

SPECTROSCOPIC INVESTIGATIONS OF LASER ABLATED GERMANIUM OXIDE

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ABSTRACT

Laser produced plumes from a GeO₂ target were investigated using both optical emission spectroscopy and laser induced fluorescence. Elemental neutral and ionic Ge and diatomic GeO were monitored as a function of O₂ pressure at 4 cm from the target surface. Data obtained from laser fluorescence experiments showed no indication of chemical production of GeO in these plumes under any conditions studied; however, the atomic emission intensities of several ionic and neutral Ge lines appeared to increase with O₂ pressure. This signified plume interactions with the background gas. The trends in the species concentrations were determined and the results are interpreted with respect to mechanisms for thin film growth.

INTRODUCTION

Our recent work in growing thin films of germanium dioxide (GeO₂) using laser ablation deposition showed that stoichiometric thin films can be fabricated under two different deposition conditions, and the results of these studies suggest the possibility of two separate kinetic mechanisms for growing these films. First, stoichiometric films could be produced by ablating a GeO₂ target in 150 mTorr of ambient O₂ [1]. At these relatively high pressures, elemental Ge in the ablation plume can react gas kinetically [2] with O₂ to form GeO, which can subsequently recombine with excess O₂ at the substrate surface in a disproportionation reaction. Generally, the oxygen content in the films increased with O₂ pressure from 10⁻⁵ to 0.15 Torr.

Performing depositions at 100's mTorr of an ambient gas causes the plume to become very highly forward directed [3] and leads to films of nonuniform thickness. For that reason, we explored film depositions at low pressures to produce plumes that are spatially more extended and allow a better opportunity to produce flat films for optical waveguides. Stoichiometric films were prepared at lower background pressures when the ablation plume was passed through a dc discharge in a 30 mTorr oxygen background [4]. In these studies, we found that the combination of the substrate temperature and the dc discharge enabled us to incorporate the correct oxygen content in the film. At these lower pressures, chemical reactions would appear unlikely because of the low collision rates between Ge and any ambient gas. However, the discharge could activate the material in the plume or the ambient gas providing additional energetic species to promote surface recombination reactions.

Reactions between elemental species in laser produced plumes and a reactive background gas are known to be important for producing good quality high T_C superconducting thin films [5]. An understanding of the potential chemical processes occurring between the plume material and any reactive gas in between the target and the substrate is needed to elucidate the important thin film growth mechanisms. Thus, the aim of this work is to explore the microscopic mechanisms responsible for forming high quality dielectric thin films under both growth conditions discussed above.

EXPERIMENT

Figure 1 shows a schematic diagram of the experimental apparatus. A pulsed ArF excimer laser [$\lambda = 193$ nm, pulse width of 28 ns (FWHM)] was focused onto the surface of a GeO₂ target at normal incidence with an energy density of 1 J cm⁻². The target was housed in a chamber that routinely achieved a base pressure of 5×10^{-6} Torr. Oxygen was metered into the chamber with a needle valve and a ring electrode biased at -1.5 kV was inserted in the plume path to determine the effect of a dc discharge on the constituents. The emission from the laser-produced plume (with and without the discharge) was imaged onto a spectrometer and the dispersed signal was detected using a linear diode array (OMA III). The time-integrated emissions were examined as a function of O₂ pressure at 4 cm from the target surface in spectral regions that covered emission features originating from electronically excited states of Ge I, Ge II, GeO, and O I.

The laser fluorescence experiments were performed using the frequency doubled output of a pulsed dye laser. The dye laser probe beam interrogated the plume perpendicular to the excimer laser beam, and the fluorescence was collected at 90° to the dye laser beam. The timing between the two pulsed lasers was varied between 1 and 50 μ sec so that the plume constituents could be probed as a function of time from the ablation laser pulse. The timing of the OMA gate was maintained so that the probe beam sampled the plume material within the 500 ns gate width of the OMA. Ge atoms were probed by exciting from the ground ³P₀ state to the ³P₁ level at 265.16 nm and observing the fluorescence from this state with the gated OMA III system. GeO molecules were probed at 261.4 nm which promoted population from the X¹ Σ ($v'' = 0$) to the A¹ Π ($v' = 1$) state. The entire $v' = 1$ progression from GeO (A \rightarrow X) was captured with the gated OMA in a single trace.

