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HgCdTe FABRICATION USING DIRECTED ENERGY TECHNIQUES

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The goal of this research is to produce large-area, thin-film, single crystal HgCdTe material for infrared detectors. This report describes initial results for the evaporation of CdTe onto insulating crystalline substrates (hot wall epitaxy), improvement of the surface morphology by pulsed electron-beam processing, and conversion to HgCdTe by evaporation and diffusion at constant temperature. Improvement in quality over past results and an increase in sample size to 2-inch diameter is expected with upgraded equipment described herein.		

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FOREWORD

The work reported in this document was performed in part at Spire Corporation, Bedford, Massachusetts, and in part at New England Research Center, Inc., Sudbury, Massachusetts, under contract MDA 903-81-C-0410, DARPA Order Number 3800. The contract monitor is Mr. Sven Roosild.

The program manager at Spire is Dr. Robert Wolfson. The principal investigator at Spire is Dr. Anton Greenwald, who is in charge of pulsed electron beam processing. The program manager at NERC is Dr. Theodore Wong. The project engineer at NERC is Dr. Robert Martineau, and the task engineer is Mr. Chris Devaney, who is in charge of the epitaxial deposition and vapor exchange processes.

The report of the main subcontractor, NERC, is included in Section 2. Work performed at Spire Corporation is described in Section 3.

SUMMARY

The goal of this work is to produce thin single-crystal films of HgCdTe at least 2 inches in diameter for use in infrared detectors.

Single crystal films of CdTe have been deposited on 1-inch diameter mica substrates by the hot wall epitaxy (HWE) method. A new furnace was constructed to handle larger samples with improved temperature control. Existing CdTe films show extensive twinning and poor surface morphology. Improvements are expected with a shift to sapphire substrates and the new furnace.

The existing films of CdTe were converted to single crystal $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ by evaporation and diffusion at constant temperature (EDICT). Sample size is currently 0.5 inch square. These films were not twinned and had better surface morphology than the original CdTe substrates. Good control of thickness and composition was shown, with the variation in the value of x less than ± 0.0006 for $x = 0.2$ throughout the entire film.

The surface morphology of these CdTe and HgCdTe films was improved by pulsed electron beam polishing (Appendix A). Apparatus for fabricating HgCdTe films by evaporation and pulse electron-beam diffusion and heteroepitaxy is being set-up.

The electron mobility of HgCdTe films produced by HWE/EDICT process was $1.5 \times 10^5 \text{ cm}^2/\text{V-s}$ at 77°K . Electro-optical devices will be fabricated in the next half-year period.

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SECTION I INTRODUCTION

1.1 PURPOSE - LONG TERM OBJECTIVE

The overall purpose of this program is to grow large, single crystal HgCdTe suitable for use in large scale detector arrays. The following material properties are design goals for this program:

- Compositional uniformity $x < 0.0006$
- Two-inch diameter, heteroepitaxial single crystal films
- Net foreign impurity concentration $< 5 \times 10^{14}$ atoms/cm³

The program objective also includes the demonstration that the process developed is capable of producing crystals with the aforementioned properties in sufficient quantities to be able to meet the future needs of DOD through the 1980's.

1.2 TECHNICAL CONSIDERATIONS

Existing melt growth methods of fabricating HgCdTe crystals are unsatisfactory for two reasons. First, the high vapor pressure of Hg at the melt temperature of HgCdTe of the desired composition limits the size of the ampoule in which the material may be grown. Second, the wide separation of the liquidus and solidus in the pseudobinary phase diagram makes it very difficult to achieve uniform composition across large specimens.

The present phase of this program is a continuation of research begun under contract number MDA903-79-C-0434 (DARPA Order Number 3800) which sought a thin-film solution to the problems discussed above. Results of the first phase of this program are summarized below:

- Heteroepitaxial single crystal films of CdTe one inch in diameter were grown using a Hot Wall Epitaxy (HWE) technique on cleaned mica substrates.
- Single crystal HgCdTe films over 1 cm² were produced by a subsequent EDICT (Evaporation and Diffusion at Constant Temperature) treatment of these CdTe films.

- The variation in compositional uniformity over 1 cm^2 was less than ± 0.0007 in the value of x for $\text{Hg}_{(1-x)}\text{Cd}_x\text{Te}$.
- High electron mobility ($1.5 \times 10^5 \text{ cm}^2/\text{volt sec}$) at 77°K in this material indicated epitaxial film quality comparable to that in bulk material.
- Good reproducibility was demonstrated for both thickness and composition.
- Pulsed electron beam polishing of the surface of CdTe was demonstrated. The feasibility of directed energy processing of HgCdTe was demonstrated.
- The feasibility of pulsed diffusion of Hg films on CdTe substrates, initially at 77°K , was demonstrated. In the current phase of this program, the size of the sample films will be increased while maintaining the uniformity achieved and reducing the contamination of the material. An improvement of the final surface finish of the HgCdTe film through pulsed processing is also sought.

1.3 GENERAL METHOD

The method used in this program attains the desired end of large area, uniform single-crystal HgCdTe films in two steps. The first step is to grow heteroepitaxially large single-crystal films of CdTe on foreign substrates by the Hot Wall Epitaxy (HWE) technique. The second step is transformation from single-crystal CdTe film to single-crystal HgCdTe film by a process of vapor growth and solid state diffusion known as EDICT (Evaporation and Diffusion at Constant Temperature).

This two step method has a number of advantages over other methods of growing large area HgCdTe single-crystal specimens. First, the film thickness is determined by the deposition of the CdTe in the initial step, whereas the critical Hg-Cd ratio is determined by the second step. This process allows critical parameters to be separately optimized. Second, since all processes take place at relatively low temperatures, the excessive mercury pressure that plagues most high-temperature melt-growth processes is not a problem. In fact, this method takes advantage of the volatility of components and grows from the vapor phase. Scaling up of the specimen dimensions is rather

straightforward relative to melt-growth methods, which are all limited by the 1/2 inch ampoule dimension as a result of high mercury pressures. Third, segregation problems which limit the uniformity of composition in melt-grown HgCdTe do not exist in this method, because melting is not required here. Furthermore, since HgCdTe is grown directly in a thin CdTe film, no compositional gradient occurs. Thus, exceptionally uniform composition should result both across and normal to the film surface. Finally, both the HWE and the EDICT processes are vapor-growth methods where the emphasis is placed on the growth of epitaxial layers under conditions as near as possible to thermodynamic equilibrium, resulting in thin films of bulk quality and crystalline perfection.

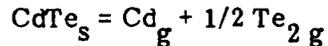
An additional processing step is necessary to produce a smooth surface. The growth morphology of the as-deposited CdTe film after HWE is faceted, with surface relief greater than one micron. The surface features after EDICT conversion to HgCdTe show many spiral growth terraces. How the surface morphology of the HgCdTe film relates to that of the original CdTe sample is not yet known. Polishing a thin film is difficult and costly. However, rapid melt and quenching by irradiation with a pulsed electron beam produces a superior surface finish. As the surface cools after melt, epitaxial crystal growth prevents degradation of structure. The short time at high temperature, less than one microsecond, minimizes outdiffusion of the volatile components. This process can be used either before or after EDICT. The process is fast, noncontaminating, inexpensive, and amenable to large-scale manufacture.

SECTION 2
REPORT OF SUBCONTRACTOR, NERC

2.1 HOT WALL EPITAXY (HWE)

2.1.1 Process Description

The HWE process consists of evaporating Cd and Te vapor from a CdTe source at a temperature T_H onto a suitable substrate held at a temperature T_L where T_H is greater than T_L . CdTe vaporizes incongruently according to the reaction:



The partial pressures of Cd and Te_2 in the gas are low but differ by an order of magnitude. (Typical pressure of Cd vapor, which is higher at the appropriate temperatures, is 10^{-2} atmospheres.) By constructing a deposition chamber which approximates a gas tight enclosure, the stoichiometry of the deposited film can be preserved.

The major parameters controlling the CdTe deposition rate are the source-to-substrate temperature differential (ΔT) and the absolute magnitude of the substrate temperature. Other factors such as the degree to which the system approximates a gas tight enclosure, the absolute magnitude of T_H , and the substrate itself exert a lesser influence upon the deposition rate. The flux of atoms arriving at the substrate surface is different for Cd and Te_2 because the component partial pressures differ. By maintaining the substrate temperature high enough, sufficient surface diffusion exists to permit the growth of stoichiometric CdTe crystals provided that the deposition rate is appropriate.

2.1.2 Apparatus

The first month and a half of this phase of the program were spent in recalibrating the existing HWE apparatus. The vacuum system for this apparatus consists of a 400 l/s turbomolecular pump backed by a mechanical fore pump. Through overnight pumping, pressures in the 10^{-8} torr range are routinely achieved in the process chamber. The vacuum vessel attached to the pump without a gate valve is a 10-inch diameter

pyrex belljar incorporating a liquid nitrogen trap. The support for the belljar contains eight high-vacuum feedthroughs for power, sensors, and a mechanical shutter to operate the furnace.

The existing two zone HWE quartz furnace, seen inside the belljar in Figure 2-1 with heat shields in place, is shown schematically in Figure 2-2. Modifications made to this furnace from the phase one design were to more closely approximate a gas tight enclosure. These modifications involved changes in the thermocouple location and attachment techniques, substrate holder and supporting envelope design. Sixteen CdTe films were grown on cleaved mica substrates in calibrating this HWE system.

2.1.3 Film Deposition

The next 2 1/2 months in this phase of the program were spent in determining the optimum parameters for reproducible deposition of single crystal CdTe films on mica substrates. Thirty-seven films were grown. Optimized values of source temperature, substrate temperature, and deposition time were determined which yield high quality CdTe films with controlled thickness.

The remaining time in the first half-year of the current program was spent in producing CdTe films on mica using these optimized parameters. Thirteen films were grown to show the reproducibility of the HWE process. These identical samples were used to study the EDICT process. Figure 2-3 shows a typical thermal cycle used in fabricating the CdTe films. Table 2-1 shows how the film thickness varies under different growth conditions.

