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GROWTH OF HgCdTe BY MODIFIED MOLECULAR BEAM EPITAXY

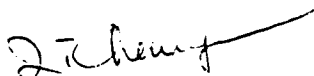
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ZnO films can be formed by evaporating from ZnO powder pellets with a pulsed CO₂ laser ($\lambda = 10.6 \mu\text{m}$). Films from 0.1 to 1.0 μm thick were deposited on various substrates in a wide range of temperatures. At substrate temperatures above 250°C, the deposited films are colorless and transparent. The surface is smooth with no discernable features, even under 1000x magnification. The films are highly oriented along the C-axis. X-ray diffraction patterns indicate a single (0001) peak with a half width (2θ) about 0.3-0.35°. This is comparable to the ZnO films deposited by the state-of-the-art magnetron sputtering technique.

λ

micrometers

2θ

degrees

λ

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SUMMARY

A novel technique of Laser Assisted Deposition and Annealing (LADA) of thin films has been developed through the technical effort of this program. It has been demonstrated that films of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and ZnO can be formed by the LADA technique. Their results will be presented separately.

$\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ films have specular surface morphology and sharp interfaces with a cross diffusion region of 1500 Å. Electron mobility at 77K as high as $19,000 \text{ cm}^2/\text{V-s}$ was observed. Secondary Ion Mass Spectroscopy (SIMS) profile analysis indicated large accumulation of impurities at the interface and near the surface. MIS devices were fabricated and their results will be presented.

ZnO films can be formed by evaporating from ZnO powder pellets with a pulsed CO_2 laser ($\lambda = 10.6 \mu\text{m}$). Films from 0.1 to $1.0 \mu\text{m}$ thick were deposited on various substrates in a wide range of temperatures. At substrate temperatures above 250°C , the deposited films are colorless and transparent. The surface is smooth with no discernable features, even under 1000x magnification. The films are highly oriented along the C-axis. X-ray diffraction patterns indicate a single (0001) peak with a half width (2θ) about $0.3\text{-}0.35^\circ$. This is comparable to the ZnO films deposited by the state-of-the-art magnetron sputtering technique.



1.0 INTRODUCTION

1.1 Program Objectives

The main objective of this program is to explore and develop a novel thin film deposition technique, i.e., Laser Assisted Deposition and Annealing (LADA). It will be demonstrated for two materials: $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and ZnO .

1.2 Overall Approach

The program started in February 1979. The work performed during the first phase (1979-1981) exclusively involved $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$.

The second phase started in May 1980. Deposition of ZnO thin film by laser evaporation was added to the program as a new task. A separate LADA system has been built to deposit ZnO in order to prevent intercontamination between these two materials. In this report, the progress on both material developments will be reported.

1.3 Accomplishments

Accomplishments in this period are:

1.3.1 $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

1. Improvement in the electrical properties. The Hall electron mobility values at 77K have been improved to $24,000 \text{ cm}^2/\text{V-s}$ for $x = 0.2$ composition and $19,000 \text{ cm}^2/\text{V-s}$ for $x = 0.34$ composition. The carrier concentration at 77K have been reduced to the range of $3-5 \times 10^{16} \text{ cm}^{-3}$.
2. Improvements in film surface morphology. We have completely eliminated the spitting from target material. Films grown on $\langle 111 \rangle \text{A CdTe}$ substrates are specular without any discernable features.



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3. Demonstration of MIS devices. We have demonstrated MIS devices fabricated on $x = 0.34$ LADA HgCdTe films.
4. SIMS profiling analysis. SIMS technique was used to profile the film composition and identify the impurities. Results indicate:
 - a. A sharp film-substrate interface with an interdiffusion region of less than 2000 Å.
 - b. High contamination level for a number of impurities accumulated at the film/substrate interface and near the surface.

1.3.2 ZnO

1. A new LADA system specifically devoted for ZnO thin film deposition has been assembled and is in routine operation.
2. We have reproduced a number of experiments to demonstrate the feasibility of depositing of ZnO film on various substrates by LADA. The experiments were carried out in a wide range of oxygen partial pressures (from a oxygen-free vacuum to 10^{-4} torr of oxygen pressure) and substrate temperatures (25°C-400°C).
3. The films deposited to date range from 2000 Å to 1 µm thick. They have been characterized by ellipsometry, x-ray diffraction and optical transmission.
4. Two types of ZnO powder pellets have been used as the target source. One is commercial hot-pressed ZnO pellets commonly used as a sputtering target and the other is in-house cold pressed ZnO pellets. These two sources yield comparable films. ZnO₂ was also tried as an alternate source.



2.0 TECHNICAL INFORMATION

This section is divided into two parts: $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and ZnO .

2.1 Thin Films of HgCdTe

In semi-annual report No. 4, we reported the growth of stoichiometric n-type films on CdTe substrates. For a $x = 0.34$ composition material after post-annealing, the typical carrier concentration at 77K was in the range of $1-2 \times 10^{17} \text{ cm}^{-3}$ and the electron Hall mobility of $3500-6500 \text{ cm}^2/\text{V-s}$. The surface of these films was rough and grainy with the presence of micron size particles spitted from the target material. Since then, we have made substantial improvements in both areas. In addition, we have also demonstrated MIS devices and used SIMS analysis for compositional profiling and impurity identification. These results will be discussed in the following sections.

2.1.1 Improvements in Surface Morphology

Spitting of the target material due to the absorption of excessive laser energy has always been a major problem in the laser evaporation and deposition process. Compared to other materials, such as ZnO or CdTe , HgCdTe is more vulnerable to this phenomenon. Small particles of a few micron in dimension were ejected from the target. The compositions of the target source, the smooth area of the deposited film and the spitting particles were examined by scanning auger microscopy and were found to be the same. Their density depends on the laser power level. At $5 \times 10^7 \text{ W/cm}^2$ radiation power density, they could cover about 70% of the film area with an average size of $3 \mu\text{m}$. At lower power density of $5 \times 10^6 \text{ W/cm}^2$, the density was greatly reduced. The average size of these particles was about $1 \mu\text{m}$.

Recently, we have further reduced the laser power density by defocusing the beam. At the same time, the scanning rate were adjusted in order to maintain a condition for congruent evaporation and a reasonable deposition rate. We discovered that at a power density of $7 \times 10^5 \text{ W/cm}^2$, the



spitting phenomenon could be completely eliminated. Figure 1 shows the appearance of a film deposited under this condition. The surface is specular and featureless. Along the lower edge of the substrate, there is a grain which is off the (111) orientation by about 5°. Film grown over this region shows rough surfaces.

2.1.2 Improvement in Electrical Properties

With the improvement in film crystallinity, their electrical properties also improved. As-deposited films under the old laser conditions had very low electron mobility at 77K. A post-annealing treatment in Hg over-pressure at 210°C could increase the mobility of a $x = 0.3$ material to the range of 6000-8000 $\text{cm}^2/\text{V-s}$ at 77K with a carrier concentration of $1-2 \times 10^{17} \text{ cm}^{-3}$. Films grown under the new laser conditions exhibit much better electrical properties. Typical electron mobility for an as-grown $x = 0.3$ film at 77K was between 7000-8000 $\text{cm}^2/\text{V-s}$. After a similar post annealing treatment, the mobility values increased to 10,000-13,500 $\text{cm}^2/\text{V-s}$. In one case, values as high as 19,000 $\text{cm}^2/\text{V-s}$ was observed. The carrier concentrations were between $3 \times 10^{16} \text{ cm}^{-3}$ to $6 \times 10^{16} \text{ cm}^{-3}$. Figure 2 shows the temperature dependence of Hall concentration and mobility of a $x = 0.34$ film measured from 5K to 300K. The mobility increased from 3000 $\text{cm}^2/\text{V-s}$ at 300K to a peak value of 17,000 $\text{cm}^2/\text{V-s}$ at 34K and then leveled off slowly at 15,000 $\text{cm}^2/\text{V-s}$ at 5K. Carrier concentration at 300K was $7.5 \times 10^{16} \text{ cm}^{-3}$. It decreased slowly with temperature but only to a value of $4.4 \times 10^{16} \text{ cm}^{-3}$.

2.1.3 MIS Devices

MIS devices were fabricated on a film with a composition of $x = 0.34$. The film was about 5 μm thick. It was post annealed at 410°C for four hours. Hall measurement showed it to be n-type with $N_D = 1.2 \times 10^{16} \text{ cm}^{-3}$ at 77K. MIS capacitors were made by using a layer of native oxide with an overlayer of E-beam evaporated ZnS as insulator covered with 3 mm square metal dots.



