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GROWTH OF HgCdTe BY MODIFIED MOLECULAR BEAM EPITAXY

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An investigation was made on the deposition of HgCdTe thin film on CdTe by irradiating the bulk source material with high power laser pulses. The morphological features and stoichiometric composition depend very strongly on the laser characteristics and the scanning rate. Under very high power operation, the dominant deposition process is the condensation of micron size molten globules "blown-off" from the source material. At lower power level, the film formation is largely due to the deposition of small molecular

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clusters. Compositional analysis of the film showed that the CdTe end of the alloy evaporated congruently, whereas the HgTe end suffered some loss of Hg. The amount of Hg loss could be reduced by varying the laser power and the scanning rate. n-type films up to 2 μm thick were deposited in this manner and photoconductive devices were fabricated and measured. We have also made a detailed mass spectrometric study of the evaporant composition under different conditions. A model on the evaporation mechanism formulated from such information will be discussed.

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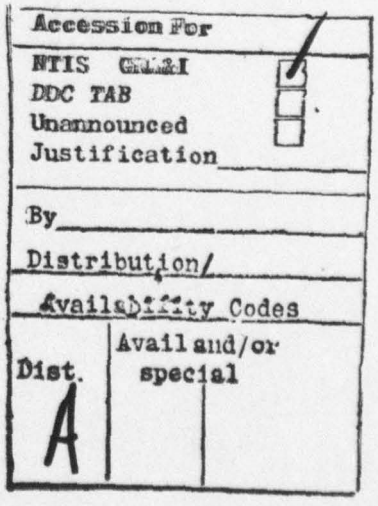

FORWARD

The work reported in this document was performed at the Science Center, Rockwell International, Thousand Oaks, California, with the support of Defense Advanced Research Projects Agency, Arlington, Virginia, under contract No. MDA 903-79-C-0188. The program monitor is Dr. Richard Reynolds.

The Principle Investigator is Dr. J. T. Cheung.

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SUMMARY

We have set up the LAMBE apparatus and integrated the pulsed laser unit into the system. The system is now operational.

We have first studied the formation of thin HgCdTe film on CdTe by evaporating from the bulk material with a single pulsed laser beam. We have discovered that the CdTe in the alloy was evaporated congruently while HgTe suffered a loss in Hg. The amount of Hg loss depended on the laser pulse characteristics such as their peak power, frequency and scanning rate. Photoconductors were fabricated from these films and their responses were measured.

We have also monitored the mass spectrum of the evaporants under various conditions. By comparing this information with the EDAX compositional analysis of the film, we were able to understand the evaporation mechanism. Such knowledge will be beneficial to our next phase of work.

1.0 INTRODUCTION

1.1 Program Objectives

The main objective of this program is to explore and develop a novel epitaxial technique for the HgCdTe system. This is a new form of vacuum deposition which combines the use of laser evaporation and in situ laser annealing. It is appropriately named LAMBE (Laser Assisted Molecular Beam Epitaxy) in order to be differentiated from the conventional MBE method. This is a low temperature process. Potentially, it can grow material with variable compositions and structures.

1.2 Overall Program Plan

Due to the pioneering nature of the subject, our initial efforts were devoted to system design, system construction and some analytic studies. The initial phase was followed by the work on material growth. The proposed approach is quite complex with many growth parameters. In order to isolate these variables, we first studied the simpler version of laser evaporation by evaporating a single HgCdTe source with laser pulses onto a heated CdTe substrate. Much can be learned from this study about the laser evaporation mechanism, problems and solutions. This accumulated knowledge will be beneficial to our subsequent work. In the next phase, we will expand our effort to study the two source laser evaporation with in situ laser annealing. Material characterization, photodetector fabrication and measurements will be carried out concurrently.

1.3 Accomplishments

During the second six-month period, we have accomplished the following:

(1) We installed the laser unit. The beam output was fully characterized. The LAMBE apparatus became operational.

(2) Before starting the experiments, there were two key technical issues to be considered. One involves the prevention of evaporant condensation onto the vacuum windows and the other concerns the possibility of evaporating CdTe with the 1.06 μm laser radiation. We examined both problems and showed that they could be solved.

(3) We have made ten depositions of thin HgCdTe film onto CdTe substrate. The films were examined by EDAX, IR transmission measurements and low temperature Hall measurements. Photo conductors were fabricated from one of the films and the spectral response was measured.

(4) We have studied the mechanism of laser evaporation under the present condition. Its mechanism was formulated based on the mass spectrometric study of the evaporants and the EDAX analysis of the thin films. Such information is valuable for improving the growth condition.

2.0 TECHNICAL INFORMATION

2.1 Background

Thus far, there have been only two types of vacuum deposition for HgCdTe films, namely, sputtering[1] and thermal evaporation.[2] The most noticeable drawback is due to the result of the high noncongruent nature of vaporization that the product films are Hg deficient. Besides, bulk HgCdTe is used as the source material, therefore the composition cannot be changed arbitrarily.

In our original proposal, we suggested two alternatives to cope with this problem: a seeded nozzle beam and the evaporation by pulsed laser irradiation. In situ laser annealing will be used in both cases. After some careful considerations, we concluded that the laser evaporation approach was more viable. The basic concept has since then been enriched with an influx of new ideas. During the last few months, we carried out some preliminary experiments to test these concepts. The results were encouraging. With more experimentation and modification, this new epitaxy technique has a good chance to be realized. We should also point out that this technique can be extended to grow other materials in particular films of compound semiconductors, oxides and refractory metals.

