Activated reactive laser deposition of GeO_2 films

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Amorphous GeO_2 optical thin films were grown in an oxygen ambient on heated Si substrates using the technique of pulsed laser deposition. The application of a partially ionized oxygen plasma generated by passing the plume through a ring electrode facilitated stoichiometric film growth in low O_2 partial pressures. Emission spectroscopy of the plume revealed an enhancement in the ionic and neutral excited Ge species. The concentration of excited neutral and ionic oxygen atoms also significantly increased when the ring electrode was activated at $P(O_2)>10$ mTorr. Coupling the results of the film property measurements with the emission studies suggested that the presence of O atoms near the substrate surface during film growth was more critical in promoting oxidation than the gas phase process in the plume. The low-pressure conditions that were utilized to deposit stoichiometric film growth identified the appropriate conditions to produce uniform films over a large area that may be suitable for waveguide fabrication.

I. INTRODUCTION

Pulsed laser ablation of a target in vacuum or in a reactive gas ambient is a well established technique for growing superconductor,[1–3] semiconductor,[4,5] and dielectric[6,7] thin films. Congruent evaporation of multicomponent systems leading to stoichiometric film growth and the ability to deposit films in high-pressure ambient gases are two of the unique advantages of this method over conventional techniques. The interaction of the laser with the target produces a plume composed of neutral, ionic, and molecular species dissociated from the bulk target whose expansion into the ambient is mainly governed by the pressure gradient across the plume. For sufficiently high particle densities desorbed from the target surface, gas-dynamic effects govern the propagation of the plume which produce the forward-directed peaking of the particle distribution.[8] The plume expands rapidly in vacuum, while at high ambient pressures [that is, pressure less than that required to form shock waves ($P\leqslant5$ Torr)] the diminished pressure gradient across the plume suppresses this expansion. This highly forward-directed plume profile has been shown to assume a $\cos^n\theta\,(8\leqslant n\leqslant16)$ functional behavior at high pressures.[9] In addition, the shorter mean-free path at higher pressures limits the plume propagation distance to a few centimeters from the from surface of the target. The gas phase interactions promoted by the collisions between the plume species and the ambient gas also play a major role in growing thin films that require the incorporation of a gaseous species to produce the desired stoichiometry.[10] Although film growth at high pressures can lead to enhanced gas phase reactions, the deposition is performed closer to the target and, thus, the films become highly nonuniform.

Amorphous GeO_2 is a promising material for the fabrication of optical waveguides that are useful towards the construction of various optical elements in integrated optical systems.[11] To date, the primary method of GeO_2 film growth has been the reactive sputtering of a GeO_2 target.[12,13] Most sputter-deposited films require long postannealing steps to produce defect-free stoichiometric films. This may be due to the ion damage caused by the constant ion bombardment of the film during the growing process. In addition to sputtering, recent advances in laser ablation deposition techniques has led to the use of this method for growing GeO_x thin films.[14,15] However, as reported by Wolf *et al.*,[15] deposition of stoichiometric GeO_2 thin films by this technique has been possible only at oxygen ambient pressures above 150 mTorr. These high-pressure film growth experiments produced thin films that are highly nonuniform and, thus, not suitable for waveguiding. In this paper, we report the use of an activated reactive laser deposition technique that facilitated the growth of amorphous, stoichiometric GeO_2 films that are uniform over a large area. The gas ambient present during laser ablation has been energetically enhanced by generating a glow discharge plasma between the target and the substrate to promote both the gas phase and the substrate surface reactions. A similar technique has been used previously in plasma assisted laser deposition of high T_c superconducting films.[2] The significance of the gas phase and substrate surface reactions towards the formation of stoichiometric films has been studied through a combination of emission spectroscopy experiments of the laser generated plume and thin-film property measurements.

