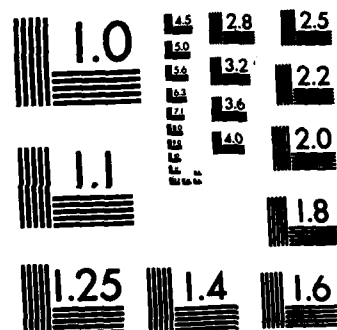


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A STUDY OF RECRYSTALLIZATION
IN CADMIUM TELLURIDE

THESIS

AFIT/GEP/PH/82D-21 Richard B. Snoddy
1st Lt USAF

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A STUDY OF RECRYSTALLIZATION
IN CADMIUM TELLURIDE

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

by
Richard B. Snoddy, B.S.
1st Lt USAF
Graduate Engineering Physics
December 1982

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Richard B. Snōddy

Table of Contents

	Page
Acknowledgments	ii
List of Figures	v
Abstract	vi
I. Introduction	1
Background	1
Problem and Scope	2
Research Limitations	3
General Approach	3
Sequence of Presentation	4
II. Review of Literature	5
CdTe	6
Si	7
Properties	10
Conclusion	13
III. Theory	14
Basis of Recrystallization	14
Application to the LESS Method	15
Advantages	15
IV. Apparatus	17
Temperature Controlled Oven	17
Vacuum System	18
Quartz Tube Oven	18
Zone Heating Unit	19
V. Procedures	23
Sample Preparation	23
Static Heating	24
Capping Evaluation	24
Zone Heating	25
VI. Results and Discussion	29
Static Heating	29
Capping Evaluation	30
Zone Heating	31

	Page
VII. Conclusions and Recommendations	34
Pressure	34
Capping Material	34
Substrate	35
General Comments	35
Bibliography	37
Vita	39

List of Figures

<u>Figure</u>		<u>Page</u>
1.	Thermal Conductivity of CdTe	12
2.	Phase Diagram of CdTe	12
3.	Zone Heating Unit	20
4.	Test Samples	26

Abstract

Solid state recrystallization of vapor grown polycrystalline cadmium telluride (CdTe) samples was studied using a zone heating method adapted from the LESS (Lateral Epitaxy by Seeded Solidification) technique developed by J.C.C. Fan, et al at Lincoln Laboratories for silicon films.

These experiments were part of an effort to produce large, twin free, single crystals of CdTe suitable for the epitaxial growth of mercury cadmium telluride compounds.

Extended, high temperature annealing of CdTe samples at 800°C and 2.5 atmospheres of nitrogen revealed no changes in the grain structure.

Zone heating experiments were performed on CdTe wafers and films at 850°C. Sputtered gold films were used as encapsulating layers. The samples were heated in a vacuum or in argon at atmospheric pressure with zone rates of 1.3 and 0.75 mm/sec. No recrystallization was observed but preferential epitaxy of amorphous CdTe films onto the polycrystalline substrate was noted. 

Further investigation should be conducted at elevated pressure, use a more compatible encapsulant, and possibly use Al₂O₃, MgAl₂O₄, or BeO single crystal substrates.

A STUDY OF RECRYSTALLIZATION IN CADMIUM TELLURIDE

I. Introduction

This research investigated the solid state recrystallization of cadmium telluride (CdTe) by zone heating. The LESS (Lateral Epitaxy by Seeded Solidification) method used to recrystallize silicon (Si) films was adapted for use on CdTe. Zone heating involves heating a polycrystalline sample to a high temperature and then passing a hotter wire over the sample. The movement of this hotter zone through the sample causes the grains in the sample to grow. In this way, polycrystalline wafers or films may be transformed into single crystals.

No process used to grow CdTe crystals has yet produced large, twin free, single crystals. Applying the LESS method to CdTe was investigated as a means of producing large area, twin free, single crystals which could be used as a substrate for the epitaxial growth of mercury cadmium telluride (HgCdTe) compounds. The HgCdTe crystals are used as IR detectors and would be grown on the CdTe substrates to form large, focal plane array IR detectors.

Background

Many methods of crystal growth have been developed to modify and improve the size, optical properties, conductivity, or other characteristics of the crystals produced. All of the available states of matter (solid, liquid, gas,

plasma) are exploited in various processes to achieve the desired qualities. One way to modify the grain patterns in a crystal is solid state recrystallization. Various techniques are used in solid state recrystallization but all of them involve adding a limited amount of energy to the crystal lattice. Just enough energy is added to make the atoms semi-mobile but not enough to form a liquid. Solid state recrystallization does not directly change the phase of the material but simply allows the grain boundaries to move.

A recent innovation in solid state recrystallization is the LESS method. The LESS method is a modification of the zone melting technique of crystal growth where thin films are recrystallized by zone heating rather than zone melting.

Up to now, the LESS method has only been used to recrystallize silicon films. If the LESS method could be successfully used on another material then it would be possible to produce large, single crystals of any semi-conducting film. The recrystallized films could be of sufficient quality for device applications and epitaxial growth.

Problem and Scope

This research was performed to determine if the LESS method can be adapted to recrystallize CdTe. The tests were performed on polycrystalline wafers and on thin, sputtered films of amorphous CdTe. The polycrystalline wafers

and the sputtering target were sliced from a vapor grown boule.

The LESS experiments were conducted in a vacuum and at atmospheric pressure in argon. The samples were heated to 850°C. A 100°C increase was produced in the sample by the moving zone heater which scanned at 1.3 and 0.75 mm/sec.

Research Limitations

Vapor grown CdTe boules were used as the starting material because of the high purity, large grains, and availability of the vapor grown material. Processing in a vacuum or argon atmosphere was chosen to reduce contamination and oxidation of the samples during heating.