2.1.4 Characterization

Back reflection Laue x-ray patterns were used to analyze CdTe films on mica. The results were similar to those obtained in the first phase of this program. This work was performed using Cu x-rays from a 20 keV, 2 mA electron beam source with a 2 hour exposure. An example of a pattern is shown in Figure 2-4. Comparison of similar patterns with CdTe films to patterns from mica alone show additional x-ray spots presumably due to the CdTe. The pattern from CdTe films on mica showed six-fold symmetry with clear spots, indicating epitaxial growth of a single crystal film. The orientation of the film is (111), which corresponds to the basal plane (c axis) of the mica substrate.

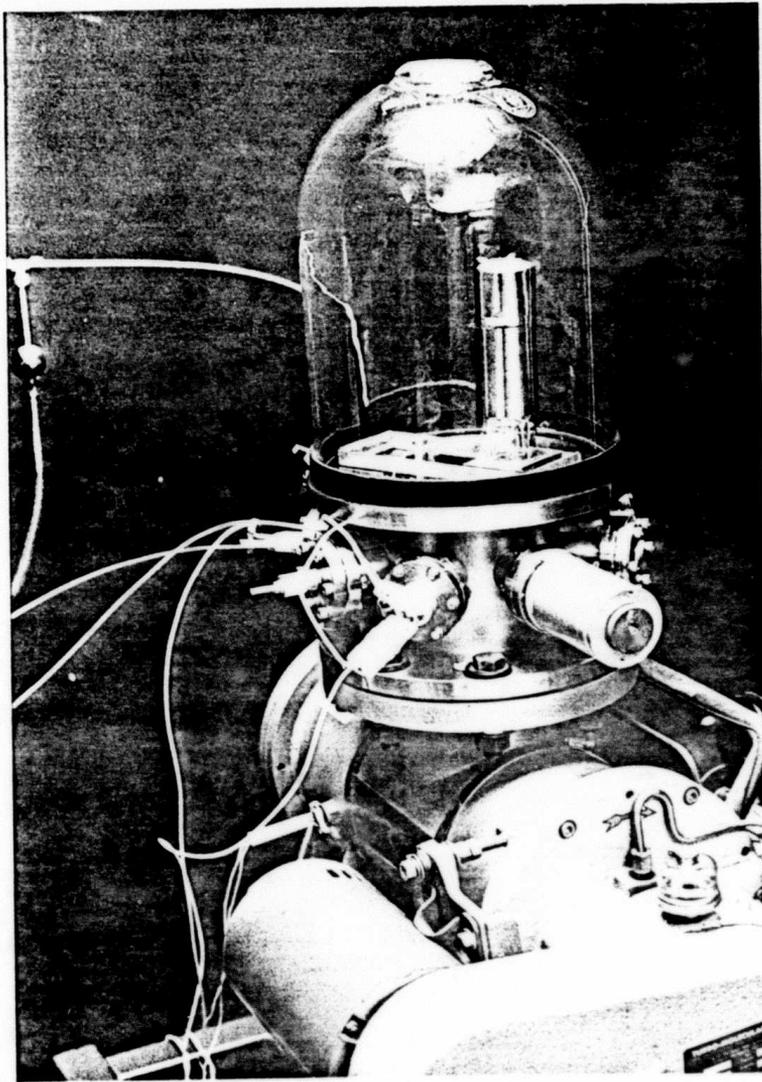


FIGURE 2-1. VACUUM SYSTEM FOR HOT WALL EPITAXY DEPOSITION OF CdTe FILMS

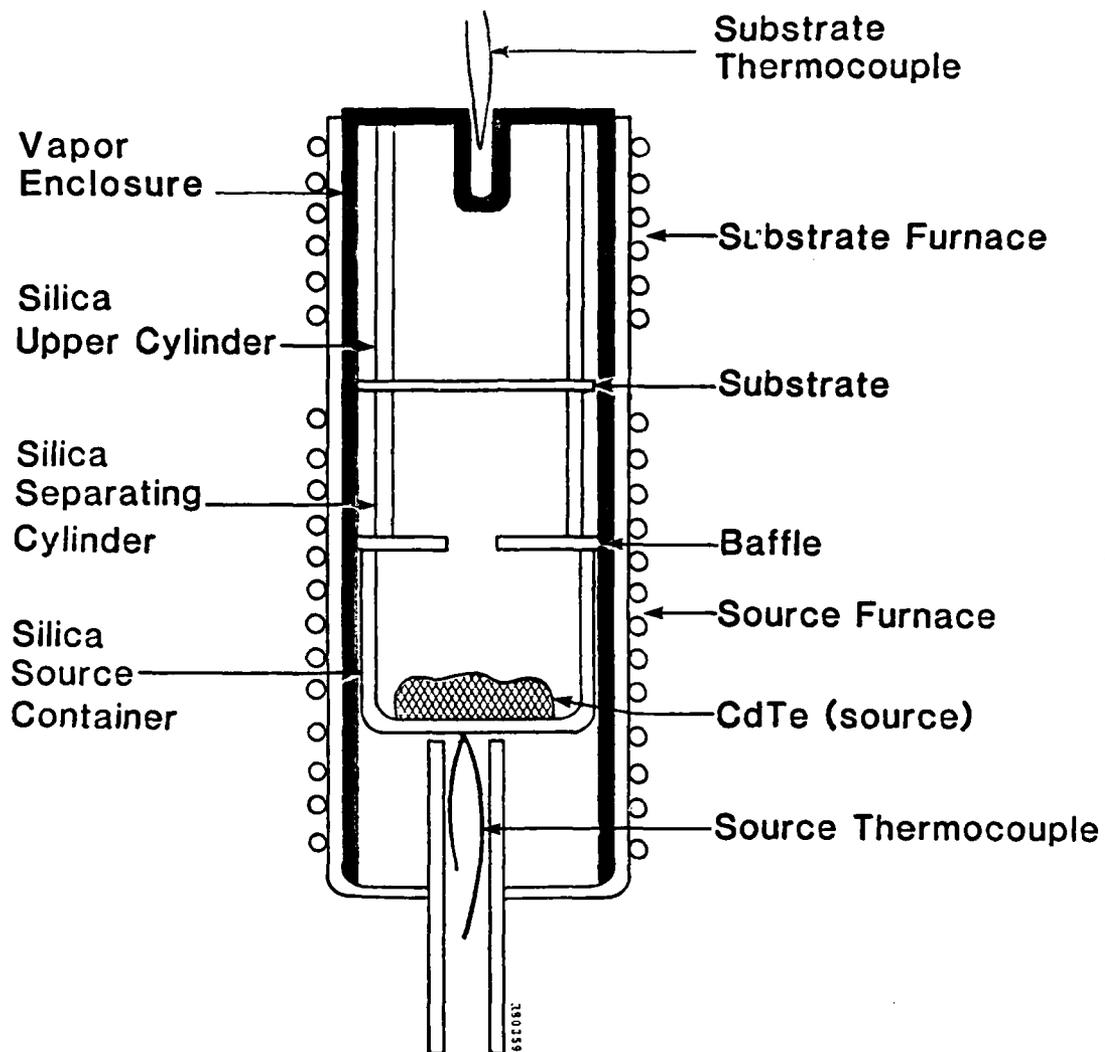


FIGURE 2-2. HOT WALL FURNACE WITH ENCLOSED SOURCE FOR EVAPORATION OF CdTe

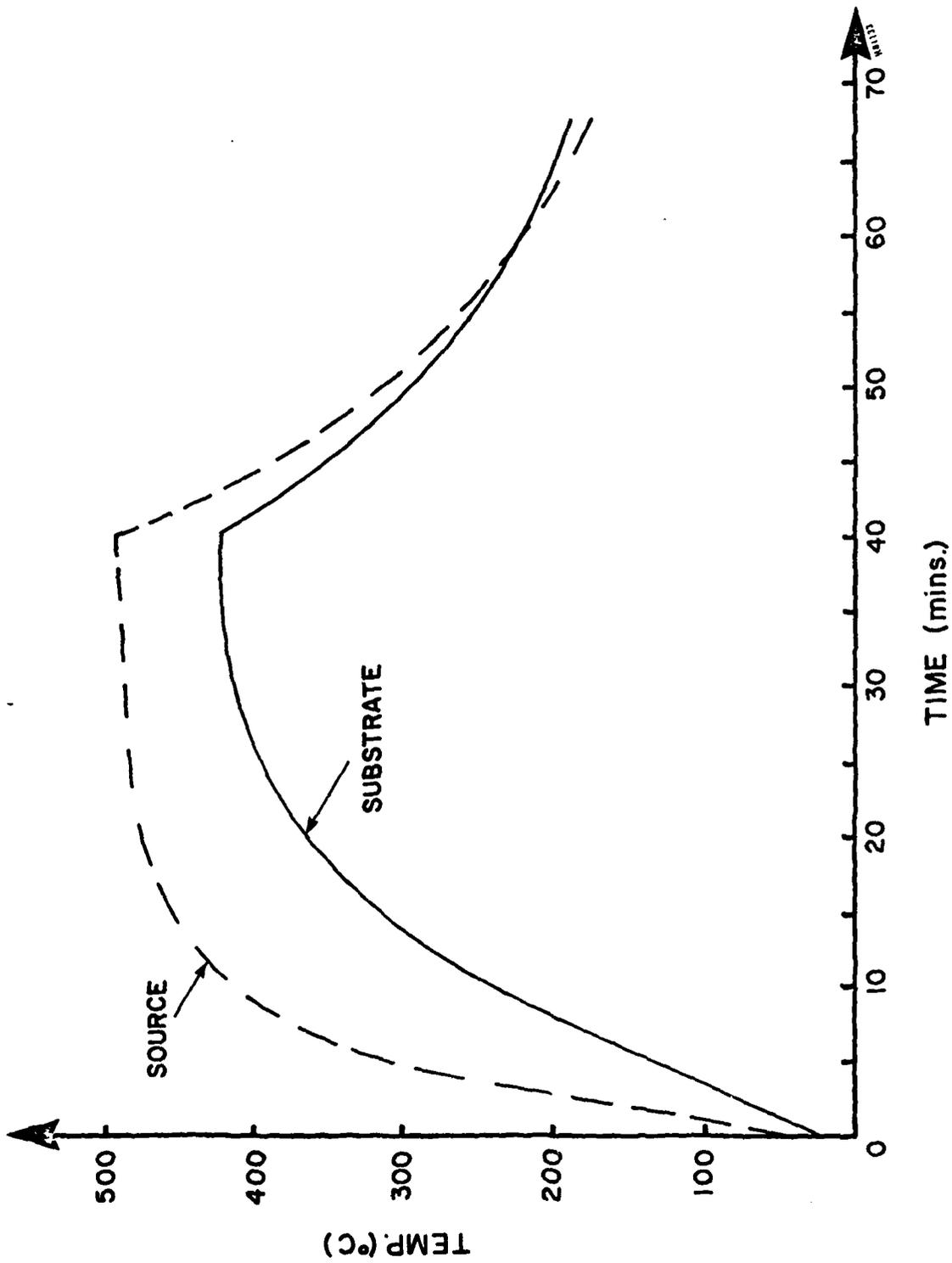
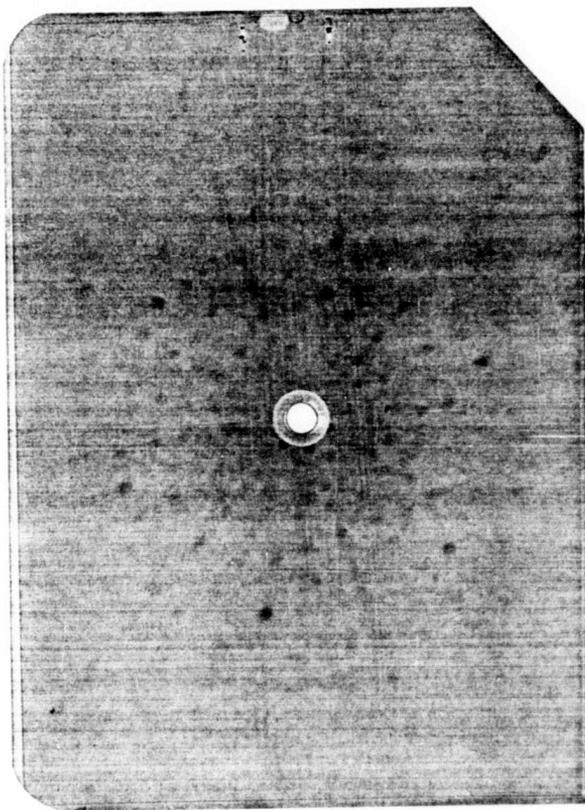


