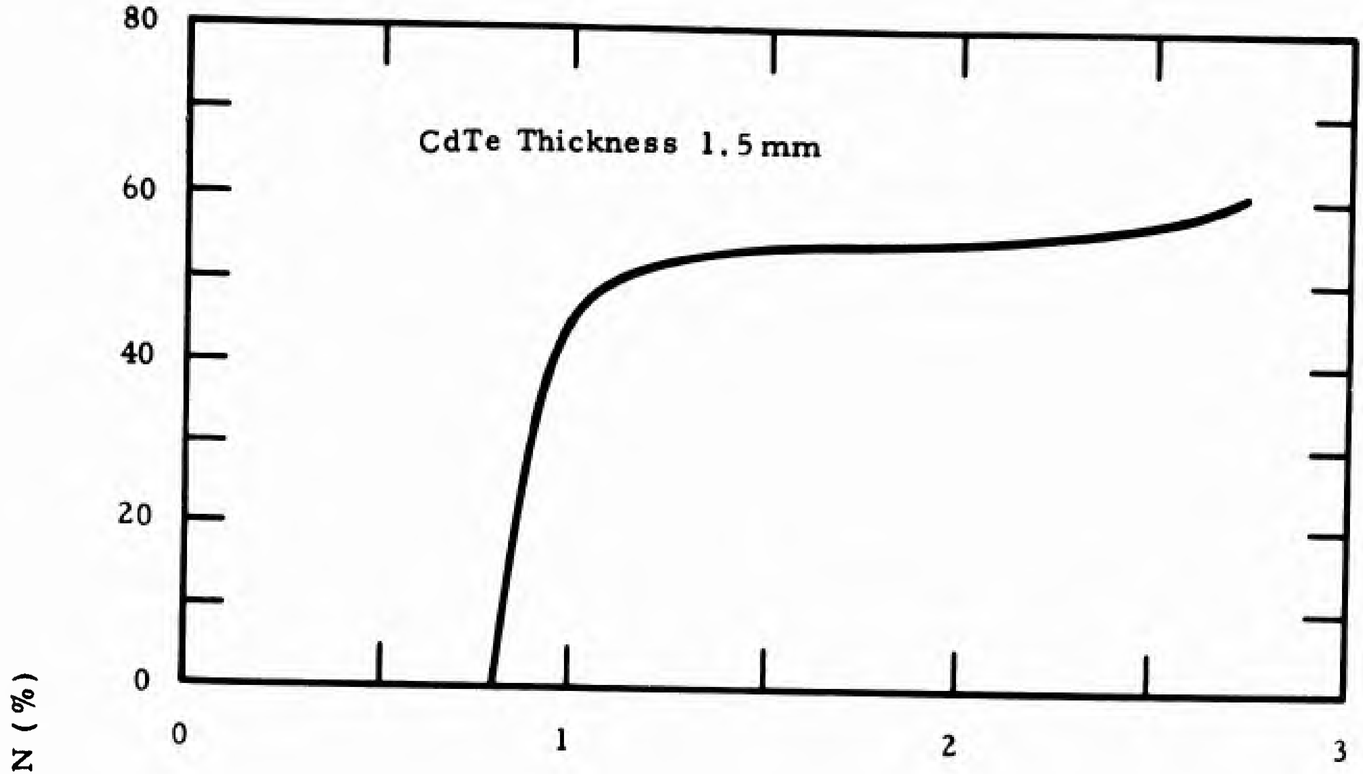
The total impurity estimate is not consistent with electrical results obtained unless, of course, the material is accidentally compensated. No definitive results were obtained on samples submitted to our Materials Characterization Laboratory for Hall measurements. The resistivity of the material was found to be too high (estimated to be greater than 10^4 ohm-cm) for routine evaluation equipment and techniques. Some difficulty was also experienced in trying to prepare ohmic contacts for the material. All routine methods failed. The resistivity estimate was made using a four-point probe. Nevertheless, the material definitely is high resistivity.

The measured transmission of a thin sample is shown in Figure 14. The sample is one of the 60 mil slices polished for transmission and does not represent the proper selection for optical evaluation. Nevertheless, one or two conclusions can be drawn. First, the absorption edge cut-on is very steep, indicating that an impurity tail is not present. An absorption tail would be present if the material were heavily compensated. Second, the transmission shows no absorption increasing with wavelength, as would be found for free carrier absorption in a low resistivity sample. The transmission was measured out to 25 μm. At that wavelength, no absorption was observed.