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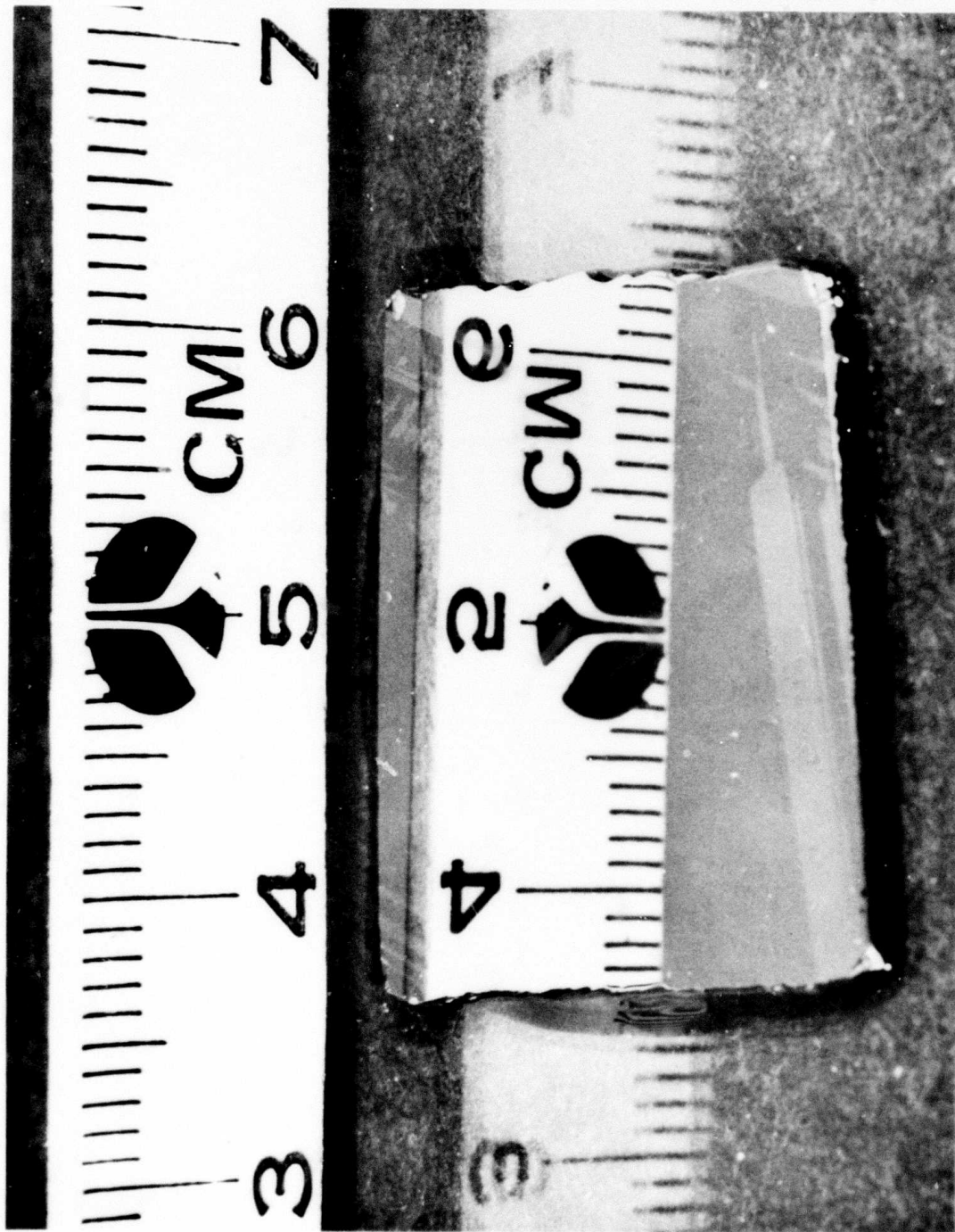


Fig. 1 Morphology of a $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ film.

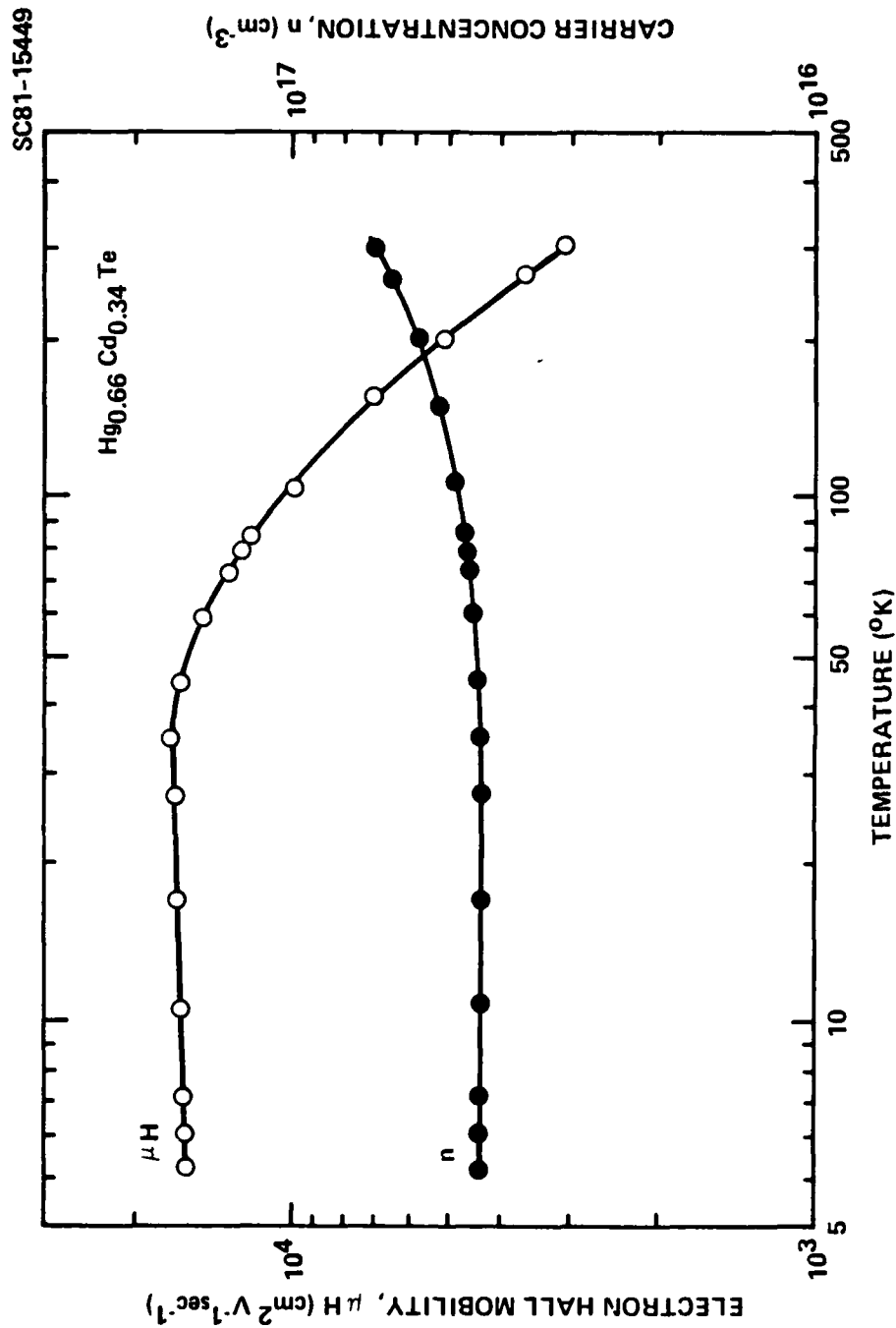


Fig. 2 Temperature dependence of mobility and carrier concentration.



Relatively uniform MIS capacitance-voltage (1 MHz) curves were obtained on all ten devices. Results are shown in Fig. 3. The data showed flat-band voltage at $V_{FB} = -4.5 \pm 0.1$ V, carrier concentration of $N_D = 7 \times 10^{15} \text{ cm}^{-3}$ and a hysteresis of 0.2 V. All measurements were performed at 77K.