2.2 Experimental

2.2.1 System Description

Figure 1 shows the scheme of the LAMBE apparatus. Detailed approach was given in the last semi-annual report. Here, only a brief description will be summarized.

The apparatus consists of two components: a UHV vacuum chamber and a Nd:YAG laser unit with assorted optics. HgTe and CdTe will be used as source materials. They are mounted on separate rotatory feedthrough flanges on the bottom of the chamber. The substrate holder located at 6 in. from the sources and its temperature can be regulated over a wide range. The laser unit produces pulses at 1.06 μm wavelength with adjustable frequency and peak power. It will be used as the power source for evaporation as well as for annealing. The dual application was achieved by periodically redirecting the laser beam with a rotating mirror. When the mirror is out of the beam axis, the laser radiation will be split into two parts and focused onto HgTe and CdTe accordingly. Evaporants condense on the substrate forming the alloy. When the mirror is in the axis, it directs the laser beam onto the substrate via a x-y scanner for in situ annealing. This deposition-annealing cycle will repeat during the entire growth. The important growth parameters are the laser pulse characteristics, the focusing conditions, the speed and duty cycle of the rotating mirror, the power density of the annealing beam and the substrate temperature.

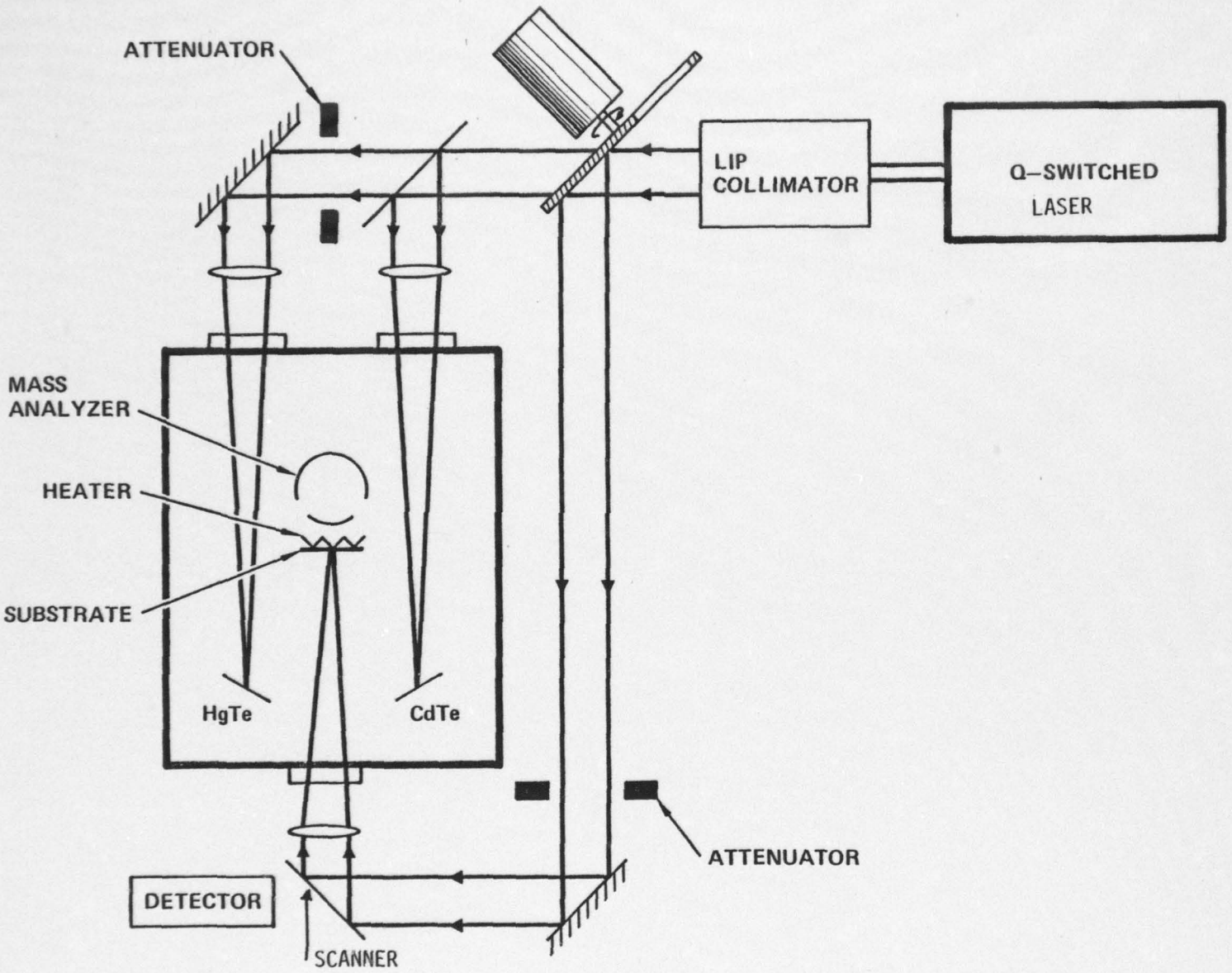


Fig. 1 Schematic diagram of the apparatus.

We have tried the single source evaporation. The work is complete and will be discussed in the later sections.