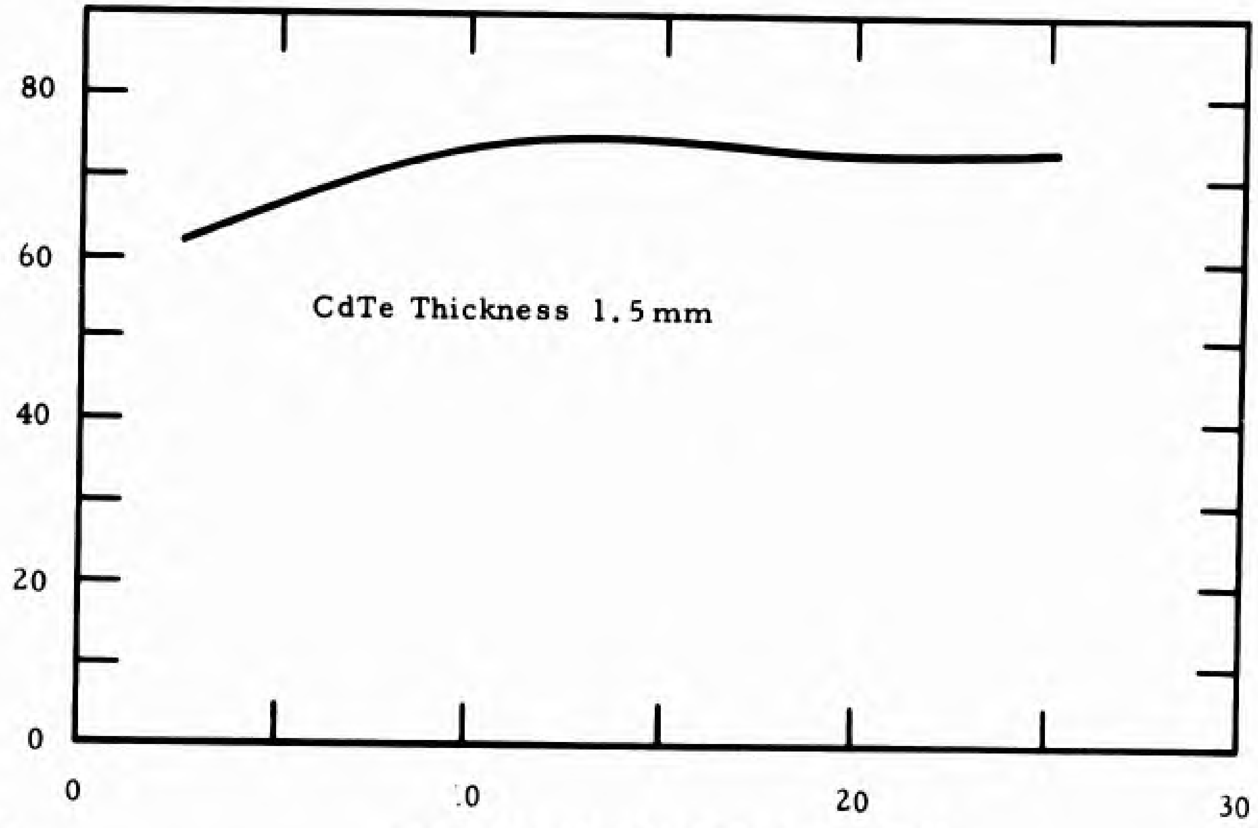
Table III

Emission Spectrographic Analysis of CdTe Crystal and Beginning Reactants

Element	Cd	Te	CdTe
Al			
Sb			
As			
Ba			
Be			
Bi		0.1-1	10-100
B			
Cd	Major		Major
Ca			
Cr			
Co			
Cu	0.05-0.5		0.05-0.5
Ga			
Ge			
Au			
In			
Fe		0.5-5	0.5-5
Pb			0.1-1
Mg	0.1-1		0.1-1
Mn			
Hg			
Mo			
Ni			
Pd			
Pt			
Si	0.1-1	0.1-1	0.1-1
Ag	0.05-0.5		0.05-0.5
Sr			
Ta			
Te		Major	Major
Sn			
Ti			
V			
Zn			
Zr			
P			



CdTe ABSORPTION EDGE



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CdTe INFRARED TRANSMISSION

Figure 14 Transmission of a CdTe Substrate

Calculated values for the free carrier absorption of CdTe are shown in Figure 15. The computer program used in the calculation was utilized in this laboratory to study damage to GaAs surfaces[6] and to calculate optical constants for semiconductor materials in the far-infrared for infrared ellipsometry studies.[7] Accurate results have been obtained predicting the optical constants as a function of wavelength for simultaneous lattice and free carrier absorption in mixed III-V compounds. Examination of the data presented in Figure 15 shows data points for only the 10^{18} to 10^{17} carrier ranges. The program as written is not suited for weak absorption or small changes in the optical constants. Extrapolation of the existing points in a linear fashion (Figure 15 is a log-log plot) shows that the free carrier absorption bulk absorption coefficient becomes less than 0.01 cm^{-1} for n-type CdTe at an electron concentration of 2 to 3 x 10^{14} cm^{-3} and less than 0.01 cm^{-1} for p-type CdTe at a hole concentration of 1 x 10^{15} cm^{-3}. The linear extrapolation appears justified upon examination of the expression given by Moss[8] for the contribution to the bulk absorption coefficient α of high mobility semiconductors due to free carriers:

$$\alpha = \left(\frac{\lambda^2 e^3}{4\pi^2 c^3 n \epsilon_o}\right)\left(\frac{N_n}{m_n^2 \mu_n} + \frac{N_p}{m_p^2 \mu_p}\right) ,$$

where λ = wavelength,
c = velocity of light,
e = electronic charge,
n = real part of the refractive index,
ϵ_o = permittivity,
N_n = number of free electrons,
m_n = effective mass of free electrons,
μ_n = mobility of free electrons,
N_p = number of free holes,
m_p = effective mass of free holes, and
μ_p = mobility of free holes.