FIGURE 2-3. TIME-TEMPERATURE CYCLES OF THE SOURCE AND SUBSTRATE



(a)

FIGURE 2-4. BACK-REFLECTION LAUE PATTERN FROM CdTe FILM ON MUSCOVITE MICA (SPECIMEN M81). Pattern as recorded, negative image; molybdenum radiation, 20 kV/20 mA, 5 h exposure.

TABLE 2-1.
FILM THICKNESS vs. GROWTH PARAMETERS

Run	ΔT	t (sec)	T _{source} (°C)	T _{subst.} (°C)	d (μm)
58	19	65	493	474	13.3
59	24	70	494	470	12.7
60	48	70	493	445	11.2
63	39	85	490	451	14.7
64	45	82	488	439	10.2
65	118	70	490	388	9.0
66	92	60	487	395	8.3
67	67	90	484	417	12.2
68	64	70	486	422	10.6
69	13	60	449	436	8.4

Photographs of two CdTe films deposited on mica substrates under optimized growth conditions are shown in Figure 2-5. The scale is in inches, showing the present size of CdTe crystals routinely grown by the HWE process. The surfaces of these films are dull, with a rough texture seen in the microphotograph of Figure 2-6. This surface morphology is related to the crystal structure and might be improved with a change in substrate.

2.1.5 Substrate Preparation

For the next six months, emphasis will be placed on the use of sapphire substrates for CdTe HWE deposition and subsequent processing. As discussed in the next section (2.2), mica was less than ideal for a substrate in the EDICT process. Mica had a low decomposition temperature and poor film/substrate adhesion characteristics. Adhesion of films should improve on sapphire substrates with a thermal expansion coefficient

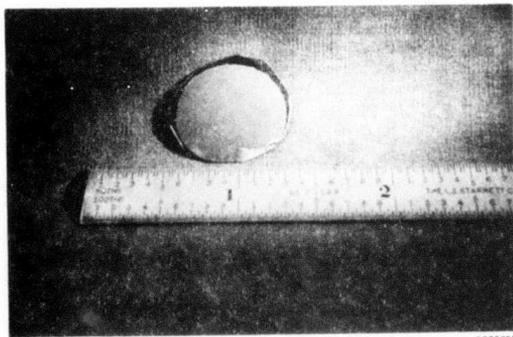
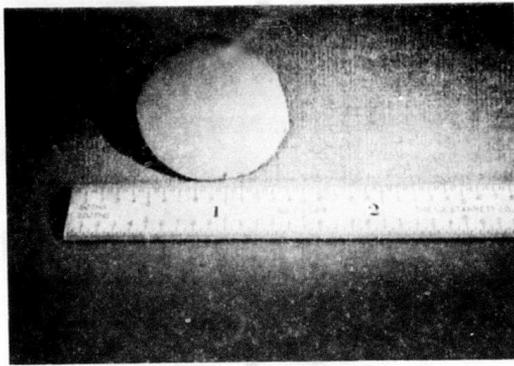
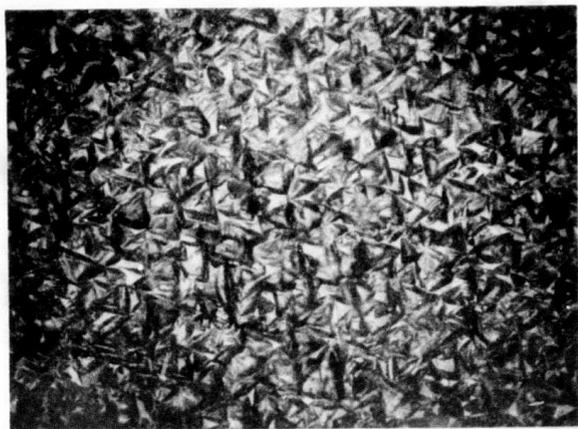
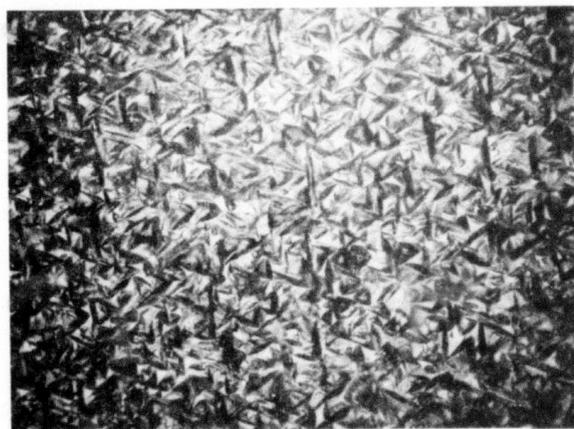


FIGURE 2-5. HWE GROWN CdTe on MICA



20 μm



LS2000 P

FIGURE 2-6. MICROPHOTOGRAPHS OF HWE GROWN CdTe/MICA SHOWING SURFACE STRUCTURE

more closely matched to that of HgCdTe than mica. Since very high purity sapphire will be used, contamination levels in the film should be reduced. Use of sapphire will facilitate characterization of the grown films, since this material is transparent in the $5\ \mu\text{m}$ spectral region. Also, it is expected that the crystal quality of the grown films will be improved due to a reduction in microtwinning defects.

Some preliminary work has been done to calibrate the new furnace. In the previous phase of this program, disappointing results for CdTe HWE on sapphire substrates were attributable to improper cleaning procedures, which have now been corrected.

Cut and polished sapphire wafers (1" o.d.) are now available for tests. In addition, a single crystal sapphire boule 1" o.d. by 3" long was purchased. This boule is presently being oriented, cut, and polished along different crystallographic planes to be used in growth comparisons.

Experiments are planned to determine the effect of sapphire substrate orientation upon the parameters of the CdTe films. No mention of a preferred orientation was mentioned in the literature for previous work on HgCdTe heteroepitaxy using sapphire substrates.⁽¹⁾ Three crystal planes will be used in the initial experiments here; the (0001) c-plane; the a-face which is 90 degrees off the c-axis; and what is conventionally known in the SOS (silicon-on-sapphire) industry as the "R" plane.

CdTe has been known to form twins (polytypes) along the (111) plane stemming from the small free energy difference between the Wurtzite (hexagonal) and Sphalerite (cubic) crystal structures. Several classes of polytypes have been identified in the literature.⁽²⁾ For growth occurring at low temperature the tendency to deposit in both structures is appreciable, whereas the equilibrium form existing in melt-grown CdTe favors the Sphalerite structure. CdTe films deposited by HWE on mica in the (111) orientation contain triangular growth pyramids perpendicular to the film surface (Figure 2-6). The triangular pyramids are actually the corners of cubes growing normal to the film. The structural variation shows up under high magnification as pyramids angularly misoriented 60 degrees from each other. Figure 2-7 is a schematic drawing showing the (100) normals for a typical twin. The stacking sequence variations (polytypes) are quite common in II-VI compounds and have been frequently reported in the literature.⁽²⁻⁵⁾