Although CdTe sublimates when heated at atmospheric pressure, a gold capping layer and rapid processing were used to minimize sublimation.

General Approach

This project involved three phases of investigation:

- 1) static heating in sealed tubes at various pressures,
- 2) rapid heating of capped samples in a vacuum, and
- 3) zone heating in a vacuum at atmospheric pressure.

The first phase was performed to determine the pressure needed to substantially reduce sublimation and to determine if any changes were made in the grain structure by heating.

The second phase determined which of the available materials was compatible with CdTe and could be used as a cap.

The last phase involved the actual application of the LESS method to prepared CdTe wafers used as substrates.

In all cases the samples were photographed before and after the various heat treatments to verify the results.

Sequence of Presentation

Chapter II reviews the crystal growth and recrystallization research performed on Si and CdTe. A brief discussion of the theory of solid state recrystallization is given in Chapter III. Chapter IV describes the equipment built for the project while Chapter V outlines the procedures used in the investigation. Chapter VI presents the operating conditions and the analysis of the information. The conclusions and recommendations for further research are detailed in Chapter VII.

II. Review of Literature

A large amount of research has been performed on Si and CdTe to grow high quality crystals which are used to make integrated circuits and solar cells (in the case of Si) or IR transparent optics (in the case of CdTe).

Crystals of Si and CdTe are grown in three basic ways: from the molten material, by zone melting the solid material, or by condensing the material from a vapor. Any of these methods may be used to produce single crystals by limiting the initial growth to only a small single crystal seed and not allowing other seed crystals to form. In growing crystals from the liquid, the purified material is first completely melted and then slowly cooled. The cooling process is initiated at one end of the liquid where crystalline seeds are formed. The solid-liquid interface progresses through the liquid until all the liquid is solidified.

Zone melting is similar to growth from the liquid but only a small region of the solid material is melted at first. This heated, molten region is moved through the solid. The crystals are formed as the molten region passes through the material.

The vapors used in the vapor growth method can be formed by subliming a mass of source material or by a chemical reaction between two molecular gasses. In either case a cool seed plate or a crystal substrate is placed in

the vapors for them to condense upon and form the desired crystals.

This chapter reviews that work which either directly or indirectly applies to recrystallization. The first section discusses some of the properties and previous attempts at growing large, twin free, single crystals of CdTe. The next section covers the development of the LESS method and its results. Lastly the properties of Si and CdTe are compared and related to the growth processes.

CdTe

Despite 35 years of research and investigation no large, twin free single crystals of CdTe have been grown although various methods have been tried. Early studies relating to the formation and growth of CdTe consisted of zone melting the compound in sealed crucibles. Single crystals (1 cm in cross section) were melt grown in tapered crucibles (Lawson, et al., 1959: 326). The crucible travelled through the hot zone at a rate of 1 cm/hr. No mention was made of the existence of twins in these crystals. To reduce seeding of the melt at the tube walls some studies used a quartz tube coated with carbon. These procedures produced boules weighing 40g with 2 or 3 single crystal grains (Ichimya et al., 1960: 107). DeNobel noted that CdTe prepared by zone melting preferentially grew in the $\langle 111 \rangle$ direction and twinned on (111) planes (DeNobel, 1959: 107). Later, vapor growth was used to produce twin

free crystals but the process yielded only small crystals (Lynch, 1962: 108).

By using a quartz rod attached to the seed plate (as a heat sink) the vapor growth was tried again. Vapor growth was chosen for growth since the lower growth temperature (850°C) would lead to the formation of fewer defects and dislocations, better stoichiometry, and higher purity crystals (Gertner, 1981: 8). One inch diameter boules were grown on single crystal CdTe substrates and quartz seed plates. No boule was twin free while only one boule was a single crystal. The seeding was ineffective since tests showed that the single crystal seed separated into several grains of different orientations at the sub-grain boundaries when the seed was heated to 850°C (Gertner, 1981: 3).

Films of CdTe have been produced on oriented single crystal substrates of Al_2O_3 , MgAl_2O_4 , and BeO. The process used is similar to chemical vapor deposition. Dimethylcadmium and dimethyltellurium were used as reactants at a growth temperature of 500°C (Manasevit, 1972: 312).

Si

Since none of the methods used to grow CdTe have produced large twin free single crystals it was felt that a method used to grow large single crystals of Si might work. This method is called zone heating or zone annealing. One used a pulsed laser (Pinizotto, et al., 1982: 388) while

another used a scanning cw laser to recrystallize areas up to $100\text{ }\mu\text{m} \times 10,000\text{ }\mu\text{m}$ (Magee, 1981: 248).

In the LESS system (mentioned earlier) the scanning laser is replaced by a moving, heated carbon rod (Fan, et al., 1981: 365). The prepared silicon sample is placed on a larger, fixed carbon heater which heats the sample to 1200°C . The upper carbon rod is then heated and passed over the sample. In early experiments, the sample consisted of a single crystal Si substrate which was coated with SiO_2 and then etched down to the Si substrate in many parallel strips $3.5\text{ }\mu\text{m}$ wide and up to $500\text{ }\mu\text{m}$ apart. After etching an amorphous Si layer was deposited over the entire sample which was then sealed with SiO_2 . The exposed Si in the strip acted as a seed for the recrystallization. As the upper heater passed over the sample (parallel to the strips) the amorphous Si was recrystallized and grew between the SiO_2 layers. In some cases the seeded crystals grew up to 4 mm from the seed and there was no evidence that the regrowth could not be propagated indefinitely if the zone heating was controlled well enough (Fan, et al., 1981: 367).