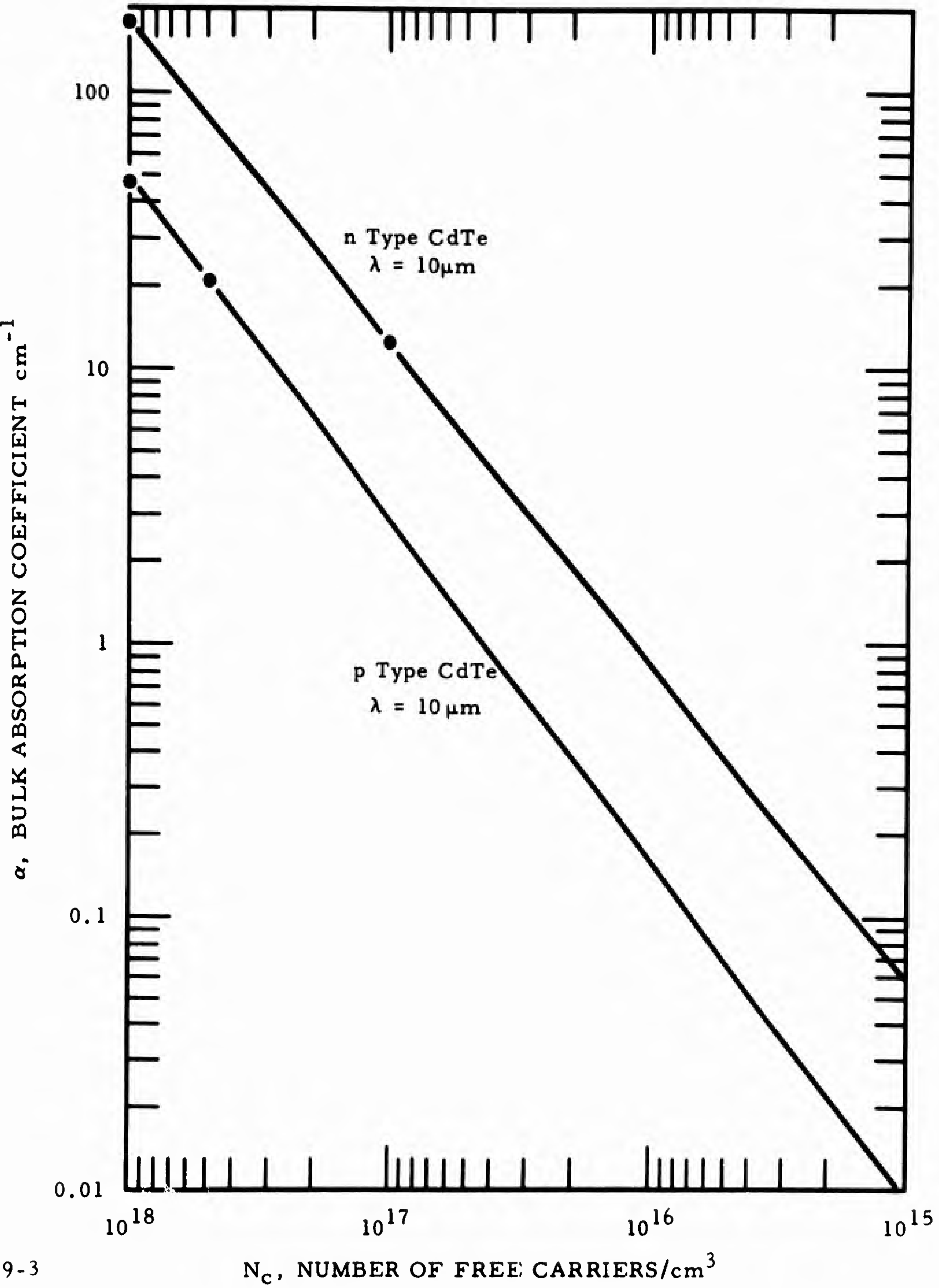

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Figure 15 Free Carrier Absorption in CdTe

However, this expression makes no allowances for impurity or lattice scattering of the electrons (or holes). The expression assumes that the mean carrier relaxation time τ is energy independent and is related to the carrier mobility by the expression:

$$\mu_c = e\tau/\langle m_c^*\rangle av \quad ,$$

where μ_c is the carrier mobility, assumed to be constant for a material of fixed resistivity and independent of radiation wavelength, and

m_c^* is the effective mass of the carrier averaged over all the involved conduction bands.

Impurity scattering, however, can increase the wavelength dependence for materials from λ^2 to near λ^4 through an energy dependence of the mobility.[9] Recent results[10] have indicated the dependence for CdTe may be of this order and have cast doubt on the validity of this type of an estimate of the chemical purity of CdTe required. The values listed below are those used in our calculations:

	Electrons	Holes
Effective mass	0.11	0.63
Mobility	1000 volt cm sec	100 volt cm sec

C. Mosaic Fabrication Methods

Two methods of obtaining a 2 inch x 2 inch mosaic substrate are illustrated in Figure 16. In Figure 16(a), a Stockbarger-formed CdTe crystal is sawed to square up the sides and is sliced into squares of proper thickness (60 mils, in this case). The squares are then pieced together to form a mosaic plate. Ideally, if the crystal is single and has assumed the orientation of a seed, the plate thus produced would be completely single and would have an orientation established as being beneficial to layer growth quality. In actual practice, of course, this ideal control cannot be obtained. As pointed out earlier, the crystals 5 to 6 inches long are not entirely single.

