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Pulsed laser ablation of silver: ion dynamics in the plasma plume

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The ion dynamics of silver ablated using 355 and 193nm pulsed laser irradiation in vacuum has been investigated by using a Langmuir probe and quadrupole mass spectrometry. The kinetic energies of the ablated silver ions were measured to be between 5 and 40 eV depending on the laser fluence. In addition, the angular distributions of ablated species showed that ionic species are preferentially ejected along the surface normal and the corresponding plasma temperature $T \approx 0.7$ eV agrees well for both techniques.

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1. Introduction

In recent years pulsed laser deposition (PLD) has evolved into a very versatile and powerful deposition technique to grow thin films [1]. When a focused laser pulse of sufficient intensity is incident on a solid surface, material removal and plasma formation occurs. The processes of ablation and deposition are linked by the transfer of material by a plasma. This deposition technique can potentially provide a stoichiometric transfer of material as plasma to the substrate. In order to understand the dynamics of the laser induced plasma plume, Langmuir probes have been used to measure the plasma density and temperature, the plasma flow velocity, and the shape of the ablation plume expansion [2,3]. Another useful technique to analyze plasma constituents such as ions, neutrals, and clusters, is mass spectrometry [4]. In this paper the combined use of Langmuir probe and quadrupole mass spectrometry as diagnostic tools is reported to study the time evolution of the ionic component within a laser generated silver (Ag) plasma expanding into vacuum.

2. Experimental setup

In Fig.1, the experimental set-up is shown. An ArF excimer laser (λ = 193 nm, 20 ns, Lambda Physik LPX 300) and a Nd:YAG laser (λ = 355 nm, 5 ns, Quantel Brilliant B) were used for the ablation of Ag in a vacuum chamber at a base pressure of 3×10^{-5} Pa. For the ArF excimer laser the beam spot size on the Ag target was about 4.3 mm^2, with laser fluences ranging from 0.69 Jcm^{-2} to 1.7 Jcm^{-2}, while for the Nd:YAG laser the spot size was about 2.5 mm^2 with fluences ranging between 1.6 to 6.7 Jcm^{-2}. The repetition rate for both lasers was 10 Hz.

Two main devices were used for these experiments: an electrostatic quadrupole mass spectrometer (EQP-QMS, Hiden), placed at an angle of 45° with respect to the incident laser beam. The second device is a home built Langmuir probe (LP) with dimensions of 5 mm x 3 mm, placed at an angle of 38° with respect to the incident laser beam and perpendicular to the sample surface and parallel to plasma plume. To determine the current of the Langmuir probe, a TDS 744A Tektronix oscilloscope was used to measure the voltage across the load resistor, and the recorded signal was averaged over 40 shots. The target-probe distance and angles, the laser fluence and wavelength were varied during the experiment.

The purpose of the combined LP and the QMS measurements is to ensure the reproducibility and matching of experimental data in order to establish a technique to analyze more complex plasmas such as those created by laser ablation from complex oxides, which contain various ions of different mass.

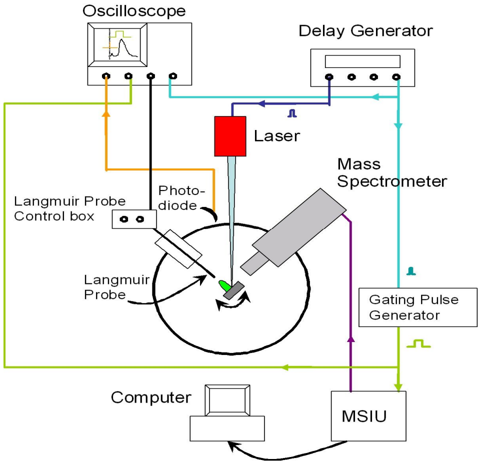

Fig. 1. Experimental setup for the plasma plume analysis performed using a Langmuir probe and quadrupole mass spectrometer.

3. Results and discussion

As discussed in the introduction, the LP and QMS experiments are performed to characterize a laser plasma plume with two different techniques. The kinetic energy distribution (KED) for a laser plume expanding into vacuum can be described by a Maxwell-Boltzmann distribution [5]

$$N(E)dE = C\sqrt{E}\,\exp\left[-\frac{E + E_{cm} - (4EE_{cm})^{1/2}}{k_b T}\right] \qquad (1)$$

with C being a dimensional constant, k_b the Boltzmann constant, T the plasma ion temperature, E_{cm} the center of mass kinetic energy.

The experimental data in Fig. 2 were obtained by QMS and show the kinetic energy distribution of Ag^+ species formed from ablation with the Nd:YAG laser at a fluence of 1.6 Jcm^{-2}. The distribution shown in Fig.2 is a least-square fit of Eq. (1) thereby neglecting the additional, smaller maxima. Here, the fitting parameters are the flow velocity u_{cm} of the kinetic energy $E_{cm} = \frac{1}{2} m u_{cm}^2$ and the plasma ion temperature T. The flow velocities are in the range 0.6 - 4 x 10^4 cm s^{-1}, while the most probable kinetic energy of the ions ranges between 6 and 41 eV at fluences between 1.6 to 6.5 Jcm^{-2} for the 355 nm irradiation. Taking the additional maxima of the energy distribution into account for the fit of Eq. (1), E_{cm} increases by 0.2-0.3 eV but the range of flow velocities is unchanged.

