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Plume investigations of the mechanisms of SiO laser ablation at 266 nm

María Jadraque¹, Margarita Martín¹, Magna Santos², Luis Díaz²,
Mirosław Sawczak³, Adam Cenian³ and Gerard Sliwinski³

¹Instituto de Química Física “Rocasolano”, C.S.I.C. Serrano 119, 28006-Madrid, Spain

²Instituto de Estructura de la Materia, C.S.I.C. Serrano 121, 28006-Madrid, Spain

³Polish Academy of Sciences, IF-FM, Fizyca 14, 80-952 Gdansk, Poland

Corresponding author: mmm@iqfr.csic.es Telephone: 34 915619400; Fax: 34 915642431

Abstract. The ablation mechanism of SiO at the laser wavelength of 266 nm has been investigated by characterizing the composition and dynamics of neutral and charged particles produced in the ablation. The neutral and ionized composition of the plume and the dynamics of neutral SiO were investigated by time-of-flight mass spectrometry. The velocity distribution of neutral SiO molecules shows contributions of slow and fast components. The velocity distributions of charged species in the plume were investigated by a Langmuir probe technique, obtaining that the distributions shift towards higher velocities with increasing distance from the target surface. The fastest component of the velocity distribution of neutral SiO overlaps the slowest part of the velocity distribution of charged species. The average rotational energy of SiO molecules, estimated by LIF spectroscopy does not allow to draw clear conclusions about the participation of silicon oxide ion clusters as the precursors of fast SiO molecules in the plume.

1. Introduction

Ablation of silicon oxide is a source of small silicon oxide clusters that are considered to play an important role in the nucleation and growth of nano-materials, such as silicon based nano-structured deposits with photoluminescent properties [1 - 5]. At the laser wavelength of 308 nm, studies on the dynamics of the ablation plume indicate that, at low laser fluences, a thermal mechanism can account for the velocity distributions of neutral species in the plume that is also characterized by the presence of neutral and ionized Si_n clusters. [5] At the ablation wavelength of 248 nm there is some evidence of a different mechanism; at this wavelength Si_n⁺ are not observed and there are some indications that the ion distribution is more forward peaked than at longer wavelengths [4]. At 193 nm a complex mechanism involving a slow varying and a highly forward directed components of the plume, can be inferred through analysis of the angular distribution and rates of the deposition films obtained in the ablation [3]. Aiming at characterizing the transition between the different mechanisms we have investigated the ablation process at the intermediate wavelength of 266 nm.

2. Experimental

Pellet samples of SiO were ablated under vacuum by the 4-th harmonic of a Nd:YAG laser, delivering laser pulses of 6 ns, at the wavelength of 266 nm. The composition of charged species in the plume was obtained by time-of-flight (TOF) mass spectrometry. The plume developed in a direction perpendicular to the flight axis of the spectrometer and was deflected by an electric field along the TOF axis. The vacuum in the ablation chamber and in the flight region of the spectrometer was respectively better than 2×10^{-6} and 2×10^{-7} mbar. Neutral species present in the plume were postionized with an ArF excimer laser (193 nm); the laser beam, mildly focused by a 40 cm focal length lens, interacted the plume perpendicularly to both the direction of plume propagation and the deflecting electric field; typical fluences of the postionizing laser were 0.08 J cm^{-2} .

The time distributions of neutral SiO was measured by post-ionizing the plume at different distances above the target surface and, for a given distance, varying the delay time between the ablating and the probing lasers. The experimental set up has been described in detail in ref. [5].

The velocity of charged species in the plume was measured with a Langmuir probe consisting of a tungsten wire (diameter 0.1 mm) surrounded by a ceramic pipe; the wire was bent 90° at its end (leaving an exposed region 5 mm in length). Ablation of the target was performed in a cylindrical vacuum chamber, 20 cm in diameter, evacuated up to 8×10^{-6} mbar. The laser beam was focused by a quartz lens ($f = 30 \text{ cm}$) on the rotating surface of the target under the incidence angle of 45° . The laser fluence was 0.5 J cm^{-2} . The Langmuir probe could be displaced along the surface normal. The probe was biased in the range of -10 to 10 V with respect to the chamber walls.

The rotational temperature of SiO in the plume was measured by recording the rotationally resolved laser induced fluorescence (LIF) spectrum of the SiO molecules present in the ablation plume. The rotational distribution of the SiO in its ground vibronic state was measured probing the transition SiO ($A^1\Pi \nu'=3, J' \leftarrow X^1\Sigma \nu''=0, J''$) by scanning a frequency-doubled dye laser in steps of 0.001 nm; the exciting wavelength was near 221.5 nm whereas the excited fluorescence was collected in the spectral region of 281-283 nm [6].

3. Results and discussion

3.1. Composition of the ablation plume

The composition of the charged and neutral species in the plume was measured at different ablation fluences (from 0.15-0.7 J cm^{-2}). In the whole range studied, the most intense silicon-containing ion was readily assigned to Si_2O^+ . Other ion clusters of silicon and silicon oxides were observed at smaller intensities. Impurities with low ionization potential as Na^+ and K^+ gave an intense signal in the mass spectra. The main neutral species observed were Si, SiO and Si_2 , recorded under similar fluence conditions as those for observation of ions. Neutral silicon oxide clusters were not observed.