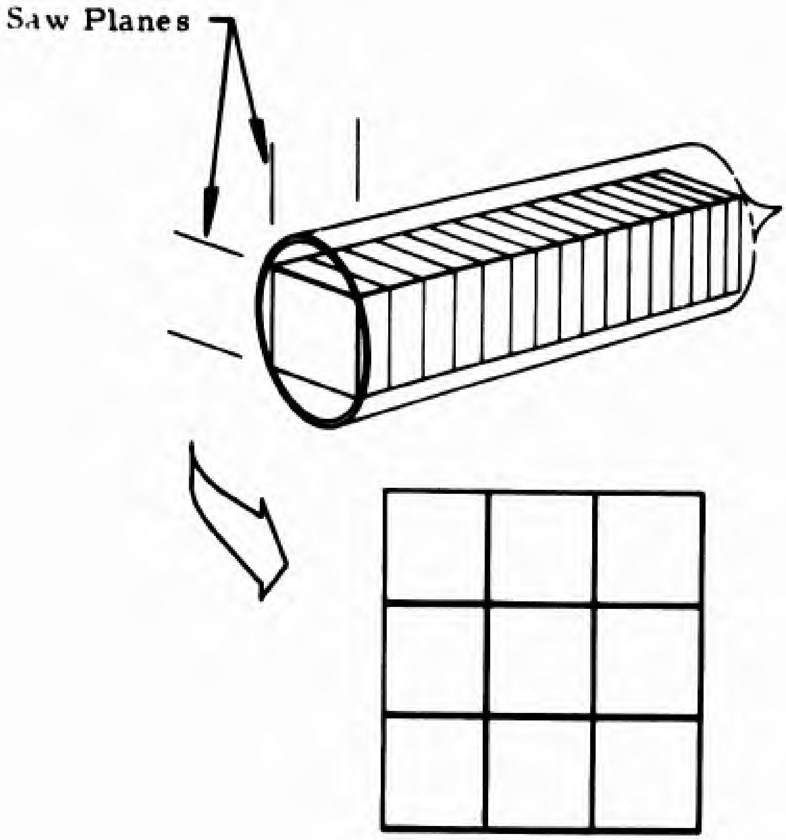

Figure 16(a) Mosaic Made from Single Crystal Squares

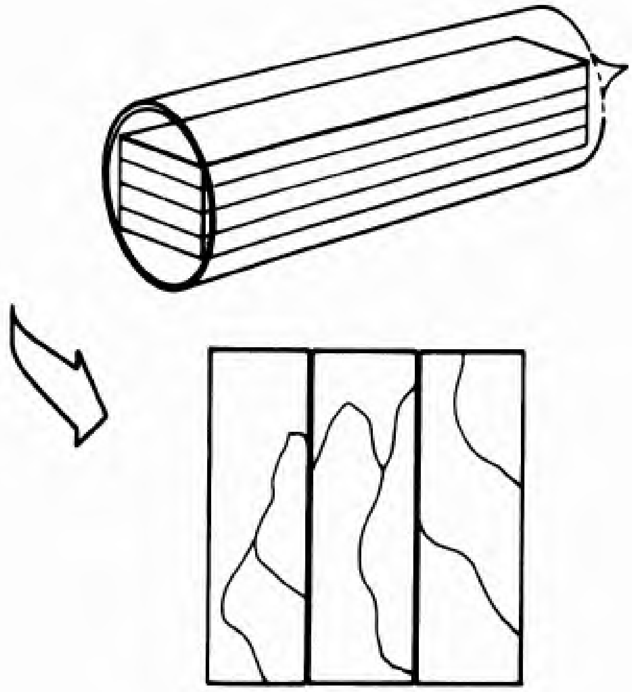

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Figure 16(b) Mosaic Made from Single Crystal Strips

The other geometrical possibility is indicated in Figure 16(b). In this arrangement, the crystal is sawed lengthwise, and strips of CdTe are placed side by side to form the substrate plate. The large grain sizes are depicted to indicate that the crystal is not single over its full length. The advantage of this method is that the pieces of CdTe can be fixed firmly in place by holding the ends of the strips so that they will not float away. One should bear in mind that CdTe is lighter than the solution from which it forms. A graphite holder used for this purpose is shown in Figure 17. The strips of CdTe are shown fixed in place. This holder was used in the rocking furnace reactor described in an earlier section of this report. The results mentioned previously indicated that the CdTe strips did not grow together. Conceivably, the CdTe pieces could grow together in two ways: (1) by growth of the CdTe layer across the cracks between pieces, and (2) by growth of CdTe on the edges between the pieces to form a continuous CdTe "glue." These two possibilities are illustrated in Figure 18. The top portion of the figure illustrates the problem of the solution wetting the surface but not penetrating into the cracks. This type of result was observed in the early experiments using the open system. It is interesting to note at this point that if the solution does not penetrate into the cracks, it cannot get under the pieces and float them out of any holder in which they are placed.

The lower portion of the figure depicts the probable result when the solution penetrates the cracks. The solution becomes entrapped in the cracks due to capillary action so that a thin CdTe layer grows only on the ends. Experiments using higher concentrations of Te ($\sim$ 90%) seemed to give this result. Examination of the samples after they had cooled showed they were stuck together; however, this examination was made at room temperature, well below the melting point of Te. Visual examination with a microscope clearly indicates the substance between the cracks is Te-rich and probably is entrapped solution. An example of results of this sort was described in Figure 9(a) for run number 17. Some tendency for the pieces to grow together was mentioned for results shown in Figures 9 through 12. However, we gave serious consideration to methods which could be used to join pieces together.