2.2.2 Characterization of the Laser Beam

We have fully characterized the laser beam output at different frequencies. The results are shown in Fig. 2. The parameters of importance are the peak power, the average power and the pulse duration. The results shown here were measured at full power operation. Lower power can be achieved by decreasing the current through the excitation flash lamp. Minimum average power at the lasing threshold is approximately 5% of the maximum level. A typical pulse used during the evaporization experiment is shown in Fig. 3. Pulse to pulse peak power variation is less than ±10%. With the present optics, the focal spot at the source surface is estimated to be $1.5 - 2 \times 10^{-2}$ cm in diameter. At 3 KHz operation, the corresponding peak power density is about 10^9 W/cm^2! This exceeds the power density of ~ 10^8 W/cm required to evaporated CdTe.

2.2.3 Experimental Procedure

In this section, we will describe the general procedure for depositing thin HgCdTe film onto CdTe substrate with a single beam of laser pulses.

<111a> CdTe wafer was cleaned in TCE and acetone followed by a HBr/Br_2 etch prior to loading into the vacuum. The $Hg_{0.8}Cd_{0.2}Te$ source material was treated in the same way. The base pressure of 2×10^{-7} torr was

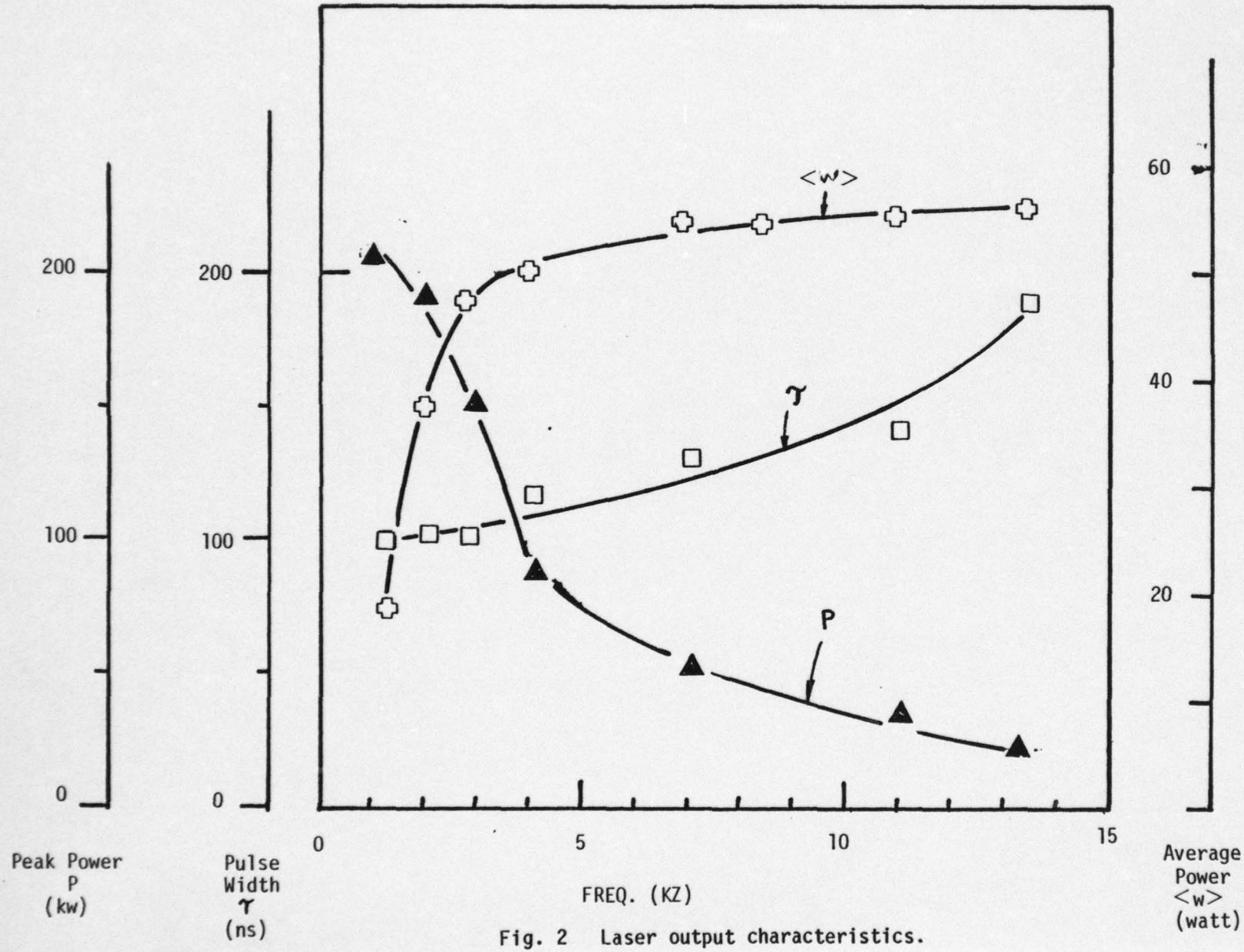


Fig. 2 Laser output characteristics.