2.1.4 HgCdTe on Sapphire Substrate

In previous experiments, we tried to deposit HgCdTe directly onto bare surface of c-axis oriented sapphire substrates. This structure could not survive the necessary post-annealing treatment. After annealing in a closed ampoule containing excess Hg pressure at 410°C, the film cracked and in some areas flaked off. This problem can be solved by depositing a HgCdTe onto a CdTe buffer layer about 1.5 μm thick which was deposited onto the sapphire at 350°C by the LADA technique. This sandwiched structure of HgCdTe/CdTe/sapphire can be annealed at high temperature without structural degradation. A transmission spectrum of such a film ($x = 0.5$, $d = 10 \mu\text{m}$) is shown in Fig. 4. The source used in this run was a pressed pellet of HgTe:CdTe (1:1) mixture which always resulted in films of more inferior electrical properties than those deposited by using a high purity bulk crystal target. The film is n-type with $N_D = 5 \times 10^{16} \text{ cm}^{-3}$ and $\mu_e = 1700 \text{ cm}^2/\text{V-s}$ at 77K.

We have modified our LADA system by adding the capability of in-situ depositing the CdTe buffer layer by laser evaporation followed immediately by the HgCdTe deposition without opening the vacuum. This should minimize the interfacial contamination. More research on the growth of HgCdTe on foreign substrates will be carried out via this approach.

2.1.5 Compositional and Impurity Profiling

Secondary ion mass spectroscopy (SIMS) was used to analyze the $\text{Hg}_{0.6}\text{Cd}_{0.3}\text{Te}$ film in order to determine:

1. The compositional uniformity of the film throughout the entire depth.



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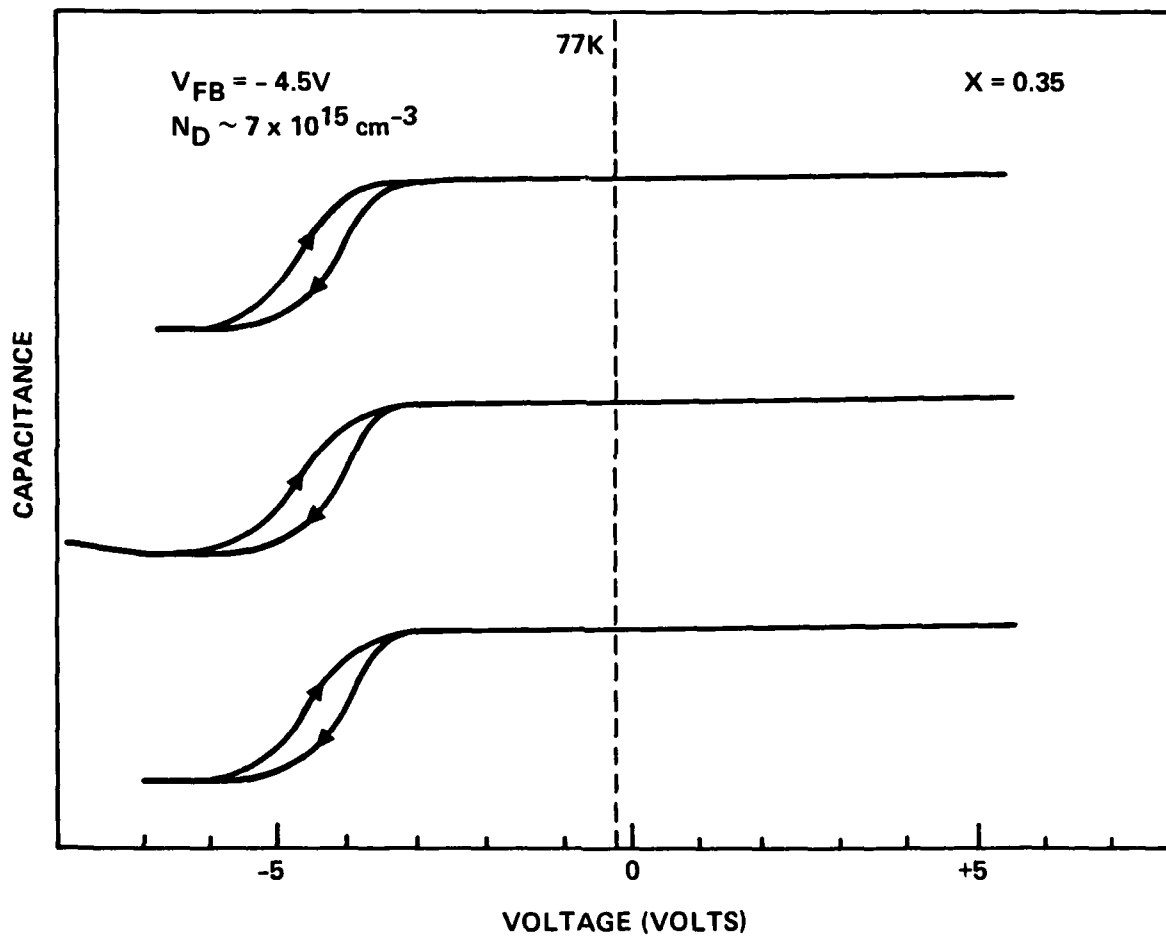


Fig. 3 Capacitance - voltage curves of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ MIS devices.



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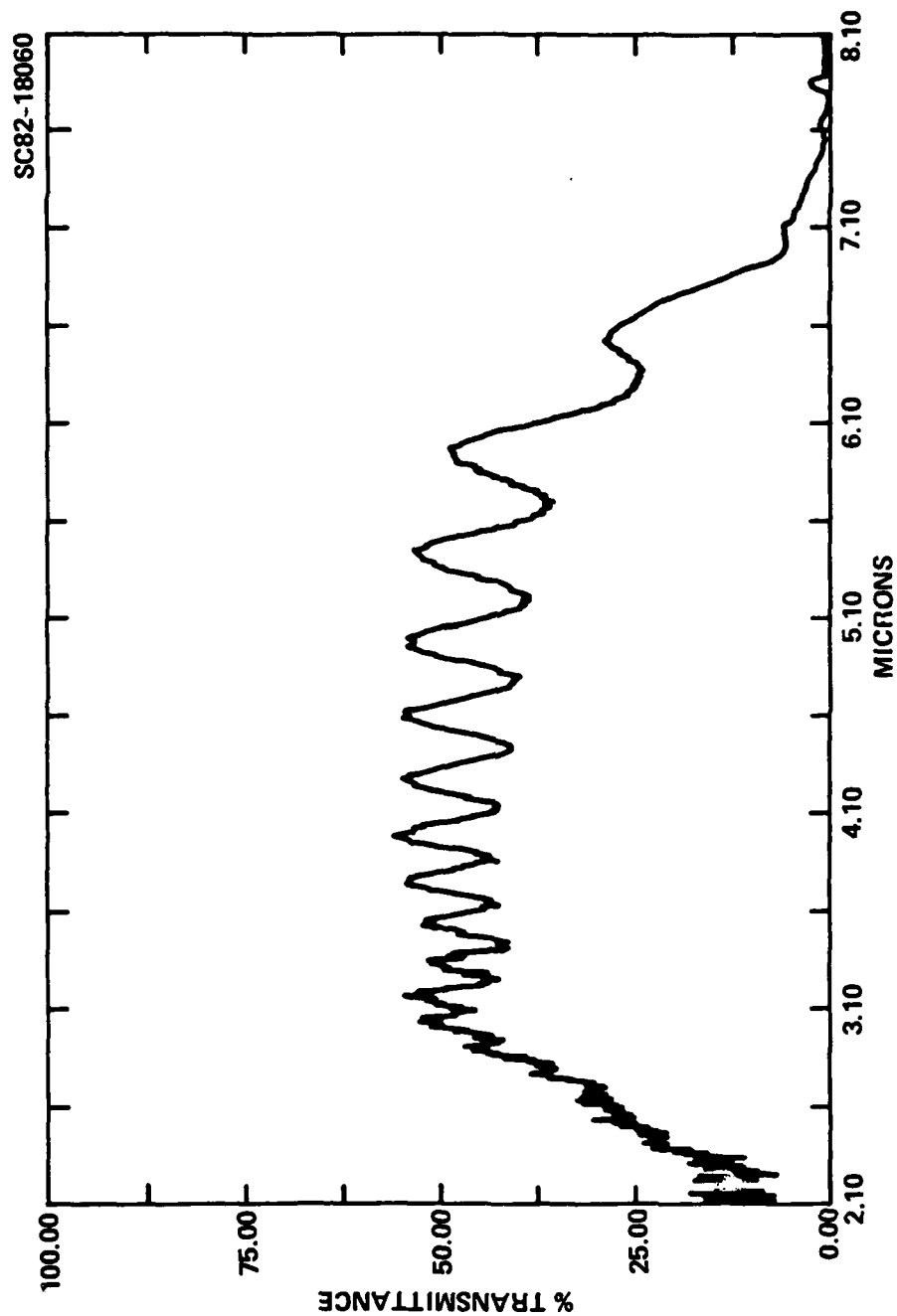


Fig. 4 Transmission spectrum of HgCdTe on sapphire.