II. EXPERIMENTAL PROCEDURE

High-purity GeO_2 targets were prepared by melting GeO_2 powder in an alumina crucible which produced an extremely smooth, high-density target suitable for laser ablation.[15] The experimental setup is shown in Fig. 1. The

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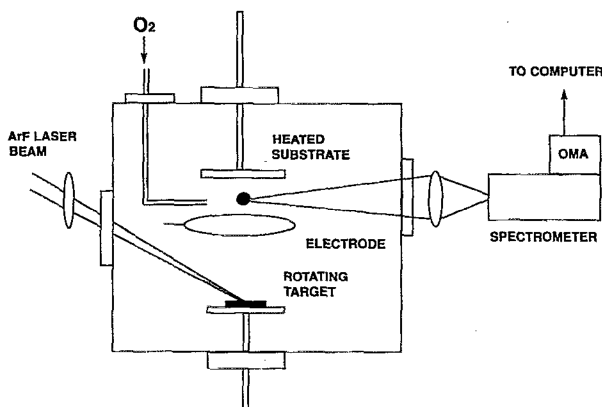

FIG. 1. Diagram of the experimental apparatus.

target was placed in a turbomolecular-pumped vacuum chamber and it was ablated by focusing an ArF excimer laser at a 45° angle of incidence. The target was rotated to prevent crater formation in a single location on the surface. The laser beam had an energy density of 1.5 J cm^{-2} over a 1×3 mm spot. This fluence was above the 0.5 J cm^{-2} threshold fluence required for ablating GeO_2.[16] The material ablated from the target produced a visible plume that extended normal to the target surface. The plume subsequently passed through a 5.1-cm-diam ring electrode which was placed approximately 0.5 cm in front of a grounded substrate holder. Oxygen was introduced through a nozzle placed near the substrate surface. An oxygen glow discharge (hereafter referred to as the plasma) was created by applying a potential of −700 to −1500 V to the electrode in an attempt to provide a more reactive environment for the ablated material. The plasma appeared only during the plume propagation at $P(O_2) \leq 10$ mTorr while at $P(O_2) > 10$ mTorr, the plasma was self sustaining.

The effect of the discharge on the propagating plume was investigated by optical emission spectroscopy. The plume emission was observed by using an image-intensified optical multichannel analyzer (OMA III). The emitted radiation from a point 4 cm above the target was imaged approximately 1:1 by two quartz aspheric lenses onto the entrance slit of a 0.5-m spectrometer with a 0.17-nm resolution. Signals were averaged over ten laser shots to provide an adequate signal-to-noise ratio.

The laser-produced plume that passed through the ring electrode was deposited on IR transmitting Si substrates whose temperature was controlled between room temperature and 500 °C. The solvent cleaned substrates were mounted on a heating block using silver print for good thermal contact. To study the effect of the ambient oxygen pressure on the gas phase reaction, a series of films were grown on ambient temperature substrates with O_2 pressures ranging from 0 to 100 mTorr. A target-substrate distance of 7.5 cm was used for ambient pressures from vacuum to 30 mTorr whereas 6- and 4-cm target-substrate separations were employed for oxygen pressures of 50 and 100 mTorr, respectively. Varying the target-substrate distance in this manner to ensure that the substrate was within the confines of the

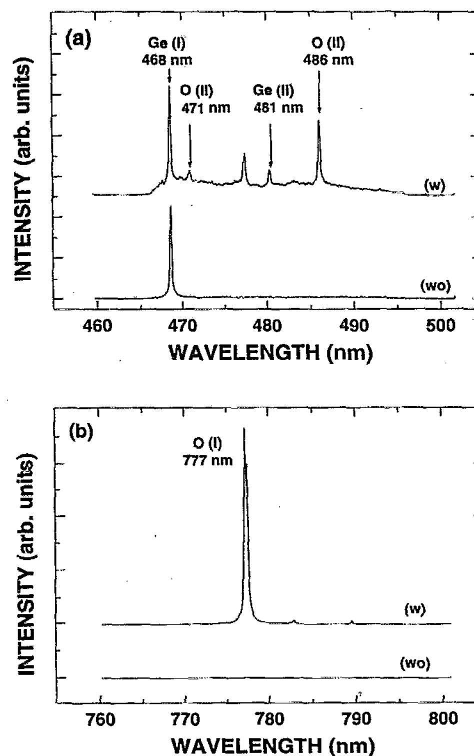

FIG. 2. Emission spectra of a laser-produced plume produced in 30 mTorr of O_2 at a laser fluence of 1.5 J cm^{-2}. The spectra were recorded at a center wavelength of (a) 480 and (b) 780 nm. Each set of spectra compares emissions with (w) and without (wo) the discharge activated.

plume was a consequence of a decreasing mean-free path with increasing background pressure. The effect of surface reactions at the substrate was investigated by depositing films at temperatures ranging from 20 to 300 °C. The oxygen content of all the films were deduced from infrared transmission spectra which were obtained using a Nicolet 510P Fourier transform infrared (FTIR) spectrometer with a resolution of 2 cm^{-1}. In addition, x-ray diffraction was used to observe any changes in the crystallinity of the films grown at elevated temperatures. The thickness variation of the films deposited under different pressures was measured using a stylus surface profiler. Multiple angle of incidence ellipsometry was also performed on several thin films to determine the refractive index n. The measurements were made at 632.8 nm at incidence angles from 55° to 80° in 5° increments. The films were assumed to be transparent ($k=0$) which gave two adjustable parameters (n and the film thickness) to simultaneously fit the ellipsometric parameters Ψ and Δ. Further details are found in Ref. 15.

