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Final Progress Report

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SPACE PROCESSING OF ELECTRONIC MATERIALS

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1. Introduction

This final report takes the form of an update of the Interim Report on NASA Contract NAS 832920, dated 26 January 1981, and covers the period 27 January 1981 to 20 August 1981.

Beginning early in 1981, the thermal models for the growth furnaces for Bridgman HgCdTe, both for ground and flight, have taken on top priority urgency. The successful growth of the crystals requires the maximum practical thermal gradient at the growth interface, and also a flat or slightly convex interface over a rather wide range of temperatures. Growth is initiated from the 20% CdTe melt at the liquidus temperature of 792°C. The first material to freeze is about 53% CdTe, and so the melt at the interface is depleted until at steady state growth, 20% CdTe solid is produced at 706°C. If growth continues until the melt is entirely consumed, the last material to freeze is pure HgTe, which solidifies at 668°C. Thus, the ideal furnace should have a sufficiently wide adiabatic zone to assure flat isotherms over this range of temperatures. Since the maximum temperature in the furnace cannot exceed 1,000°C (because of the excessive vapor pressure of mercury) and since a high thermal gradient is required to maintain interface growth stability, it is clear that compromises must be made in furnace design.

In a given furnace configuration, the location of the freezing interface will depend on the thermophysical properties of the crystal material. In particular, if the melt thermal conductivity is high

relative to that of the solid, then the growth interface will be "pushed down" toward the cold end of the system where it becomes concave. If, on the other hand, the solid has the higher conductivity, then the material in the adiabatic zone will be cooled and the growth face moves up toward the hot end of the furnace where it becomes convex. Thus, the relative values of thermal conductivity of solid and liquid HgCdTe are critically important. As long as these values remain unknown, proper predictive control of the crystal growth will be impossible.

During the period of this report, Dr. Holland has spent nearly all of his time working on the experimental approaches to measuring the thermal conductivity of HgCdTe and on related topics such as the density change on melting.

2. Thermal Conductivity Measurement

A. METHODS OF MEASUREMENT:

As explained in the Interim Report, the high vapor pressure of mercury in the temperature range of interest requires the use of sealed ampoules to contain the HgCdTe. This, in turn, precludes the use of direct temperature sensing to do steady state measurements which require the measurement of heat flux and thermal gradient.

The thermal diffusivity of a material is closely linked to the conductivity by the defining relation

$$D = \frac{k}{\rho c}$$

where D is the diffusivity, k is the thermal conductivity, ρ is the density, and c is the specific heat. Since ρ is very well known and c

can be estimated fairly accurately on theoretical grounds, a measurement of D should yield a good picture of the behavior of k on melting. The dimensions of D are [length^2/time], rather than [heat x length/temperature] as for k, and hence a determination of D is relatively easy. There are two broad categories of diffusivity measurement; those which use transient heating, and those which use periodic heating. These types of experiment each have distinct advantages and disadvantages. Both types are being pursued.

B. TRANSIENT HEATING:

The method to be used here is that of Taylor and Cape (Appl. Phys. Lett, Vol 5, p 212 (1964)). In this method, the sample is a thin wafer, heated on one face by a laser flash. The rise of temperature on the back face, monitored optically, follows a characteristic delay related to the thickness of the sample and the diffusivity. If the time delay and the thickness are measured, the diffusivity can be calculated. The drawbacks of the method are first, that if the thickness is not accurately determined, then the error turns up doubled in the diffusivity because of the length^2 dimension, and second, that if liquid, the sample must be contained in a flat cell whose windows affect the thermal response.