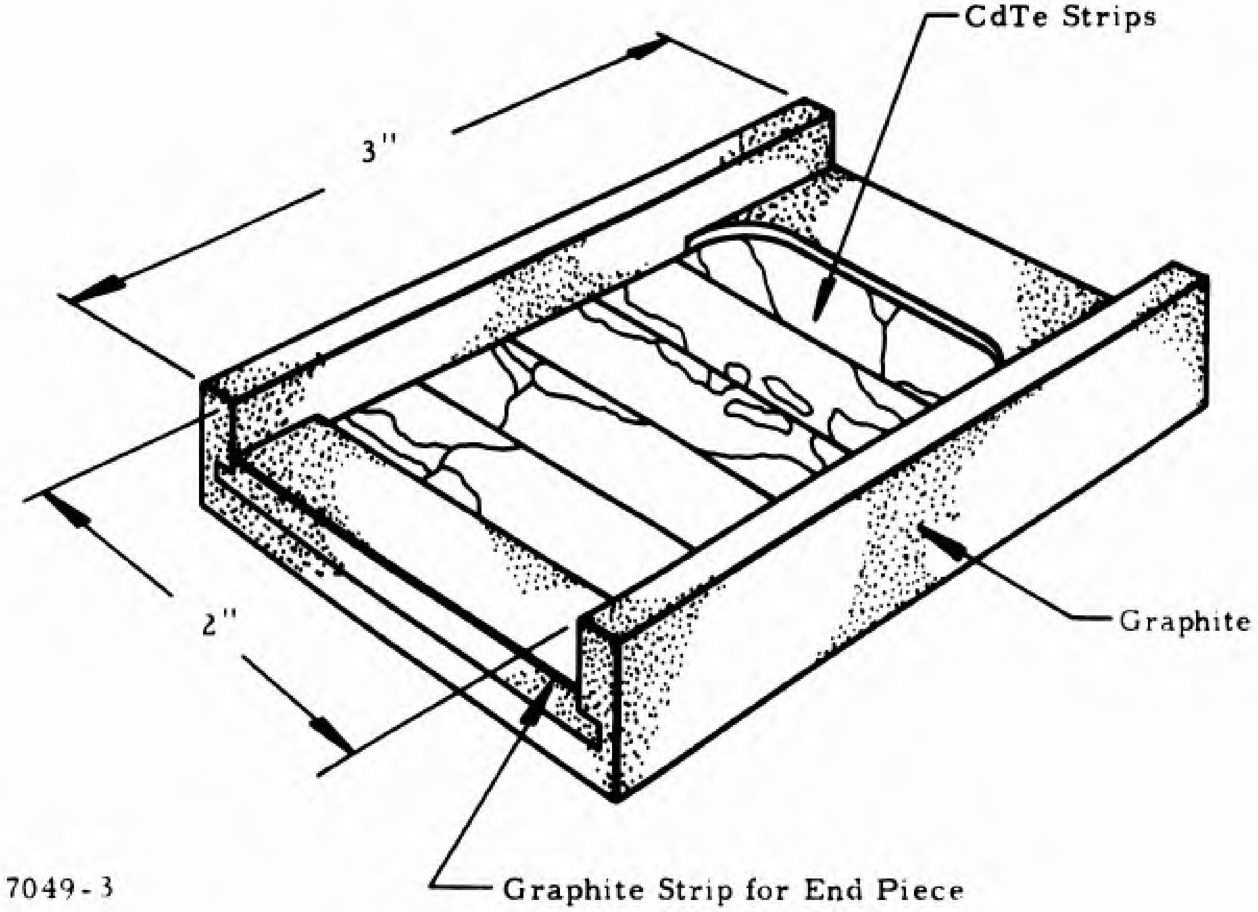
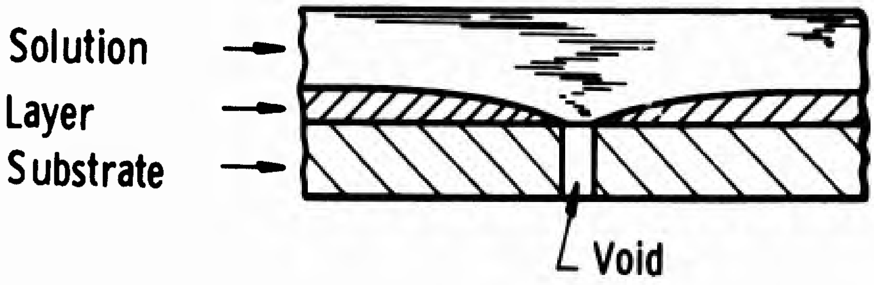
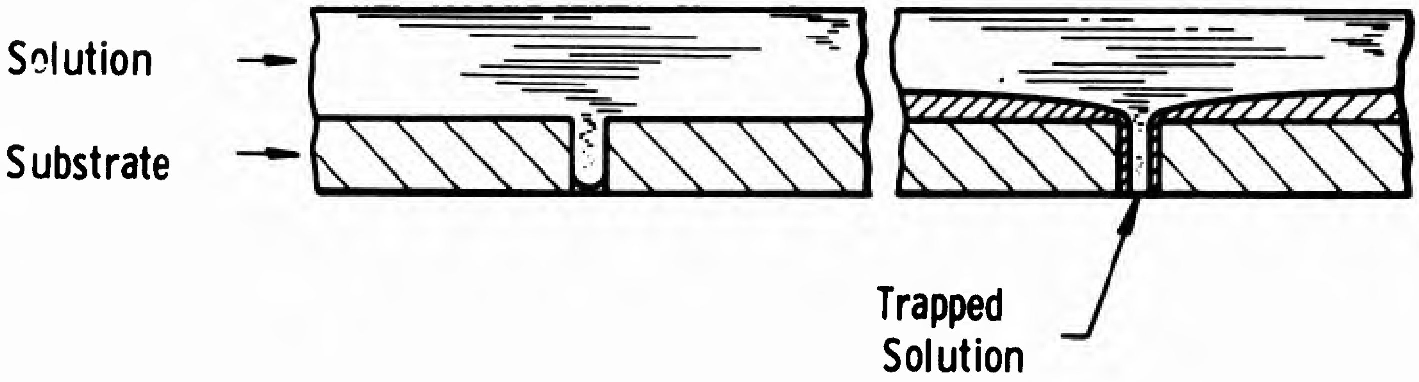


Figure 17 Graphite Holder for CdTe Strips Used to Form Mosaic Substrate



(a) Individual pieces do not grow together. Solution does not penetrate into the spaces between the pieces because of capillary action.