III. RESULTS AND DISCUSSION

Emission from the laser generated plume was recorded with and without the oxygen plasma in the wavelength region between 250 and 850 nm. In the absence of the discharge, the spectrum produced at a laser fluence of 1.5 J cm^{-2} consisted mainly of excited neutral Ge atoms (Ge I). Applications of the discharge produced strong emission from excited Ge ions (Ge II) and enhanced the neutral atomic

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emissions. Figure 2(a) shows a sample emission spectra centered at 480 nm. The emission wavelengths are shown for each prominent feature. These emission features resided on a continuum background which indirectly indicated the presence of electrons that can potentially interact with the plume constituents and the ambient gas. The intensity of the line at 468 nm, which corresponded to an electronic transition in Ge I, increased by approximately a factor of 1.5 in the presence of the plasma. Emission from Ge II, absent without the discharge, also appeared under the activated conditions. Surveys at higher laser fluences without the plasma revealed Ge II emission in addition to electronically excited neutrals, and a significant enhancement of the ion line intensities occurred with an activated ambient. The results of the optical emission survey presented here are consistent with those reported in Ref. 16. Since the emission intensity was directly proportional to the number density,[17] the increase in the intensity of these emission features translated to an increase in the population of the emitting states. Clearly, the O_2 plasma interacted with the material in the plume to produce a higher density of electronically excited neutral and ionic Ge atoms.

The plasma enhancement also produced excited and highly reactive species of neutral atomic oxygen, O I. Figure 2(b) shows emission spectra centered at 780 nm with and without the oxygen plasma. Emission at 777 nm clearly showed the presence of the $O(^5S)$ state which was not observed without plume enhancement. There were also significant increases in other oxygen emission lines, notably the O I metastable ^1D state observed at 715 nm and oxygen ions O II as shown in Fig. 2(a). The enhancement in the oxygen emission was probably a direct result of an interaction between the discharge (electrons) and the ambient oxygen with little contribution from O or O_2 produced from the laser ablation process. Although we found significant enhancement in the ionic and electronically excited-state content of the plume, we observed no signatures from gas phase chemical reactions as a result of plume/plasma interactions.

The oxygen content of films deposited under the enhanced plasma conditions at different pressures and substrate temperatures were analyzed by infrared spectroscopy. The structure of amorphous GeO_2 can be described as Ge-Ge_yO_{4-y} tetrahedra connected by bridging oxygen atoms. The asymmetric stretch vibration mode (ASM) of Ge-O-Ge in stoichiometric GeO_2 resides at 885 cm^{-1}. The vibration frequency of oxygen deficient structures, for $y=0$ to 4, changes linearly from 885 to 740 cm^{-1} according to the empirical equation[18]

$$\nu(x)=72.4x+743 \quad (cm^{-1}), \tag{1}$$

where x is the oxygen content that ranges from 2 to 0. The stoichiometry of the films produced in these studies has been computed using this equation. Figure 3 shows sample IR spectra of GeO_x films deposited in 30 mTorr of discharged O_2 at three substrate temperatures. The asymmetric stretch vibration mode described by Eq. (1) is the most prominent absorption peak, as observed in Fig. 3. All the IR absorption measurements have been made near the center of the film where thickness variations are minimal. The broadening of the absorption band at high temperatures may have resulted

