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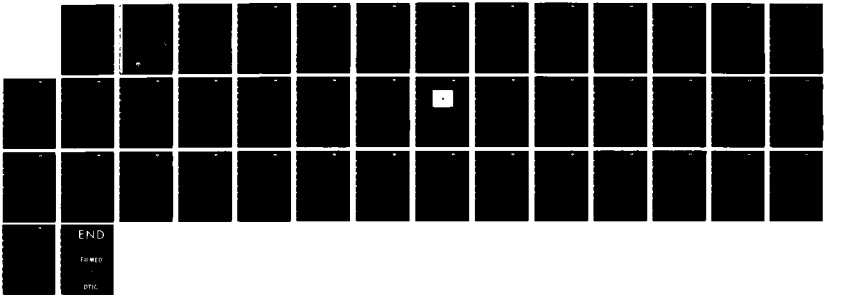

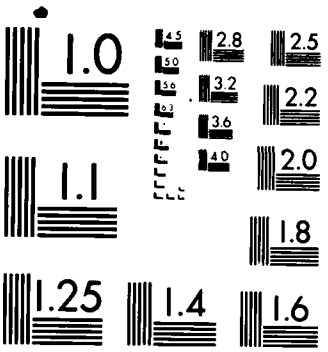

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LASER EVAPORATION STUDIES

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H. Sankur
Principal Investigator

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The use of a pulsed laser to evaporate dielectric materials for optical thin film deposition was investigated. Studies were performed to analyze the species present in the evaporant plume generated by a 1.5 Joule TEA-CO_2 laser. The materials investigated were Al_2O_3, SiO_2, ZnO, PbF_2, TiO_2, and HfO_2. Experiments were performed in a cryopumped system with a base pressure of 10^{-8} torr. The evaporant plume was characterized using luminescence spectroscopy, mass spectroscopy, and ion current analysis.

Luminescence studies indicated the existence of excited state neutrals and singly, doubly and triply ionized species. Plasma electron temperatures of 6500K were deduced from a study of neutrals in the plumes of SiO_2 and Al_2O_3. Molecular species were found in significant concentrations only for higher (10^{-3} torr) residual gas pressures. Ion current analysis demonstrated the existence of several species for each compound, each with different velocities. Velocities of 1.5×10^7 cm/sec indicated very high kinetic energies for the ionized species.

In the following phase of the program, the effects of excited state and energetic species on thin film growth will be investigated.

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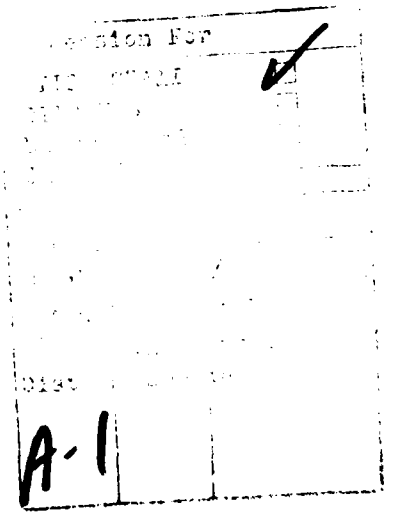
TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (concluded)

LIST OF TABLES



1.0 INTRODUCTION

This is the first annual report on the program Physics of Thin Film Growth by Laser Evaporation. The goal of this study is a fundamental understanding of the laser evaporation process and how the unique physical phenomena inherent in this process affect the nucleation and growth of thin films of optical materials.

Laser-assisted material processing techniques, including laser-assisted evaporation (referred to as LADA for laser-assisted deposition and annealing) have drawn considerable attention since the advent of powerful lasers in the past two decades. Considerable research has been done in the areas of laser-generated plasmas at very high fluences, material processing techniques by lasers such as annealing, recrystallization, and thin film deposition methods by laser-assisted pyrolysis, photolysis and laser-assisted thermal (or flash) evaporation.

In the past, most of the above research has been applied to metals and semiconductors using such high power lasers as CO_2, Nd:YAG, ruby and excimer lasers. Recently, laser-assisted evaporation has emerged as a versatile and powerful thin film deposition technique, especially for dielectric and semiconductor materials. There are unique advantages offered by this technique as a result of using a high power laser ($> 10^5$ W/cm^2) which is focused on the evaporation target surface. As discussed in this report, the evaporant plume is found to contain highly excited, energetic and ionized species in amounts and relative concentrations dependent on the laser and material parameters.

In spite of recent successes in the deposition of high quality optical and electronic thin films [R1], a systematic investigation of the nature of the evaporants and the effect of these on thin film parameters has not been carried out. The effect of energetic and ionized species in the evaporant plume on the nucleation and structure of thin films has been seen in studies of sputtered films. [R2] Therefore, development of a fundamental

understanding of the laser evaporation process and control of the abundance and energy of evaporant species is necessary to be able to control the physical parameters of thin films deposited by LADA.

This work addresses some of the fundamental issues mentioned above. In the first phase, the evaporant plumes generated by a high power ($P > 10^8$ W/cm^2) pulsed CO_2 laser beam impinging on absorbing targets (Al_2O_3, SiO_2, TiO_2, HfO_2, PbF_2, ZnO) have been analyzed using a variety of techniques. At the same time, properties of some thin films deposited by LADA have been analyzed to identify materials that show substantial differences in their properties when deposited by pulsed LADA as opposed to conventional techniques. This phase of the work proved the utility and limitations of the experimental approaches and provided significant data on the nature of the evaporant plume generated when pulsed laser radiation is incident on highly absorbing dielectrics. The analysis of luminescence data indicated the presence of highly excited neutral and ionized atomic species; ion current measurements revealed ionic species with hyperthermal velocities ($> 10^7$cm/s); and the thin film studies were helpful in the selection of materials for future studies (see Results).

In the subsequent phases of this project, control of the features of the evaporant plume that are specific to laser-induced evaporation, their effect on thin film parameters and the properties of thin films of the above materials deposited by LADA will be studied in detail (see Future Studies).

2.0 EXPERIMENTAL

The experiments in which we investigated the nature of the evaporant plume were performed using materials such as Al_2O_3, SiO_2, ZnO, HfO_2, TiO_2, and PbF_2 evaporated with a TEA-CO_2 pulsed laser (Lumonics model 820) (Fig. 1). These studies included luminescence spectroscopy, ion current time behavior and quadrupole mass analysis.

Experiments were carried out in a stainless steel vacuum chamber where the base pressure was between 2×10^{-8} and 2×10^{-7} Torr. Pressures of reactive gases could be maintained at any desired level by throttling the vacuum and by means of a fine leak valve. The chamber was fitted with several windows that are transmissive from the UV (200 nm) to the far IR (25 μm). The position and angular orientation of the targets with respect to the laser beam could be varied to expose fresh surfaces or different materials to the laser beam.

The CO_2 laser beam was focused on the targets using a 40 cm focal length AR-coated ZnSe or NaCl lens, whose focus could be adjusted to vary the power density on the targets. The laser power was attenuated using Fresnel reflection from plates of ZnSe, NaCl, GaAs, Si and Ge, which, when used in various combinations, provided incremental attenuation in 5% steps from full power to a minimum of ~ 10%. The power could also be varied by adjusting the discharge voltage of the laser. However, since this method also altered the beam modes and the beam divergence, making control of the power density more difficult, the first method was used exclusively. Laser pulse energy was measured with an energy meter (Gentec Model ED-500). The maximum pulse energy at the output of the laser was 1.5 J, whereas the energy at the target surface was measured to be ~ 1 J due to losses from lenses, windows, and the molybdenum mirrors used to steer the beam onto the targets. The absorbed energy was less than this value due to reflection at the target surface. The reflectivities of some of the target materials are listed in Table 1.

Table 1

Reflectivity (R) Values
for the Materials
Studied at 10.6 μm [R3]

Material	R
Al_2O_3	0.16
SiO_2	0.15
TiO_2	0.21
PbF_2	0.32
ZnO	0.20

Luminescence spectroscopy was performed using an f/3, Jarrell-Ash monochromator with a 600 lines/mm grating and an optical multichannel analyzer (OMA), (Tracor Northern Model 1710). The luminescence within 2 cm of the target surface was collimated using a 15 cm focal length NaCl lens and was directed through the vacuum viewport onto the monochromator slit (Fig. 1). Optical alignment was performed with a HeNe laser. The resolution of the OMA - monochromator combination was approximately 2Å per channel. Since the plasma luminousity was high, the plasma emission was not focused on the slit. Neutral density filters were required in some cases to prevent saturating the amplifiers. Spectra were obtained from 200 to 900 nm with spectral intervals of 190 nm. The OMA was calibrated using a low pressure Hg lamp. The pressure in the chamber was maintained at 2×10^{-7} Torr during most of the experiments. In studies of the effect of ambient gases on plasma properties, controlled amounts of O_2, Ar, He, N_2 gases were introduced at pressures of 2×10^{-5} Torr - 1 Torr.