(b) Even with penetration into cracks, pieces will not grow together due to capillary action.

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Figure 18 Possibility of Growing a Layer Across Pieces of a Mosaic Substrate

D. Alloying Experiments

Ideally, growth of CdTe between pieces of CdTe would produce the best configuration for a mosaic substrate. Methods are found in the semiconductor literature covering the "alloyed junction" period which should be adaptable for this application. Figure 19 illustrates the method used by Kleinknecht[11] to alloy pieces of InAs together. An In-rich solution is used to stick the pieces together. They are then placed in a thermal gradient so that CdTe can be transported in the solution in a direction along the crack. As shown in the diagram, the crystalline material grows from the top down in a direction parallel with the thermal gradient. In the case of CdTe, this procedure would result in pieces of CdTe joined together with a CdTe layer. All that might be different at the surface is the existence of grain boundaries.

A modified bell jar apparatus used in an attempt to develop an alloying procedure is shown in Figure 20. Two commercially available, flat heat[illegible] were placed inside a machined graphite holder. The holder had a the [illegible] chamber next to a machined recess in which the CdTe pieces and grap[illegible] are placed. Wires for the heaters and thermocouples are attached t[illegible] in the bottom plate of the chamber. The heater temperatures are co[illegible] by controllers operating on the thermocouple voltages and are set to [illegible] the required thermal gradient. The entire assembly is wrapped in quartz[illegible] to decrease heat loss by emission. An asbestos plate at the bottom helps to decrease the heat loss to the bell jar plate.

Experiments were begun using a graphite plate relieved in the same manner as used in the boat so that two pieces of CdTe in substrate form (1 cm in diameter, 60 mils thick) could be placed in a thermal gradient. Precompounded solution for the 700 to 750°C range was used to stick the pieces together. The graphite plate with pieces in place was heated in a hydrogen-flushed tube furnace until a piece of solution, placed over the crack between the substrates, melted and flowed down, joining the two pieces together. The plate was then removed and placed in the bell jar apparatus. As described in Figure 19, the top temperature was raised to a point corresponding to the liquidus point on the diagram.