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2. The width of the cross diffusion region at the interface.
3. The impurities and their distribution profiles.

The depth resolution is about 500 Å. Figure 5 shows the distribution profile of Hg, Cd and Te, with excellent compositional uniformity throughout the entire film. The transition region at the HgCdTe/CdTe interface is very sharp due to the low growth temperature. The width of the cross diffusion region is less than 1500 Å.

Both the target $\text{Hg}_{0.6}\text{Cd}_{0.3}\text{Te}$ bulk crystal as well as the thin film were analyzed by SIMS for a number of impurities such as: Li, Na, Al, Si, Fe and B. In the bulk crystal, the contamination level of these impurities are too low to be detected. Therefore, the contamination must come either from the substrate or from the deposition ambient. Figure 6 shows their distribution profiles. All impurity profile show accumulation at the interface and near the surface with a minimum near the center of the film. Impurity distributions were also profiled for a thicker film (10 µm thick) shown in Fig. 7. Same trend showed with even more promising build-ups at the interface and near the surface. The most likely source is the impurities initially present on the substrate surface as a result of handling and exposure to the ambient. During the deposition, the film surface and the film/substrate interface acted as getters, toward which the impurities diffused. Therefore, it is essential to clean the substrate surface in-situ prior to deposition. Configuration changes are being made to the apparatus to carry out this task.

2.1.6 The Problem With the Heated Mirror, Its Effect on Film Properties and Solutions

One difficulty in obtaining thick films by LADA technique involves the condensation of evaporants onto the vacuum chamber window through which the laser beam transmits. Condensation gradually reduces the transmission of the laser beam (i.e., the evaporation rate) until the window becomes



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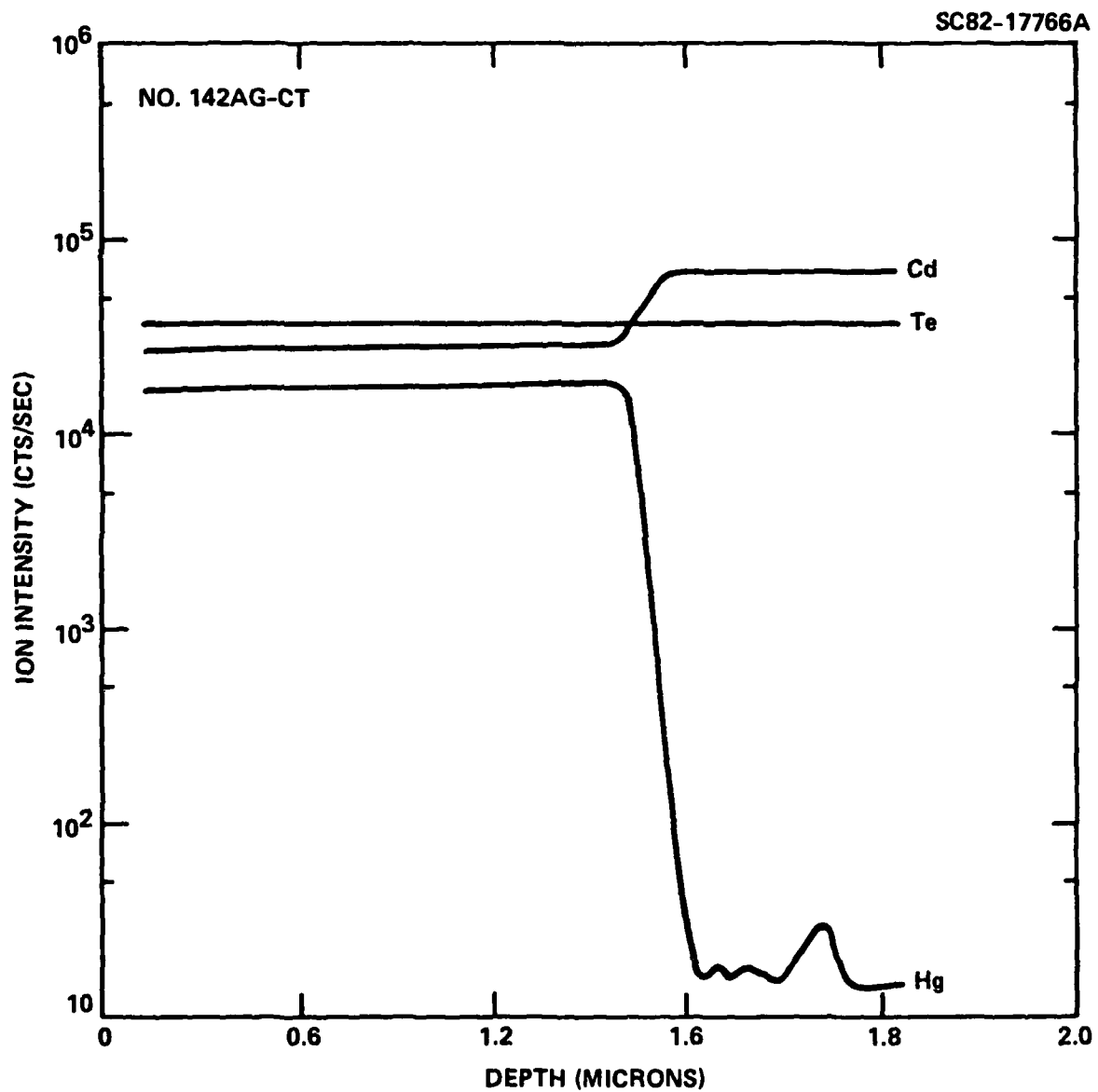


Fig. 5 Composition profile.