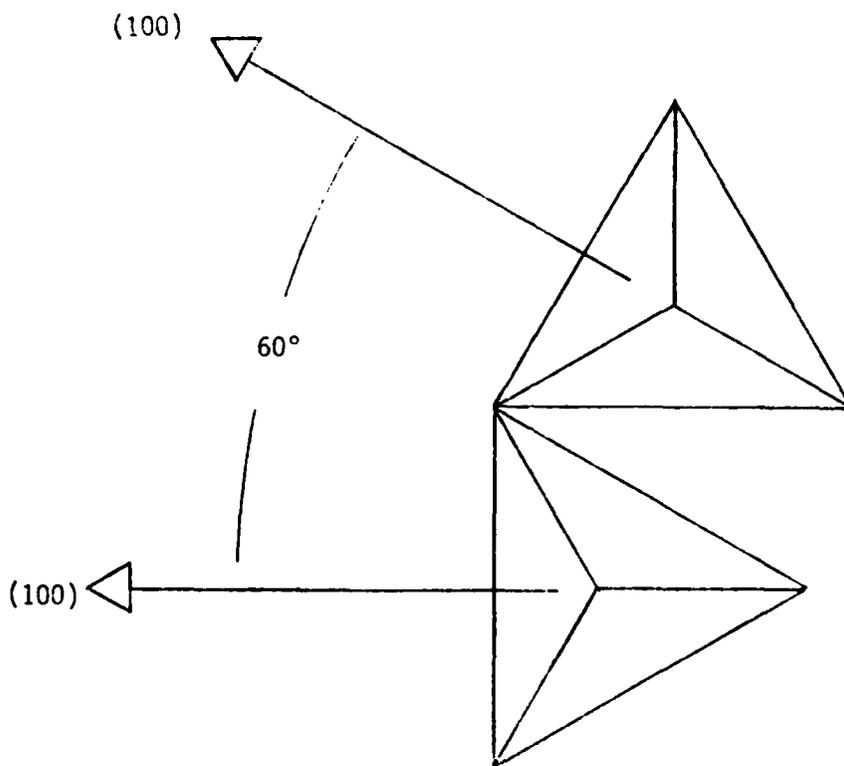


FIGURE 2-7. SCHEMATIC ROTATIONAL TWINNING ON (111)
PLANE PERPENDICULAR TO PAGE

Faceted growth results in poor surface morphology as shown in Figure 2-6. Polytype formation prevents the pyramids from coalescing and even forming a smooth growth surface. The existing stepped morphology has large variations in surface height, which led to the work on pulsed electron beam polishing of these films. An alternative approach to obtaining a mirror surface finish is to change growth orientation of the film and/or reduce twin formation. The possibility of obtaining a crystallographic orientation having more cubic symmetry was one reason for choosing sapphire substrates with the "R" or 90 degrees off C-axis planes. This choice should lead to enhanced morphologies free from microtwinning.

2.1.6 Other Substrate Materials

Besides mica and sapphire, other substrate materials were considered for HWE deposition of CdTe films. Two deposition runs were performed on each of the following materials: barium fluoride (BaF_2), stabilized cubic zirconia (ZrO_2), and fused quartz (SiO_2). Barium fluoride was tested because it has a cleavage plane which allows easy preparation of clean surfaces; however, only polycrystalline films of CdTe were deposited on BaF_2 . Structural and chemical compatibility were reasons for testing zirconia, but CdTe films deposited on these substrates were also polycrystalline. Films deposited on fused quartz had large grain structure and were of poor quality compared to films deposited on mica.

2.2 EDICT CONVERSION OF CdTe FILMS TO HgCdTe FILMS

2.2.1 Process Description

The conversion of a CdTe film into single crystal $Hg_{1-x}Cd_xTe$ of controlled x value is performed using the EDICT process (Evaporation and Diffusion at Constant Temperature). This process involves the vapor transport of a precise quantity of HgTe onto the CdTe film and the homogenization of the film by isothermal diffusion.

The EDICT process requires a substrate, a source, and a control medium to be enclosed together in an evacuated ampoule. In the case that concerns us the substrate is a CdTe film supported on an inert base of mica or sapphire. The source which will be transported and which will diffuse into the substrate is HgTe. The control medium is excess mercury. The method by which the source and substrate interact, and how the control medium affects that interaction is examined next.

The substrate is a CdTe film epitaxially deposited on a foreign substrate and very carefully weighed. The source is an amount of purified HgTe calculated to be just sufficient to change the CdTe film into $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ for a given x (for this example $x = .416$). The weight of the control medium, a small drop of mercury, is calculated using an ideal gas approximation to be that which will give the required overpressure of mercury at the isothermal reaction temperature used. (The internal volume of the ampoule must be known in advance.)

The reaction mechanism is driven by the equilibrium pressure of the three elements (Hg, Cd, and Te) in the ampoule. This does not imply that equilibrium exists in the ampoule. Equilibrium does not exist until the reaction is complete, but the equilibrium vapor pressures indicate the way in which the reaction will proceed. In this example the process temperature is assumed to be 830°K . The vapor pressure of mercury, cadmium, and tellurium in equilibrium with the components of the ampoule at 830°K is given in Table 2-2.

TABLE 2-2.
ELEMENTAL EQUILIBRIUM VAPOR PRESSURES
AT 830°K (atmospheres)

	<u>Hg</u>	<u>Cd</u>	<u>Te</u>
Hg Liquid	15.1	0	0
HgTe Solid	4.9	0	8×10^{-3}
$\text{Hg}_{.584}\text{Cd}_{.416}\text{Te}$	1.28	1.1×10^{-7}	2.3×10^{-4}

Now consider what occurs as the temperature of the ampoule is raised from 298°K (room temperature) to 830°K . If the amount of mercury added in liquid form to the ampoule is sufficient to give an excess pressure of 0.5 atmospheres at 830°K , then all of the excess mercury will have vaporized before this temperature is reached. By the time the substrate is at the process temperature of 830°K , the CdTe surface will be

bombarded by mercury atoms at a pressure of between 0.5 and 4.9 atmospheres. The former pressure is that calculated due to the excess added mercury, and the latter figure is the vapor pressure of Hg over HgTe at 830°K. Because the quantity of HgTe in the ampoule is quite small (on the order of milligrams), even if it were completely evaporated it would not raise the mercury pressure to 4.9 atmospheres. The overpressure of mercury on the CdTe film will therefore be near 0.5 atmospheres. A small amount of mercury will initially be evaporated from the HgTe leaving a surface of excess Te, so that the vapor pressure of Hg over the HgTe source will also fall toward 0.5 atmospheres.

The surface of the CdTe, being bombarded by Hg, will be covered with a mobile layer of adsorbed mercury which cannot react for reasons of stoichiometry. The HgTe will be covered by a partial layer of excess Te, which will reduce the equilibrium mercury pressure over the HgTe to a value close to that determined by the excess mercury added (0.5 atmospheres in this example). The situation is a quasi-equilibrium one, and no growth occurs if the other atomic species are ignored.

Now consider the motion of Te in the EDICT process. The vapor pressure of Te over the HgTe source will be between that of HgTe at 830°K (2×10^{-3} atm) and that of the excess Te on the surface of HgTe (8×10^{-3} atm) which results from the evaporation of mercury. The vapor pressure of Te over $\text{Hg}_{.584}\text{Cd}_{.416}$ at 830°K is 2.3×10^{-4} atm.⁽⁶⁾ Therefore, even after completion of the reaction, there is a chemical driving force for transfer of Te through sublimation from the HgTe source to the HgCdTe substrate due to the difference of equilibrium Te vapor pressure. Molecules of Te_2 proceed by gaseous diffusion from the source to the substrate, where they can be adsorbed on the surface and react with the excess mercury. The tellurium chemically bonds the mercury to the substrate, resulting in physical growth of the film epitaxially. Bonded mercury atoms diffuse into the substrate under the Cd-Hg concentration gradient. Capture of tellurium molecules on the surface continues until all of the HgTe source has been transferred to the substrate. Inter-diffusion of Hg and Cd continues until a uniform depth distribution for x has been achieved. Since the substrate is a thin film, inter-diffusion will be completed in a reasonably short time at the typical process temperature (830°K). The defined end point is a variation in x less than ± 0.0007 .

Gaseous diffusion of Cd from the substrate to the HgTe source can be neglected because the equilibrium partial pressure of Cd (Table 2-2) over $\text{Hg}_{.584}\text{Cd}_{.416}\text{Te}$ is very small compared to the pressure of tellurium or mercury. Because the molecular concentrations in the gas in the ampoule at any given temperature are proportional to the partial pressure of that component, the amount of Cd in the vapor phase is less than 10^{-6} that of Hg.

The reaction rate, or the rate of vapor growth of the HgCdTe film, is controlled by the difference in the partial pressure of tellurium over the source (HgTe) compared to the pressure over the HgCdTe substrate. The pressure of Te_2 in equilibrium with the source is affected by the excess mercury pressure. If the pressure of Hg exceeds the equilibrium vapor pressure of mercury over HgTe, then evaporation of mercury from the surface of the source will cease. In this case the vapor pressure of Te will drop because the surface of the source is no longer enriched with Te. With sufficient mercury pressure, the pressure of Te will fall to the equilibrium value over the substrate, and the reaction will stop without the driving force.

Previously published data on the isothermal growth of HgCdTe have come from experiments on bulk samples. Parameters are quite different for thin film specimens in EDICT. As previously mentioned, the limited weight of the HgTe source in EDICT limits the Hg pressure to a value close to that due to the excess liquid mercury initially admitted to the ampoule. In the bulk case, a considerable build-up of mercury pressure occurs from the available bulk of HgTe, and tellurium saturation does not occur in the gas phase. Hence, the reaction parameters of mercury pressure, reaction temperature, etc., will have to be determined again under the new boundary conditions of a finite HgTe source.

2.2.2 Apparatus/Results

The EDICT apparatus has not yet been modified from that described in the final report of the previous phase.⁽⁷⁾ The sealed ampoule containing the CdTe film (and inert substrate), HgTe source, and excess Hg is formed by the space between two glass tubes with sealed ends, one fitting inside the other. After filling and evacuation, the glass outer tube is crimped for a seal, and inserted into a furnace with careful temperature control. Total process time is about 200 hours in current work.

Macrophotographs of typical EDICT samples are shown in Figure 2-8. The scale, in inches, shows the present size of HgCdTe crystals grown by the HWE/EDICT process. The surface of the film after EDICT has a smoother, more mirror-like appearance when compared to the CdTe films (Figure 2-5).

Microscopic examination of the surface of HgCdTe films formed by EDICT reveal spiral growth terraces. It is not known how this surface relief relates to the surface morphology of the CdTe films. There may be no connection between the two for the HgCdTe crystal is four times as thick as the CdTe film for $x = 0.2$, and the two surface structures have very different length scales. Smoothing of the surface features is discussed more fully in Section 3.