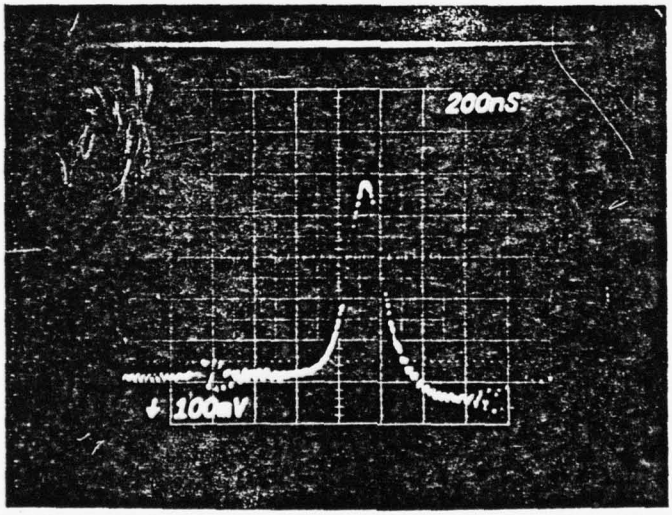


Fig. 3 Shape of a laser pulse.

achieved with a 800 L/S Hg diffusion pump. Residual gas analysis showed the presence of a minute amount of Hg ($<10^{-11}$ torr) background. The substrate was then heated to 120°C. Once the steady state was established, the source surface would be cleaned by scanning over with the laser beam for 5 minutes, the substrate shutter was closed during this time. During deposition, the pressure raised to 1×10^{-5} torr. The source was rotating at 5 sec/turn and the focused laser beam was repositioned by turning the steering prism at two minute intervals. We found that this scanning arrangement was much too slow. A pair of 300 Hz galvanometer scanner will be installed to improve this situation.

Deposition usually lasts 1-1/2 hours, yielding films between 1-2 μm thick. By measuring the film thicknesses vs deposition time, we discovered that the deposition rate was not uniform. The rate decreases with time. We believe that it is due to the improper geometric configuration of the source and the substrate. New design of source holder will be tested.

During the course of evaporation, two sets of parameters were closely monitored. First, the laser pulses were monitored with an in-line laser photodiode. The laser pulses showed good uniformity over the entire period. We also monitored the evaporant composition with a quadrupole mass analyzer. The results will be correlated with the film composition.

2.3 Results

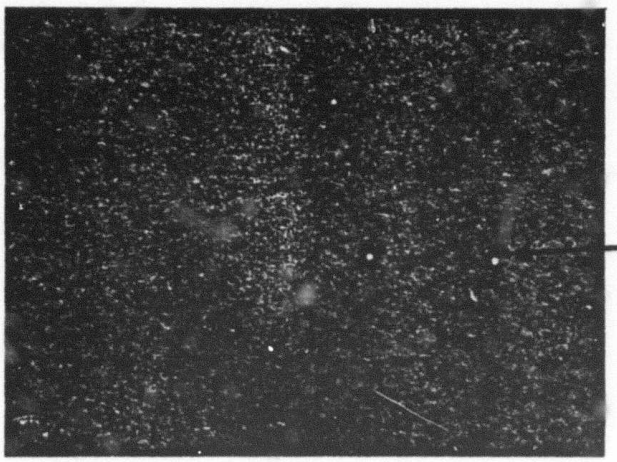
A total of ten HgCdTe thin films were grown under different conditions.

2.3.1 Film Morphology

Figure 4 shows the surface and cross section of a film. Observation via optical microscopy revealed that the films were of uniform smoothness and thickness, with no crystalline structure discernable. The surface also exhibited the condensation of molten globular droplets of a few microns in diameter. This feature was also seen in other early work on laser evaporization. It is believed that the globules are small pieces of the source material "blown-off" onto the substrate during the strong interaction between the laser irradiation and the surface. EDAX analysis showed the globules and the source material having the same composition, thus confirming this speculation. We discovered that the density of globules could be reduced by lowering the laser peak power. The result is shown in Fig. 5.

2.3.2 Film Properties

Figure 6 shows the IR transmission spectrum of a 1.5 μm thick film. The closeness of the absorption edge at different locations of the film is a strong indication of compositional uniformity. This was also verified by EDAX analysis over various parts of the film. Comparing the EDAX measurement of the source material with the thin film. We notice that there is little change



SURFACE

CROSS SECTION

Fig. 4 Film appearance.