An analysis of these recrystallized films showed that there was a subgrain boundary located midway between the seed stripes. These subgrain boundaries are not abrupt changes in the crystal structure but are a set of dislocations. The crystal structure on each side of this boundary was misoriented by less than 0.3 degrees (Pinizotto, et

al., 1982: 388). The LESS process has been more effective than laser annealing because the carbon heater scans the sample much more slowly than the laser, slowing down the growth rate. Also, the larger size of the heated area under the strip heater and the more gradual temperature gradient gives a smoother transition as the sample is scanned. These effects combine to produce the much larger recrystallized films from the LESS method (Pinizotto, et al., 1982: 389). However, the Si film contained SiC contamination resulting from small particles falling from the upper carbon heater (Pinizotto, et al., 1982: 390).

In the following experiment the amorphous Si film was seeded from the top, using a separate polished piece of single crystal Si placed on the film. Seeding from underneath was accomplished by recessing the SiO_2 layer into the single crystal substrate except for a strip across one edge. This strip was not coated with SiO_2 and was used as the seed. The amorphous Si film was deposited next and capped with a SiO_2 and Si_3N_4 combination. The addition of Si_3N_4 made the capping layer more stable and increased the quality of the recrystallized films (Tsaur, et al., 1981: 562). These recrystallized films had completely smooth surfaces and the twins formed near the stripes in the SiO_2 layer were eliminated by using a recessed SiO_2 layer (Tsaur, et al., 1981: 562).

The next series of experiments used no seed. The Si substrate was coated with SiO_2 , the amorphous Si layer

deposited, and the wafer sealed with SiO_2 and Si_3N_4 (Geis, et al., 1982: 158). The recrystallized Si films had many long, thin grains running parallel to the motion of the heater. The grains were all of (100) orientation with the $\langle 100 \rangle$ axis in the general direction of the motion of the heater (Geis, et al., 1982: 159). One of these long grains was used to seed the rest of the film by rotating the sample 90 degrees and zone heating again. The resulting film was a high quality single crystal (Geis, et al., 1982: 160).

The latest experiments also used samples without an internal seed. A seed was provided for the Si film by scribing a groove in the top surface of the sample which penetrated through all of the deposited layers and into the Si substrate (Fan, et al., 1982: 187). Up to 20 cm² of single crystal film were produced with the $\langle 100 \rangle$ axis in the direction of growth (Fan, et al., 1982: 187). As in the previous experiments, many microscopic subgrain boundaries were formed (Fan, et al., 1982: 187).

Properties

The physical and chemical properties of Si and CdTe essentially determine the crystal growth techniques which can be successfully used for their growth. Therefore, a comparison of the properties of CdTe and Si is needed.

Since both CdTe and Si crystallize in an FCC structure (CdTe in the zinc-blende phase and Si in the diamond phase), there are many similarities in their growth

patterns. The solid-liquid interface is a {111} plane and growth occurs in the $\langle 111 \rangle$ direction in both Si (Wagner, 1967: 347) and CdTe (DeNobel, 1959: 107). It has been noted that the growth direction in Si can be changed by applying a force during solidification (Wagner, 1967: 347) and in thin films of Si the growth is in the $\langle 100 \rangle$ direction (Geis, et al., 1982: 158). Also growth from screw dislocations (evidenced by the formation of growth spirals) is seen in both Si (Sandulova, et al., 1966: 99) and CdTe (Teramoto, 1963: 108).

The similarities observed in their crystallography do not carry over into their physical properties. Si is a good thermal conductor while CdTe is a very poor conductor its thermal conductivity being 23 times smaller than that of Si (Pamplin, 1981: E-99). The thermal conductivity of CdTe is plotted in Figure 1 as a function of temperature and doping level.

The other major difference between Si and CdTe is their vapor pressure. At 1000°C the vapor pressure of Si is 10^{-6} torr (Sandulova, et al., 1966: 98). Since CdTe sublimes as Cd and Te_2 vapor the vapor pressure of CdTe is controlled by the vapor pressure of Cd. The pressure versus temperature phase diagram for CdTe is shown in Figure 2. For CdTe the vapor pressure at 1000°C is approximately 7 atmospheres (DeNobel, 1959: 84).

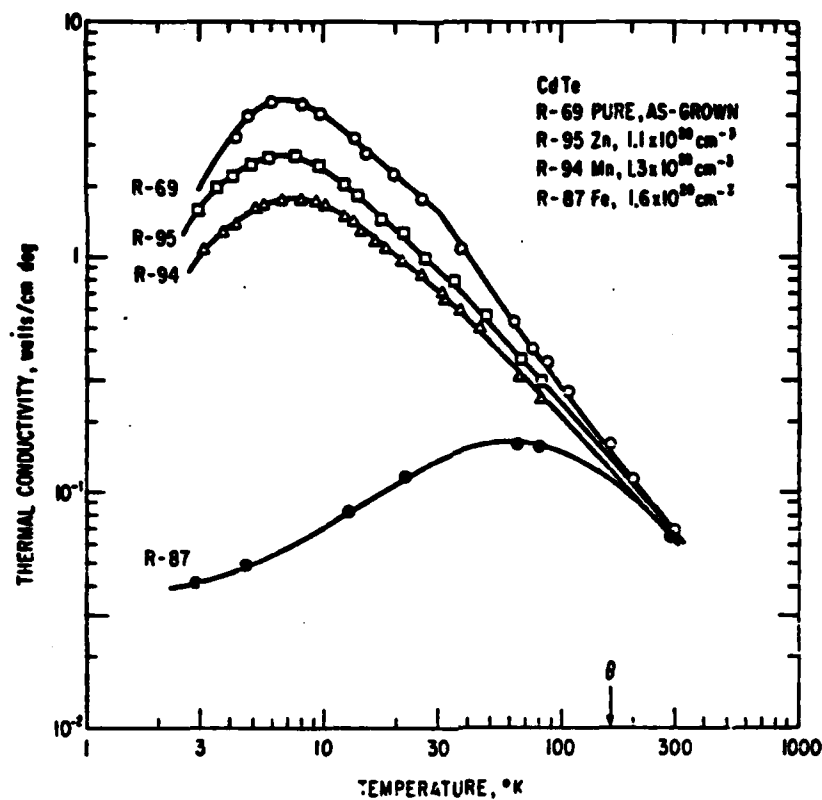


Figure 1. Thermal Conductivity of CdTe
 (Slack and Galgaitis, 1964:576)