3.2. Velocity distributions of neutral and charged species

In order to compare the evolution in the plume of the charged and neutral species we have measured the velocity distribution of SiO and the velocity distribution for positively charged species and electrons. The time distributions, $I(t)$, of neutral SiO were measured at distances from 0.5 to 2 cm above the target surface and at laser fluences in the range of 0.15 to 0.5 J cm^{-2} . The time distributions were converted to velocity distributions, $f(v)$, by the transformation: $f(v_z) \propto I(t) \cdot t^2$. The latter assumes that the postionization takes place along the column in the plume interacted by ArF laser beam and therefore the signal intensity at a given time is proportional to the density integrated along the column, instead of integrated at a point [7]. The velocity distributions of positive ions and electrons were measured at distances of 1 and 2 cm above the target surface and at the same laser fluence as for the neutral SiO; the distributions are shown in figures 1 and 2 and compared to the velocity distribution for SiO measured at 1.5 cm.

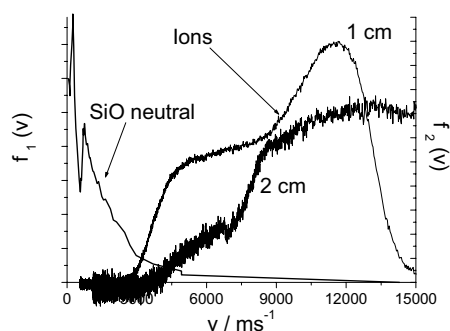


Figure 1: Velocity distribution of SiO and positive ions in the plume at distances above the surface of 1.5 cm for SiO and 1 and 2 cm for the ions. Laser fluence is 0.5 Jcm^{-2}

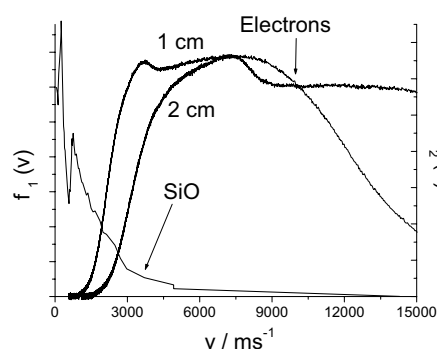


Figure 2: Velocity distribution of SiO and electrons in the plume at distances above the surface of 1.5 cm for SiO and 1 and 2 cm for the ions. Laser fluence is 0.5 Jcm^{-2}

It can be observed that the SiO distribution is multi-component indicating that several mechanisms contribute to the formation in the plume of neutral SiO. Regarding positive ion and electron distributions, the data depicted in figure 1 and 2 shows that the distribution shifts towards higher velocities at increasing distance above the target. In this range of distances, comparison of neutral SiO distribution, with that of charged species shows that the fastest part of the SiO velocity distribution overlaps that of charged species in the range of velocities of 3000 to 6000 ms^{-1} . This suggests that the formation mechanism of SiO responsible for the fastest component of the velocity distribution is related to charged species in the plume. Regarding ion species that could be precursors to SiO formation, we note that the most abundant silicon-containing species detected in the mass spectra is the Si_2O^+ cluster. Neutral Si_2O is stable against dissociation in $\text{SiO}+\text{Si}$ by $\sim 2\text{eV}$ [8], but excited Si_2O formed by ion-electron recombination could have enough energy to undergo dissociation leading to neutral SiO. Ion-electron recombination has been invoked to explain velocity distributions of neutral and ionised Zn and O atoms produced in the ablation of ZnO and also to account for the fast velocity component of neutral atoms produced in the ablation of YBCO at 351 nm [9, 10]. On the other hand, the shifts towards higher velocities of the electron and positive ion distributions would be compatible with depletion of those species due to ion-electron recombination processes. However, other mechanisms of plume acceleration cannot be excluded; thus, double layer effects involving significant laser / plume interaction, has been shown to lead to plume acceleration in the Nd:YAG laser ablation of graphite at moderate fluences and nanosecond laser pulses [11].

Aiming at a better characterization of the internal energy content of the plume species, that could help to elucidate if the observed species could be result from electron-ion recombination processes, in the next subsection we report experimental data on the rotational energy content of the SiO molecule in the plume.

3.3. Rotational energy of SiO in the plume

The rotational population was probed by LIF of SiO ($X^1\Sigma v''=0, J''$) at 1 cm above the target surface and at a delay of 3 μ s with respect to the ablating pulse. By comparing the intensity of pairs of transitions: P(26), P(27) and P(28) respectively to R(36), R(37) and R(38) and assuming Boltzmann rotational equilibrium, the rotational temperature at the ablation fluence of 0.3 Jcm⁻² is estimated as 1170 K corresponding to an average rotational energy of 0.1 eV. The energy appearing as internal energy of SiO, if the latter were formed in the plume by an electron-ion recombination mechanism, can be estimated assuming that the precursors are the small clusters observed in the mass spectra, Si₂O⁺ or Si₃O⁺. Taking as the ionization potential of neutral Si_nO a value of ~8eV and ~2 eV as the dissociation energies to SiO product formation [8, 12], the excess energy of the process largely exceeds the rotational energy measured above. We note however that the rotational temperature, calculated assuming equilibrium, may not be appropriate to characterize the complete rotational distribution; beside this, in order to obtain a complete energy balance of the process it should be taken into account the energy appearing as vibrational excitation of SiO and that carried by other fragmentation products.

4. Summary and conclusions

The ablation mechanism of SiO at the laser wavelength of 266 nm has been investigated by characterizing the composition and dynamics of neutral and charged particles in the ablation plume. It is concluded that several mechanisms contribute to the velocity distribution of neutral SiO molecules in the plume and that the mechanism responsible for the fastest velocity component is related to that of charged particles. The participation of recombination processes electron - silicon oxide ion clusters, is not consistent with the estimated rotational temperature of SiO molecules. A complete characterization of the SiO ro-vibrational distribution and of the energy disposal on other possible co-fragments of the dissociation is needed to elucidate the latter point.

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