The effects of strong electric and magnetic fields were investigated by applying a DC electric field of (0-4000V) whose direction was perpendicular to the plane defined by the laser beam and axis of the collimating lens (Fig. 1). The magnetic field was applied by placing a permanent magnet (600 gauss)

around the target materials with the same orientation as for the DC electric field.

Velocity analysis of the ionic species produced by the pulsed laser evaporation was performed using a time-of-flight technique. Source materials in this experiment consisted of a piece of single-crystal Al_2O_3, a pellet of fused quartz (SiO_2) and pellets of highly compressed ZnO and PbF_2 powder. The positive ion current was collected on a biased (-30 V) wire loop (~ 4mm dia) which could be positioned from 0 to 20 cm from the source. The angle between the incident laser pulse and the ion detector was 45°.

Source pellets were positioned such that their surface normals were ~ 22 1/2° from the incident laser and the detection direction (Fig. 2). Current on the ion collector was measured with a Tektronix noninvasive current probe. The passive amplifier at the end of the probe was connected to a 100 MHz Tektronix (Model 7854) oscilloscope which displayed the temporal behavior of the current. The current signal was averaged over ~ 100 laser pulses and then was recorded on film.

Mass analysis of the evaporant plume was achieved using a quadrupole mass analyzer (QMA) (UTI Model 100C) whose ionizer element was positioned 15 or 35 cm from the target surface. The current at the output of the electron multiplier within the QMA column was further amplified by a current to voltage amplifier and then was displayed on an oscilloscope. With this experimental arrangement, neutrals emitted from the target surface are ionized by the QMA and then are detected, while ionic species can be isolated by operating the QMA with its ionizer off. The temporal behavior of both neutrals and ions was displayed and photographed on the oscilloscope.

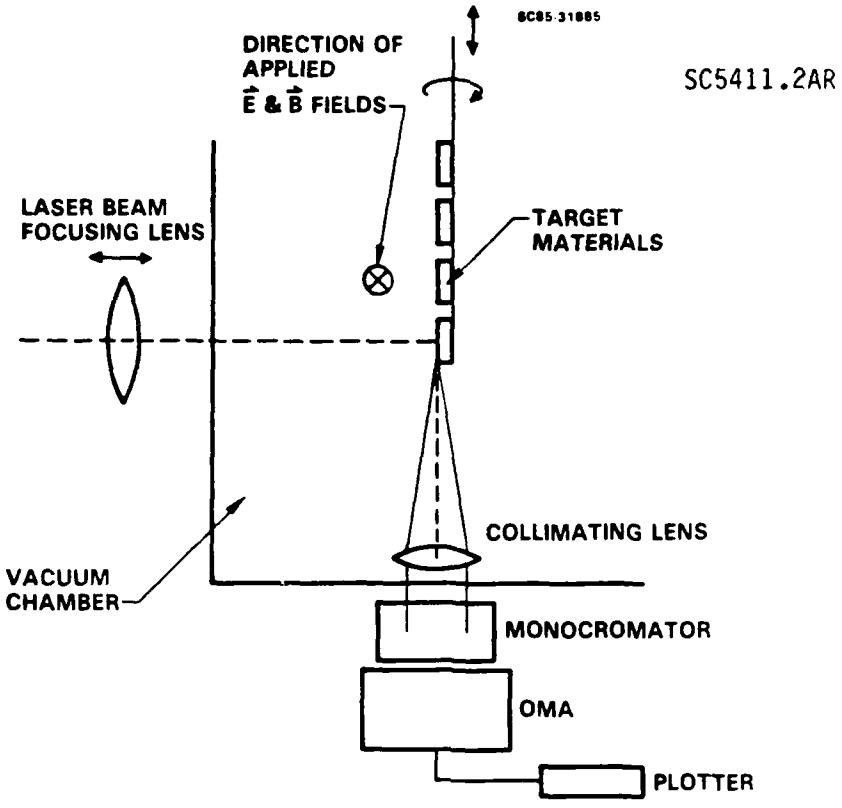


Fig. 1 Schematic of the experimental apparatus used in the luminescence studies.

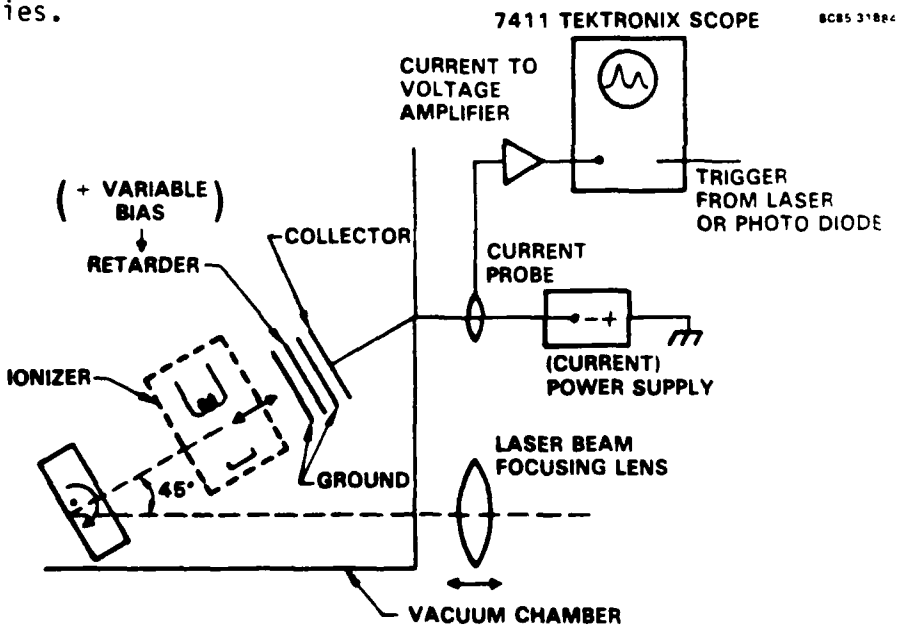


Fig. 2 Schematic of the experimental apparatus used for ion velocity determination and quadrapole mass analysis.

3.0 RESULTS

3.1 Luminescence

The spectrum of Al_2O_3 is shown in Fig. 3a,b where the prominent lines are labeled. Most of the 222 lines in this spectrum, with the exception of a few (14) weak lines, were identified as neutral, singly and doubly ionized Al and oxygen lines. The typical temporal behavior of the emission is shown in Fig. 4a. The decay time is comparable to the laser pulse width (~ 1 μs), an example of which is shown in Fig. 4b.

In the case of Al_2O_3 and SiO_2, the relatively fewer lines of the cations (due to their low Z number) made the identification of most lines unambiguous. For TiO_2 and HfO_2 such was not the case since the cations in these compounds have richer emission spectra. [R4] The problem was further compounded by a slight nonlinearity of the wavelength axis of the OMA display. When one or both ends of a given wavelength interval were fixed using a Hg lamp, the midsection of this axis was found to deviate by as much as 4-5Å (0.5 nm). In future studies, use of a holographic, higher resolution diffraction grating in the monochromator will simplify the identification of the spectral features.

The plasma temperature (assuming local thermal equilibrium) can be estimated if the relative number density of the excited species can be calculated using the relative emission intensity and the published data on the spontaneous emission coefficient (A) and the degeneracy factor (g). [R5] The emission intensity (I) is related to the number density (n) of the species, and the number density is determined by the electron temperature (T) via the relationships

$$I \quad \frac{An}{E_i - E_f}; \qquad n \propto g\exp(-E_i/kT) \quad .$$

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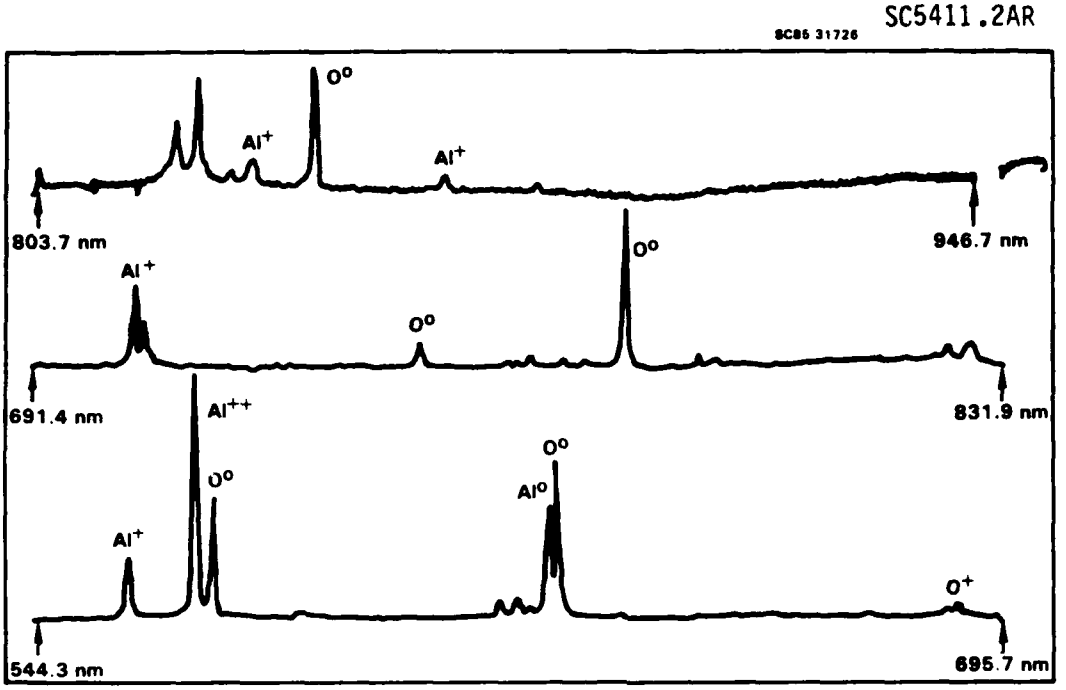