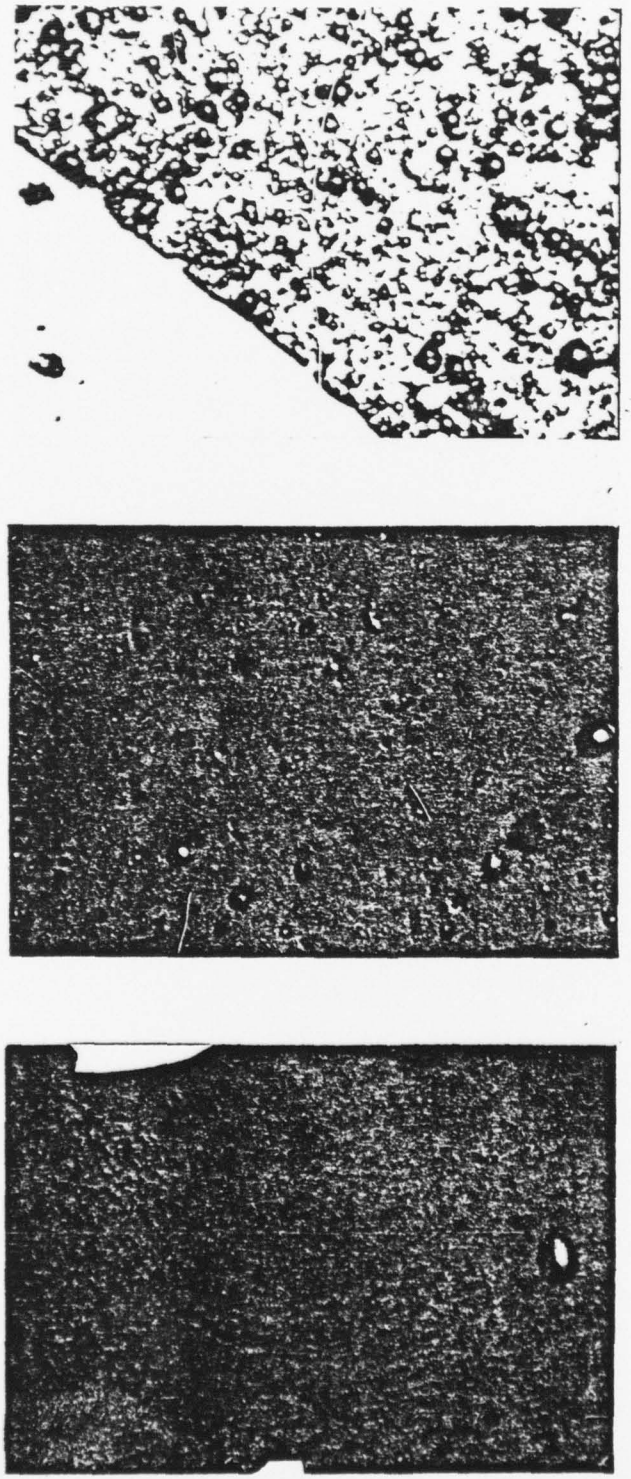


Fig. 5 Surface morphology vs laser power.

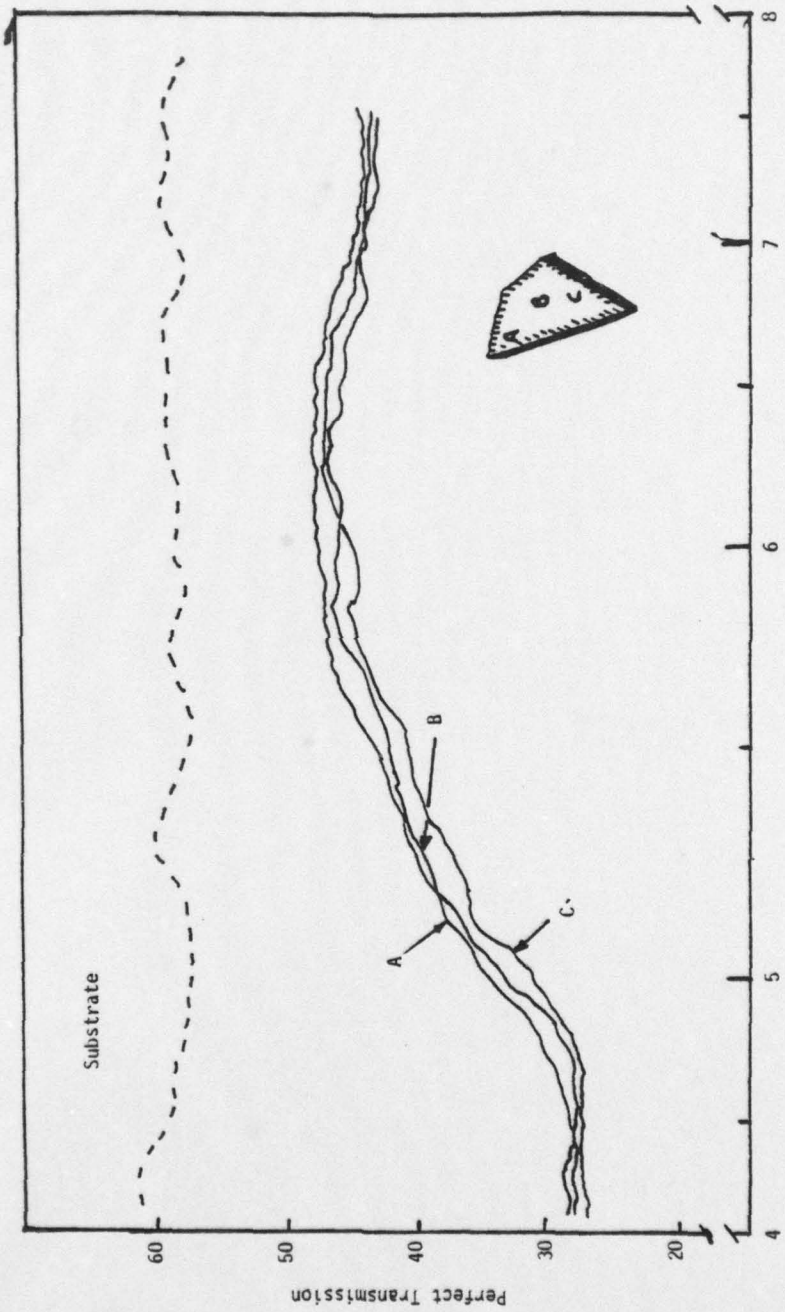


Fig. 6 Transmission spectra of a film.

in Cd content whereas the Hg content showed considerable loss. The loss was reduced by using higher laser power and faster scanning rate. By fixing the scanning rate at 5 sec/turn and increasing the laser power level, we can obtain film with absorption edges varying from 3.7 μm (32% Hg) to 5.2 μm (27% Hg) at room temperature.

Liquid nitrogen temperature Hall measurements indicated n-type films with carrier concentration from 10^{16}-10^{17} carriers/cm^2 and mobility from 400-600 cm^2/volt sec. No annealing effort has yet been attempted to improve the electrical properties.

We fabricated a photoconductor from one of the films by making contacts on both ends of a film strip 1 mm x 5 mm in dimension. The spectral response at 77°K is shown in Fig. 7.