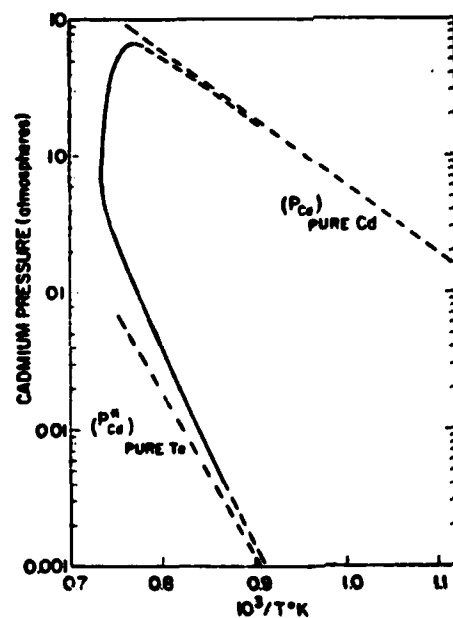


Figure 2. Phase Diagram of CdTe
 (Lorenz, 1967:84)

Conclusion

Both CdTe and Si have been studied in depth, producing many advances in crystal growth for both materials. Large twin free single crystals of CdTe have not yet been produced while large crystals of Si are routinely produced as are single crystal films. The similarities in the crystallographic properties of CdTe and Si provide a reason to expect that LESS recrystallization will work well on CdTe. The difficulties associated with a lower thermal conductivity and higher vapor pressure should only change the parameters for growth rather than prevent growth.

III. Theory

This chapter describes briefly the theory involved in solid state recrystallization. The theory is formed from the observations and results of the experiments reviewed in the previous chapter. The first section gives an overview of the recrystallization process. The application of this theory to the LESS process is described in the second section and is followed by a section covering the advantages of LESS recrystallization over other techniques.

Basis of Recrystallization

The process of solid state recrystallization is one in which a polycrystalline material is changed into a less severely polycrystalline material or, in the best case, into a single crystal. This process is aided by releasing some of the potential energy bound up in the polycrystalline material. Grain boundaries, sub grain boundaries, and individual dislocations or defects are the sources and locations of the trapped potential energy.

By adding a controlled amount of energy to the lattice as heat the atoms become more mobile. This allows the atoms to seek an area of lower potential energy by moving in the lattice or diffusing across a grain boundary. In amorphous or finely polycrystalline Si films, heating a small area (e.g. with a laser pulse) will cause recrystallization over an area much larger than the heated region (Luke, 1982). This is due to the large amount of energy trapped in the amorphous starting material.

Application to the LESS Method

The LESS method also utilizes the trapped energy in the material to aid in recrystallization but does so in a controlled manner. Before zone heating the entire sample is heated to high temperature (slightly lower than what is needed for recrystallization). This reduces thermal stresses, transport of material from the heated zone, and the amount of power which must be supplied to the movable heater to cause recrystallization.

As the zone heater moves across the sample, a narrow region is heated sufficiently to increase the mobility of the atoms. In this region the atoms move to occupy their appropriate place in the lattice, the position of lowest potential energy. The atoms become locked into place as the heater travels and the material cools. The broad temperature gradient produced by the heater and the slow scan speeds allow the atoms ample time to "find their place," reducing defects produced by recrystallization. Twinning should be reduced or eliminated by this process since the growth of a twin is statistically less likely. This is drawn from the reduced number and area of twinned regions as compared to the area of the bulk material.

Advantages

The LESS method of zone heating has several advantages:

- 1) In solid state recrystallization the material is not melted so the crystal structure is not destroyed,

however sufficient energy is added to break the weaker bonds at grain boundaries and allow the crystal to readjust to the single crystal phase. Also the purity of the material can be better maintained by keeping the sample as a solid.

2) The method can be used as an additional step to recrystallize high purity polycrystalline material grown in another manner.

3) The process is very rapid and yields high quality single crystals.

IV. Apparatus

The equipment used in the three stages of the investigation are described in this chapter. The first section describes the temperature controlled oven used in the static temperature testing of samples at various pressures. The second section describes the system used to produce a vacuum or contain an argon atmosphere when samples were heated in the quartz tube or the zone heater. The following section describes the heated quartz tube used to test the compatibility of the films (which could be used as a sealing layer) with the CdTe. The last section describes the zone heating unit used to investigate the fully prepared samples. The zone heating unit was used in the vacuum system described in the second section in place of the heated quartz tube.

Temperature Controlled Oven

Initial recrystallization tests were run on CdTe samples sealed in quartz tubes. These samples were tested in a resistively heated oven with a proportional temperature controller. The oven consists of eight heater rods imbedded in fire bricks and placed symmetrically around a mullite tube. The mullite tube is sealed at one end and provides the housing for the encapsulated samples. The signal from the thermocouple (TC) placed against the mullite tube in the hottest region of the oven is used to control the temperature. To monitor the temperature another TC was placed next to the sensing TC of the

controller and connected to a digital display. During the tests the temperature of the oven was not seen to vary by more than 5°C.