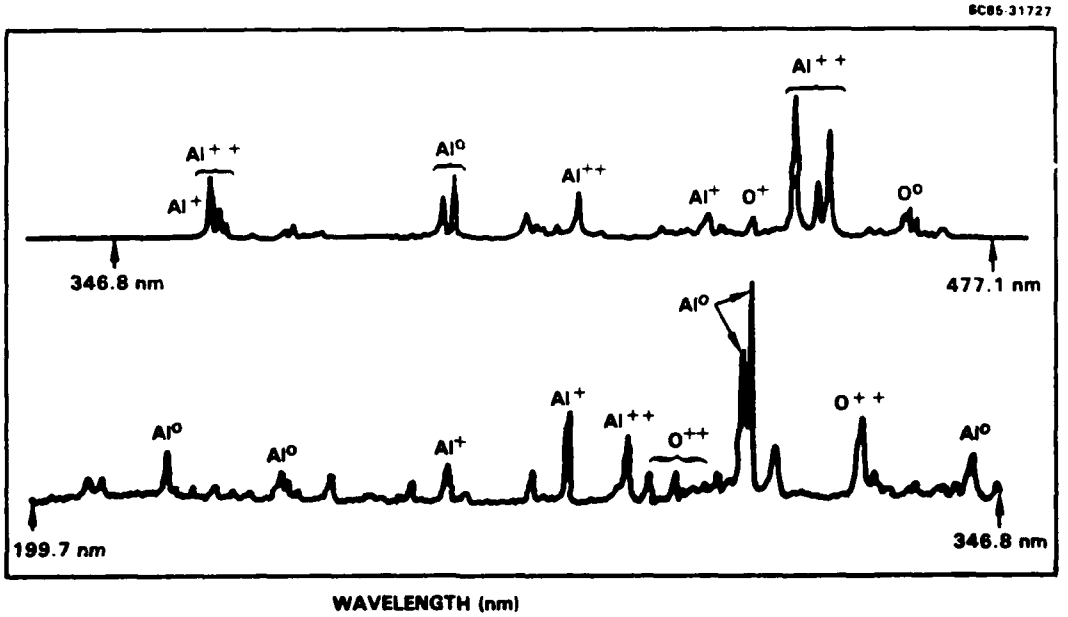

Figs. 3a,b Spectrum of the luminescence of the evaporant plume of Al_2O_3 under TEA-CO_2 laser radiation. (Power density $>10^8$ W/cm^2.)

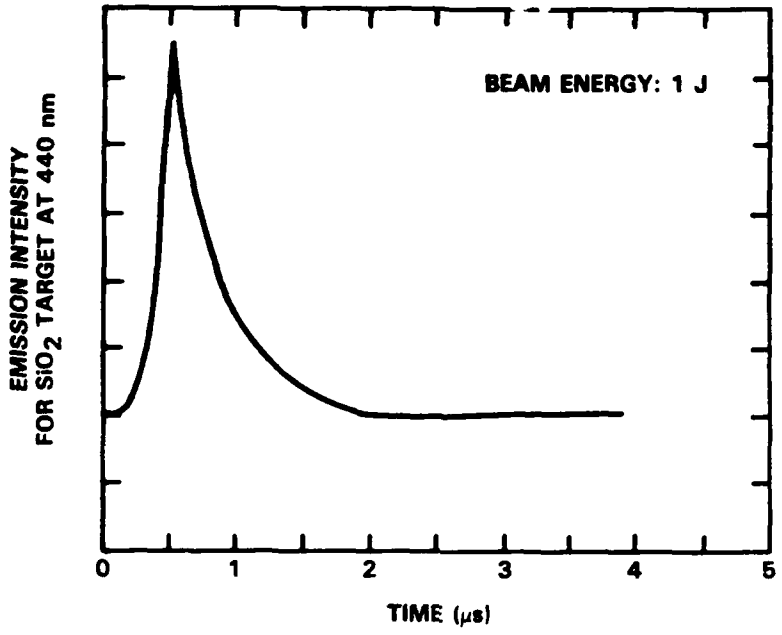

Fig. 4a Temporal behavior of the luminescence signal of the evaporant plume of SiO_2 at 440 nm wavelength.

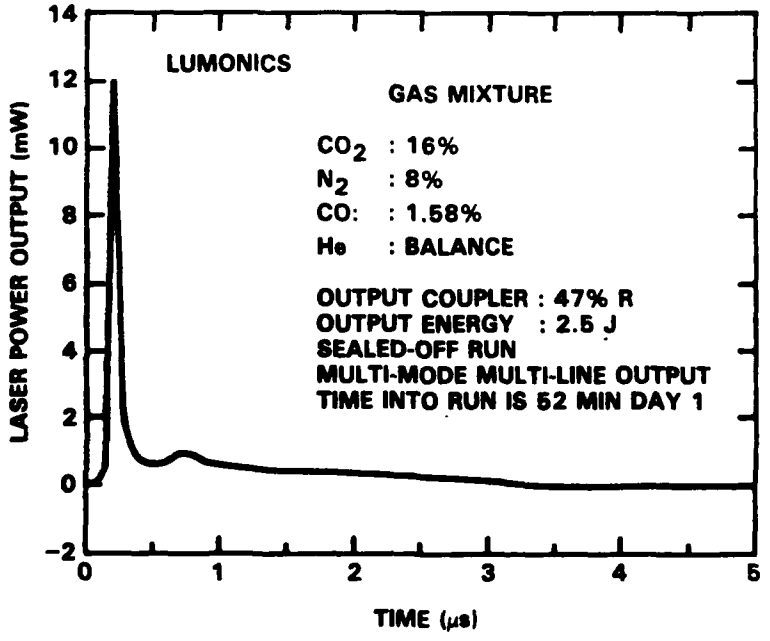

Fig. 4b Temporal behavior of the TEA-CO_2 laser output, as given by the manufacturer.

Here E_i, E_f refer to initial and final state energies, and k is the Boltzmann constant. Rearranging and taking the natural logarithm of both sides, the following expression is obtained where the slope is inversely proportional to the temperature

$$\ln \left(\frac{I}{Ag\ (E_i - E_f)}\right) = -\frac{E_i}{kT} + C \quad .$$

Fig. 5a, 5b show such plots for Al^o and Si^o. The temperature calculated from the slope is 6550 ± 250 K for Al, 6700 K for Si^o. Similar plots for Al^{++} gave a temperature of ~ 25000 K. The higher temperature for doubly ionized species may indicate the existence of an accelerating potential at the surface of the target.

3.2 Power Dependence

The dependence of emission intensity on laser power for some of the major lines is shown in Fig. 6a,b for Al_2O_3 and SiO_2. In general, the major lines of neutral and ionized species show the expected monotonic increase with beam energy. However, for Al, the saturation energy increases from neutrals to higher ionization states. This is thought to arise from screening of the target surface at high plasma densities when the laser radiation is absorbed mostly in the plasma itself, thus raising its temperature. The energy absorbed in a plasma of a given density will increase the concentration of the highly ionized species at the expense of neutrals or lower energy species.

3.3 Molecular Lines

In the luminescence experiments performed under high vacuum conditions (10^{-7} Torr), Al_2O_3 was the only material to exhibit molecular bands. These bands, attributed to Al-O, were very weak and were superimposed on top of several atomic lines (Fig. 7). Many lines, and the presence of

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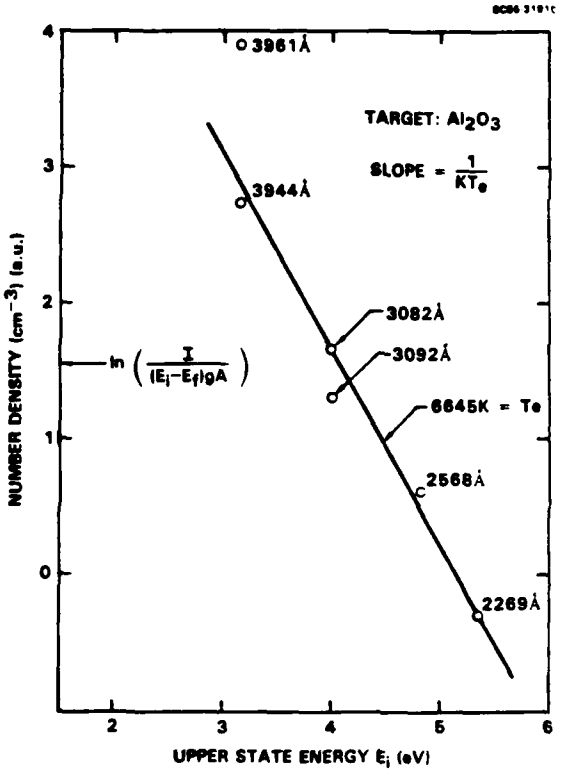

Fig. 5a *Number density of the* Al^0 *luminescent species plotted vs (initial) excited state energies in the evaporant plume of* Al_2O_3.