2.3.3 Mechanism of Laser Evaporation

Thermal evaporation of HgCdTe was recently investigated by Farrow, et al.,[3] using modulated mass spectroscopy under Knudsen effusion condition. The results showed that it proceeded incongruently through five stages. At low temperature (<200°C), Hg is the only significant dissociation species. In the second stage, (200°C-300°C), both Hg and Te_2 were present. The dissociation vapor pressure of Te_2 increases rapidly in this regime but the Hg signal increases much slower than at low temperature. By 320°C, the ratio of P_{Hg}/P_{Te_2} reach a temperature independent value. This situation represents a

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Fig. 7 Photoconductor response.

steady rate of effusion in which HgTe was lost from the source change. The progressive fall in P_{Hg} and P_{Te_2} over the temperature range 400°C-450°C was due to this selective depletion of charge composition. Above 450°C, the predominant species were Cd and Te_2 corresponding to the dissociation of the residual CdTe.

Mass spectra of the evaporants by laser irradiation at low and high power are shown in Fig. 8a,b, respectively. The differences are obvious:

(1) We observe all three atomic species Hg^+ (Hg^{++}), Cd^+ and Te^+. The Cd^+ and Te^+ intensity ratio is close to unity. The Hg^+ (Hg^{++}) is much more abundant.

(2) We do not see any molecular Te_2^+.

(3) There is a large abundance of species with mass/charge ratio greater than 360. They correspond to clusters such as $CdTe_2^+$, Te_3^+, $Hg_2Te_3^{+2}$, etc. Unfortunately, due to the detection limit of the spectrometer, clusters with mass charge ratio (m/e) of more than 400 cannot be observed. The spectra shown here are not corrected for the mass dependent calibrations such as the spectrometer gain, transmission and ionization efficiency. The gain and transmission factors are readily available from the operational manual, and it is reasonable to assume the ionization efficiency proportional to the geometrial cross