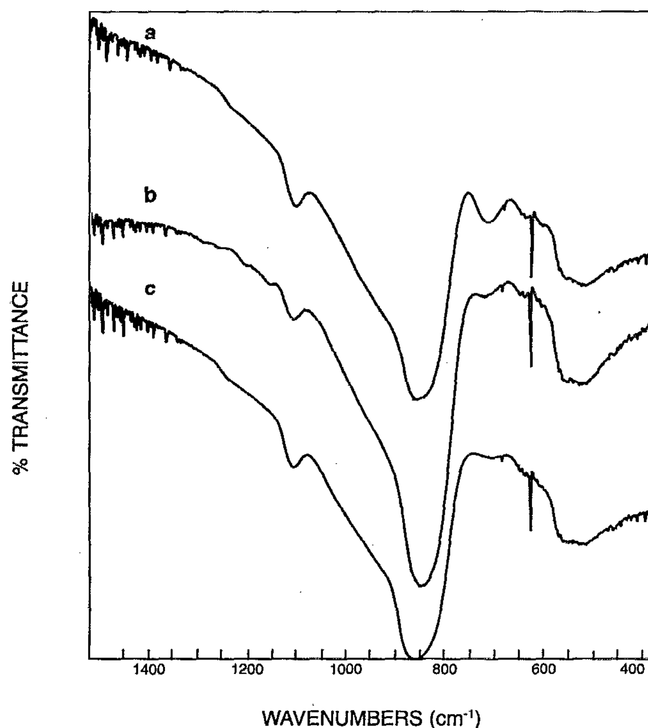

FIG. 3. IR transmittance spectra recorded at the center of GeO_x thin films deposited in 30 mTorr of activated oxygen at three substrate temperatures: (a) ambient, $\nu=875.8$ cm^{-1}; (b) 100 °C, $\nu=874.8$ cm^{-1}; and (c) 300 °C, $\nu=881.6$ cm^{-1}. Note the shift in the Ge-O-Ge asymmetric stretch mode as the substrate temperature increases to 300 °C which indicated a more complete oxidation of the film.

from interfacial strain due to a thermal-expansion mismatch between Si and GeO_2. This mismatch, defined as the difference in the thermal-expansion coefficients of Si and GeO_2 divided by the thermal-expansion coefficient for the substrate, is approximately 0.82.

The films deposited at different pressures and substrate temperatures were analyzed to gauge the effectiveness of gas phase and substrate surface reactions. Figure 4 shows the changes in the oxygen content as a function of both the ambient oxygen pressure and the substrate temperature. These

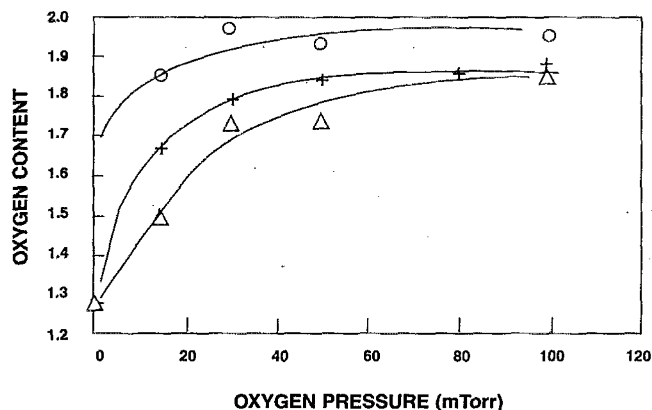

FIG. 4. The effect of the ambient oxygen pressure on the film stoichiometry with the oxygen plasma. The data depict film grown at the following substrate temperatures: (△) room temperature; (+) 200 °C; and (○) 300 °C.

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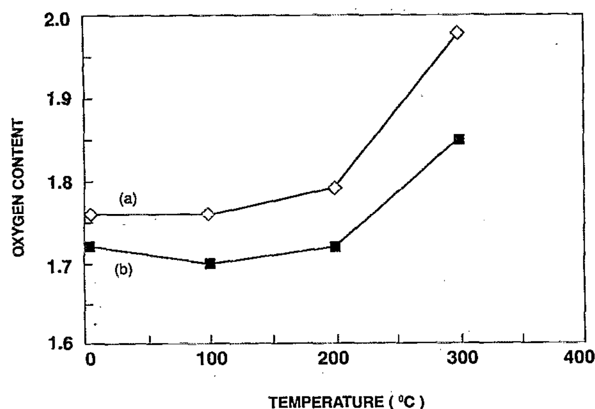

FIG. 5. Variation in the film oxygen content at different substrate temperatures: (a) with the oxygen discharge and (b) without the oxygen discharge. The O_2 pressure remained constant at 30 mTorr for these comparisons.