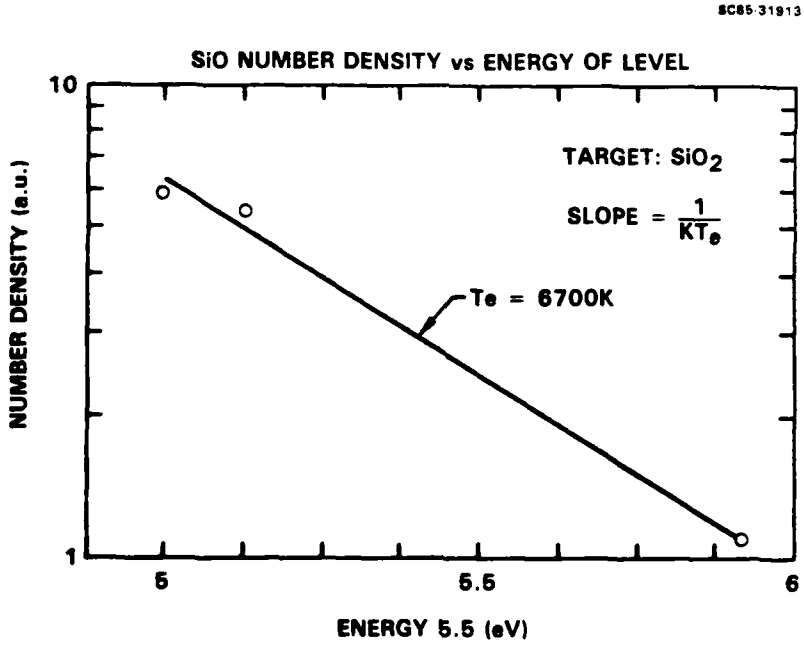

Fig. 5b Same as Fig. 5a for Si^0 in the evaporant plume of SiO_2.

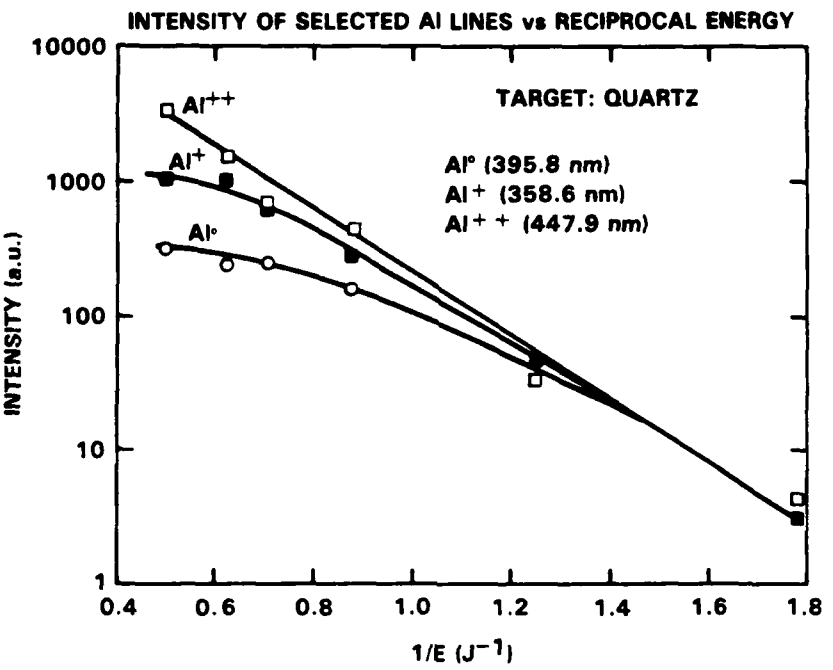

Fig. 6a Incident laser power dependence of selected neutral and ionized emission line intensities in the evaporant plume of Al_2O_3.

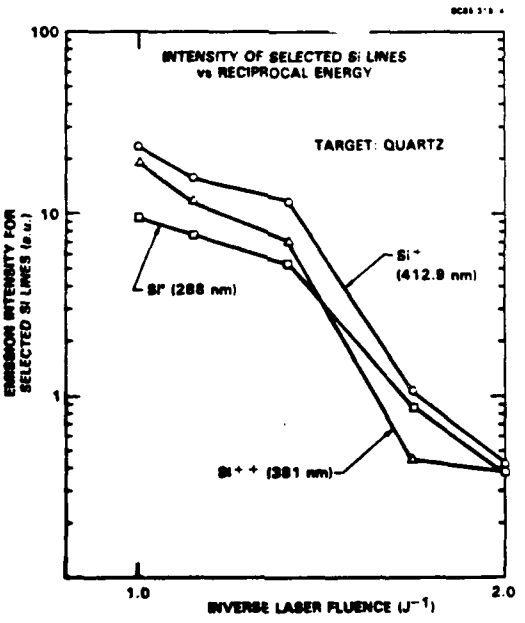

Fig. 6b Same as Fig. 6a for Si species in the evaporant plume of SiO_2.

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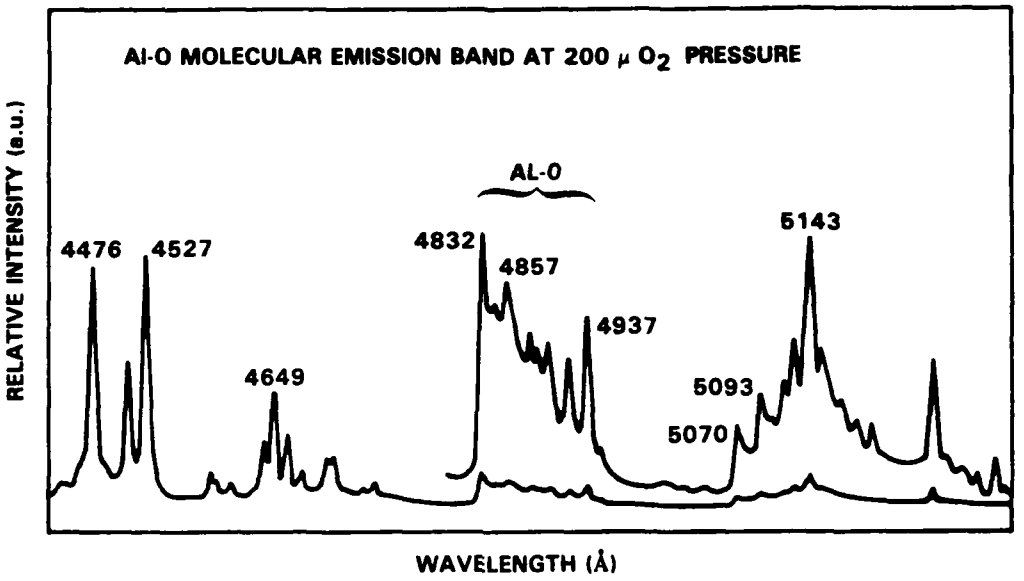

Fig. 7 *Luminescence spectrum of the molecular emission band in the evaporant plume of* Al_2O_3 *in the presence of 200 microns of* O_2.

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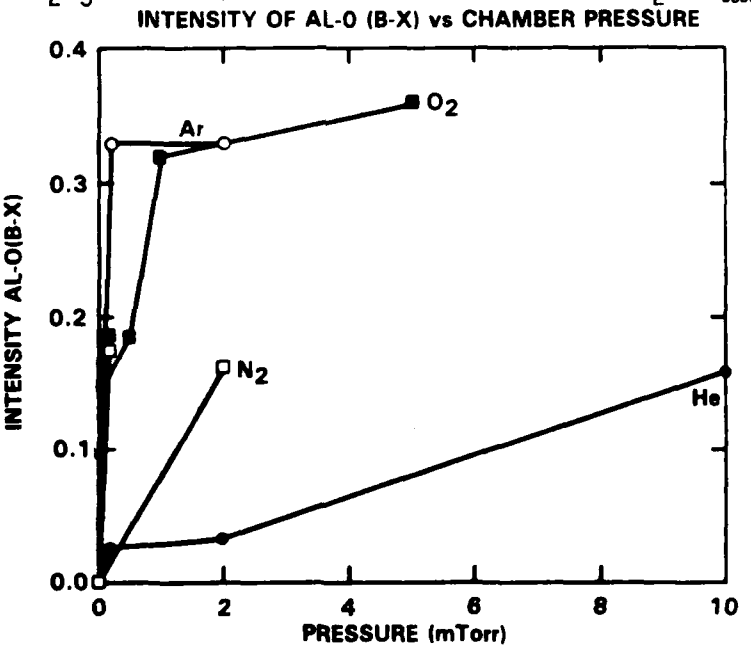

Fig. 8 Ambient gas pressure dependence of the molecular band emission intensity for Al-O (B-X) in the evaporant plume of Al_2O_3.

atomic transition lines and continuum background, made determination of the population of the molecular vibrational states impossible to calculate.