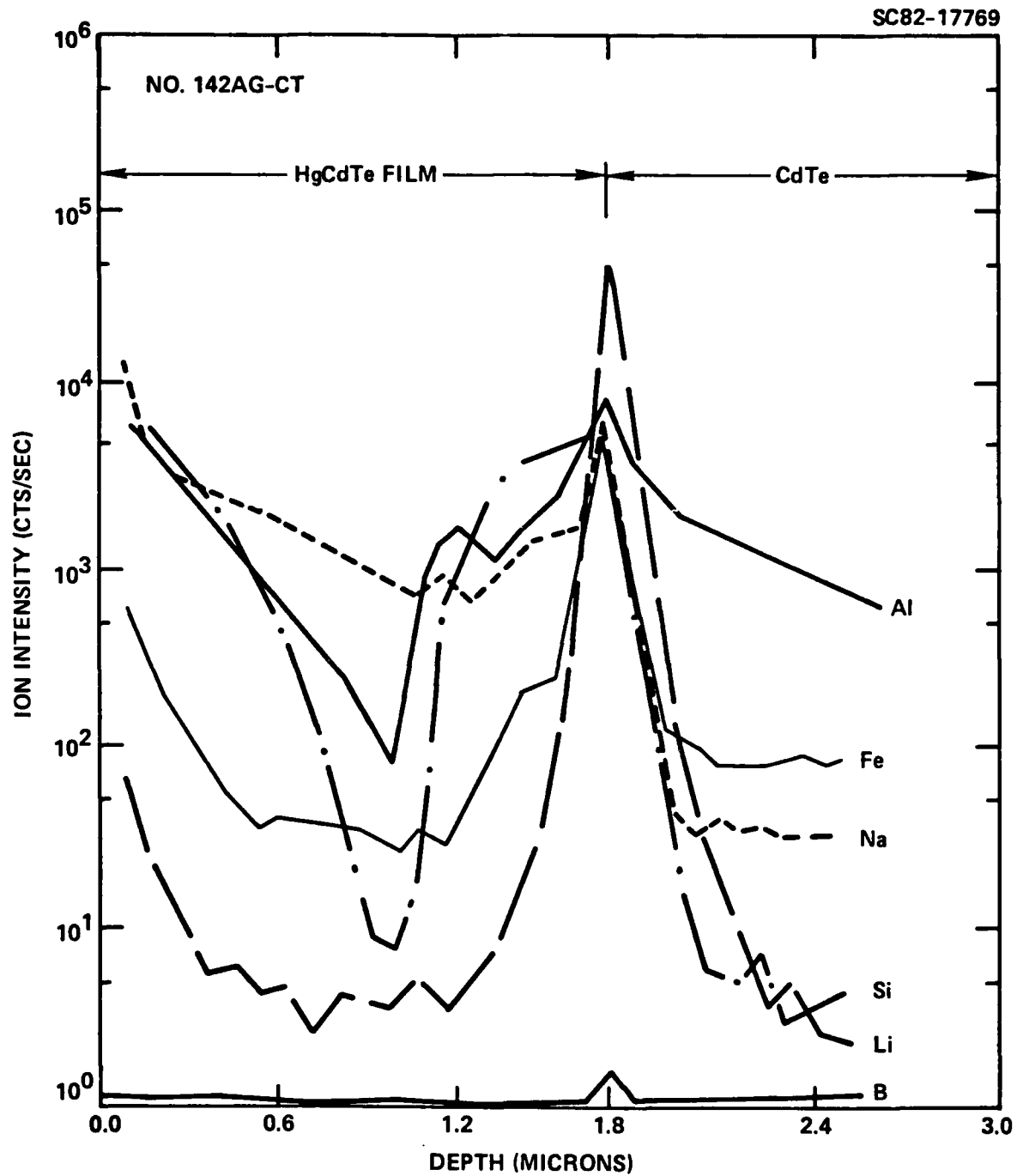


Fig. 6 Impurity profile of a 2 μm thick Hg_{0.7}Cd_{0.3}Te film.



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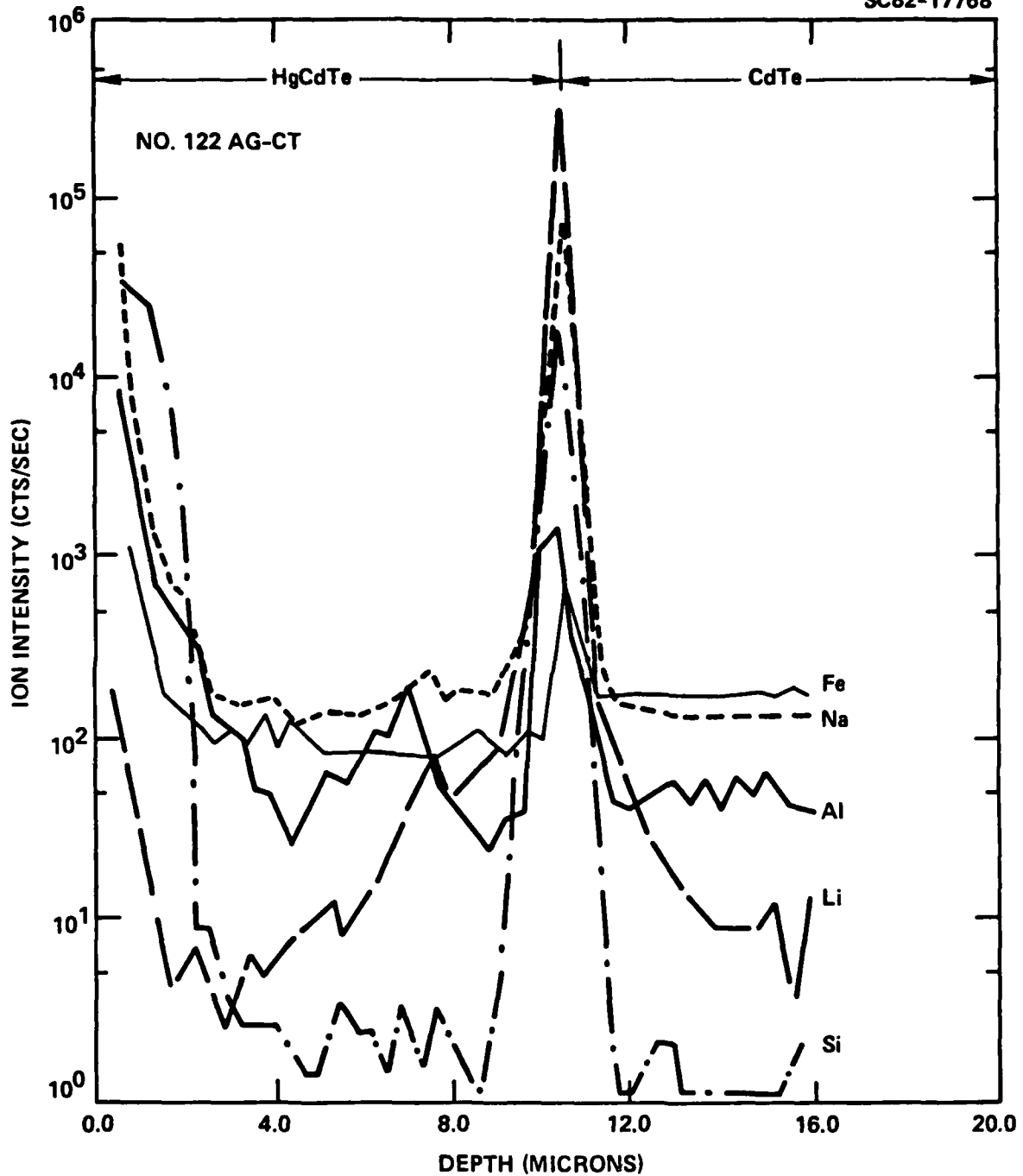


Fig. 7 Impurity profile of a 10 μ m thick $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$ film.



completely opaque. Therefore, constant deposition rate cannot be maintained. To circumvent this problem, we first installed a light baffle to eliminate the line of sight between the target and the window. A first surface mirror, mounted on a tantalum wire heater, was installed inside the vacuum chamber to reflect the laser beam onto the target. The mirror coating consisted of 2500 Å aluminum covered with 2500 Å SiO. Upon heating the mirror to 210°C or higher, the evaporants from the HgCdTe target did not stick to the mirror. Therefore, the mirror remained reflective all the time and thick films could be deposited.

However, there are some drawbacks. First, the SiO/aluminum coated window can only be heated to a maximum temperature of 300°C. At this temperature, evaporants from HgCdTe do not condense but the evaporants from CdTe still does. Therefore options such as depositing in-situ CdTe buffer layers cannot be carried out. Second, HgCdTe evaporants can bounce off the hot mirror surface onto the window. Although this is a secondary effect, nevertheless, over a long period of time the window will eventually become opaque. This limits the thickness to be less than 12 µm. The third effect is perhaps the most important of all. Under the experimental conditions, the laser radiation can cause damage to the mirror by melting and evaporating the coating material. This is evident by examining the mirror under the microscope. SIMS analysis showed high levels of Al and Si. Since both impurities are donors, their incorporation onto the HgCdTe film can probably explain why these films cannot be annealed into p-type. To solve this problem, we have changed the configuration of the apparatus by replacing the mirror with a heated sapphire window through which the laser beam transmits. The sapphire window will be heated to 500°C to avoid the condensation of not only HgCdTe but also CdTe. Therefore, both CdTe and HgCdTe can be deposited at a constant rate.



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2.2 Thin Films of ZnO

ZnO thin films were deposited by the LADA technique in a separate apparatus. The new LADA system was designed and assembled in-house and became operational in February. The basic principle is similar to the deposition of HgCdTe films, namely to induce congruent evaporation by pulsed laser heating. In early experiments, we consistently obtained films rich in metallic zinc. After trying different laser conditions such as: power, pulse rate and scanning rate, we discovered the existence of a window of parameters within which ZnO films could be deposited. These films have surprisingly good quality. Within another month's effort of optimization, their metallurgical and optical qualities became comparable to those deposited by magnetron sputtering. The success of these early experiments suggests the great potential of LADA as a unique technique for depositing ZnO films and possibly films of other dielectric materials. This report gives an account of experimental approach, the film qualities as characterized by x-ray diffraction, ellipsometry and optical transmission.

2.2.1 The Apparatus for Depositing ZnO

The apparatus is similar to the one described in earlier reports for depositing $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ films, as shown in Fig. 8. The main vacuum chamber is an all stainless steel structure with copper gaskets. Its interior is lined with liquid nitrogen shrouds for trapping the condensable ambient gas such as water and CO_2 . The system is pumped by a Perkin-Elmer 8 inch diameter cryopump. Ultimate pressure in the chamber is in the low 10^{-8} torr range. Reactive gas can be introduced through a variable leak. Partial pressure can be varied from 10^{-6} torr to 10^{-3} torr.