RESULTS

Figure 2 shows a sample of a time-integrated plasma emission spectrum. The plume luminescence was caused by electronic transitions in neutral Ge (Ge I), singly ionized Ge (Ge II), and neutral O (O I) atoms. At pressures below ≈ 50 mTorr and with no discharge, the emission emanated solely from excited Ge I. The emission intensities remained constant from vacuum to about 10 mTorr of added O₂ and increased by a factor of 10 between 10 and 100 mTorr. This behavior could be attributed to species confinement at higher backing gas pressures which increases the number of emitters per volume [6]. Application of the discharge at low pressures (i.e., P(O₂) < 50 mTorr) enhanced both the Ge I and O I atomic emissions as shown in Fig. 2. No GeO emission was observed under any conditions in these experiments.

The various channels that are open to creating these electronically excited states in the plume material make it difficult to monitor the behavior of any one species independent of the formation mechanism. In order to circumvent this limitation, the behavior of species in the plume was monitored as a function of ambient gas pressure using laser induced fluorescence (LIF). Figure 3 shows a sample LIF spectrum of Ge I. The ground state Ge I concentration appears to decrease with increasing O₂ pressures as illustrated in Fig. 4. The decay, when converted to a rate coefficient, is consistent with the known reaction rate coefficient for Ge + O₂ \rightarrow GeO + O [2]. The Ge LIF intensities were also monitored as a function of N₂ pressure to test whether or not the decay is due to this reaction scheme. Collisions between N₂ and Ge are non-reactive and should yield little or no decrease in the Ge I concentration with pressure. We found, however, that the Ge concentration decreased with increasing N₂ pressures with a rate that was only 40% slower

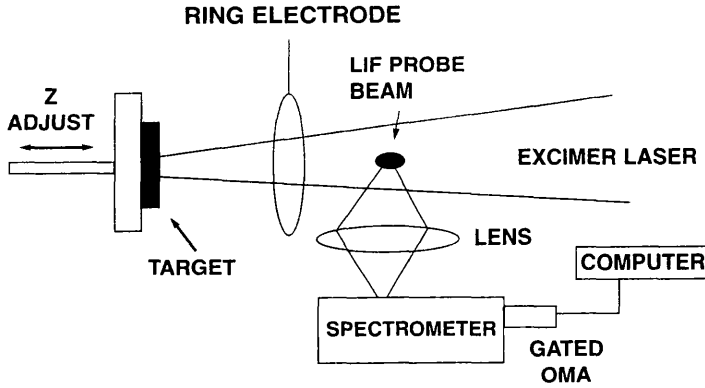


Figure 1. Diagram of the experimental system. The diagram shows the arrangement for the LIF studies. The set-up for the optical emission studies changes by removing the dye laser beam and operating the OMA in an ungated mode.

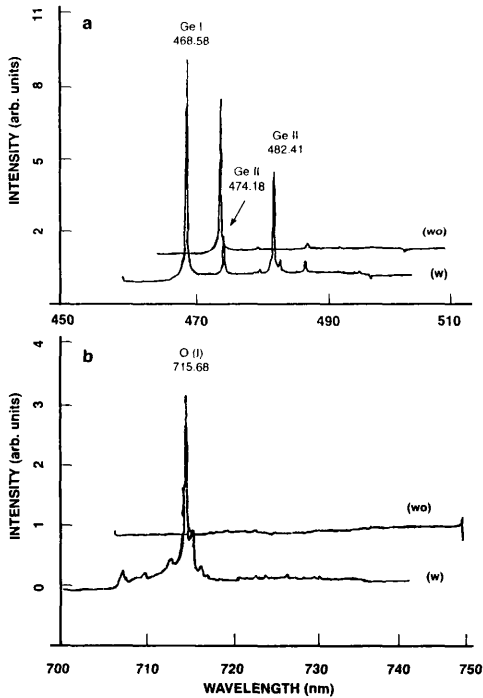


Figure 2. Time-integrated plasma emission spectrum recorded at an oxygen pressure of 30 mTorr and at 4.0 cm from the target surface. Trace (a) shows Ge emission with (w) and without (wo) the discharge while trace (b) shows the behavior of atomic oxygen.