Vacuum System

The vacuum system consists of a bell jar, feed through ring, mechanical pump and a TC gage for pressure measurements.

The bell jar has a 14-1/4 inch inside diameter and is 14 inches high. The feed through ring has 12 ports of which eight are fitted with various sizes of electrical connections. One port has two valves and fittings for backfilling with a gas, and three ports were unused. The mechanical pump is a two stage pump with a capacity of 500 liters/sec. The TC gage was not calibrated so only relative pressures were measured and used in testing. A cylinder of high purity argon is connected to one of the gas fittings on the feed through for purging and backfilling the bell jar.

Quartz Tube Oven

The following heater design was used in the bell jar under vacuum conditions during testing: The heater is a 6 cm long section of quartz tube wrapped with 10-3/4 turns of 0.040 inch diameter nichrome heating wire. The quartz tube has a 2.3 cm inside diameter and a 1 mm wall thickness. The nichrome wire coils are evenly spaced over the center 5 cm of the tube and resistively heated using a 15 ampere Variac. Molded asbestos sheet covers the lower 75% of the

tube and also forms two 3.5 cm tall posts which support the heater. A TC (with digital display) monitors the temperature in the tube and an AC ammeter is used to monitor the current flowing in the circuit to avoid damaging the Variac.

Zone Heating Unit

A zone heater was built for use in the bell jar so that samples could be processed in a vacuum or in argon at atmospheric pressure. A simplified top view of the zone heater is shown in Figure 3 with the upper (movable) and lower heaters separated. The drive screw on the base plate passes through and engages the threads in the drive screw holes which allows the upper heater frame to be moved by the motor. The base plate stands on four supports (each one being 9 inches tall) to elevate the heater to the center of the bell jar for easier operation. The upper and lower heater sections are examined in detail in the following two sections while the third describes the power sources.

Upper heater. The upper frame is made of 1/4 inch thick cast aluminum with an anodized surface. The upper frame supports a rod made of machinable ceramic which provides electrical and thermal insulation of the upper heater. The ceramic rod is 1/2 inch in diameter, 5-3/8 inches long, and is notched halfway through on each end to align the bottom of the ceramic rod with the lower surface of the frame. The heating element is a tungsten ribbon

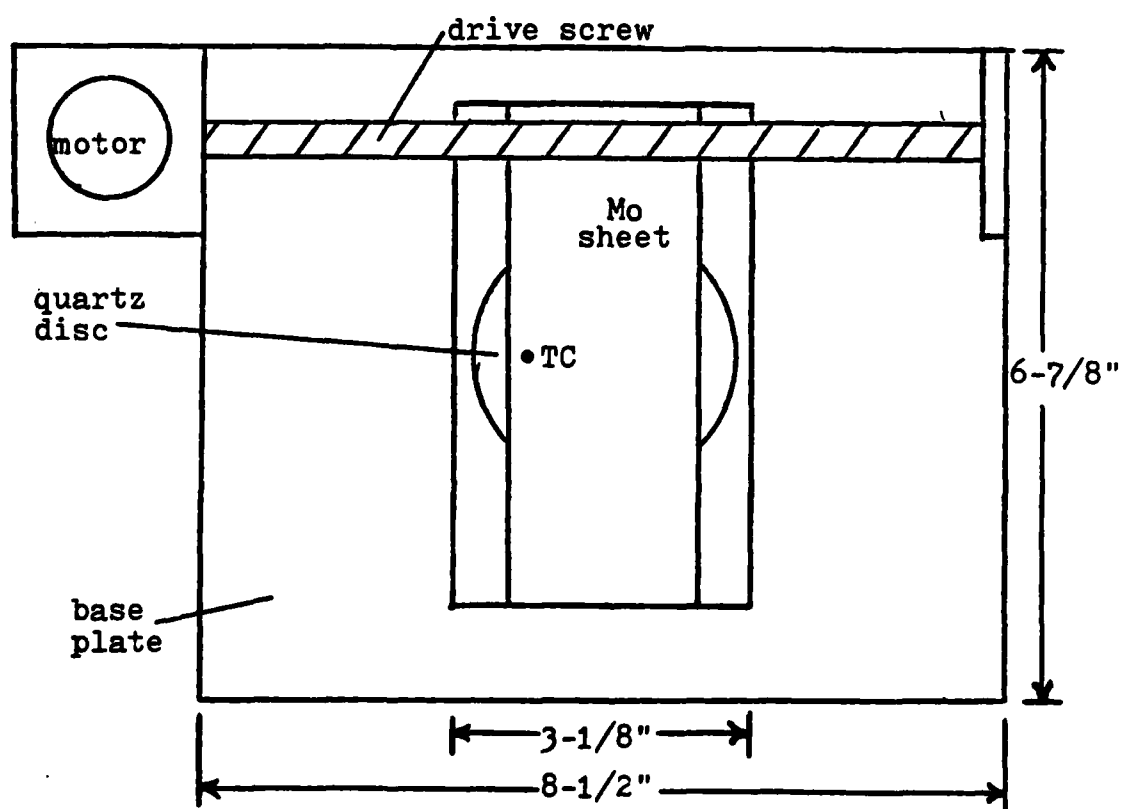
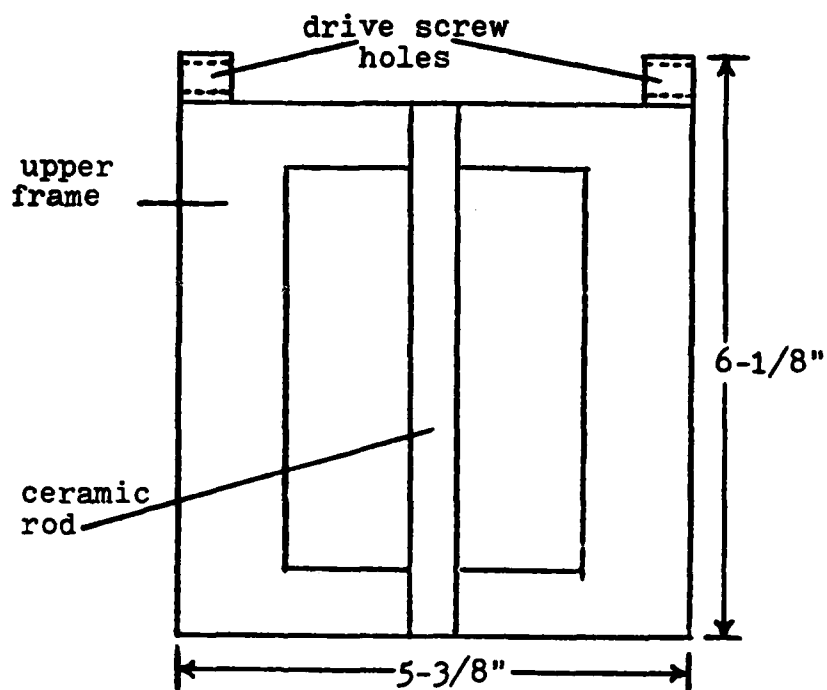