data were collected for films grown under discharge conditions. The oxygen content of the films deposited at room temperature increased from 1.3 to 1.8 as the deposition pressure was changed from 5×10^{-4} Torr to 100 mTorr. The increase in the oxygen content as a function of pressure for ambient temperature substrates indicated that collision dominated processes, such as gas phase chemical reactions, may be important for growing stoichiometric films even at very low pressures. As the substrate temperature was raised to 300 °C, the oxygen content in the films clearly increased at a constant oxygen pressure. The data depicted in Fig. 3 shows that the absorption maximum in the Ge-O-Ge asymmetric mode shifted toward higher energy as the substrate temperature increased to 300 °C. According to Eq. (1), this implied an enrichment of oxygen in the film matrix. The atomic emission experiments illustrated that the activated oxygen environment not only increased the concentration of Ge ions and neutral excited states, but, most importantly, significantly enhanced the concentration of energetic oxygen. In addition, no chemical reaction product (i.e., GeO) was found in the plume. Therefore, the dependence of the oxygen content on the substrate temperature may indicate an enhancement in substrate surface reactions and revealed that potential surface reactions at high temperatures may be more efficient in presence of the plasma. Under these plasma conditions, the films deposited in 30 mTorr of oxygen became stoichiometric at a substrate temperature of 300 °C. The IR spectra and x-ray diffraction of the films deposited at this temperature gave no indication of crystalline structure. The average value for index of refraction for these films was 1.591 ± 0.003, which was slightly lower than the accepted value for bulk GeO_2 ($n=1.61$). The film thicknesses that were output from the model used to calculate n agreed with the surface profiler results to within $\pm5\%$.

In an earlier work,[15] increasing the substrate temperature while depositing material from laser ablated GeO_2 targets worked primarily to reduce the porosity in the film. FTIR analyses of these films showed no significant change in the oxygen content with increasing substrate temperature when the deposition was performed in a 150-mTorr ambient O_2 environment. Figure 5 shows the effect of the oxygen plasma on the film oxidation for films deposited in 30 mTorr of O_2. The results revealed that the oxide content was higher in films deposited with the plasma present. Generally, we observed a 10%–15% increase in the oxygen content for films deposited with the discharge at a constant substrate temperature. The films attained stoichiometric proportions ($x\approx1.98$ as measured at the center of the film) in the oxygen plasma for a 300 °C substrate temperature while the films deposited without the plasma achieved a Ge to O ratio of only 1:1.8. Although the plume became more energetic with the oxygen plasma, the presence of these higher energy species appeared not to affect the film quality (i.e., surface morphology, thickness variation).

FTIR measurements were made for several films as a function of distance along the major axis to determine the uniformity of the oxygen content in the film. The position of the ASM absorption peak did not remain constant along the film's major axis, but shifted to lower energy toward the outer region of the film. This suggested that the films became oxygen deficient away from the center. For example, a film deposited at $T=400$ °C and $P(O_2)=50$ mTorr had an ASM peak located at 881 cm^{-1} ($x=1.91$) near center which corresponded to a near stoichiometric film. The ASM peak shifted to 869 cm^{-1} approximately 2 cm from the center of the film, which translated to a 1:1.74 Ge to O ratio. Generally, the composition of the films within a half angle of $\approx20°$ from the normal of the target was stoichiometric with respect to the target. However, the oxygen content in the laser deposited films deviated from ideal by approximately 2%–3% at angles greater than 20°. Similar results were recorded for films grown without the discharge at higher oxygen partial pressures.[15]

As shown in Fig. 4, the films deposited above 30-mTorr oxygen pressure attained stoichiometric proportions at a 300 °C substrate temperature. Depositions at these low pressures could have an impact on the growth of thin films for waveguide applications. The rectangular laser spot focused at the target produced a plume with an elliptical cross section which expanded perpendicularly to the laser spot on the target. The ejected material was highly forward directed so the majority of the material removed from the target was within 20° half angle. This expanding material was subsequently collected on the substrate surface which formed a film with an elliptical pattern having its major axis perpendicular to the laser spot formed on the target surface. Two films were grown to compare the thickness variation: one in 100 mTorr of O_2 with a target-substrate separation of 4 cm (no discharge) and one at $P(O_2)=30$ mTorr at 7.5 cm from the target in an oxygen plasma. The thickness variations are shown in Fig. 6 for both the major and minor axes. The film grown at low ambient pressure was more uniform over a larger area. The thickness along the major axis of the elliptical profile varied only 10% over a 1.75-cm length on each side of the center of the film for those grown at 30 mTorr, while for the film grown in 100 mTorr of oxygen the thickness varied 10% within a 0.6-cm length on each side of the film's center. The thickness variation was more prominent along the minor axis, as indicated in Fig. 6. The full width at