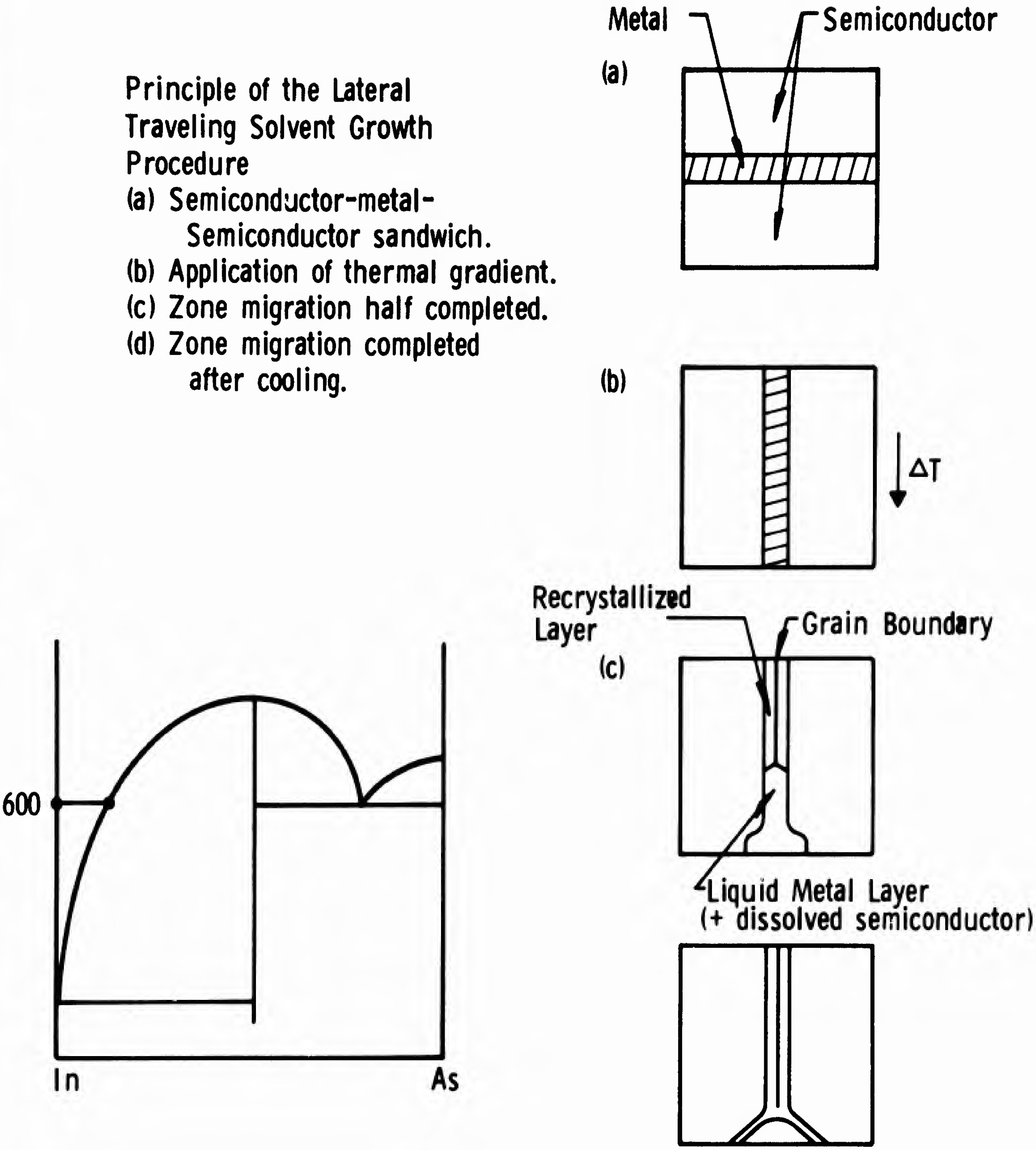

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Figure 19 Lateral Traveling Solvent Growth Method

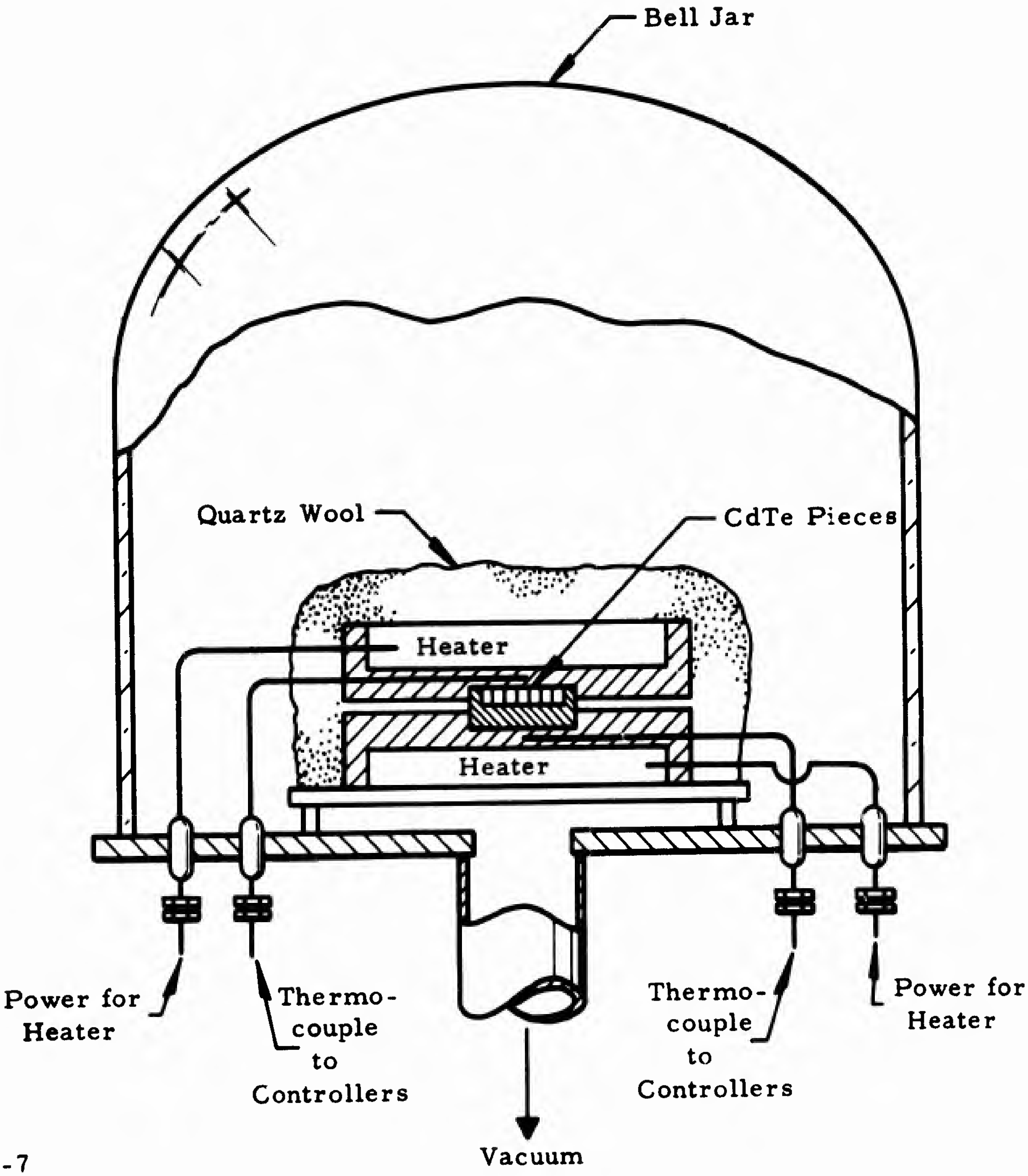

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Figure 20 Apparatus for Alloying Experiments

The bottom plate was regulated for a temperature 100°C lower than the top to produce the gradient. Samples were left in the apparatus for 25 to 48 hours. Complete loss of substrates and solutions occurred at these temperature ranges. Sublimation under these conditions was very often complete.

Drops in temperature were attempted, of course. In the vacuum (reduced pressure) environment, temperatures were dropped all the way to the melting point of pure Te. No success was obtained in growing the pieces together under these conditions. A microscopic photograph of results obtained after 41 hours at a top temperature of 450°C and a bottom temperature of 350°C is shown in Figure 21. Very little evidence of growth between the pieces can be seen; in fact, there were fewer signs of growth than in the solution growth attempts.