Figure 3. Zone Heating Unit

0.060 inches wide and 0.0008 inches thick. This ribbon fits into a 0.062 inch wide slot 0.020 inches deep in the bottom of the ceramic rod. An access hole is drilled from the top of the rod into the slot near the frame at each end. The ends of the tungsten ribbon extend out of these access holes where electrical connections are made.

Lower heater. The base plate is made of 1/4 inch thick anodized cast aluminium plate as is the upper heater frame. The drive screw (which moves the upper heater frame) is supported at each end by ball bearings. A 24 VDC motor is connected to the drive screw by a pair of brass bevel gears. These gears allowed the motor shaft and the drive screw to operate at a 90 degrees angle.

The lower heater consists of a molybdenum (Mo) sheet on top with a quartz disc, heating element, and asbestos insulation underneath. The Mo sheet is 2 inches wide, 0.010 inches thick, and is secured at each end to provide a firm, smooth, level surface. The quartz disc is 1/8 inch thick and electrically insulates the heating element from the Mo sheet. The heating element is a commercially available, coiled resistive wire heater found in many small home ovens. The heater is bent into four short segments to fit under the quartz disc and to provide a more uniform temperature profile. Molded asbestos sheet thermally and electrically insulates the heater from the two stainless steel support straps and keeps the coiled sections separated.

Power supplies. Power is supplied to the upper heater by a 25 ampere Variac and to the lower heater by a 40 ampere Variac. The temperature of the lower heater is measured directly by a TC attached to the Mo sheet near one edge and indirectly by an optical pyrometer. The temperature of the upper heater is measured with the optical pyrometer. A variable, 0-30 VDC power supply allows the motor to operate from 4 to 30 volts producing a 0.11 to 1.3 mm/sec range in speed for the upper heater.

V. Procedures

This chapter describes the process used in preparing, measuring, and recording the results of measurements on various samples. All the samples were prepared and analyzed in the same manner. The procedures for preparing and analyzing the samples is presented first. The following three sections give the procedures used in static heating, evaluation of various capping materials, and in zone heating.

Sample Preparation

For all experiments, the CdTe wafers were prepared in the same way. First, the wafers (less than 1 mm thick) were sliced from the vapor grown boule and mechanically polished. Since the wafers were polycrystalline the mechanical polishing did not produce a mirror smooth surface and many wafers were broken into four or more pieces by the mechanical polishing. Other than very careful handling of these samples would also cause them to break demonstrating the brittleness of the polycrystalline CdTe. This brittleness is due to crack formation at the inherently weak grain boundaries. A crack will then propagate either along a cleavage plane or along the grain boundary. After mechanical polishing, each piece was etched in a 5:1:1 mixture of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (to bring out the grain structure) and then photographed. The samples were then chemically polished in a mixture of 10 ml HNO_3 , 20 ml H_2O , and 4 g $\text{K}_2\text{Cr}_2\text{O}_7$. The sample was then coated as needed for

the subsequent heat treatment. After heating, each sample was photographed, etched if necessary to reveal the grain structure, and photographed again to record any changes in the grain pattern. The samples with gold coatings were soaked in a KCN solution (Technistrip Au) at 60°C to remove the gold film.

Static Heating

Samples of CdTe were statically heated in sealed quartz tubes to determine if there would be any enlargement of the grains and to determine the pressure needed to substantially reduce sublimation. The clean, polished sample of CdTe was placed on a flat quartz plate in a quartz tube which had one end sealed. The tube was then evacuated, backfilled with nitrogen to a specified pressure, and sealed. The quartz tube was then placed in the center of the hot zone of the oven and heated for approximately one week. At the end of the week the oven was shut off and allowed to cool slowly. When cool, the quartz tube was removed and the sample examined.

Capping Evaluation

Different capping materials were investigated to determine the compatibility of the various materials with the CdTe sample during rapid heating. An acceptable material needs to be well matched to the thermal expansion of CdTe and strong enough to withstand the vapor pressure at high temperatures.