In the case of mercury cadmium telluride, NASA has contracted with Dr. R. E. Taylor of CINDAS to make the actual flash measurements at Purdue University. Dr. Holland has been assigned to try to construct a cell to contain the sample. The cell windows must have the following charateristics:

1. Optical flatness

2. Accurate parallelism

3. Accurate spacing

4. Large diameter relative to spacing

5. Transparency to the laser pulse

6. Transparency to the infrared radiation used by the temperature monitor

7. Strength to withstand 100 atmospheres of mercury vapor pressure

8. Chemical inertness to HgCdTe

The only possible material for this is fused silica, and consequently, an all silica cell has been chosen. The cell size specified is 1 cm diameter and 2 mm thick. Since the cell must be completly filled (otherwise, the laser pulse would destroy the optical heat sensor), the cell must have a side arm for filling, as shown in Figure 1.

Various methods of fabricating the cell were tried before a technique which could meet the minimum requirements was worked out. The resulting, time consuming, multistep process is as follows:

1. The windows are cut from 10 mm diameter fused silica rod, and polished on one end, which will be the inside surface. This must be done with care because the high friability of cut and polished fused silica makes the edge of the polished surface tend to crumble. No visible chip at this point is tolerable, as it will later cause a stress riser which could provoke failure of the cell under pressure. The required time is about three weeks.

2. The windows, with the required 2 mm spacing are fused into a silica tube of 16 mm OD and 10 mm ID nominal. The tubing must be hand selected for a close fit. Fusion is done under vacuum, which necessitates using a graded seal to connect to the pumps (silica acts as a radiant heat pipe which would burn the tubing). A small diameter silica rod attached to the back of each window and tacked to the inside of the 16 mm tube holds the windows in place. The heat must be very carefully controlled so that the vacuum does not cause the cell cavity to collapse or distort.

3. The 16 mm tube with the fused windows is given a 24 hour annealing.

4. A 2 mm hole is drilled in the side of the cell with a diamond drill, and the hole is fired polished.

5. The side arm is attached for loading, and the excess length of 16 mm tube is sawed off each end of the cell.

6. The ends of the cell are ground and polished to complete the windows, and a flat is ground on the side to facilitate optical measurement of the cavity geometry.

7. The polished cell and side arm assembly is given a 24 hour annealing.

8. The cell sidearm is loaded with purified mercury, cadmium, and tellurium and sealed.

9. The elements are reacted in the rocking furnace and cast into the cell as HgCdTe.

10. The excess sidearm length is removed and the shortened seal annealed.

11. The HgCdTe is annealed at 650°C for a week to homogenize the material in the cell.

At this point the charged cell is sent to CINDAS for the measurement of the diffusivity. One successful cell has been delivered and five more cells are under construction.

C. PERIODIC HEATING:

The method to be used here is a modified Angstrom measurement, in which one end of a long thin sample is heated periodically at a low frequency (say one cycle per hour), and the resulting heat wave is monitored for velocity and attenuation as it travels down the rod. Of course, the "rod" to be used here will not be unsupported liquid HgCdTe, but rather, a composite system of HgCdTe contained in a sealed ampoule. The result of such a measurement is not the diffusivity of the HgCdTe,

but rather that of the composite system of HgCdTe plus the silica ampoule. Therefore, it will be necessary to do a parallel measurement of the pure silica, so that the effect of the silica can be compensated in the composite system.

The proposed measurement is schematically diagrammed in figure 2. The pure silica rod and the sealed silica ampoule containing HgCdTe are individually packed in silica wool and placed together in a furnace muffle which brings them to the desired background temperature. Heaters are wound on each end of the rod and the ampoule, and resistance thermometers are wound at the locations marked "Tsense". For the measurement of diffusivity, a very low frequency ac voltage is applied to one end of the rod or ampoule, while an equal average power in dc is applied to the other end. In this way, the resultant constant thermal gradient near the center can be neutralized. The thermal fluctuations from the ac heater will be picked up by the two sensors, and from the phase and amplitude difference in the signals, the speed and attenuation of the wave are determined. These, in turn, give the effective diffusivity.