The substrate holder is made of molybdenum for cleanliness. Its temperature can be regulated at higher than 500°C . The target is mounted on a rotatable platform. The substrate-target distance is variable, typically ~ 8 cm.



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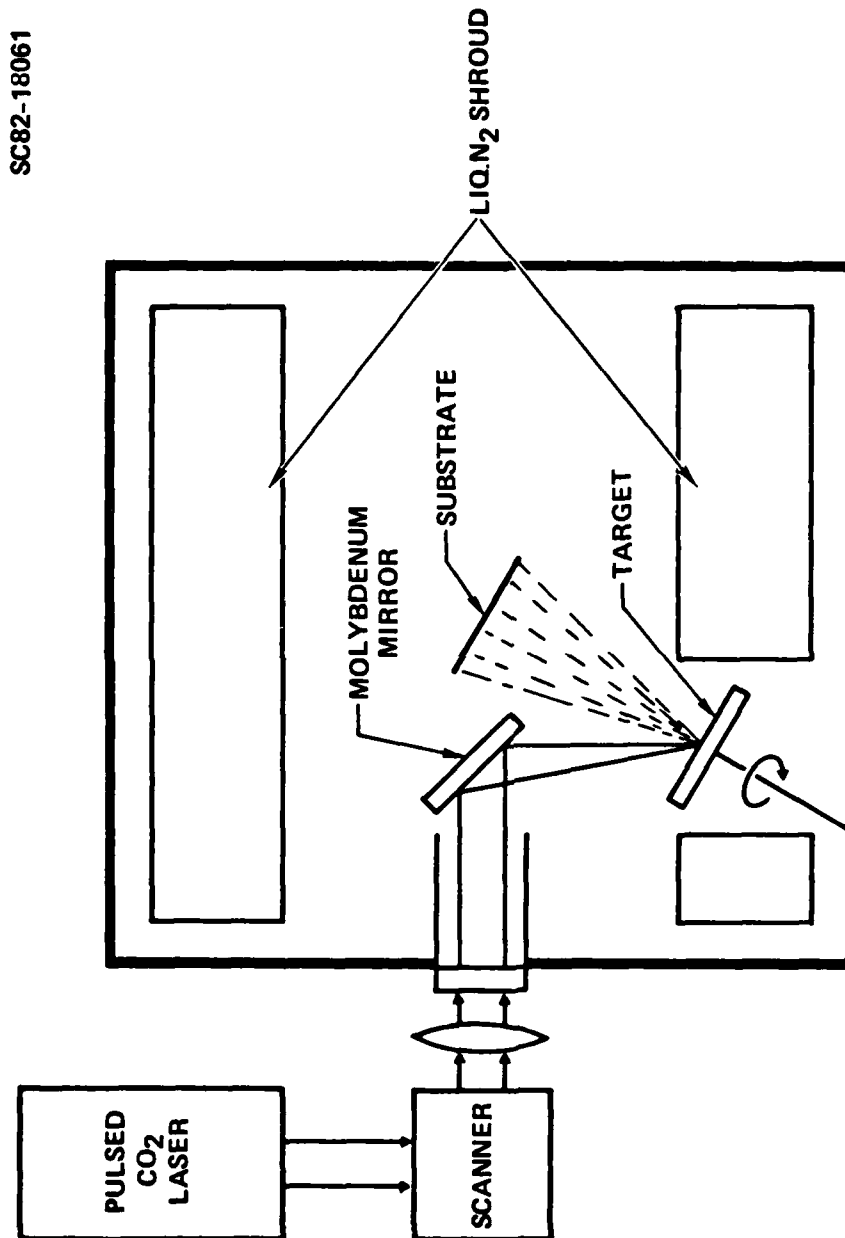


Fig. 8 LADA apparatus for depositing ZnO films.



The main power for evaporation derives from a CO_2 laser. It can be operated either in cw mode or pulsed mode. Pulse duration and frequency are also variable. The maximum output is 80 W. The 10.6 micron wavelength radiation is focused onto the target via a ZnSe lens, ZnSe vacuum window and a polished molybdenum mirror. The beam can scan over the target with a galvanometric mirror scanner.

2.2.2 Target Materials

Two types of pressed powder pellets of ZnO were used. One is a hot pressed pellet available commercially as a sputtering target. The other is pellets of high purity ZnO powders cold-pressed at the Science Center under a pressure of 10 ton/cm². Films deposited from the two are of comparable quality. However, the home-pressed targets are more flexible especially for future counter doping experiments. The dopant (such as Li_2CO_3) can be premixed with ZnO powder to any desirable level.

The absorption of the 10.6 μ radiation is most important in determining the required power level. Figure 9 shows an IR transmission spectrum of a ZnO pellet. ZnO is transmissive at 10.6 μ with an absorptivity $\alpha \approx 20 \text{ cm}^{-1}$. The low absorptivity suggests the need of high laser power density and large number of pulses for pulse overlapping. The latter requirement has been discussed in an early report (Final Report of Phase 1). Overlapping pulses can heat up the ZnO surface in a stepwise fashion. The absorption at 10.6 μm can be aided by the free carriers generated by the sequential heating.

We also tried ZnO_2 as an alternative target source, since this material may absorb more 10.6 μm radiation than ZnO. ZnO_2 were synthesized by reacting ZnO with hydrogen peroxide. When it was irradiated with the 10.6 μm laser beam, it heated up rapidly, followed by decomposition by the release of a large amount of oxygen. Consequently, the pellet exploded to powder form.



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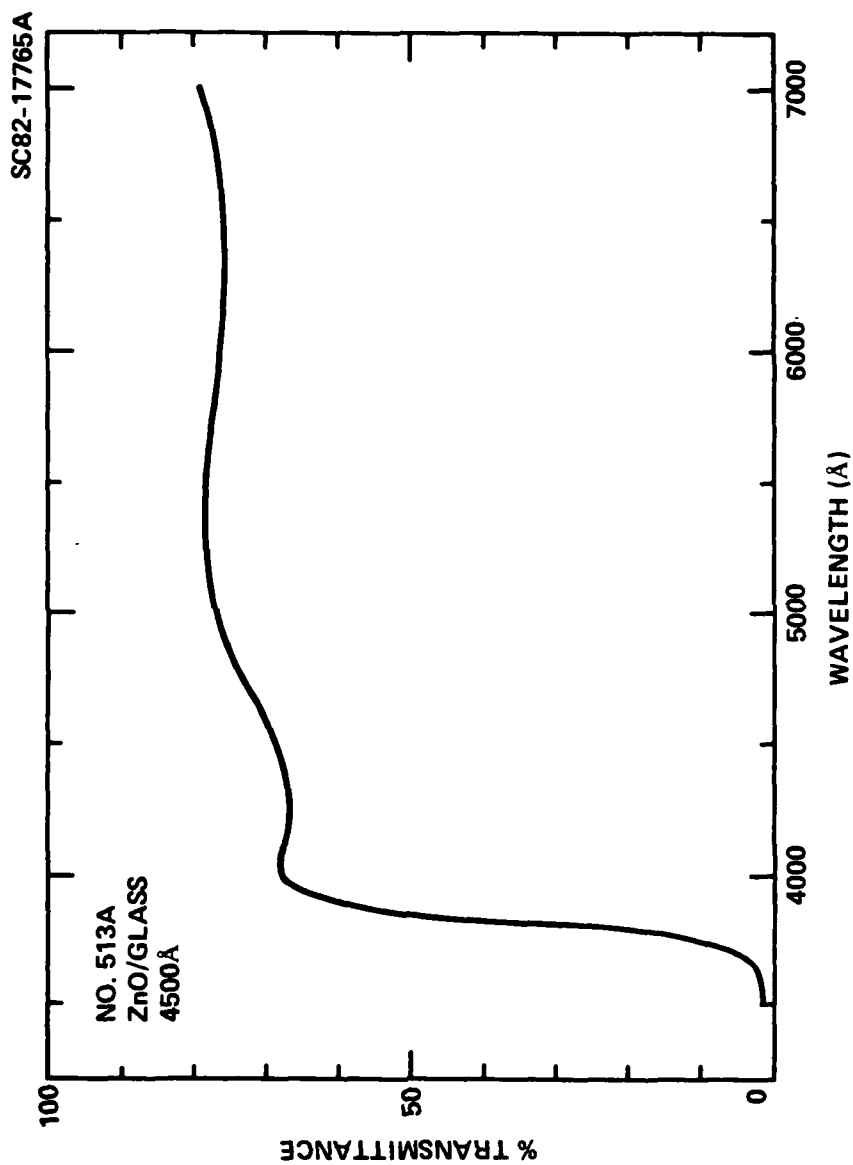


Fig. 9 IR transmission of ZnO.