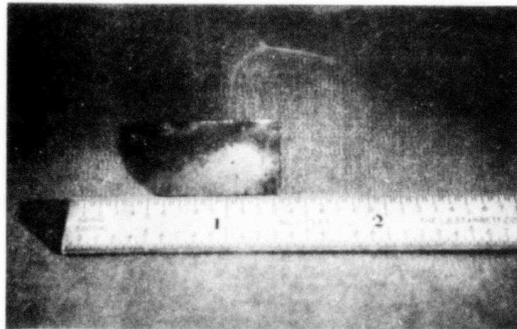
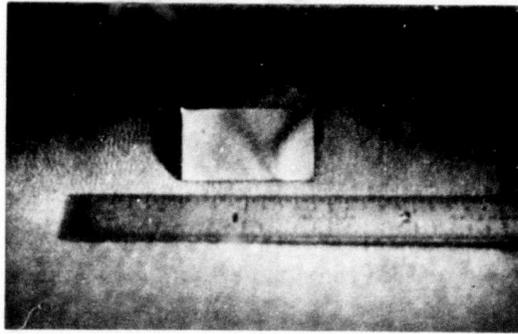
Microscopic examination of the surface of HgCdTe films formed by EDICT reveal irregular depressed regions and/or spiral growth terraces. The terraced regions show aligned six-sided polyhedra indicative of crystal structure with a scale length much different than the scale for the pyramids seen on the CdTe films. The depressed areas may be those regions between the original pyramids in the CdTe films. The composition of the structure seen on the surface of the HgCdTe film was checked using EDX with an SEM. Within the resolution of this method the composition and stoichiometry of the film were constant everywhere on the surface. A connection between the surface morphology of the CdTe films and the final HgCdTe films cannot be well established, for the increase in thickness in going from the first to second film is as great as a factor of four for $x = 0.2$. Smoothing of the surface features is discussed more fully in Section 3.

During this phase of the program, a variable temperature Hall station was set up to measure the electrical properties of the HgCdTe films grown. However, due to the poor film/substrate adhesion, electrical data have not been obtained. If better adhesion is achieved, as expected, on sapphire substrates, these measurements will be performed routinely.

2.3 FUTURE PLANS

2.3.1 New Hot Wall Epitaxy Furnace

A major objective for this phase of the current program is to produce 2-inch diameter single-crystal HgCdTe films on sapphire substrates. During the past six months a new HWE growth system capable of depositing up to 2-inch diameter CdTe films has been designed, and fabrication is now almost complete. The new system has increased



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FIGURE 2-8. HgCdTe CRYSTALS GROWN BY EDICT

control over the deposition parameters of source temperature (T_H), substrate temperature (T_L), growth time, and temperature ramp rates. Provision has been made for separating the source and substrate during heating and cooling, a feature lacking in the existing apparatus shown in Figure 2-2.

Figure 2-9 is a composite view of the new HWE system. Thermal control is enhanced by using microprocessor-run temperature controllers to independently control the source and substrate heaters to desired set point or differential. The quartz wall is kept hot by a third heater adjusted so that CdTe condensation does not occur on the wall. Temperatures of all three heaters can be automatically ramped up or down during the process to enhance growth reproducibility.

A high-purity graphite slider acts as a shutter to automatically place the substrate in the growth position (as shown in Figure 2-9) when the desired T_H and T_L conditions exist. After deposition the sample can be moved into a non-growth position for the purpose of thermally cycling the new CdTe film. The shutter is moved using a magnetically coupled pulley. Completion of the furnace assembly only awaits delivery of this graphite slider.

During the next six months the construction of this furnace will be completed, the furnace controls and temperature measuring apparatus will be calibrated, and the initial determination of the relationship between regimes of furnace temperatures and the rate of film deposition will be made.

2.3.2 Determination of the Effect of Growth Parameters on Epitaxial Films of CdTe on Mica Substrates

This work will be done in the new furnace. The important growth parameters for these films are T_L , T_H , and the amount of source material present in the furnace. The stoichiometry and surface morphology of the epitaxial films are functions of the growth rate and the temperature differential ($T_H - T_L$) during growth. The films will be characterized for three essential criteria:

- (a) Reproducibility of thickness: This property is essential if the HWE/EDICT method is to be used in device manufacture.
- (b) Surface morphology and stoichiometry: This property will be assessed by optical and SEM examination, and EDX.
- (c) Crystal Structure: Crystal perfection as a function of deposition parameters will be assessed by x-ray analysis.

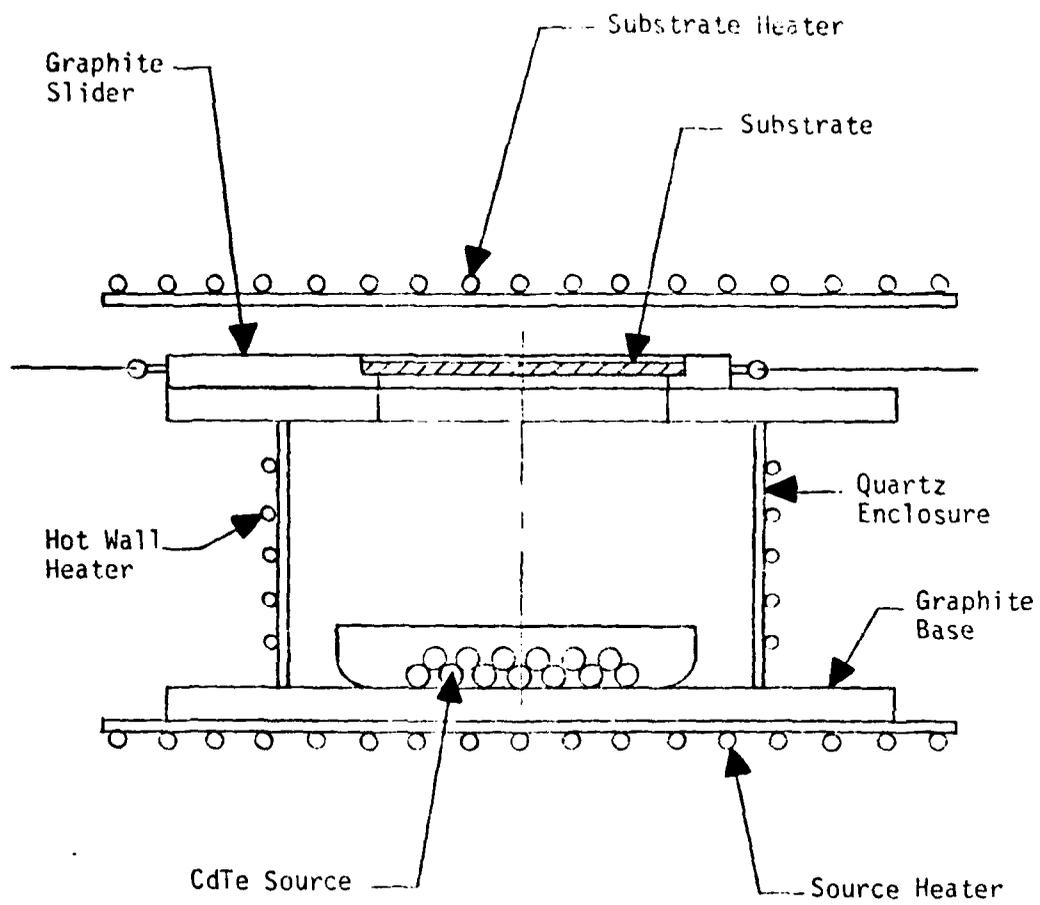


FIGURE 2-9. NEW HOT WALL EPITAXY SYSTEM

2.3.3 Determination of the Effect of Growth Parameters on Epitaxial Films of CdTe on Sapphire

This task is more complex than the previous one because there are more options in the preparation of the substrates. All mica substrates were prepared by cleaving. The orientation and surface cleaviness were pre-determined by the cleavage properties of mica. Sapphire is more versatile because any substrate orientation is possible as the crystal samples are sawed and polished rather than cleaned. However, substrate cleaning techniques have to be developed for these polished substrates.

In addition to standard cleaning methods, an electron bombardment treatment will be used. In this technique the sapphire substrate will be bombarded by an electron pulse in vacuum to clean it, and the surface will be coated by a thin film of tellurium before removal from the vacuum. This tellurium layer will keep the substrate surface clean until it is placed in the HWE furnace for CdTe deposition. The protective coating will be thermally removed before deposition of the epitaxial CdTe layer, thus insuring complete cleanliness of the substrate.

The new HWE furnace will be used for this task. Growth parameters will be determined as for the films on mica, with substrate orientation on additional variable.

2.3.4 Optimization of the EDICT Process

This last task will optimize the process by which CdTe films are transformed into $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ films with x value of 0.3. The parameters to be optimized are:

- a) time of EDICT transformation
- b) temperature of EDICT transformation
- c) the amount of excess Hg used in the ampoule.

The effect of variations of these parameters on HgCdTe film growth from films of CdTe on mica and/or sapphire will be determined. Correlation between the quality of the initial CdTe film and that of the final $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ film produced by the EDICT process will be measured.

The HgCdTe films will be characterized by the following techniques:

- a) Optical and/or SEM microscopy will be used to determine the surface morphology.
- b) X-ray analysis using Laue and/or Berg Barrett techniques will be use to determine crystal structure and defects.
- c) Optical transmission measurements using a Fourier Transform Spectrometer will be used to determine the value of x , and the uniformity of composition across the film surface.
- d) Hall measurements will be used to determine carrier concentration, type, and mobility.
- e) Electro-optic devices (either PC or PV) will be fabricated in HgCdTe films and tested.

SECTION 3
REPORT OF THE MAIN CONTRACTOR
SPIRE CORPORATION

3.1 PULSED ELECTRON BEAM PROCESSING OF HETEROEPITAXIAL FILMS

3.1.1 Objective

The goal of this program task is to improve the characteristics of the final HgCdTe films through one of three possible techniques:

- a) Smooth the surface of the final HgCdTe crystal film.
- b) Smooth the surface of the HWE CdTe film.
- c) Improve the crystal structure of the HWE CdTe films.

The crystal defects in the as-deposited CdTe films are discussed in Section 2.1. The typical irregular topography of these CdTe films is shown in Figure 2-5. It is not known how the surface morphology or crystal structure of the initial CdTe film contributes to the surface irregularities in the final HgCdTe sample; however, it is plausible that an improved initial substrate will improve the final film qualities.

Pulsed electron beam processing is the technology proposed to smooth the film surfaces and/or to improve the crystal structure. A large diameter, low electron-energy beam is used to melt a thin surface layer of CdTe. The short duration of the irradiation (less than 0.1 microsecond) and low total energy (less than 1 joule/cm²) insure that only a thin layer of the sample is melted. The liquid cools quickly by heat conduction to the solid substrate. Epitaxial crystal regrowth and surface smoothing are observed.