To assure that inequalities in the sensors do not distort the wave speed and attenuation measurements, the roles of the two heaters will be interchanged so that the wave travels in the reverse direction. A second measurement will then be made and the results of the two measurements appropriately averaged.

Much new mathematical theory has had to be developed for this system. Present status of the theory indicates that there will be no

problems with end effects or surface losses. If the standard 12 mm OD ampoule tubing is used, the diffusion length "l" in figure 2 should be set at about 3 cm, which would require a heat frequency of about 1-1/4 cycles per hour, and an electric power frequency of half that or 175 microhertz. At this time, the theory is not quite complete, as the exact eigenfunctions for the lowest mode of the composite rod are still to be worked out. There is every indication that this can be done in closed form. An approximate error analysis indicates that the sensitivity of the system should be adequate for a satisfactory determination of the diffusivity.

3. Ongoing Tasks

Routine work has been accomplished at SSL, among which the following have been the larger efforts:

a. Further development of the facility for distillation loading of HgCdTe ampoules. This facility now has a liquid nitrogen cooled heat extractor, which will make possible much more rapid deposition of the distillate in the ampoules. A new transparent, multilayer heater is also under construction.

B. A new furnace has been specified, ordered and received for the rocking furnace homogenization facility. This will be equipped with all new high temperature components which will permit a much improved control and uniformity of temperature.

C. There have been ongoing conferences with TRW concerning the design and construction of flight and DVT ampoules. It has been a major effort to defend the mechanical integrity of this system.

4. New Technology

Dr. Holland has invented and put into practice a new system for securing and extracting heat from silica or glass tubes under high

vacuum conditions. This system may have much wider application than the original need, which was for a way to hold the ampoules in the distillation facility. This is because it has proved to be a means of holding tubes which have large dimensional tolerances with a security which approaches the strength of pristine glass and with a remarkable ability to position the tube to high precision.

While the outstanding mechanical advantages of the new system may be, in the long run, its most important feature, they are, in fact, a fringe benefit. The original design goal was for a reliable means of thermal contact to remove heat under high vacuum conditions. Since it was assumed that an irregular cylinder held in a rigid tube would have only six contact points, a system of spring fingers was devised in which dozens of fingers each have one contact point. Beryllium copper was selected as a spring material for its high thermal conductivity. A set of ten to fifteen rings (figure 3) is fastened into a metallic tube, either by soldering or spot welding. Then the glass tube or rod is simply forced into these rings, thus compressing the fingers outward. Fifteen rings, each with sixteen fingers, would give a total of 240 contact points on the glass. The force exerted by each finger may be quite small, but the total force is formidable. Thus, a pressure approximating a hydrostatic pressure is exerted on the glass.