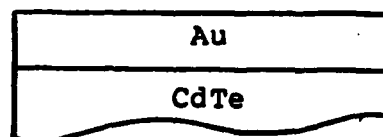
After polishing, each sample was sputter coated with 1 μm of the capping material to be evaluated. The sample was placed in the quartz tube and the thermocouple placed at one edge of the sample. The vacuum system was then sealed, evacuated, and power applied to the heater. A temperature of 800°C was achieved in one minute and 1000°C in two minutes. Changes in the coating were observed and recorded as the temperature increased. After the temperature passed 800°C the heater was turned off and the temperature allowed to drop to 200°C before backfilling with argon. When fully cooled the sample was removed and processed as described in the first section.

Zone Heating

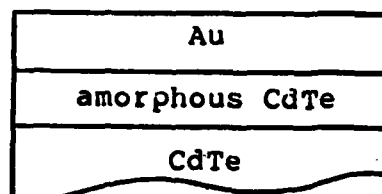
The zone heating experiments investigated how zone heating would affect the polycrystalline substrate and the sputtered films. The first two experiments were to determine whether there would be any change in the grain structure of the substrate as a result of the zone heating. The following experiment investigated the solid state recrystallization of a zone heated film sputtered directly onto the substrate. The final experiment examined the recrystallization of a sputtered CdTe film which was isolated from the substrate.

For these experiments the CdTe samples were coated in three different ways as shown in Figure 4. Figure 4a shows how the samples were coated for the first two experiments; the polycrystalline CdTe samples were coated with 1 μm of

a)



b)



c)

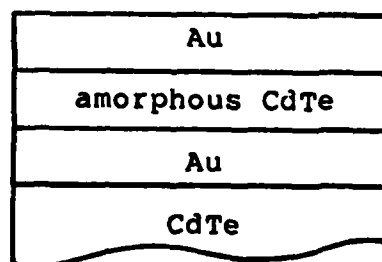


Figure 4. Test Samples

gold. In the following experiment a $1\text{ }\mu\text{m}$ layer of amorphous CdTe was sputtered onto the substrate and then capped with a $1\text{ }\mu\text{m}$ layer of gold (Figure 4b). In the final experiment a $1\text{ }\mu\text{m}$ layer of gold was first sputtered on the top of the sample (Figure 4c). Next, a $1\text{ }\mu\text{m}$ layer of amorphous CdTe was added and then the sandwich was capped with $1\text{ }\mu\text{m}$ of gold.

After the sample was coated it was zone heated in the following manner:

- 1) The sample was placed in the center of the Mo sheet next to the TC.

- 2) The lower and upper heater frames were positioned so that the tungsten ribbon was directly over the TC.

- 3) The bell jar was placed in position and evacuated.

- 4) The bell jar was then backfilled with argon and evacuated to purge residual gasses.

- 5) Step 4 was repeated.

- 6) At this point the lower heater was turned on and the temperature allowed to stabilize at 800°C (on the TC display at the edge of the Mo sheet; the temperature in the center of the Mo sheet was 850°C).

- 7) The upper heater was turned on to the high setting and then reduced to the desired temperature (to remove any sag in the ribbon).

- 8) The drive motor was turned on.

9) After the upper heater had passed over the sample, the heaters and motor were turned off.

10) When the temperature dropped to 200°C the bell jar was backfilled with argon and the bell jar removed.

11) After the system was cool the sample was removed and analyzed as described in the first section.

VI. Results and Discussion

This chapter describes the results of the experiments. The experimental parameters, expected and actual results, and any observations noted during the investigation are discussed. The static heating experiments are described first followed by the experiments on capping materials and then the zone heating experiments.

Static Heating

Three samples were investigated at different pressures and temperatures. The initial pressure (obtained by back-filling with nitrogen), oven temperature, and final pressure (pressure in tube at the oven temperature) for each sample are presented below:

Sample #	Initial Pressure (Torr)	Temperature (°C)	Final Pressure (atm)
1	180	1000	1
2	365	900	2
3	500	800	2.5

The CdTe sample #1 totally sublimed and condensed at both ends of the tube forming two small, polycrystalline buttons. A small, thin section of the sample #2 remained but the majority of the material had sublimed and condensed in the ends of the tube as in sample #1. Any changes in the grain structure of the remaining piece could not be measured due to the small size of the sample.

Sample #3 remained whole and only a thin, semi-transparent film of CdTe coated the inside of the tube. After removing the sample no changes in the size or grain structure were detected. This showed that a pressure of 2.5 atmospheres will keep CdTe from subliming significantly over an extended period of time. Therefore, it is possible to reduce sublimation for short periods of time by capping the sample and performing the experiment at a pressure less than 2.5 atmospheres. Capping the sample would then make zone heating at reduced pressure feasible.

Capping Evaluation

These evaluations compared the compatibility of CdTe and Si_3N_4 (silicon nitride), Mo, tantalum, and gold. These materials were selected because of their high melting point (greater than that of CdTe, 1041°C), high strength, and availability. Si_3N_4 layers were applied by chemical vapor deposition while the metals were sputtered.

Of the materials tested only the sputtered layer of gold remained intact. The Si_3N_4 layer was deposited on a heated CdTe sample and would pop off if the temperature changed by only a few degrees. As the CdTe samples coated with Mo and tantalum were heated in the quartz tube oven the film peeled off in very small flakes resembling a powder.

As the sample coated with gold was heated no changes in the film were noticed. Under close examination after the sample had cooled the gold film looked unchanged except

for a small area which had several wrinkles. The reason for the success of the gold film may be due to a closely matched thermal expansion or to the high ductility of the gold film at elevated temperatures. Although gold is an excellent conductor (and an insulating cap is more desirable) gold was used as the capping material in the zone heating tests. Gold is also naturally found in a compound with tellurium, gold ditelluride (AuTe_2), and may combine with the tellurium in the sample.