For this phase of the program, it was considered desirable to process the CdTe films, although the feasibility of pulsed electron beam processing of HgCdTe for surface smoothing was shown in the first phase. Processing CdTe samples is considered easier because the entire film thickness typically deposited by HWE could be melted by the pulsed electron beam (or PEB) for complete epitaxial growth from the substrate. The HgCdTe films, whose parameters are determined by device requirements, are generally thicker than the layer which can be melted and cooled in its entirety with minimal loss of stoichiometry.

3.1.2 Processing Description and Results

The results of pulsed polishing heteroepitaxial CdTe films were presented at the Materials Research Society Conference held in Boston in November 1981 at the symposium on "Laser and Electron-Beam Solid Interactions and Materials Processing." This paper will be published as part of the proceedings edited by B.R. Appleton and G.K. Celler (North-Holland in April or May of 1982). A copy of the paper acknowledging DARPA support is attached in Appendix A.

At the start of this phase of the program Spire pulse irradiated three samples supplied by NERC. These samples were:

- a) HWE CdTe film on mica
- b) HWE CdTe film on mica, which was converted to HgCdTe by EDICT after pulsing.
- c) HWE CdTe film on mica, which was converted to HgCdTe by EDICT before pulsing.

Each sample was pulsed irradiated at two or three fluences between 0.3 and 0.65 J/cm² in non-overlapping regions about 1/4 inch square. Some material on all sample films was not processed by the electron beam.

Microscopic examination of the specimens showed that: the surface of the CdTe film (a) was polished by pulsed processing, the surface of the HgCdTe film (c) was polished by pulsed processing, and in sample (b) although the surface of the CdTe film was polished by the electron beam it did not appear to affect the surface morphology of HgCdTe film after EDICT. The reason for failure in (b) is not known. This failure could have been caused by defects/contamination in the CdTe, defects/contamination in the HgCdTe layer, an initially polycrystalline CdTe layer, or an error in pulsed or EDICT processing of the sample. These samples were returned to NERC for further analysis. To date, only one sample like (b) was successfully processed in this program. The experiment will be repeated when further samples are available.

3.1.3 Apparatus

The experiments previously described, and the work performed in the first phase of this program, used an electron beam with an area of approximately 1 cm^2 of uniform fluence at the appropriate level. Previous work on this apparatus had generated electron beams of nearly 100 cm^2 area at higher fluence (1 J/cm^2) for processing silicon⁽⁸⁾. A series of tests were run to determine how a large area, uniform pulsed electron-beam could be produced at a lower fluence ($0.2\text{-}0.6 \text{ J/cm}^2$).

Tests of uniform fluence for processing HgCdTe were performed on the SPI-PULSETM 7000, which is a production oriented, pulsed electron-beam processor for semiconductor materials. The fluence was measured at 29 points in the sample plane, simultaneously, by an array of small calorimeters each 0.25 inch diameter. The temperature rise of the calorimeters after one pulse was recorded by a multiplexed readout and analyzed by a small laboratory computer. There is a "hot spot" on the beam axis with a radius of about 12 mm. This spot is surrounded by a large area over 112 mm diameter of uniform fluence. This is sufficient for processing three, 2-inch diameter HgCdTe films simultaneously.

On a fine linear scale, the fluence of the electron beam cannot be measured directly. The uniformity of processing by the pulsed electron beam is shown in Figure 3-1. A two-inch diameter p-type silicon wafer was implanted with 2.5×10^{15} ions/cm² of arsenic at 25 keV and annealed by a pulsed electron beam on the SPI-PULSETM 6000. The variation in sheet resistivity is less than $\pm 10\%$ over most of the wafer surface. A bad spot is shown opposite the wafer flat. It is believed that samples pulsed at low fluence on the SPI-PULSETM 7000 will have a smaller variation in properties.

3.1.4 Future Plans

Further tests await the delivery of large samples from NERC. The experiment of pulse polishing a CdTe film, followed by HgCdTe conversion by EDICT, will be repeated.

3.2 PULSED ELECTRON BEAM PROCESSING OF AMORPHOUS/ POLYCRYSTALLINE FILMS

3.2.1 Objectives

There are two objectives to this task: the first is to show that amorphous or polycrystalline films of CdTe with the correct stoichiometry can be converted to

SPIRE

ARSENIC RS

WAFER NO. 2055-6

AVERAGE R(SHEET)=34.5 OHMS/SQUARE

STD. DEV. = +/-3.73 RANGE = +/- 7.45 OHMS/SQUARE

IMPLANT CONDITIONS-

TILT= 7

ENERGY= 25KEV

FLUENCE = $5 \times 10^{15}/\text{cm}^2$

ANNEAL SPEC- PEBA 280

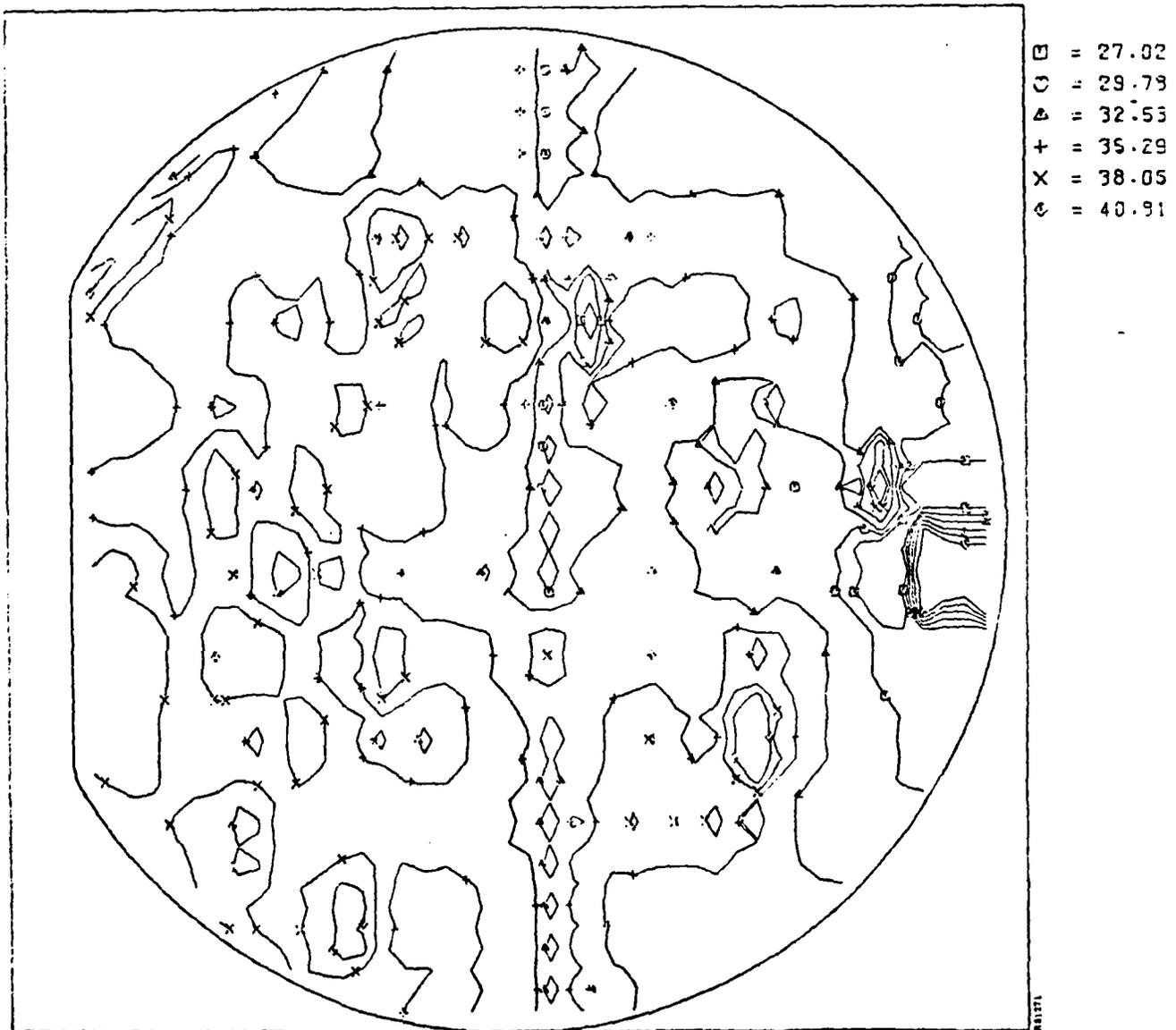


FIGURE 3-1. RESISTIVITY MAP FOR A PEBA ANNEALED WAFER

single-crystal films by liquid-phase heteroepitaxial growth; the second is to show that an evaporated layer of Hg and Te with the correct stoichiometry can be converted to a single-crystal film by liquid-phase heteroepitaxial growth. For both cases, a pulsed electron beam will be used to melt a thin film without melting the crystalline substrate. If successful, the thin CdTe films might have better structure and surface morphology than the HWE produced films and would be used as substrates in the EDICT process; the in situ Hg and Te evaporation/pulsing process has the capability of producing HgCdTe directly, without EDICT.

3.2.2 Apparatus

Previous work in the first phase of this program had shown that elemental mercury could be evaporated onto a liquid nitrogen cooled sample of CdTe, and chemically bonded to the surface by in situ pulse heating using an electron beam. The apparatus used in prior experiments is now being modified so that Hg and Te can be evaporated at independently controllable rates onto a liquid nitrogen cooled sample of crystalline CdTe. This apparatus is shown in Figure 3-2. Only the sample holder and two small furnaces are being constructed with funds from this contract.

Current design criteria call for low deposition rates. Samples of appropriate thickness will be built up by multiple layers of pulse-processed films. Evaporation of mercury will be done at room temperature; however, a small heater can be added. Shutters are not required since the sample can be turned away from the source.

3.2.3 Future Plans

Experiments in pulsed processing evaporated Hg and Te films are scheduled to begin at the end of May. Initial work with CdTe will be delayed until after completion of HWE experiments by NERC, as the new furnace would be used to produce the films.