Alloying the pieces together could probably be accomplished at much higher temperatures. However, the system would have to be closed, not evacuated, and (considering our results with 800°C solution growth attempts) a small volume reactor would have to be used. At this point in time, it appears that the possibility of growing a continuous layer across the substrate pieces is better than alloying the pieces together.

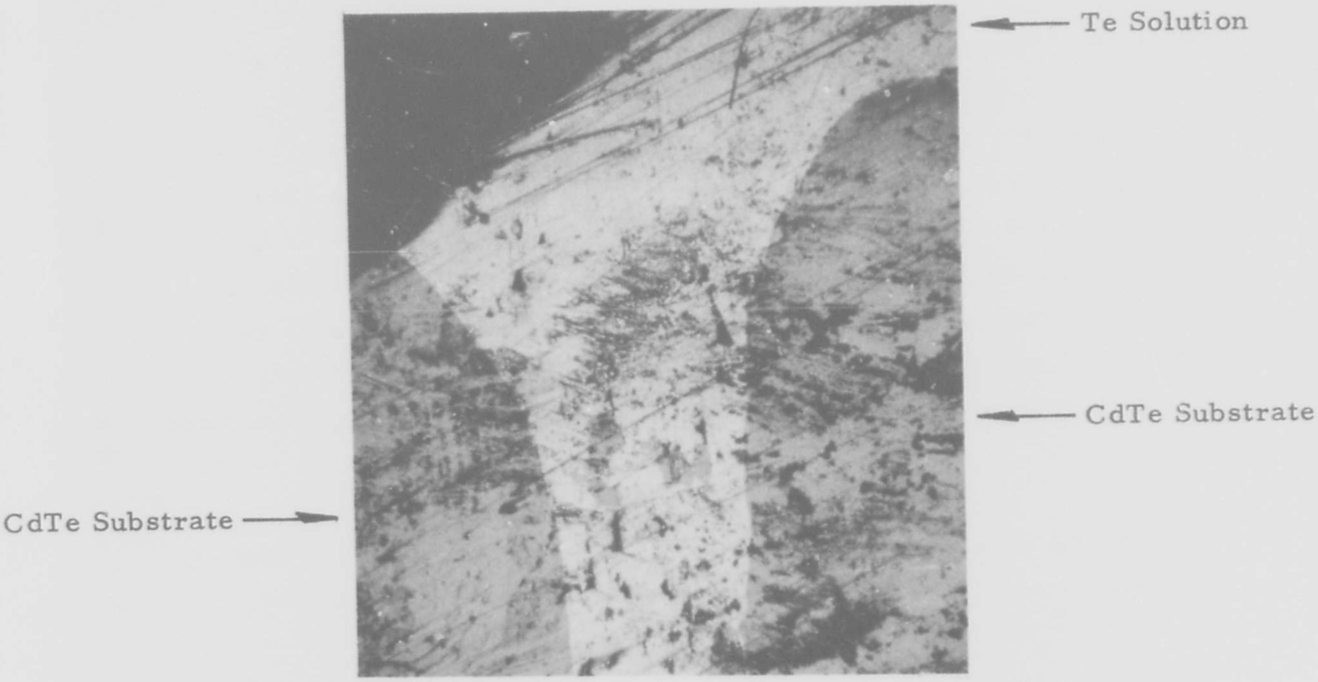

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Figure 21 Microscopic Photograph of Cross Section Showing Results of an Attempt to Alloy Together Two Pieces of CdTe at About 500°C (44 X)

SECTION IV

CONCLUSIONS

1. The program goal of developing a practical method for growing large, thick plates of CdTe on a mosaic substrate cannot be met using solution epitaxy.

2. Growth of CdTe layers was obtained from Te-rich solutions, but in all cases constitutional supercooling occurred. Growth of 10 to 20 mils was obtained at 750°C in closed systems, but not without solution entrainment of the deposit. Temperature differences of only 2°C between the solution source and substrate chambers improved the quality of the deposit, but not sufficiently to avoid solution entrainment. Mechanical movement of the solution across the substrates added to the interface instability, resulting in irregular growth. Attempts to escape these bad effects by going to higher temperatures leads to sublimation of CdTe and substrate loss.

3. Attempts to alloy pieces of CdTe together using the lateral traveling solvent growth technique applied while the pieces were under reduced pressure failed due to CdTe and Te solution sublimation.

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Wright-Patterson Air Force Base, Ohio

13 ABSTRACT

The goal of this program was to grow thick, large-area plates of CdTe using a solution epitaxy method. Solution epitaxy was chosen as the method for growth in the belief that fast reaction rates could be obtained at lower temperatures than those used for vapor growth. Operating at a temperature well below the wide existence region found for CdTe would reduce the trouble with impurities and lead to greater control of stoichiometry.

Generally, solution epitaxy is a batch process used to grow thin layers. The process as used is rate-limited by diffusion of one constitutent through the solution. Mechanical motion of the solution was used in an effort to overcome the batch-type nature of the process. Motion of the solution in the vicinity of the substrate led to extremely irregular layer growth along with spontaneous nucleation and growth of CdTe dendrites and platelets. Solution entrainment was observed for all deposits. Solution growth is not a good method of forming thick pieces of CdTe. For the finished process, the large-area substrate would be a mosaic made up of pieces of single crystal CdTe cut from a crystal grown in a conventional manner. Several methods of fabricating the substrate are discussed, along with efforts to alloy the mosaic pieces together.

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