The intensity of the molecular emission band increased with gas pressure as shown in Fig. 8, but the shape of this band did not change with gas pressure. Rather unexpectedly, the molecular emission band intensity was enhanced not only in the presence of O_2 but also in the presence of other gases, namely He, N_2, and Ar at comparable pressures. The fact that the intensity of molecular band emission is dependent on the gas pressure and less dependent of the gas species indicates that the collisions in the gas phase promote this emission in the vicinity of the surface. Pending further experiments, it is not known whether this enhancement is due to the collisional cooling of the plasma that would allow gas phase formation of the molecular species, or whether the slowing of the plasma expansion front in the presence of any gas allows emission of longer-lived molecular species that would normally escape the detection area before relaxing to the lower energy state. In view of the fact that Al-O lifetimes (τ) are relatively long (e.g. τ[Al-O(v^i = o to v^f = o transition)] = 236 ns [R6]) and that the velocities of many species are relatively large (V ion = 2×10^7 cm/s), the probability that molecular species may escape the optically sampled volume (within 2 cm of the target surface) is nonnegligible. To answer the above question the emission from a larger volume must be sampled.

3.4 Effect of an Ambient Gas

Experiments carried out in the presence of a gas showed that the evaporant plasma interacted with the gas in the chamber and produced discharge in the latter. Photographs (Fig. 9) of the plasma taken with various filters indicated a central luminous core surrounded by one or two halos of paler color. In general, the relative and absolute intensity of the atomic lines of the target did not change appreciably with gas pressure, whereas the intensity of atomic lines of the ambient gas (e.g. Ar) increased monotonically with pressure (Fig. 10).

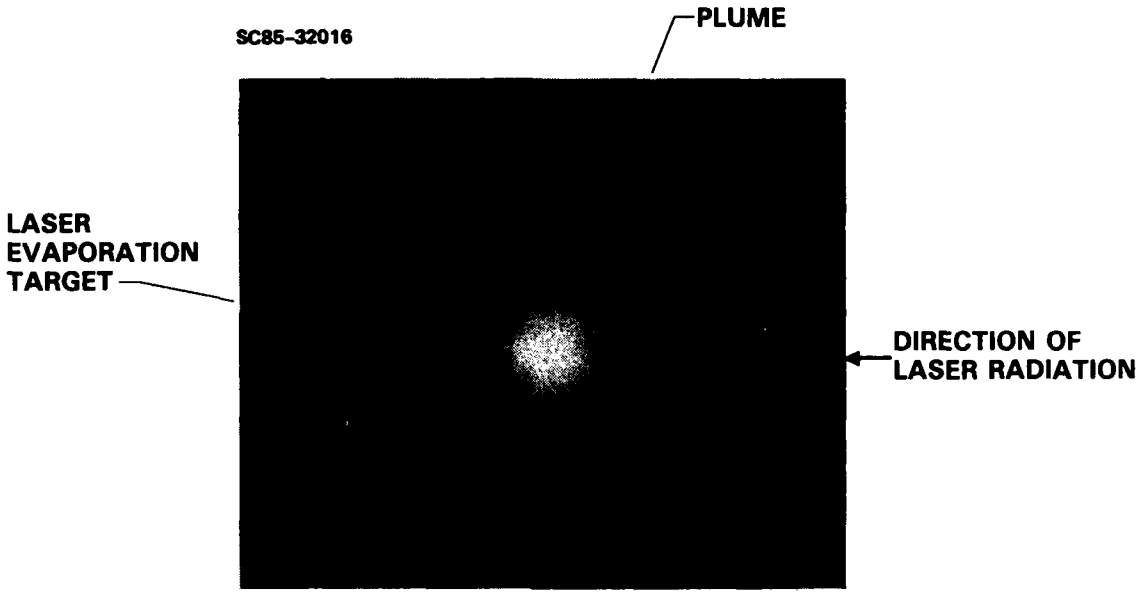

Fig. 9 Photograph of the evaporant plume emission of ZnO in the presence of 200 microns of O_2. Photograph was taken through a high pass red filter.

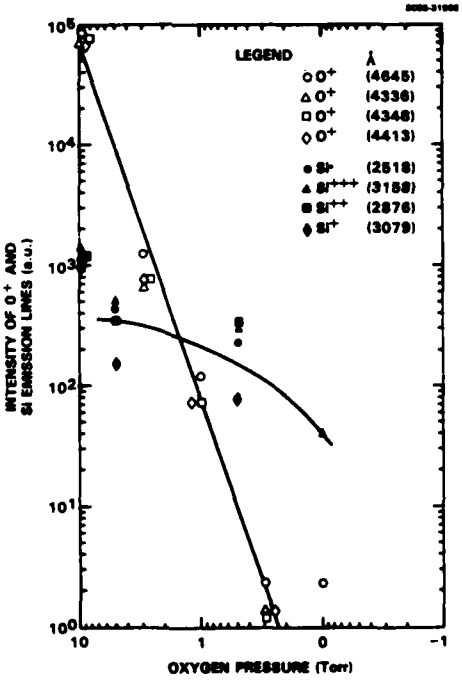

Fig. 10 O_2 pressure dependence of the O and Si emission line intensities.

The possibility that the laser beam may cause breakdown in the gas itself or at even lower powers in the presence of a solid surface, was tested. No breakdown was observed in the gas even under the highest pressures in which the experiments were carried out. The other condition was tested by directing the laser beam onto Al and Si target materials. No gas discharge was observed when concurrent target material emission did not take place. In these experiments, the molecular bands mentioned in Section 3.3 could be generated, albeit somewhat weaker, for the same power levels. Not known at this point is whether the molecules are formed as a surface reaction or gas phase reaction.

3.5 Magnetic and Electrical Fields

The effect of static electromagnetic fields on the plasma emission was studied using a DC electric field (1 to 4 kV), and in a separate experiment a magnetic field (600 gauss). In both cases the field was oriented perpendicular to the plane of the laser beam and the axis of observation (Fig. 1). The electric field was expected to "quench" the plasma by separating the charges in the initial phase of plasma formation before the electron temperature could rise due to inverse bremmstrahlung. Similarly a rise in the electron temperature was expected due to spiraling of the electrons in the presence of a magnetic field. Neither of these effects was observed. Relative and absolute intensities of the emission lines remained the same in the region of observation, even though the color of the plasma changed in the presence of an electric field due to sputtering of the electrode plates (made out of Al) and possibly to break down of the plasma at these locations. The relatively poor resolution (2Å per channel) of the monochromator-OMA setup precluded observation of any Stark broadening in the electric field experiment.

3.6 Velocity Analysis of Ionic Species

One of the unique features of laser-assisted deposition techniques is the ability to generate evaporants with high kinetic energy. [R8] Evaporants with high kinetic energies have been found to improve film growth due to enhanced adatom surface mobility. [R9] To control and use this added dimension of LADA, quantitative measurements of the velocity or kinetic energy of the evaporant species must be made. The velocity of the ionic species produced by a pulsed laser is most easily measured by the time-of-flight technique. By varying the distance between the biased wire detector and the evaporant source, temporal changes in the ion current can be monitored as a function of distance. Figure 11 shows traces of ion current versus time for two different collector-to-source distances. The shift in the arrival time of the peaks labeled A-D can be seen. Using this type of plot, the velocity of the ionic species can be calculated by three methods. First, the source-to-collector distance can be divided by the transit time to obtain a velocity. Second, velocity can be calculated using the change in distance and the change in time of traces at any two distances. Third, the velocity can be obtained by plotting time versus distance for a particular peak (Fig. 12). The velocity is simply the slope of the straight line which best fits the data.