than that for O_2 . This may indicate that the decays are not caused by a chemical depletion of ground state atoms. Electronic quenching could account for these decays, but the radiative lifetimes of the states under study (≈ 250 ns) prohibit such encounters [7]. For example, the time between collisions in an equilibrium mixture is about $12 \mu\text{s}$ so the electronic states will never see a collision. These pressure experiments were repeated with the dc discharge with no difference in the results.

Although the emission studies did not reveal the presence of GeO^* , the removal of ground state Ge I by reaction is not totally ruled out. Reactions between Ge and O_2 produce GeO in the electronic ground state with $\Delta E = +1.2$ eV [7]. The exothermicity of the reaction is sufficient to populate $\text{GeO}(X)$ up to $v'' = 5$ so no visible emission would be produced. We searched for vibrational excitation in $\text{GeO}(X)$, which would indicate chemical formation of GeO, by pumping from various X state vibrational levels ($0 \leq v'' \leq 5$) to the A state using the strongest Frank - Condon allowed transitions. We discovered strong emission lines from the molecule upon excitation from only $v'' = 0$. No LIF emission was observed after exciting from $v'' \geq 1$ even in the presence of various pressures of O_2 . In experiments similar to those performed with Ge I, the GeO LIF emission intensities decreased with increasing O_2 pressures. The $\text{GeO}(A \rightarrow X)$ LIF signals became undetectable at O_2 pressures near 40 mTorr. The radiative lifetime for $\text{GeO}(A)$ is not known, but, assuming typical values of 3-5 μs , a significant number of collisions would not occur eliminating electronic quenching as the source of the intensity decrease. Although the mechanism for these intensity decreases at various O_2 pressures is currently not understood, the results do indicate that chemical production of GeO via interactions of the plume material with the background O_2 does not occur.

Since the chemical production of GeO via plume-ambient gas interactions does not appear to be important, we traced the origin of diatomic GeO by monitoring LIF signals as a function of distance from the target surface. These LIF experiments showed that GeO molecules were present in the plume at distances as near as 2.5 mm from the target surface. Molecular LIF emission was also observed in vacuum. These results indicate that GeO is either produced as a result of recombination of material in the plume near the target surface where the ion and neutral number densities are high or the molecule dissociated directly from the target.

DISCUSSION

These experiments showed that interactions between the plume material and the ambient O_2 gas directly affected the concentrations of the excited neutral and ionic states of Ge and O atoms as well as molecular GeO. Two possible mechanisms can be postulated to explain the observed emission and LIF behavior described above. The first mechanism involves non-reactive plume - ambient gas interactions. Plume interactions with the background gas, especially at the higher gas pressures (> 50 mTorr), spatially confine the plume and should cause both the atomic emission features and the LIF intensities to increase. However, we observe increases in only the atomic emission intensities and not in the LIF signals. Therefore, this mechanism may not be plausible. The second mechanism involves reactive encounters between the plasma and the ambient gas. Scattering events between electrons and atoms or molecules and high kinetic energy collisions between atoms could produce neutral electronic excitation as well as additional ionization. Therefore, atomic emission experiments would show an increase in emission intensities as was observed here. These interactions would also result in a concurrent decrease in ground state species which is consistent with the LIF results.