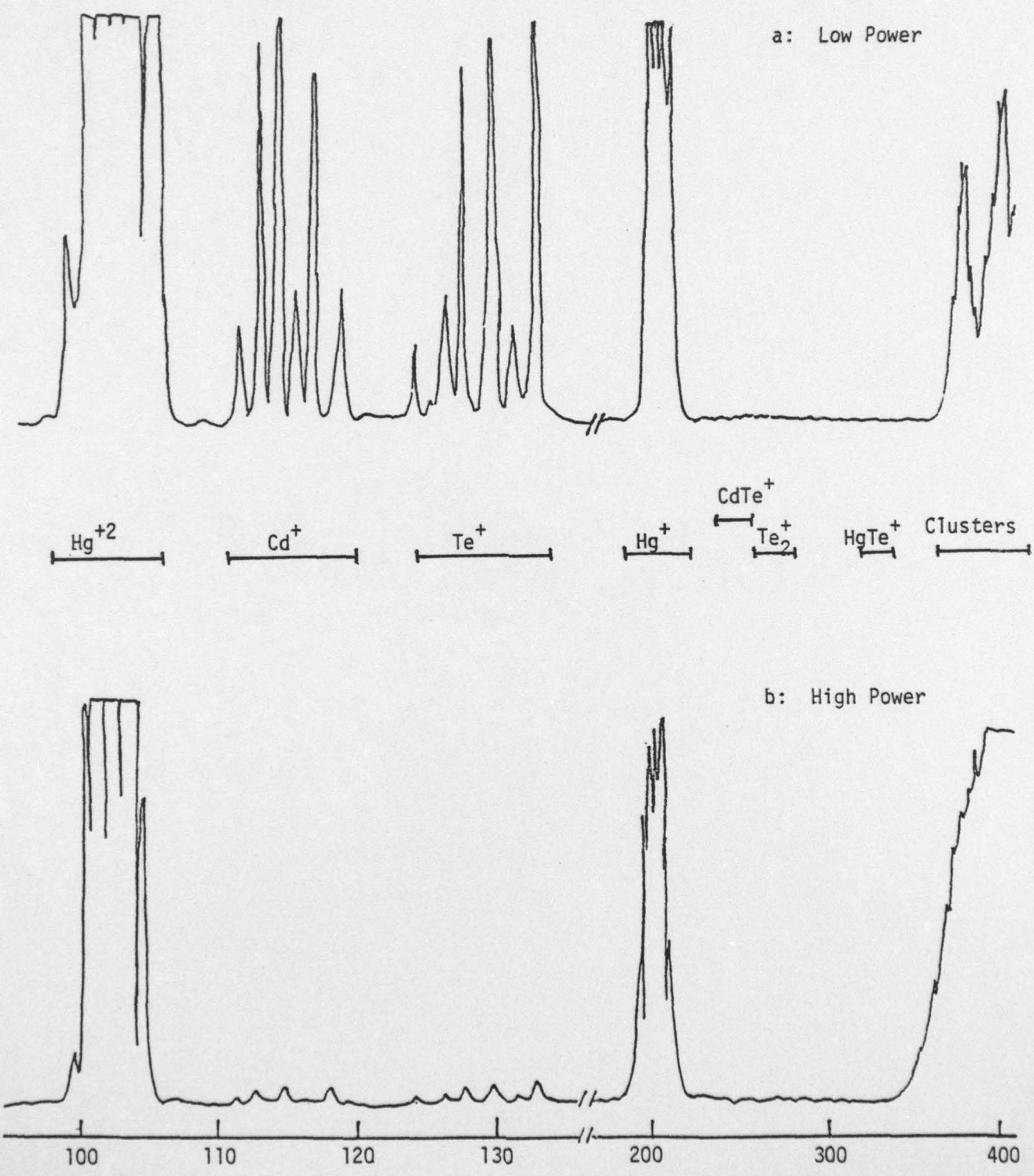


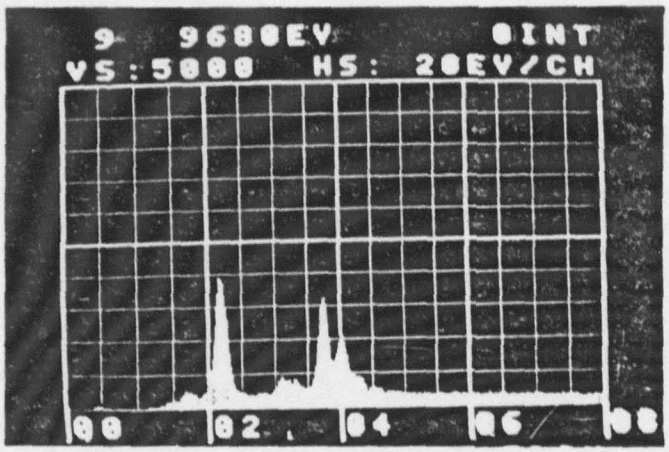
Fig. 8 Mass spectra of laser evaporated beams.

section of the clusters, namely $(N)^{2/3}$ where N is the number of atoms in the cluster. Applying these correction factors, the intensity ratios for clusters (m/e) from 360 to 400), Hg (Hg^+ and Hg^{++}), Te^+ and Cd^+ are approximately 40:20:1:1 for the lower laser power case and 500:100:1:1 for the high laser power case, respectively. Bearing in mind that there are at least 3 atoms per cluster, therefore the actual ratio of clustered atoms to free single atoms is even higher. Cluster formation during laser evaporation was also observed in other previous works,[4] but none had shown this kind of dominance.

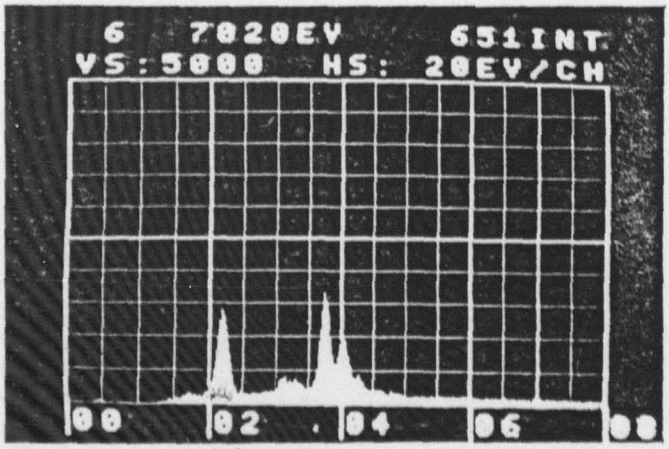
EDAX analysis of the film and the source material after irradiation with high power laser pulses are shown in Fig. 9. Comparison shows that there is some loss in Hg, but the Cd/Te ratio remains virtually the same.

To determine whether Hg loss is a result of high substrate temperature or is due to Hg deficient evaporants, we deposited two films under the same laser condition but different substrate temperature. One was at 120°C and the other at room temperature. Results indicate same Hg content in both cases. We then conclude that the Hg loss occurs in the evaporant beam.

The above observations allow us to reach the following conclusions regarding the present evaporation scheme:



SOURCE



THIN FILM

Hg Cd Te

Fig. 9 EDAX analysis results.

(1) Under the present condition, CdTe was evaporated congruently but HgTe suffers the loss of Hg.

(2) Unlike the thermal evaporization where CdTe decomposes into Cd and Te_2:

$$CdTe \rightarrow Cd + 1/2\ Te_2$$

the surface temperature during laser irradiation is much higher that the molecular compound dissociates directly into atoms

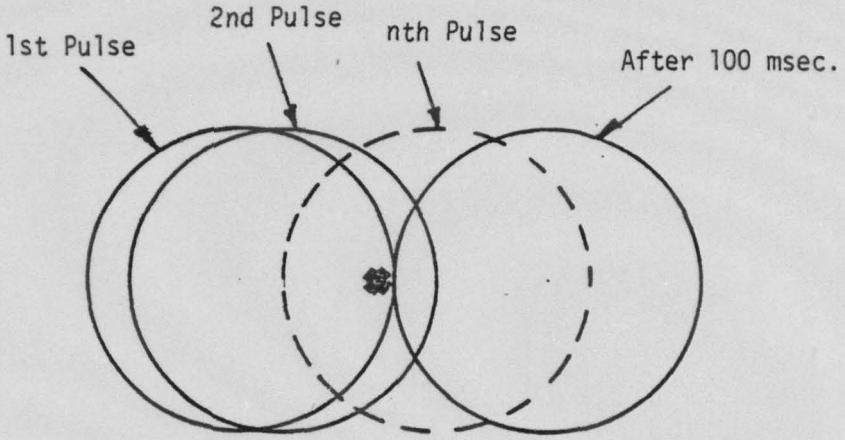
$$CdTe \rightarrow Cd + Te$$

(3) Previous studies in the similar area showed that the laser evaporated species have a large kinetic energy of a few eV.[5] In order for the evaporants to adhere to the substrate, it will be necessary to transfer all its kinetic energy to the substrate in a single collision. The efficiency is very low for atomic projectile but quite plausible for large clusters. When a cluster, consisting of N atoms, impinges the surface, the impact energy can be redistributed into its (3N-6) vibrational modes to promote surface adhesion. Atomic projectile does not have this property. Therefore, we can reason that the resulting film is

a result of cluster deposition. Since we have shown that the evaporant is rich in Hg, atomic, therefore the film will be Hg deficient.