Data were collected for Al_2O_3, SiO_2, PbF_2 and ZnO at source to collector distances of between 0.5 and 19 cm. In the region from 0-9 cm, the current versus time traces were usually characterized by a single broad peak. This was due to the fact that, at short distances, the transit time of the various ionic species was too short to be resolved into discrete peaks. At ~ 10 cm, individual peaks, such as those seen in Fig. 12, began to be discernible. Using data collected between 10 and 19 cm from the source, the velocity of the various species was calculated by all of the methods described above. Table 2 shows a summary of the results of this experiment. These numbers were obtained by averaging the various velocity values obtained from traces at different distances. For each material, several different velocity species were found. In all cases, the velocities are surprisingly high,

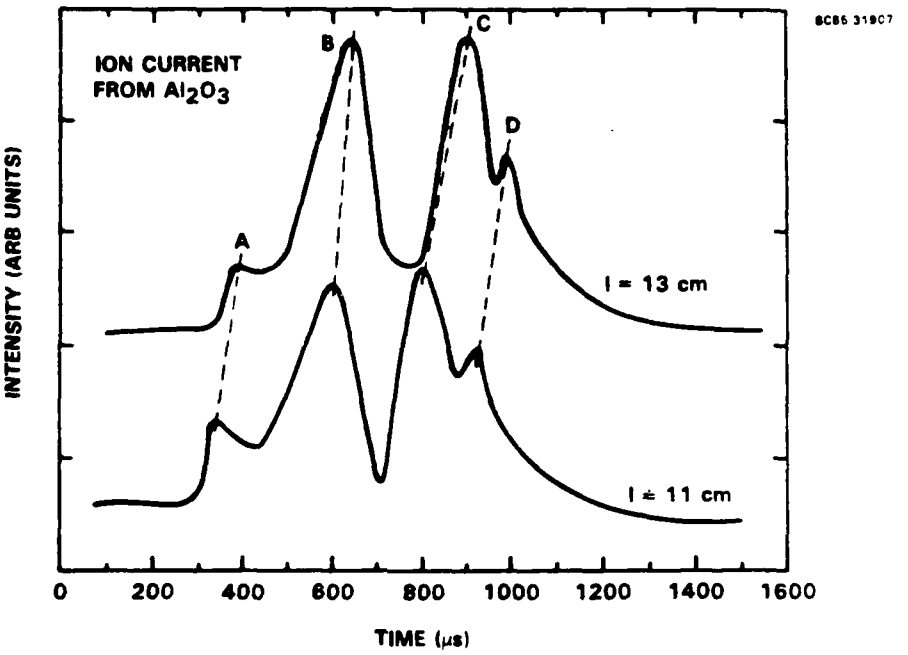

Fig. 11 Temporal behavior of the ion current due to positively ionized species in the evaporant plume of Al_2O_3. A collector was placed at 11 and 13 cm away from the evaporation target and biased at -30V.

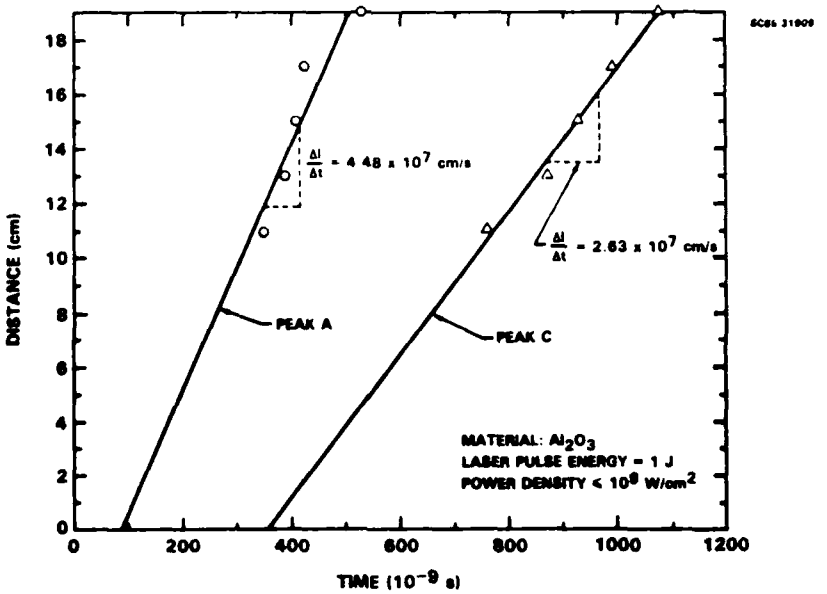

Fig. 12 Data of Fig. 11 plotted as relative temporal position vs collector-target separation. The slope of these plots gives the velocity of the species.

varying from (0.6 - 4.3) × 10^7 cm s^{-1}. Unfortunately, measuring ion current with no mass resolution allows only the velocity and not the kinetic energy to be determined. However, assuming various mass values for different species, an estimate of the kinetic energy can be obtained. Using the mass of an oxygen atom, a velocity of (0.6 - 4) × 10^7cm/s corresponds to 200 - 15000 eV of kinetic energy. The upper limit value is much higher than expected but not completely without precedent, since values as high as 11000 keV have been reported. [R10] *Further studies in this area are needed to confirm that these* ionic species have such a high kinetic energy.

Table 2
Velocity of Evaporant Ionic Species

Compound	Species	Velocity (10^7cm/s)	Std Deviation
SiO_2	A	3.27	0.11
	B	2.30	0.19
	C	1.48	0.05
	D	0.98	0.05
Al_2O_3	A	3.56	0.34
	B	2.46	0.23
	C	1.62	0.13
	D	1.38	0.10
PbF_2	A	4.28	1.7
	B	1.16	0.05
	C	0.59	0.08
ZnO	A	3.00	0.29
	B	2.06	0.13
	C	1.00	0.06
	C	0.78	0.05

3.7 Mass Analysis of Neutral and Ionic Species

Determining the relative concentrations of the different species emitted during a laser pulse is of primary importance in correlating thin film properties with laser growth conditions. The size of the evaporant species cluster should play an important role in the nucleation and growth of thin films. In this area, we have used a quadrupole mass analyzer (QMA) to determine the relative amounts of different size clusters emitted during the evaporation pulse. Unfortunately, to date, we have had only limited success with our current experimental setup. The most difficult aspect of this part of our study is measuring the very small amount of material which reaches the QMA in a very short period of time (5×10^{-7} s). A signal at the appropriate mass/charge ratios expected for a particular material system is observed, but there is also an unusually large background signal at smaller and larger mass values, which decreases as the QMA is scanned to lower or higher masses. This apparent mass insensitivity is being explored further; we hope to resolve the problems either by reconfiguring the position of the QMA with respect to the source or by using a faster, more efficient, amplifier on the QMA output.

3.8 Thin Film Growth

Thin film growth experiments were carried out to explore material systems whose study would feature some of the peculiarities of pulsed and CW LADA deposition. These experiments were done in high vacuum (2×10^{-6} Torr) using a TEA-CO_2 laser with graphite, Al_2O_3, SiO_2, PbF_2, and yttria stabilized zirconia as source materials. Films were characterized by x-ray diffraction, optical spectroscopy and optical microscopy.

In general, the problem of spitting of particulates, even after extensive degassing, produced films with excessive scatter. Particulate density was reduced by reducing the pulse energy. In future studies, higher repetition rate and lower peak power laser pulses will be used to reduce spitting and to maintain an acceptable growth rate.

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X-ray diffraction spectra of PbF_2 films grown by pulsed LADA (Fig. 13) show that the films consist of oriented PbF_3 with very small amounts of free Pb. The CW LADA or thermally evaporated films are a mixture of α and β-phase similar to source material composition. The pulsed LADA films were smooth and showed slight absorption in the visible, presumably due to free Pb clusters.

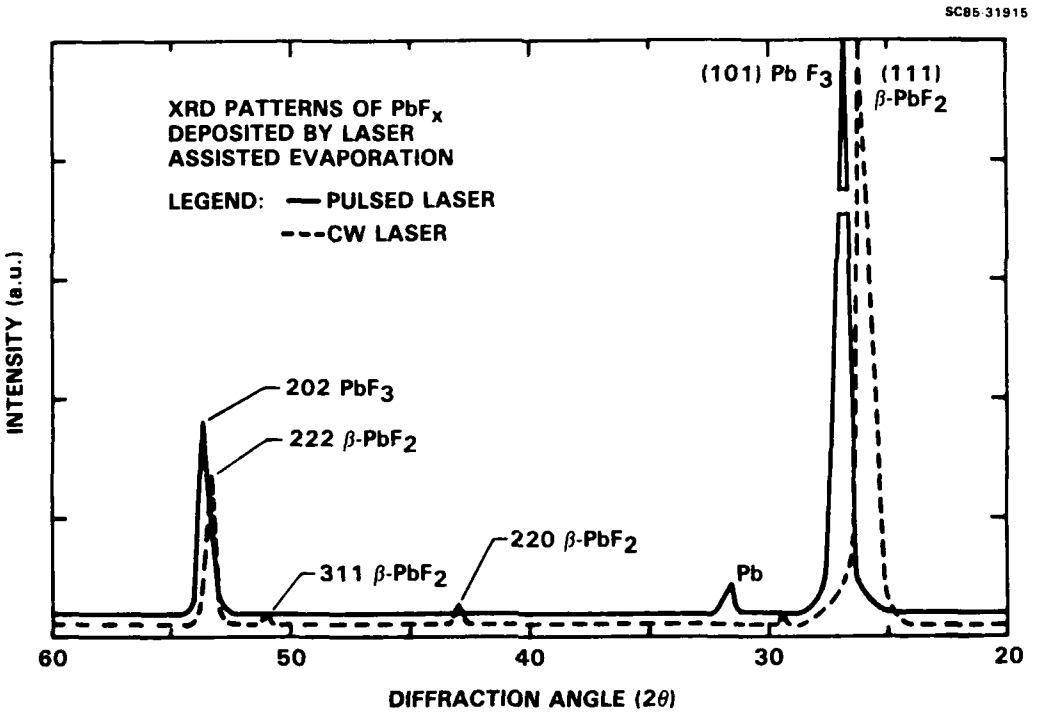

Fig. 13 X-ray diffraction pattern of PbF_x grown by CW and pulsed LADA. Glass substrates were held at room temperature. The evaporation source material was a high purity mixture of α and β PbF_2.