Zone Heating

The following four zone heating experiments were performed on samples of CdTe prepared as shown in Figure 4. This section first described the experimental parameters for the tests and then a separate discussion of each test is presented.

Experimental Parameters. The first two samples were prepared as in Figure 4a. The third and fourth samples were prepared as illustrated in Figure 4b and Figure 4c, respectively.

The first three experiments were conducted in a vacuum while the fourth experiment was run in argon at atmospheric pressure to further reduce sublimation.

The upper heater was passed over the sample twice in the first experiment. Both passes were run at 1.3 mm/sec with the ribbon temperature at 1305°C for the first pass and at 1375°C during the return run. The remaining three

experiments were zone heated at 0.75 mm/sec with the upper heater set at 1375°C.

In no case were any changes in the grains observed.

Experiment #1. During the first zone heating pass of this sample a tungsten support wire for the upper heater pushed the sample onto the TC. The action of the moving wire put a crease and bend in the sample. The return pass of the wire moved the sample to the opposite side of the moly sheet.

Further examination of the cooled sample showed that the gold film was intact except along the crease in the sample where the moving wire had rubbed it off. The existence of the bend and the crease in the sample indicate that the CdTe was in a plastic region where solid state recrystallization could take place. The tungsten support wires were removed after this experiment.

Experiment #2. In this experiment it was observed that as the sample was being heated by the lower heater, the gold film became thinner in the middle. This phenomena was also observed in the following experiments. When the upper heater scanned the sample the ceramic rod lightly brushed the sample removing small amounts of the gold film. When the remaining gold film was removed it was noted that a small amount of AuTe_2 , formed during zone heating, remained on the crystal surface.

Experiment #3. Examination of the sample after zone heating revealed that small amounts of the gold film had

again been rubbed off. A steel shim was placed under each end of the ceramic rod for additional clearance. Removal of the gold film revealed a small amount of AuTe_2 and the very rough surface texture of the CdTe substrate. Under magnification, it appeared that the sputtered layer of amorphous CdTe had epitaxially grown on some orientations and not on others. This indicates that thin amorphous films can epitaxially grow during zone heating.

Experiment #4. This experiment was performed at atmospheric pressure to reduce sublimation in an effort to preserve the $1\text{ }\mu\text{m}$ layer of amorphous CdTe sandwiched between the gold films. However, while the lower heater was heating the sample white vapors were observed coming from the edges of the sample and later from the middle. The vapors seemed to come up through the gold film, leaving the gold film intact.

The gold film on the surface of the sample (after cooling) had a dark spot in the center surrounded by a lighter colored ring. The rest of the gold film retained its metallic gold color. Etching revealed a thin ring of AuTe_2 which marked the outer limit of the light colored ring. No trace of the sputtered CdTe film was found.

VII. Conclusions and Recommendations

Although none of the CdTe samples were recrystallized by the LESS method in these experiments the results do not indicate that LESS recrystallization of CdTe is unfeasible. To achieve this goal several changes need to be made concerning the application of the LESS method to CdTe. These modifications need to be made in the pressure at which the sample is zone heated, the material used as a cap or sealing layer, and in the material used as a substrate. These areas are discussed below in addition to a few general comments.

Pressure

These tests were performed in a vacuum or at atmospheric pressure. These pressures are too low to keep the CdTe from subliming even when using a cap. Future experiments will need to be performed in a pressure vessel where elevated pressures of argon or any other non-reactive gas can be maintained.

Capping Material

Gold proved to be unsuitable as a capping material. A capping material must be found which incorporates the following properties:

- 1) compatible with CdTe
- 2) does not react with Cd or Te
- 3) have a high melting point
- 4) have good strength properties

Any material which meets these qualities should provide a tight cap in future tests.

Substrate

LESS recrystallization of Si used large, single crystal wafers of Si as a substrate.

While using polycrystalline wafers of CdTe in these tests caused no problems, future attempts at recrystallizing films may be affected. The results of experiment #3 indicated that seeding of the sputtered film was dependent upon the orientation of the substrate. While CdTe is isotropic in many of its properties, it may not be in others, such as its thermal expansion. For these reasons future substrates should be single crystal wafers of materials compatible with CdTe. CdTe has already been grown on substrates of Al_2O_3 , BeO_2 , and MgAl_2O_4 (Manasevit, 1972: 312) and should be tried in future LESS experiments.

General Comments

While the previous three sections outlined the major areas of improvement for future tests, there are several other areas which need refining.

First, the lower heater should be redesigned to provide a more uniform temperature profile, allow faster heating of the sample, and simplify the construction of the heater.

Since it is recommended that future tests be run at high pressure, heating of the system components will be a greater problem. All components made from low melting

point materials (aluminum, copper, etc.) should be replaced by steel or other high melting point materials. This will reduce the possibility of mechanical failure from the heat or contamination of the sample. Also, the drive motor should be mounted outside the pressure vessel using a sealed feed through to transfer the motion to the drive screw. This will protect the motor from heat damage and will maintain accurate speed control.

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(block 20 continued)

Extended, high temperature annealing of CdTe samples at 800° C and 2.5 atmospheres of nitrogen revealed no changes in the grain structure.

Zone heating experiments were performed on CdTe wafers and films at 850° C. Sputtered gold films were used as encapsulating layers. The samples were heated in a vacuum or in argon at atmospheric pressure with zone rates of 1.3 and 0.75 mm/sec. No recrystallization was observed but preferential epitaxy of amorphous CdTe films onto the polycrystalline substrate was noted.

Further investigation should be conducted at elevated pressure, use a more compatible encapsulant, and possibly use Al_2O_3 , MgAl_2O_4 , or BeO single crystal substrates.

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