2.2.3 Effect of Deposition Conditions

There are three kinds of existing techniques to deposit ZnO films. First is CVD either by chemical vapor transport or MO-CVD. This process generates ZnO film with good crystallinity. The disadvantages are the high substrate temperature and poor morphology. Surfaces are usually faceted and rough. Second technique is sputtering. Although ZnO films can be prepared by different forms of sputtering, the most promising is the magnetron sputtering. The ZnO films prepared this way are considered as the state-of-art. Substrate temperatures used in sputtering of ZnO are usually higher than 200°C, below which the films are sometimes amorphous. A high oxygen background pressure is often required during sputtering in order to maintain the film stoichiometry. The third technique involves the oxidation of thin films of zinc compounds such as ZnSe. The films usually have poor crystallinity. We should also point out that throughout an extensive literature, we could not find any work on direct evaporation of ZnO either by resistive heating or by E-beam heating. A possible reason is the decomposition and non-congruent evaporation of ZnO at elevated temperatures. LADA is actually a special form of thermal evaporation, we found that this technique can grow ZnO thin film under a wide range of experimental conditions.

2.2.3.1 Substrate Temperature

ZnO films can be obtained at any substrate temperature from 25°C to 500°C or higher! This result came as a surprise since it differs from all the techniques described earlier. The uniqueness can be attributed to the non-equilibrium evaporation generated by pulsed heating. A good fraction of the target probably evaporated as a ZnO molecule without decomposition. Transparent films were obtained at all substrate temperatures. Nevertheless, film deposited on a room temperature substrate has a slight yellowish shade, whereas on a hot substrate (400°C) the films are colorless and clear.



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2.2.3.2 Oxygen Partial Pressure

Just like the effect of substrate temperature, the effect of oxygen partial pressure during deposition is also quite unexpected. ZnO film can be obtained from hard vacuum (10^{-7} torr) to 10^{-4} torr or more oxygen partial pressures! This can also be due to the possible nondissociative molecular ZnO evaporation by pulsed laser heating.

2.2.3.3 Film Properties

ZnO films were deposited on a number of substrate materials including amorphous substrates (e.g., fused quartz, Corning glass 7059, SiO₂/Si, Au/Ti/Si) and crystalline substrates (e.g., <111> Si, <111> GaAs). Film thickness can be varied from 0.1 μ m to 1.0 μ m. Their surfaces are smooth, featureless with no discernable structures even under 1000X magnification. The films are very hard and their adhesion to the substrates are excellent.

Figure 10 shows an x-ray diffraction pattern from a ZnO powder sample. The three major peaks are all in the 30°-40° range (2 θ value). For surface acoustic wave device application, the (0002) or the c-axis orientation is the most ideal. Films deposited on substrates at room temperature show all three orientations. However, at higher substrate temperature (> 200°C), c-axis (or (0002)) is the only orientation for films deposited on any substrate, amorphous or crystalline. Therefore, the affordable growth temperature is lower than other techniques, likely, the strain due to thermal expansion mismatch between the ZnO and the substrate will also be reduced. Figure 11 shows an x-ray diffraction spectrum of a LADA ZnO film (2000 Å) deposition on quartz at 250°C. The full width at half maximum (FWHM) of the (0002) peak (2 θ value) is between 0.3° to 0.35°. On a c-axis cut sapphire substrate at 400°C, the FWHM of this peak is only 0.2°. These values compare favorably with the best magnetron sputtered ZnO films and natural crystalline zincite.

The index of refraction is another useful parameter to gauge the film quality. In addition, this value is also vital for optical devices



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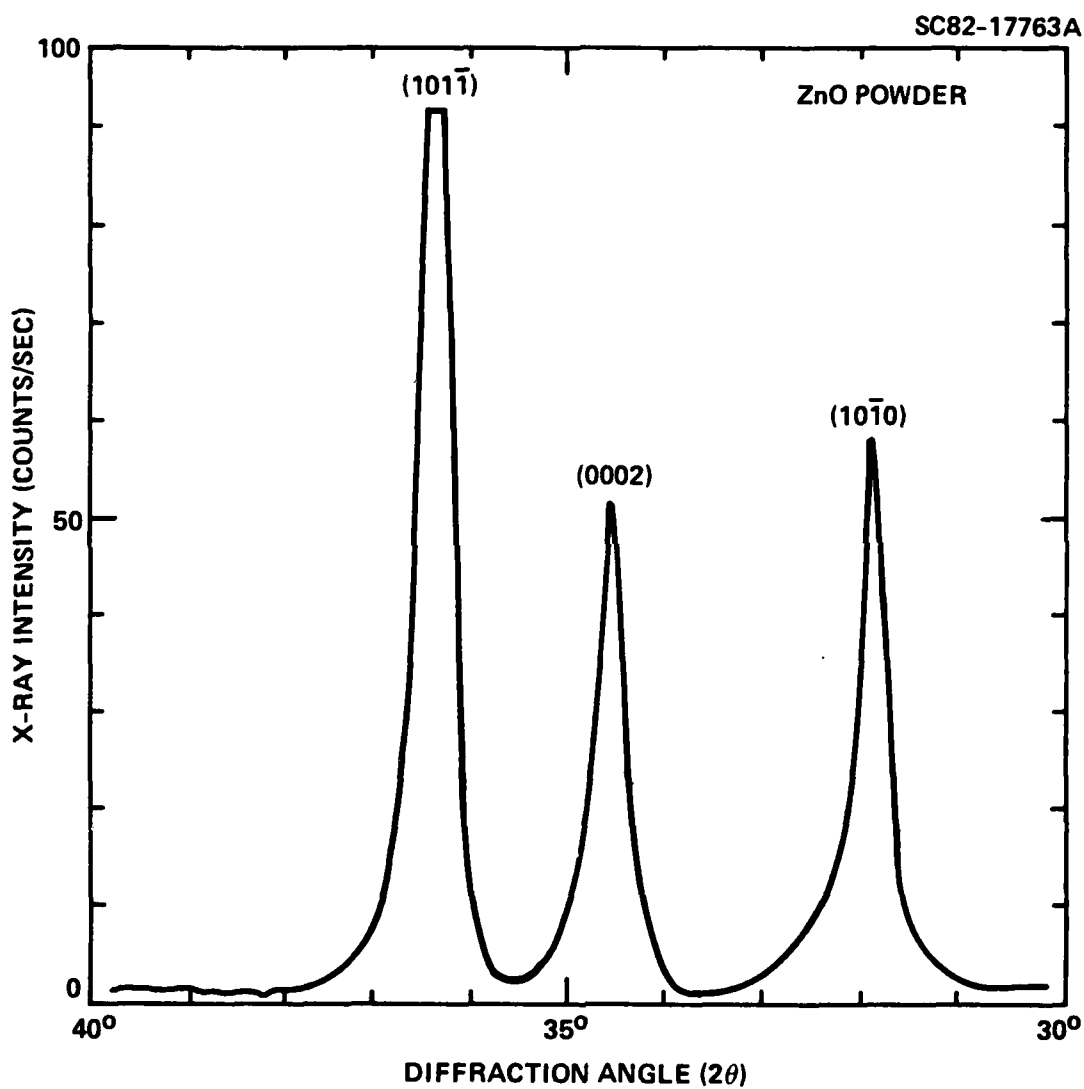


Fig. 10 X-ray diffraction spectrum of ZnO powders.