4.0 FUTURE STUDIES

The studies performed during the first year of this program have demonstrated the variety of unique phenomena to be observed in laser evaporation of optical materials. Experiments so far have been performed in the nature of a survey to identify key features which might be used to probe the laser source interaction. As many new questions have been raised as have been answered. A more detailed study of the evaporant plasma luminescence under various conditions of laser illumination will provide information necessary to establish control of deposition conditions.

Studies planned for the remainder of this program are directed toward a more quantitative analysis of the evaporant plume and to determine the effect of energetic and excited state particles on film nucleation and growth. Films grown by pulsed LADA will be studied in detail to relate their structure to conditions in the laser-generated evaporant. For the duration of this program, we plan to undertake a number of studies suggested by previous experiments, as described below.

4.1 Experiments with TEMoo and Temporally Controlled Laser Pulses

The experiments performed to date used multimode laser pulses to maximize the energy per pulse and to enhance the amount of evaporated material for analysis. As a result, the laser spot is not spatially uniform, resulting in hot spots on the source. In addition, the pulse is followed by a lower power tail (Fig. 4b). This tail can cause heating of the plasma and additional evaporation of low energy neutrals and can therefore mask the effects of pulsed laser interactions.

In this study, the laser will be operated in the TEMoo mode to achieve predictable power density profiles and to eliminate hot spots. The shape of the pulse and its subsequent tail can be tailored by varying the nitrogen concentration in the laser gas mixture. Laser pulses will be analyzed using a photon drag meter, and the spatial distribution will be determined using a pyroelectric detector array.

Subsequent measurements of laser source interactions will be more readily related to fundamental processes with a quantitative measure of the incident laser energy.

4.2 Plasma Scaling Factors

The dependence of plasma temperature on laser power density will be determined by monitoring changes in the luminescence spectrum over a range of laser power densities. This information will allow control of the evaporant plume constituents as a function of the laser power.

The power density can also be varied while maintaining constant fluence by varying the position of the focusing lens, thus varying the size of the focal spot. This will allow the same total energy to be incident on the material but with varying power densities. The purpose of this experiment is to maintain a high evaporant flux with lower energy constituents.

4.3 Spatial Distribution of the Luminescent Species

The spatial distribution of the plasma constituents will be studied by the luminescence spectroscopy technique described earlier and with the use of slits or apertures to limit the volume of emission under investigation. The importance of this work is to assess the optimum position of the substrates with respect to the evaporation targets.

The spatial nonuniformity of the emission, because of expansion of the plasma front, decay of energetic species and general cooling of the plasma with time (or distance), as well as inherent nonuniformities, will be studied as functions of laser power density and type of energetic species. This will be done by varying the separation and angular position of the substrates with respect to the evaporation target.

4.4 Ion Energy Analysis

Our preliminary studies indicated the presence of high velocity, high kinetic energy species in the laser-generated evaporant. These measurements need to be refined and extended to a wider range of materials. Thin film properties will certainly be influenced by the presence of highly energetic particles, making this an issue of fundamental importance to the development of LADA as a thin film growth technique.

Additional studies of the kinetic energy of emitted ions are also planned. Using a high-pass energy analyzer, the kinetic energy of ionic species can be measured directly without using the time-of-flight technique. In this experiment, a positively biased high transmission grid acts as a high-pass filter for the ionic species. Only ions with kinetic energy greater than the bias voltage reach the collector. By varying the bias voltage, the kinetic energy of the various ionic species can be determined. Using results of this experiment in conjunction with those of the velocity analysis study, the mass of the ionic species can be calculated and compared with results obtained with the QMA. Ion current measurements will also be carried out with single constituent materials that are highly absorptive at CO_2 laser wavelengths (e.g. graphite). These experiments will simplify the interpretation of data, which consist of velocity peaks, and may provide energy data as well since the mass of the evaporant species will be better defined (i.e. C, C_2...). Concurrently, the possibility of detecting neutral species will be investigated by means of an ionizer placed between the source and the collector plate.

These experiments may also help us to understand whether the observed velocity peaks (Section 3.6) represent different mass species, as would be the case if the ion acceleration occurred due to some surface potential, or if they correspond to different energy peaks of the same species (e.g. slow ions, fast multiply charged ions).

4.5 Mass Analysis

Measuring the relative amounts of different size clusters is important in understanding the physics of LADA. This makes the QMA experiment a necessary part of this study. The apparent insensitivity of the analyzer system to the mass/charge ratio may be related to the time response of the QMA. The RF field in the quadrupole oscillates at approximately 2 MHz, which is comparable to the transit time of the species (0.5-1 μs). This means that species of different masses may be able to traverse the field region before the oscillating field can do its job of mass selection. One possible solution to this problem is to move the QMA further away from the source, thus temporally separating species having different velocities. This effectively lengthens the transit time of the species, giving the QMA more time to mass select the appropriate m/e ratio. Another possibility would be to use a QMA which oscillates at 20-50 MHz, making the mass filtering more efficient. A third possible solution would be to defocus the laser slightly, keeping the energy/pulse constant. This reduces the power density while delivering the same amount of energy to the target surface. Less energetic species are expected, making it possible for the QMA to perform quantitative mass analysis.

Preliminary results obtained to date show that our current experimental apparatus is close to providing the needed information. We believe that this study has shown sufficient promise to warrant the additional time and energy needed to refine the experiment to a point where more exact data can be obtained.

4.6 Energy Distribution of the Neutrals

The energy distribution of the neutrals and a quantitative assessment of their spatial density will be studied with two complementary techniques.

In the first phase, the neutrals will be studied by the ion current detection measurement explained above with the addition of a precollector ionizer (Fig. 2). The ionization efficiency is expected to be about 0.1% and this process is not expected to alter the trajectories of the evaporant stream

significantly. The ion current with the above stated ionization efficiency is expected to be comparable to or larger than the current due to plasma ions observed in the studies to date.

An alternative technique is atomic absorption spectroscopy in the evaporant stream. This technique is amenable to those elements for which discharge lamps are available. The measurement will be carried out by observing the absorption of the light from a glow discharge source (e.g. Zn) by the evaporant stream of ZnO. The detection system, consisting of a monochromator and a photomultiplier tube connected to a fast oscilloscope, can be tuned to a particular transition. The temporal behavior of the absorption line will provide information about the velocity of the species, essentially in a time-of-flight experimental configuration. The quantitative sensitivity of this technique is very good and may be as high as 10^9 particles/cm^3.

4.7 Role of Ions in Thin Film Deposition

The role of ions in the nucleation and growth of thin films will be studied by controlling the energy and density of ion flux incident on the substrate. Ionized species may be readily accelerated, decelerated, or deflected by means of electrical and magnetic fields. A fine, semitransparent biased metal mesh in the path of the ion flux can slow down or speed up positively charged ions. Alternatively, a pair of deflecting plates along the path of the ions can be used. The amount of deflection is determined by their mass/charge ratios and velocities. By judicious selection of the deflecting voltage, adjacent areas of the same substrate can be bombarded with different amounts of ions and ion energies. [R11] In this way, the effect of high and low energy ions on film deposition can be studied on a single large area substrate.

4.8 Growth and Characterization of Thin Films

Systematic investigation of the deposition and characterization of thin films will be carried out to study the nature of materials deposited with this novel depositon technique (LADA). Based on the results presented in Section 3.7, a few select materials will be studied. These are PbF_2, SiO_2, Al_2O_3 and TiO_2.

The growth of thin films will be carried out in high vacuum (2×10^{-7} Torr) or in various reactive atmospheres. The substrate temperature, deposition rate, reactive gas pressure and substrate type and orientation are the usual thin film deposition variables that will be controlled or monitored.

The optical, mechanical, chemical and structural properties of these films will be studied using a wide variety of analysis methods. Of particular interest is the determination of the crystallinity, stoichiometry, and film defects. A number of the parameters of practical interest for optical thin film coatings will also be investigated.

4.9 Shock Wave in the Evaporation Target

The possible presence of a shock wave in the evaporation target generated by the evaporation pulses will be investigated by means of a wide band ultrasonic detector bonded to the target. The shock wave may be one source of the unexpectedly high ($> 10^{-7}$ cm/s) ion velocities observed in experiments to date.

The experimental arrangement can also be used to investigate the pressure wave due to recoil momentum of the departing evaporant stream. This pressure will be given by the integrated mass and velocity component perpendicular to the target surface. [R12] The degree of shielding of the laser radiation by the plasma may also be determined. For instance, the apparent saturation of the excited neutral species with pulse energy, as observed in the luminescence experiments (see section 3.1), may be explained if the temporal behavior of pressure wave was available. In this case, the pressure due to recoil momentum is also expected to saturate.