(4) Obviously, the key to congruent evaporation is to reduce the atomic Hg generation. The answer lies in the inadequate scanning rate in the present setup. According to the description of thermal evaporation by Farrow, Hg atoms first diffuse out to the bulk surface and then leave the surface. This process is slow. "Blowing off" clusters from source surface by laser pulse takes a short time. Therefore, we would like to reduce the heating time so short that cluster formation takes place without Hg loss.

Although the pulse width is about 10^{-7}, the surface actually experiences a much longer heating time in the current setup due to slow scanning. For example, the scan rate is 5 sec/turn or 0.2 cm/sec, the focal point is about 0.02 cm in diameter and the pulse frequency is 5000 Hz therefore as many as 500 pulses can overlap. The situation is exampled in Fig. 10. During the onset of the first laser pulse, the point "x" on the source surface near the edge of the focal spot absorbs some radiation energy and raises its temperature. When the second pulse strikes 2×10^{-4} sec later, the location of the focal spot has



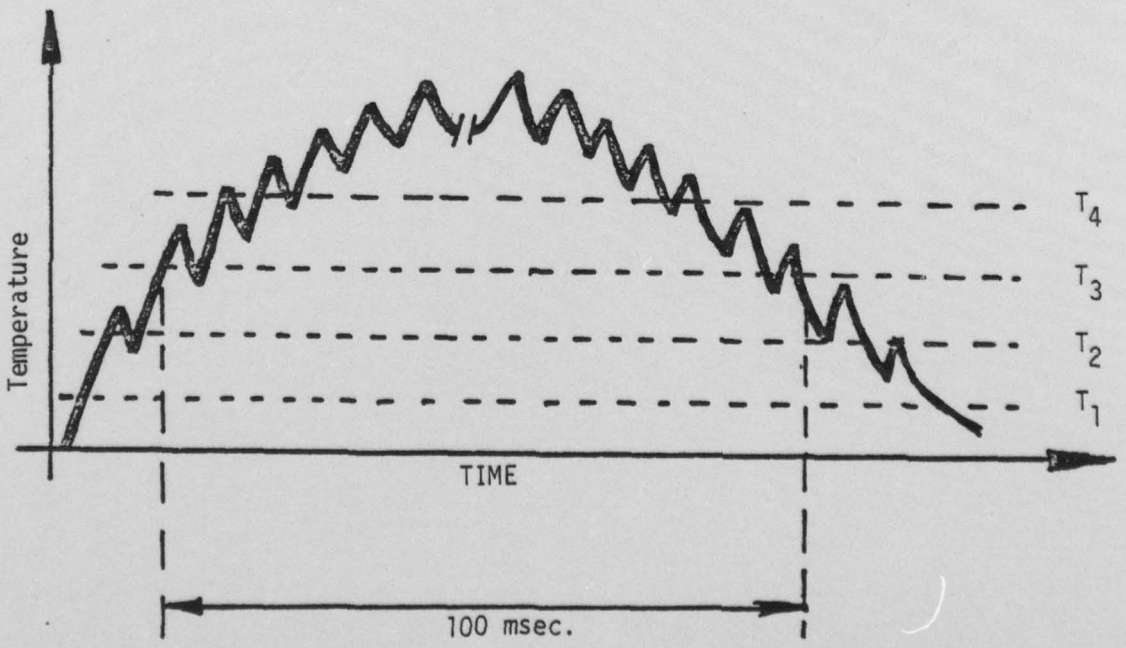


Fig. 10 Surface temperature vs time.

only moved 0.4 x 10^{-4} cm. HgCdTe is a very poor thermal conductor, 2 x 10^{-4} sec is not long enough for the surface to relax to its original temperature. Therefore, the surface temperature raises again to a higher value. This process repeats until about 100 msec later when the laser spot moves at least 0.02 cm away from the initial hit. Consequently, the time dependence of the surface temperature at this location takes the form illustrated in Fig. 10b. Therefore, because of the slow scan, the surface is effectively heated up by long (100 msec) pulses instead a few 100 nsec if there was no overlapping. The slow heating and cooling is responsible for Hg loss.

In conclusion, we can describe the overall picture in the following picture shown in Fig. 10b:

The time dependence of the surface temperature can be divided into four regions. When the surface temperature is higher than T_1 and the duration is long enough for Hg outdiffusion to the surface, Hg loss takes place. At higher temperature (T_2), CdTe decomposes congruently into atoms and leaves the surface. Cluster formation takes place at even higher temperature (T_3). Finally, when the surface temperature exceeds T_4 in a short time, molten globules can be ejected.

3.0 FUTURE PLANS

Our future plans are:

(1) Modify the system by installing the liquid nitrogen cold shroud, and the sample loading air lock. These parts have just been completed by our machine shop.

(2) We have ordered a x-y optical scanner and two single motion scanners, their deliveries are scheduled for early April. The x-y scanner will be used for in situ annealing and the single motion scanners will be used for scanning over the source materials. They will be installed and aligned.

(3) After the above work is completed, we will start the co-evaporation of HgTe and CdTe and in situ annealing studies.

(4) We will try to establish a thin film characterization routine, both electrically and metalurgically.

(5) We will carry on the furnace annealing study on the as-grown films.

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