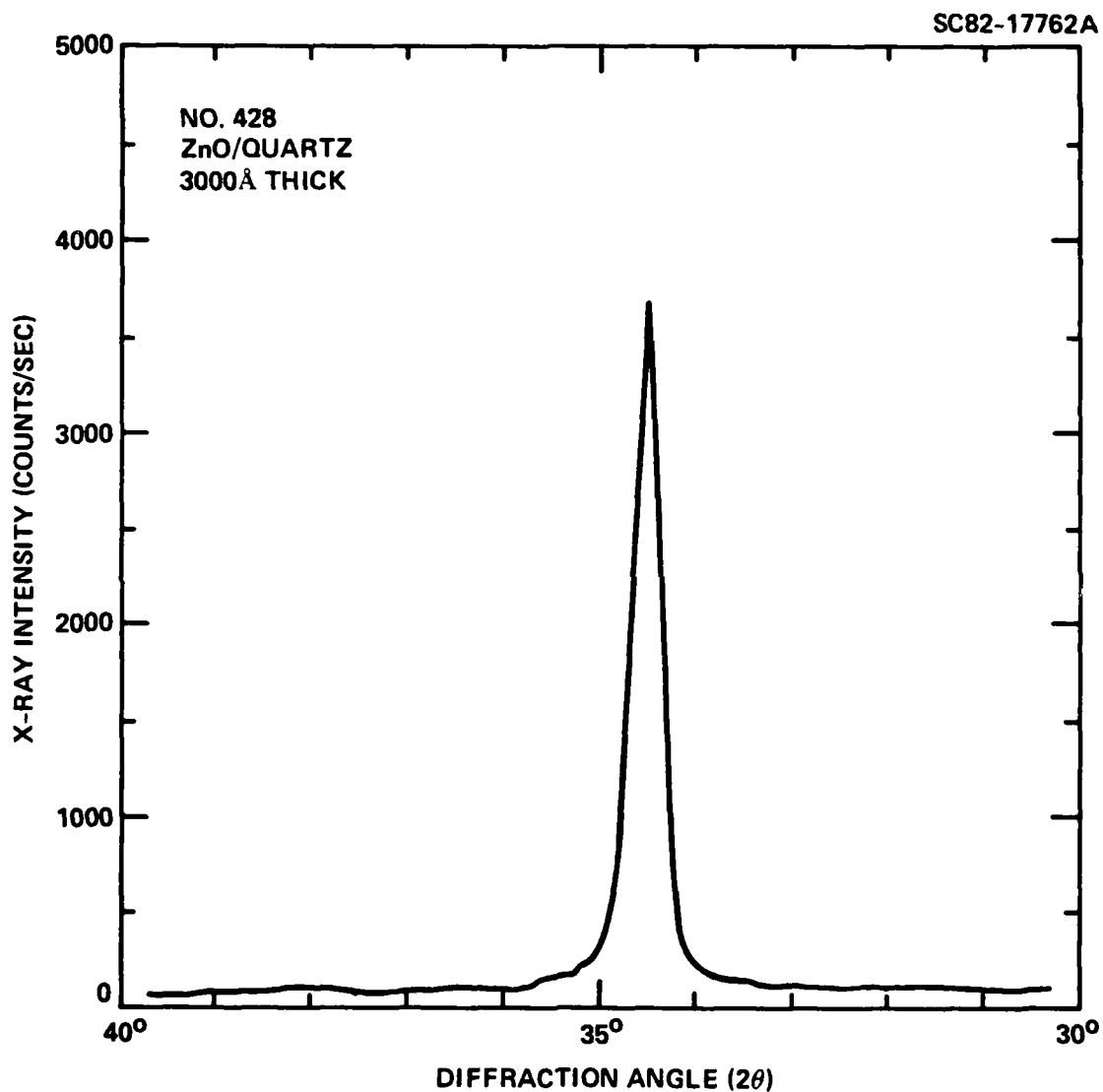


Fig. 11 X-ray diffraction spectrum of a ZnO film deposited on quartz.



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application, such as waveguides and AR coatings. The index of refraction was measured at 6328 Å wavelength using an ellipsometer. The values range from 1.93 to 2.0. They are considerably higher than the vapor transport CVD grown films and are comparable to the magnetron sputtered films. The refractive index of a bulk crystal ZnO is about 2.02. Closeness to the bulk value is indicative of a dense and highly oriented film.

Optical transmission spectra were also taken. The absorption edge was found to be very sharp at 380 nm corresponding to a 3.2 eV bandgap. The transmission spectra of some films showed the interference maxima and minima indicating good uniformity. An example is shown in Fig. 12.



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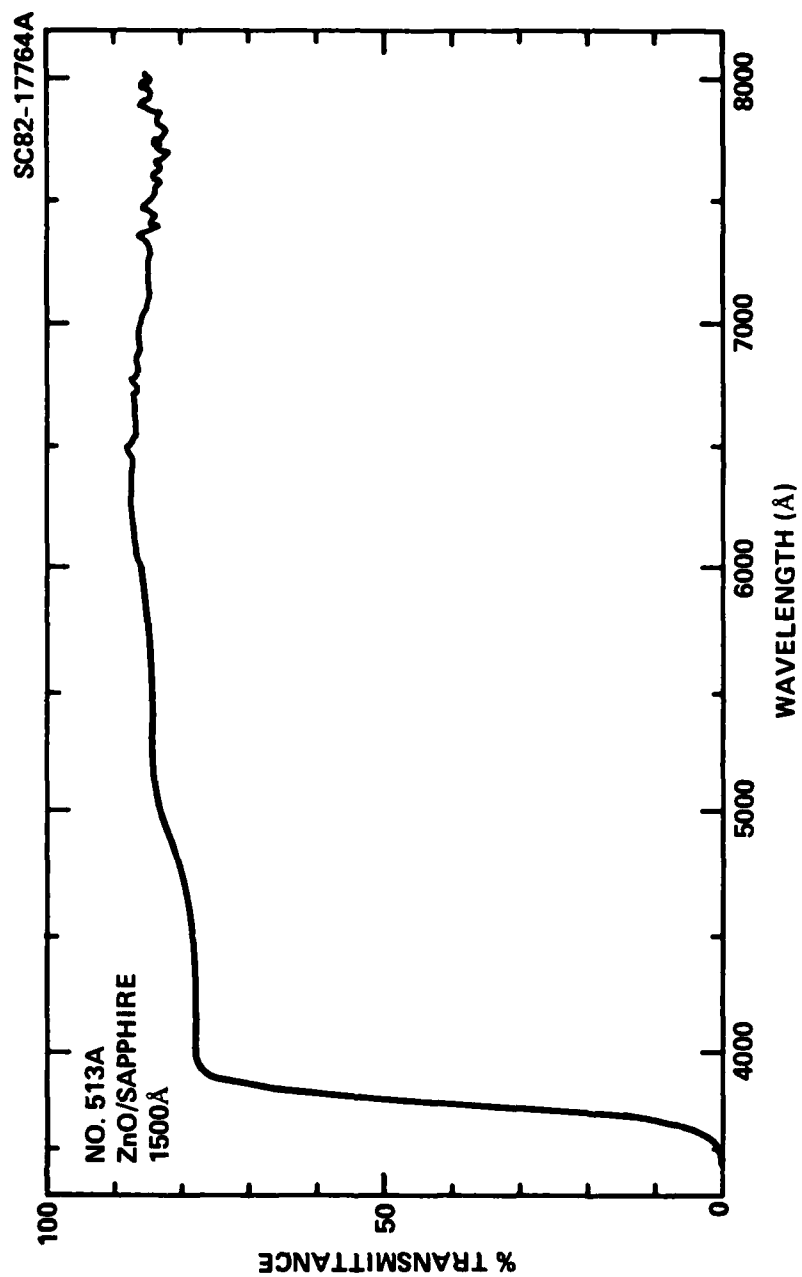


Fig. 12 Optical transmission spectrum of a ZnO film deposited on c-axis sapphire.



3.0 FUTURE PLANS

3.1 HgCdTe

Plans for the next six months are:

1. To reduce the impurity levels by:
 - a. Improving the substrate surface preparation such as etching and rinsing.
 - b. In-situ cleaning of the substrate surface by sputtering (being installed).
 - c. Replacing the heated mirror with a heated sapphire window. (Installed and operational). This will reduce the Al and Si contamination in the film.
2. To grow very thick ($> 15 \mu\text{m}$) films at a constant deposition rate with modification 1c.
3. To fully characterize these films and to attempt to convert to p-type by annealing.

3.2 ZnO

Future plans will focus on systematic characterization of the evaporation process, characterization of films with other techniques, and development of device structures.

1. The evaporation process, rate, and the film growth will be systematically studied as functions of substrate temperature, laser power density, ambient gas (hard vacuum, O_2 , N_2O), oxygen



excitation source (dc glow discharge, microwave plasma, ultraviolet light), type of laser power (CO_2 , Nd:YAG, pulsed vs cw), substrate type (Si, GaA, 7059 Corning glass, quartz).

2. Films will be characterized for light scattering and absorption in ZnO/SiO_2 waveguide structures; for dielectric constants in metal/ZnO/metal capacitive structure; for oscillation frequency and "Q" factor in piezoelectric device structure, for photoluminescent in as-grown form, at 4K, 77K and room temperature.
3. Finally, after optimizing film properties, prototype device structures will be built and characterized.