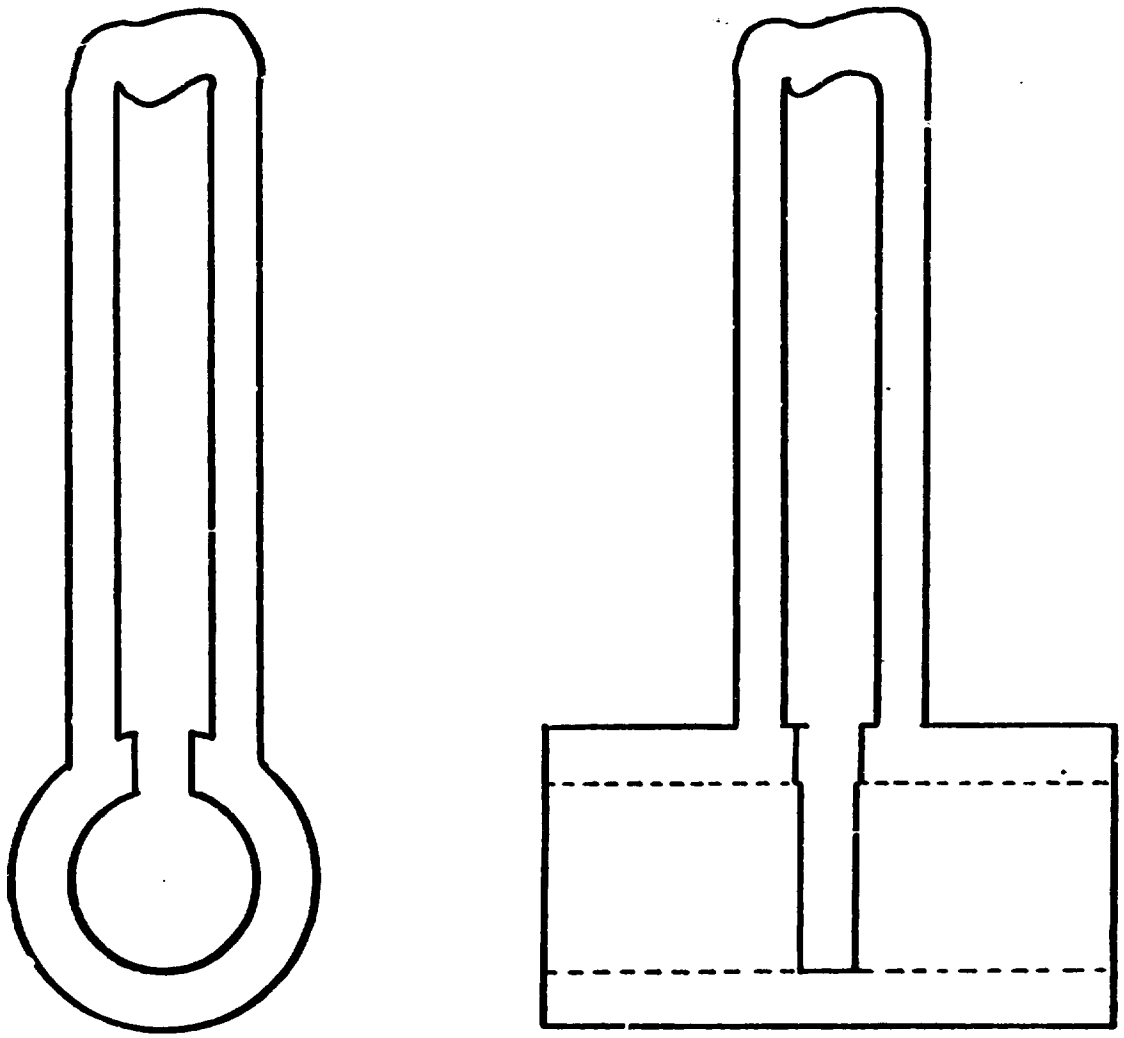


FIGURE 1

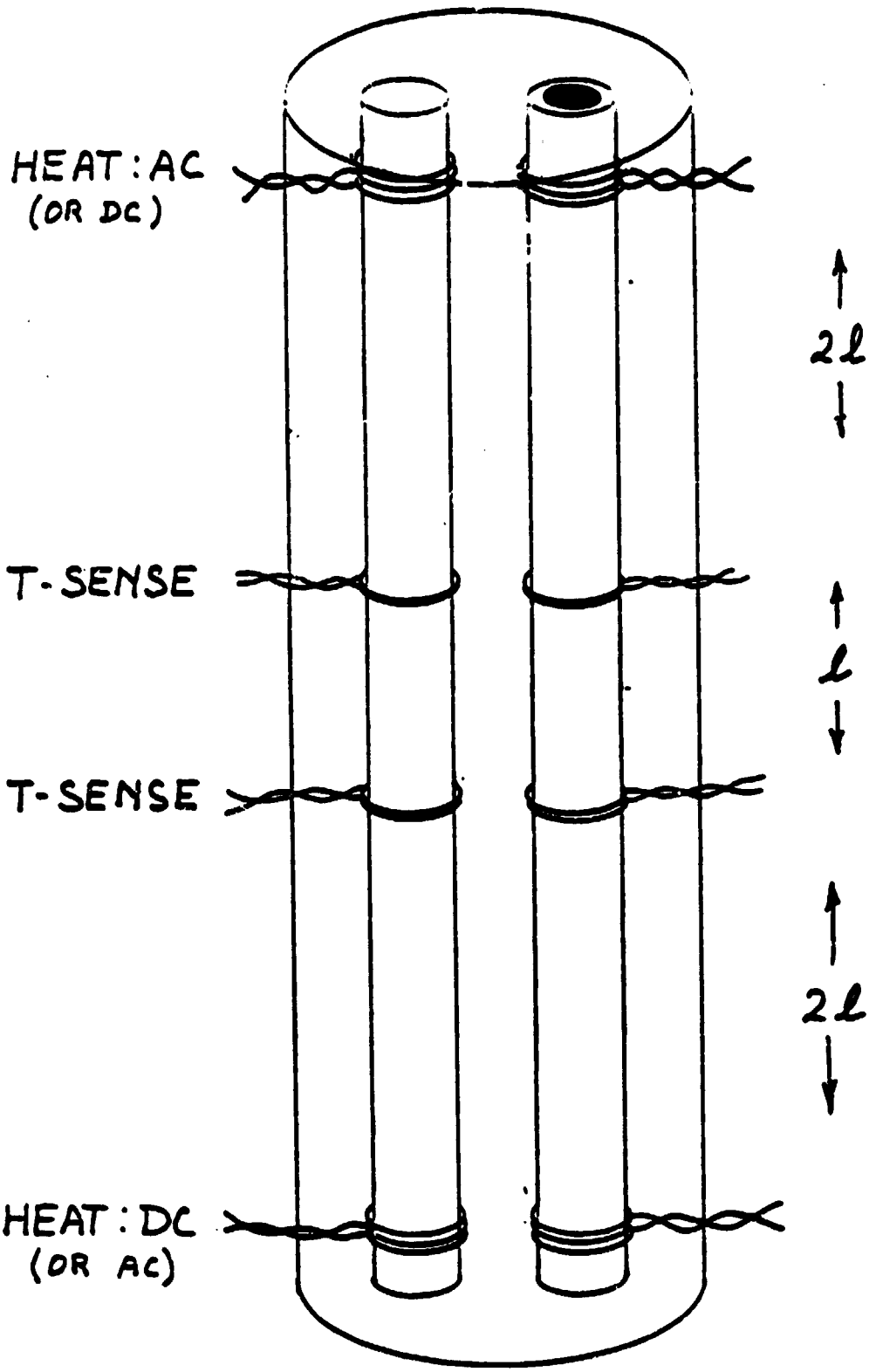
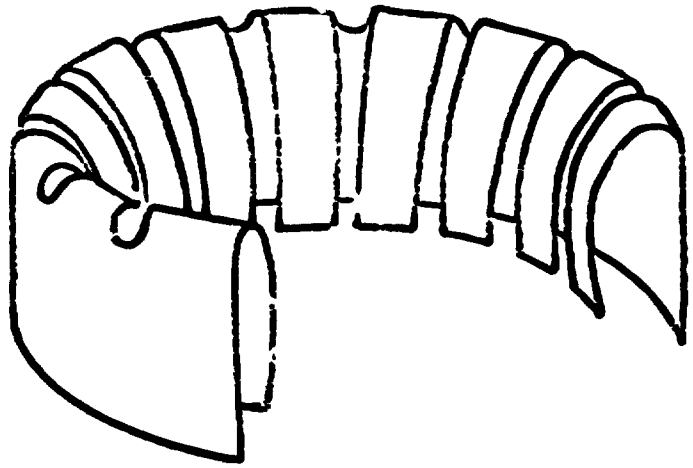


FIGURE 2



CUT-AWAY OF SPRING RING

FIGURE 3