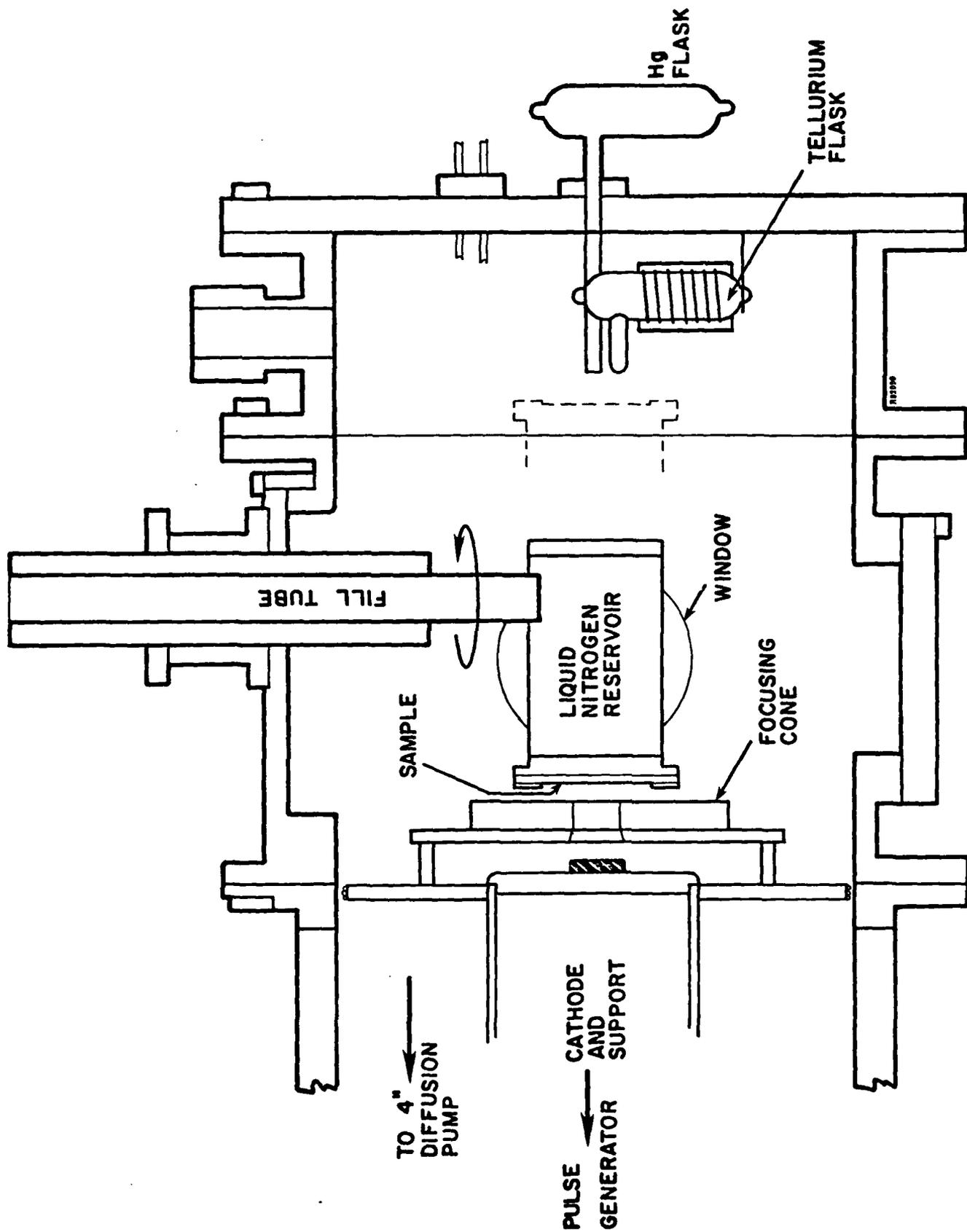


FIGURE 3-2. APPARATUS FOR EVAPORATION OF Hg AND Te,
AND PULSED PROCESSES IN CANU

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APPENDIX A

A NEW ELECTRON BEAM POLISHING TECHNIQUE
FOR HETEROEPITAXIAL THIN FILMS

A NEW ELECTRON BEAM POLISHING TECHNIQUE FOR HETEROEPITAXIAL THIN FILMS

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ABSTRACT

We have developed a novel technique for improving the morphology of as-grown monocrystalline thin films on foreign substrates. A pulsed electron beam briefly heats the surface of the film above its melting temperature, allowing surface tension in the liquid to erase irregular features. Crystallinity of the layer is preserved by rapid resolidification with the underlying material acting as a seed. Pulse polishing has been applied to two heteroepitaxial systems exhibiting rough as-deposited surfaces: germanium on silicon and cadmium telluride on mica. In both cases the surface morphology was dramatically improved while crystallinity and other critical properties of the layers were maintained. We believe this technique has potentially wide application to many thin film systems and should allow a greater degree of freedom in the growth conditions for heteroepitaxial thin films.

INTRODUCTION

The fabrication of semiconductor devices generally requires smooth, specular surface layers which are free of residual damage. For bulk-grown materials these surfaces are prepared by a combination of mechanical polishing and chemical etching. For thin films, in the micron or submicron range, conventional polishing is impossible; it would remove the layer of interest. Thin films must therefore be extremely smooth as-grown, placing additional and sometimes contradictory requirements on the growth conditions. Especially in the case of heteroepitaxial thin films, i.e., single-crystal films grown epitaxially on foreign substrates, mirror-smooth surfaces can be difficult to obtain, even when other constraints on crystallinity, interface abruptness, stoichiometry, etc. can be met.

We have recently encountered problems with as-grown surface morphology in two heteroepitaxial materials systems of interest: cadmium telluride on mica and germanium on silicon. In both cases growth conditions were defined which gave high-quality films in all respects except surface smoothness. The technique to be described in this paper allowed us to improve the morphology of the as-grown films without disturbing their other favorable properties. The idea is rather simple: a thin surface layer of the film is melted by a high-intensity pulsed electron beam; surface tension in the liquid serves to smooth the surface before the film recrystallizes. To our knowledge this is the first reported use of pulsed beams specifically to improve the surface morphology of thin films. Previous related work has tended to emphasize the degradation of smooth surfaces by pulsed or scanned lasers due to optical interference [1], standing acoustic waves [2], shock waves [3], or surface tension gradients [4].

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DESCRIPTION OF PULSED E-BEAM POLISHING PROCESS

A schematic diagram of the polishing process is shown in Figure 1. The rough-surfaced sample is uniformly irradiated by a large-area electron beam pulse at an energy density high enough to melt to a depth greater than the surface relief. During the brief interval when the surficial material is molten, protrusions slump and depressions fill. Subsequent solidification is epitaxial, seeded by the underlying crystal.

The melt depth and time are functions of the material properties of the film and substrate, as well as the pulsing parameters of electron energy spectrum, energy density, substrate temperature, and number of pulses. We have used a computer solution of the one-dimensional heat flow equation, similar to others recently published for laser melting [5, 6] to simulate the dynamics of the pulsing process. This has given melt times and depths consistent with the experimental results insofar as the two can be checked. In particular, melt thresholds are in good agreement, and conditions which should give larger melt depths and times do result in greater morphology changes. We are thus satisfied that the polishing process can be described solely by thermal effects.

Spire Corporation's SPI-PULSE 5000 e-beam generator was used for this work; it has been described earlier in connection with the annealing of ion implantation damage in silicon [7]. The beam was modified slightly for use with Ge and CdTe from that used for Si, due to the lower melting points of the former. The mean electron energy was raised to 20 keV for deeper penetration; the energy density ranged from 0.2 to 1.0 J/cm². The beam was about 3 cm in diameter. Provision was also made for heating the samples during pulsing to a maximum of 400°C, to allow more control over the melt time.

For the pulsed polishing process to be successful it must at least maintain the other critical parameters of the film/substrate structure while improving the morphology. Particular properties to be preserved might include:

- Degree of crystalline perfection
- Interface abruptness
- Electrical properties of interface
- Stoichiometry
- Surface cleanliness
- Freedom from damage

In the following examples from our work it will be shown that all these criteria can be satisfied by the pulsed e-beam polishing process.

EXAMPLE 1: CdTe ON MICA

One of the biggest problems facing the development of Hg_{1-x}Cd_xTe infrared imaging technology is the need for large-area materials of exceptional compositional uniformity and structural perfection. To address this problem we have pursued the approach of growing heteroepitaxial CdTe films on mica substrates by a hot-wall epitaxy process [8], then converting the films to Hg_{1-x}Cd_xTe by vapor exchange with HgTe [9]. Single-crystal, stoichiometric CdTe films have been grown on mica substrates; however, the films are characterized by uneven coverage and hillocks, faceted growth morphologies, or crystallographic etch figures, depending upon the substrate temperature and the deposition rate. Such growth features are ubiquitous in films deposited on mica [10].

Pulsed electron beam polishing was applied to a 2.5 micrometer thick CdTe film characterized by faceted 1 micrometer surface relief, with results shown in Figure 2. The original surface structure has been erased by this pulse of 0.5 J/cm², leaving a specular film. We confirmed that no CdTe had been lost in the process by careful weight measurements before and after. There was a clear progression in results as the e-beam fluence was varied; at lower fluences the melting was only partial with peaks slumping and valleys filling, while above 0.5 J/cm² the sample was damaged. To investigate possible changes in stoichiometry caused by the e-beam pulse, the Auger sputter profiles shown in Figure 3 were measured. Although measurement artifacts are visible near

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the surface for both virgin and pulsed samples, it can be seen that a surficial loss of Cd in the pulsed sample extends no more than 60 nm deep. Such shallow effects can be removed by light etching. Another concern was the degree of crystalline perfection of the film after the rapid melting and recrystallization process. X-ray diffraction patterns were found to be virtually identical for pulsed and non-pulsed areas of the sample. The pulsed electron beam polishing process was therefore quite successful in the CdTe-mica system, where no other existing technique could have produced comparable results.

EXAMPLE 2: Ge ON Si

We investigated the growth of thin Ge films on Si wafers by chemical vapor deposition (pyrolysis of GeH_4), for application to low-cost, high efficiency GaAs solar cells. The Ge coating, being well matched in material properties to GaAs, would allow the growth of thin-film GaAs solar cells on relatively low-cost Si substrates. A thin ($<1\ \mu\text{m}$) single-crystal layer of Ge was required, with a specular surface for later GaAs growth and device processing. It was found that single-crystal layers of Ge could be grown on Si relatively easily in the temperature range of 600-850°C, but the layers were not smooth. Typically islands of Ge nucleated and grew until they coalesced at 0.5 to 1 micrometer in thickness; surface ripples or facets remained during further growth.