4.10 Nucleation Studies

The nucleation of the dielectric films will be studied using surface analysis techniques. The deposition on the substrate in the initial stages can be studied by means of high resolution SEM and X-ray dispersive energy analysis. Alternatively, spatially resolved XPS and Auger techniques may be useful in mapping the formation of nuclei on the surface. The shape, distribution, size and sites of these nuclei will depend on deposition conditions (e.g. ion bombardment..) and substrate surface conditions (e.g. native oxide..).

The same techniques can be applied to the study of the evaporation conditions by analyzing the target surface. The alteration of the morphology and the stoichiometry at the laser beam impingement site can indicate some aspects of the evaporation such as hot spots (beam burn pattern), material evaporated per pulse, and fractionation of compound targets. These data will also be used to optimize the laser parameters to obtain good quality thin films.

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6.0 PERSONNEL

J. T. Cheung: Member of Technical Staff, Applied Optics Department, Rockwell International Science Center. B.S., Chemistry, with the highest distinction, UCLA (1969), Ph.D., Chemistry, Harvard University (1974). He was an IBM Post-doctoral Research Fellow from 1974 to 1975 and a member of the Research Staff at Oak Ridge National Laboratory from 1975 to 1977. His original field of specialization is gas phase kinetics and in particular, the use of molecular beam experiments to study the collisional dynamics between atoms, ions, molecules and clusters. He has also studied the exo-ion and exo-electron emissions from surface induced by chemical reactions. Since joining the Science Center, his initial responsibility has been in the development and characterization of PbSnTe/ PbTe inverted mosaics. He is the pioneer on the development of the laser-assisted deposition (LADA) technique. This technique has successfully demonstrated the growth of various semiconductor and dielectric thin films, including epitaxial growth of $Hg_{1-x}Cd_xTe$, and CdTe. He has also grown HgTe/CdTe superlattice for two-dimensional transport studies. He has over 20 publications.

W. J. Gunning: Manager, Optical Devices Department, Rockwell International Science Center. B.S., Physics, Rensselaer Polytechnic Institute (1973); Ph.D., Solid State Physics, Univ. of Pennsylvania (1978). Dr. Gunning joined Rockwell International Science Center in 1978 as an MTS. An experimentalist, he has developed a number of novel optical devices including a multiple cavity electro-optic Fabry-Perot tunable filter, reflective electro-optic Fabry-Perot filter, liquid crystal tunable Fabry-Perot, cryogenic solid Fabry-Perot for CO_2 laser wavelengths, and a narrowband, extremely wide field of view filter for visible laser receiver applications. For this last project he was the overall program manager as well as technical contributor. This project culminated with the integration of these filters into optical receivers which were successfully tested by the Navy and Air Force. He has studied and improved the properties of visible polarizers and has studied the optical properties of new electro-optic materials.

Since assuming the responsibilities as Manager in 1983, Dr. Gunning has been directing the activities in gradient-index optical thin film research. He has made numerous contributions to the conceptual development of gradient-index deposition processes and to device applications. This activity has been quite successful and is becoming recognized by the community as at the forefront in thin film research.

Dr. Gunning has 25 publications and 1 patent. He is a member of the Optical Society of America, The American Physical Society, and the Society of Photo-Optical Instrumentation Engineers.

H.O. Sankur: Member of Technical Staff, Applied Optics Department. Dr. Sankur received his M.S. and Ph.D. degrees in Electrical Engineering from California Institute of Technology in 1971 and 1975, respectively. While at Caltech, his field of research was semiconductor-metal interactions. He successfully developed a novel solid state epitaxial growth technique for Si from Si/Al thin film structures. From 1974 to 1976, he worked at Jet Propulsion Laboratory on degradation mechanisms and on effects of electrostatic discharge on CMOS IC devices. Dr. Sankur was a senior research fellow at University of Southern California, between 1977 and 1979, working on CVD and high pressure synthesis of GaN. From 1979 to 1982, he worked at Hewlett Packard Optoelectronics Division. His work involved designing epitaxial production reactors, optimizing quantum efficiency of $GaAs_xP_{1-x}$ LED material by improving the epitaxial growth process. He developed a novel technique of measuring nitrogen concentration and techniques to measure and characterize structural defects in GaAsP and GaP. He joined the Rockwell Science Center in 1982 and has been working on laser-assisted deposition of dielectrics and semiconductors. Dr. Sankur has six publications and is a member of the American Physical Society and Electrochemical Society.

J. Nelson: Member of Technical Staff, Optical Devices Group. Dr. Nelson received his B.A. degree in Chemistry with high honors from the University of Tennessee in 1979, and his M.S. and Ph.D. degrees in Physical Chemistry from UCLA in 1982 and 1984, respectively. While at UCLA, his field of research involved studies of clean metal and semiconductor surfaces and characterization of MBE grown thin films using techniques such as angle-resolved photoemission, Auger electron spectroscopy, low-energy electron diffraction and electron-energy loss spectroscopy. Since joining the Rockwell International Science Center in December 1984, his initial responsibility has been the design and construction of a vacuum deposition chamber dedicated to the growth of optical thin films using a novel growth technique called Atomic Layer Epitaxy (ALE). Dr. Nelson has seven publications and is a member of the American Physical Society, American Vacuum Society, American Chemical Society and the Materials Research Society.

7.0 INTERACTION

7.1 Publications

1. H. Sankur, J. Nelson, "Luminescence Analysis of Pulsed Laser Induced Evaporation Plume of Solids," in preparation.

2. J. Nelson, H. Sankur, "Mass and Energy Analysis of the Constituents of a Laser-Induced Evaporant Plume," in preparation.

7.2 Presentations

The following abstracts have been submitted for presentation at the annual meeting of the Optical Society of America, Washington, D.C., October 1985.

OPTICAL THIN FILMS DEPOSITED BY PULSED AND CW LASER EVAPORATION

H. Sankur

ABSTRACT

The properties of thin films of PbF_2, ZrO_2 and other optical materials grown by pulsed and CW laser evaporation are compared.

SUMMARY

Laser evaporation for the deposition of optical thin films is a very promising new technique for thin film fabrication. Localized heating, stoichiometric evaporation, and energetic deposition are a few of its novel features. In this work, thin films of PbF_2, ZrO_2 and other thin film materials, deposited by CW and pulsed CO_2 laser radiation, are compared. Optical, structural and chemical analysis are discussed.

This work was supported by AFOSR and Rockwell International under Contract No. F49620-84-C-0091

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PLASMA LUMINESCENCE GENERATED IN LASER EVAPORATION OF OPTICAL THIN FILM MATERIALS

H. Sankur, C. Pritt, J. Nelson

ABSTRACT

The plasma generated in laser evaporation of materials for thin film deposition is analyzed using an optical multichannel analyzer. Various excited state neutrals, ions and molecules are identified.

SUMMARY

The emission of the plasma generated when a pulsed CO2 laser is used to evaporate an optical thin film material is analyzed by means of an optical multichannel analyzer in the 200 - 900 nm region. Source materials were Al_2O_3, SiO_2, HfO_2, TiO_2, and ZnO, which are absorbing at 10.6 microns. Very rich atomic spectra were obtained indicating the presence of excited neutrals, as well as singly, doubly, and triply ionized anions and cations. Molecular emission (e.g. Al-O) was observed when background gas pressures of O_2, He, Ar, or N_2 were increased to the range of 0.1 to 10 torr. The optical power dependence of the emission intensity is nonlinear, indicating saturation behavior.

This work was supported by AFOSR and Rockwell International under Contract No. F49620-84-C-0091.

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MASS AND ENERGY ANALYSIS OF THIN FILM EVAPORANT STREAMS GENERATED BY PULSED LASER HEATING

J. Nelson

ABSTRACT

The mass and kinetic energy spectra for optical thin film materials, evaporated using a pulsed CO_2 laser, are analyzed using a quadrupole mass analyzer.

SUMMARY

Little is known about the physics of film growth with laser evaporation, as compared with more conventional techniques such as thermal or sputtering. For example, there is evidence that the atomic nature of the laser evaporated materials may be responsible for the observed epitaxial growth at comparatively low temperatures. It is of fundamental interest to study the physical processes which lead to such results. Oxides (ZnO, Al_2O_3, SiO_2) and fluorides (PbF_2), which have been used to form high quality optical thin films, were evaporated using a CO_2-TEA laser with power densities exceeding 10^9 W/cm^2. The chemical state (atoms, molecules or clusters) of the evaporants was determined using a residual gas analyzer (RGA). The relative concentrations of the different chemical species were measured as a function of laser conditions. Using the RGA in conjunction with a time-of-flight apparatus, the kinetic energy of the evaporants was also studied as a function of laser conditions. Finally, the effect of reactive (O_2) and inert (N_2, He) gases on the evaporation process was also studied.

This work was supported by AFOSR and Rockwell International under Contract No. F49620-84-C-0091.

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