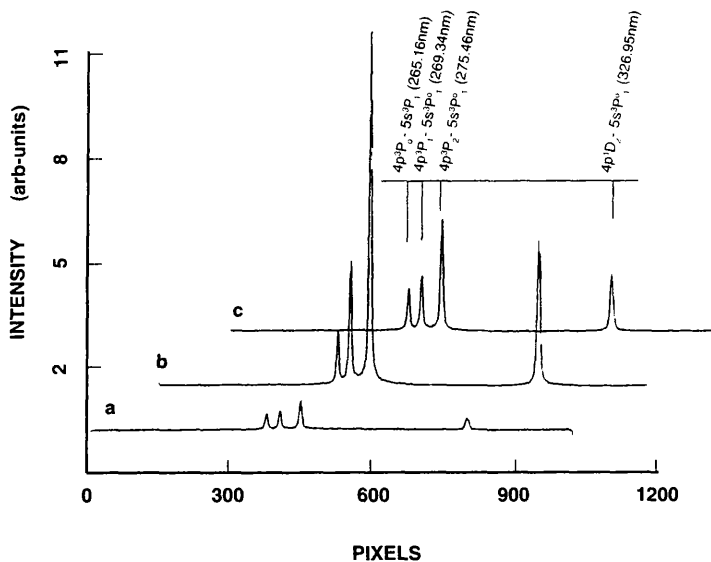


Figure 3. LIF emission spectra from Ge as a function of O_2 pressure: (a) $P(O_2) = 25$ mTorr, (b) $P(O_2) = 0$ mTorr, and (c) $P(O_2) = 10$ mTorr. These spectra were recorded 4 cm from the target surface with a $10.5 \mu s$ delay time between the excimer and the probe lasers.

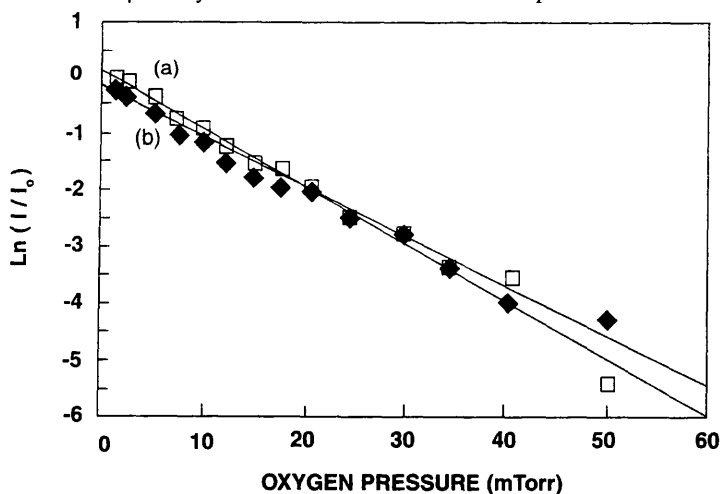


Figure 4. Plot of the natural log of the relative fluorescence intensities vs. O_2 pressure. Decays from two LIF emission lines are plotted: (a) $\lambda = 326.9$ nm and (b) $\lambda = 275.5$ nm. The cause of this decay may be due to a combination of reactive and non-reactive collisions with the ambient oxygen.

These results may have significance in determining the mechanisms for GeO₂ thin film growth. Since chemical reactions do not appear to dominate the plume-ambient gas processes, surface reactions must control the thin film growth. At high ambient gas pressures (i.e., P(O₂) = 150 mTorr), excess O₂ may be required to complete recombination reactions on the substrate surface, whereas at lower pressures, the discharge produces excited O atoms which can then interact more energetically with the substrate. These processes produce the same result: stoichiometric thin films. The importance of GeO in the film formation process is not completely understood. Diatomic GeO is abundant in vacuum but disappears as the O₂ pressure is increased. Since we cannot detect population in other vibrational levels of the ground state, GeO may either be scattered from the excitation region or the molecule could be dissociated as a result of plasma-O₂ interactions.

SUMMARY

Constituents of a laser-produced plume from a GeO₂ target have been spectroscopically examined. The results indicate complicated processes that occur when the plume interacts with the ambient O₂. High kinetic energy species are produced and the behavior of individual species in the plume may be governed by several reactive and non-reactive encounters. Chemical production of diatomic species, which are critical for growing good quality high T_C thin films, does not occur for laser ablated GeO₂ plumes in O₂, and thus does not appear to be important for growing stoichiometric GeO₂ thin films.

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