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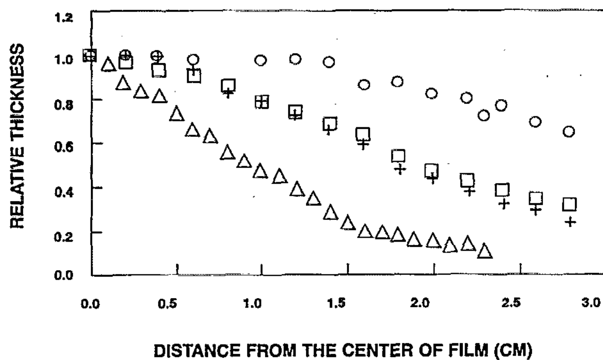

FIG. 6. The thickness variation across the major and minor axes of a film deposited at various O_2 pressures: (+) $P(O_2)=30$ mTorr, minor axis; (○) $P(O_2)=30$ mTorr, major axis; (Δ) $P(O_2)=100$ mTorr, minor axis; and (□) $P(O_2)=100$ mTorr, major axis. The substrate temperature was 300 °C. The discharge was activated only at an ambient pressure of 30 mTorr.

half maximum (FWHM) along the major axis in the films deposited at low pressure was nearly 3 cm while the minor axis had a FWHM of almost 2 cm. The expansion of the laser generated plasma under these low-pressure discharge conditions suggested that one can employ an axial geometry of a stationary heated substrate and a rotating target with a tilt of approximately 20° or less to the target rotation axis to deposit large area films. With this simple approach, a film thickness uniformity of better than 10% should be obtained over a 6×4 cm area with good compositional uniformity.

The oxygen content of the film is determined by gas phase and substrate surface reactions. The experimental results indicate that gas phase reactions may contribute to the formation of stoichiometric films, even at a very low pressure. The absence of GeO molecular emissions in the plume made it difficult to confirm the formation of GeO in the gas phase and, thus, the importance of molecular species in producing stoichiometric thin films. Since the exothermicity of the $Ge+O \rightarrow GeO+O$ reaction is only 1.93 eV,[19] molecules are expected to be in the electronic ground state and, therefore, nonemitting. The GeO molecules formed either in the gas phase through plume-ambient gas collisions or as a direct result of the laser ablation mechanism can undergo a disproportionation reaction $2GeO \rightarrow GeO_2+Ge$ on the substrate surface. The atomic oxygen produced by the plasma and the elevated substrate temperature lead to more efficient oxidation of the excess Ge at the substrate. However, recent results of probing molecular GeO at low pressures in laser generated plumes using laser induced fluorescence demonstrate that gas phase chemical reactions are not important when the plume interacts with atomic or molecular oxygen.[20] This result has been indirectly corroborated in this study. The presence of the plasma does not result in an appreciable change in the oxygen content (1.72–1.76 at 30-mTorr pressure) of the films grown with and without the plasma at room temperature. Stoichiometric films can be deposited at low pressures only with the correct combination of substrate temperature and activated oxygen concentration. That is, reactions at the substrate surface appear to be significantly affected by the plasma at high substrate temperatures. This result illustrates the importance of substrate surface reactions over gas phase processes in growing films with the desired composition.

IV. CONCLUSIONS

The results of this study showed that stoichiometric GeO_2 thin films can be deposited using laser ablation deposition at low reactive gas pressures. The high-pressure depositions reported previously[15] appear to depend on gas-phase reactions to incorporate the appropriate quantity of oxygen into the film. In contrast, the low-pressure depositions must rely on material impinging on the substrate with substantially higher energy. In this regime, surface reactions appear to dominate the growth process. This condition is achieved with the use of a ring electrode to provide activated atomic oxygen at the substrate surface to promote film oxidation. Collisions between high-energy atoms, ions, and electrons within the plasma are responsible for increasing the populations of electronically excited neutral and ionic Ge atoms. The activated oxygen background may also contribute to the collisional excitation of the atoms. The material used to grow the film clearly becomes more energetic with the plasma, as signified by the presence of energetic oxygen atoms and ions, and these highly excited species probably play an important role in the film growth process. No molecular species were observed in this study, so it is difficult to directly gauge the importance of these species for depositing good quality thin films. The higher energy depositions performed at low pressures also define the appropriate conditions to grow relatively flat films over large areas suitable for waveguiding experiments.

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