Pulsed electron beam polishing was again applied with good results, although the improvements were not as spectacular as for CdTe due to better starting morphology. Figure 4 shows Nomarski micrographs of an as-grown 0.6 μm Ge film and the results of 3 pulsing experiments. A single pulse reduced the as-grown surface relief from 0.20 to 0.10 micrometer, as measured by angle sectioning. The same pulse at a sample temperature of 400°C reduced the relief to 0.08 micrometer; with three pulses the relief was too small to be measured. Increased sample temperature or number of pulses increases the duration of the melt and therefore the surface smoothness, in agreement with our conceptual model. Although not shown in the figure, increased pulse fluence had the same effect.

Our numerical simulations of these experiments indicated that the entire Ge film should melt for cases (b) through (d), but the Si substrate should not, due to the higher melting point of Si and the rapid decrease of the temperature profile with depth. For case (c), however, the Si should have reached melting temperature at the interface. Calculated surface melt times were 30 ns for room temperature pulsing and 1.7 μs for 400°C pulsing. With melting of the entire Ge film indicated, there was concern about maintaining the abruptness of the Ge-Si heterojunction. The composition profiles shown in Figure 5 were measured by Auger sputter profiling to address this question. The as-grown profile is somewhat misleading, due to variations in film thickness caused by surface rippling. Using angle sectioning we confirmed that the as-grown Ge-Si interface actually was abrupt, and that the extent of apparent grading in the profile agreed with the measured surface relief. After a single pulse the interface remained abrupt; again the apparent interface profile is attributed to surface relief. The interface was also quite abrupt after 3 pulses, but for pulsing at 400°C, interdiffusion of Ge and Si was indicated. Higher interface temperatures and a larger melt time explain the latter result. It is, however, possible to smooth the surface while avoiding significant interfacial alloying, as in cases (b) and (c).

Other critical parameters in this structure were the degree of crystalline perfection in the Ge layer and the electrical properties of the Ge-Si interface. The films were found to be good single crystals both before and after all pulsing conditions by RHEED and electron channeling patterns. Electrically, the interface was required to be ohmic and of low resistance, for future application as a back contact to a GaAs solar cell. The as-deposited samples and those pulsed at room temperature met this criterion; there was no change with pulsing. The results for the hot-pulsed sample were nonuniform and non-ohmic, possibly due to the interfacial alloying of Ge and Si. Overall, the samples pulsed at room temperature were able to satisfy all requirements and exhibited significantly improved morphology over the as-grown material.

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SUMMARY AND DISCUSSION

Pulsed electron beam polishing of thin films has been quite successful in the applications discussed above, where no other existing technique could have solved the morphology problems. We have found that the simple conceptual model of surface melting, liquid flow, and recrystallization is capable of explaining all the observed results. These include the effects of varying pulse energy density, number of pulses, and sample temperature. A one-dimensional heat-flow model has been able to adequately simulate the melting and recrystallization process, allowing us to determine suitable pulsing conditions without extensive experimental work. It is applicable to virtually any single or double layer materials system whose thermophysical properties are known.

We believe the pulsed polishing process has application to many more situations than those we have examined. It addresses a fundamental problem in thin-film growth: the need for smooth surfaces, independent of other growth constraints. Without the requirement for a specular surface, growth could be carried out over a much wider range of conditions, extended for example to different temperature or growth rate regimes, or to different orientations. Other promising applications include the elimination of pinholes from thin films, and surface texture modification in general for non-semiconductor materials.

The types of materials amenable to pulsed polishing would have the following characteristics. The surface features to be eliminated must be smaller than the maximum melt depth in the material; this could be up to a few micrometers, depending on the melting point of the layer and other thermal properties, and the pulse conditions. The pulse conditions must be chosen to give a significant melt time, but not to exceed the damage threshold in the material. This requirement can be eased by using multiple or hot pulses, to increase the melt time. If alloying of the film and substrate is a problem it is advantageous to have a lower melting point in the film than in the substrate, as in the two examples. Melting can then be effectively restricted to the film. The same purpose is also served if the film is thicker than the melt depth. In compound semiconductors or other materials where a loss of stoichiometry is caused by heating, this problem will be restricted to the very near surface region by the short duration of the melt. The melt time can be minimized by adjusting the pulse conditions, or light chemical etching could be done to remove the non-stoichiometric layer.

ACKNOWLEDGEMENTS

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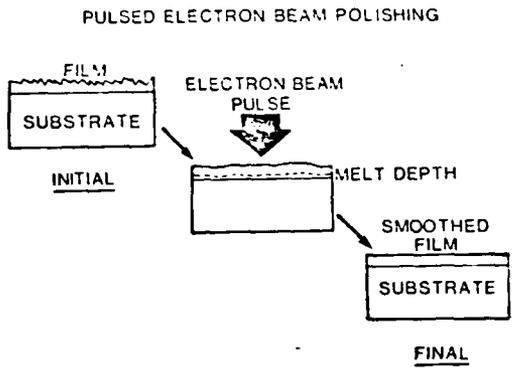
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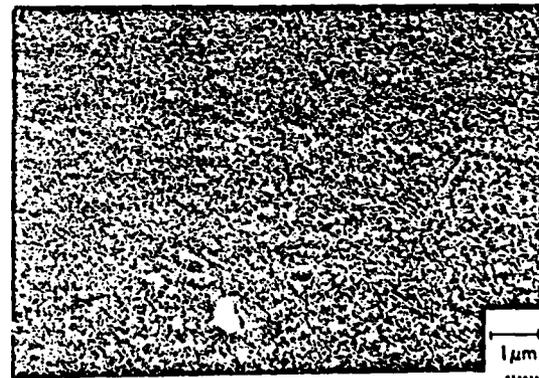
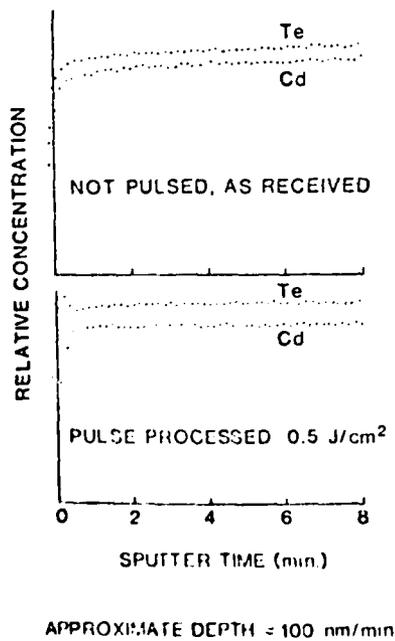
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AS-DEPOSITED CdTe FILM

Fig. 1 Conceptual diagram of pulsed electron beam polishing process.



CdTe FILM PULSED ELECTRON BEAM PROCESSED AT 0.5 J/cm²

Fig. 2. SEM photos of CdTe film before and after 0.5 J/cm² electron beam pulse.

Fig. 3. Auger depth profiles of Cd and Te for samples of Fig. 2.

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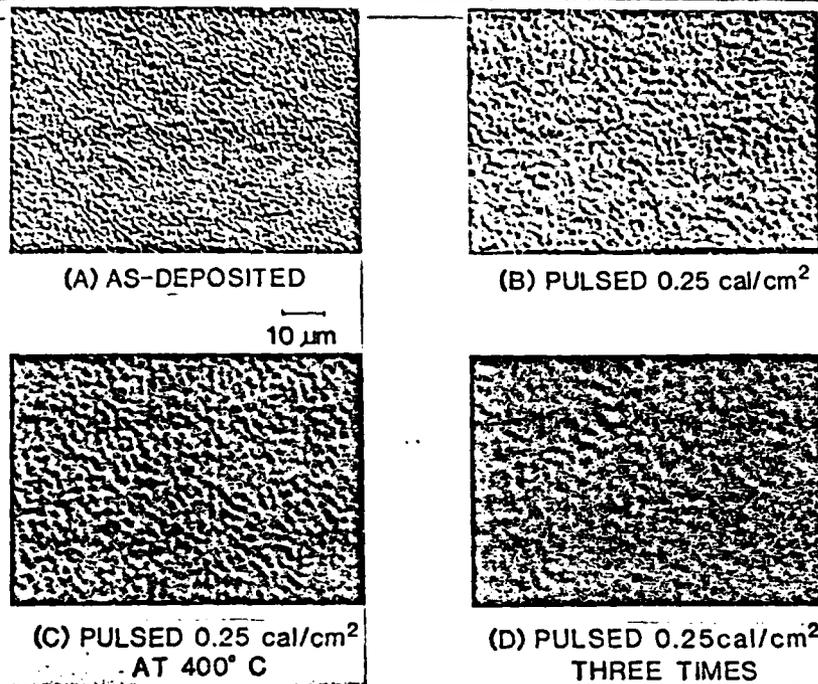


Fig. 4. Nomarski micrographs of 0.6 μm CVD Ge layers on Si, before and after pulse polishing.

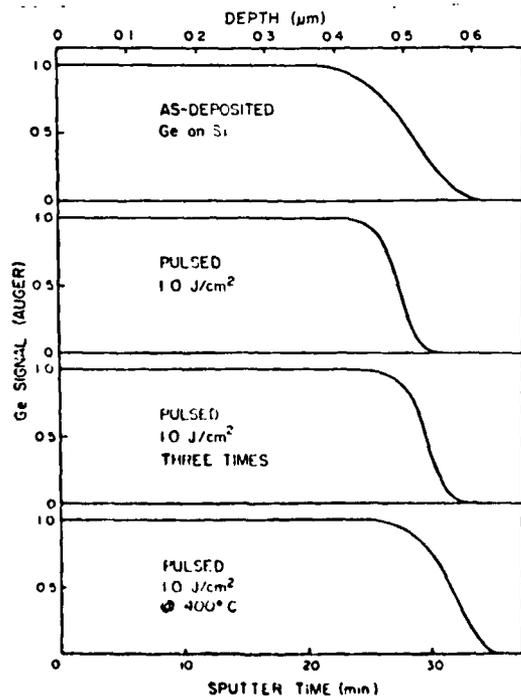


Fig. 5. Auger depth profiles of Ge for samples of Fig. 4. (1.0 J ≈ 0.25 cal).

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