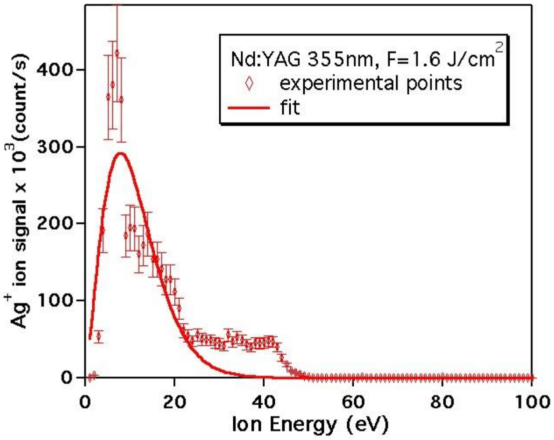

Fig. 2. Kinetic energy distribution of Ag^+ ions as measured with QMS. The plasma was created with a Nd:YAG laser at wavelength of 355nm and a fluence of F = 1.6 Jcm^{-2}.

The kinetic energy distribution shown in Fig. 2 has two experimental maxima, one at 6.2 eV and a second, very broad one at ~ 40 eV. The second maximum, as well as its shape, is unexpected and one explanation for the appearance of this second very broad maximum is an inhomogeneous energy beam profile of the applied Nd:YAG laser at the irradiation wavelength of 355 nm. The shape of such a shoulder suggests several smaller maxima between 20 and 40 eV which requires fluences of up to 6 Jcm^{-2} to create species with KE of ~40 eV. This seems a likely scenario as the measured energy profile of the Nd:YAG laser contains several hot spots. An alternative explanation for the observed line shape is the contribution of differently ionized species like Ag^+ and Ag^{++} to the KE distribution. The latter ones are faster and some of them will capture an electron to become single ionized prior detection with the mass spectrometer. Hence Ag^{++} with a recaptured electron could contribute to the unusual line shape. However, we have not observed any indication of Ag^{++} in the plasma and therefore consider this explanation as unlikely.

When the ion signal is determined by the ion time-of-flight (TOF) measurements using a Langmuir probe, the measured ion current will be dominated by the ion flux, (appropriate voltage criterion for the LPs I-V characteristic) and is given by [6]:

$$I_{i,sat} = Aen_i u_i \qquad (2)$$

here, A is the probe area, n_i the ion density (without mass resolution) and u_i the ion flux velocity. An example for TOF measurements as obtained from a Langmuir probe experiment is shown in Fig.3 where the variation of the ion signal as a function of the probe-target distance d is shown. As expected, the TOF signal vs. distance shows the expected $1/d^2$ dependence for the integrated signal [7]. The maximum of the TOF signal corresponding to the time of maximum ion flux, gives an ion velocity of $u_i = 2.3 \pm 0.1 \times 10^4$ cms^{-1}. The peak maximum of 43 mA (Fig. 3, plasma-probe distance of 6 cm) corresponds to an ion density, as calculated from Eq. (2), of $n_i \approx 2.9 \times 10^{11}$ cm^{-3}.

The TOF signals were converted into energy distribution spectra under the assumption that the dominant species in the plasma plume are monoatomic and single charged silver ions, as confirmed by the QMS measurements. The ion energy distribution within the plasma can also be determined from the ion TOF signals using the following relationships:

$$I(t) = eA\frac{dF}{dt} \text{ and } E = \frac{1}{2} m_i u_i^2 \qquad (3)$$

$$\frac{dF}{dE} = I(t) \times \frac{t^3}{emAd^2} \qquad (4)$$

where $I(t)$ is the measured ion current, m_i the ion mass, u_i the ions flow velocity, e the electric charge, d the probe-target distance, A the probe area, and t the time of flight.

Fig. 4 indicates the most probable ion energy of ~ 5 eV at 1.55 Jcm^{-2} for an irradiation at 193 nm and ~ 40 eV at 6.25 Jcm^{-2} for the ablation of silver at 355 nm.

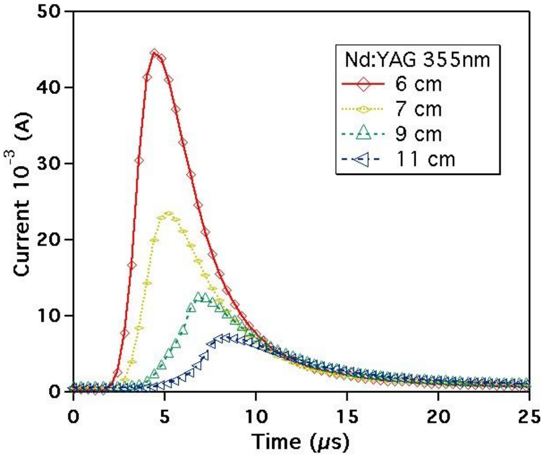

Fig. 3. Ion TOF signals for various target-probe distances. The plasma was created with a Nd:YAG laser at a wavelength of 355nm and a fluence of F = 6.25 Jcm^{-2}.

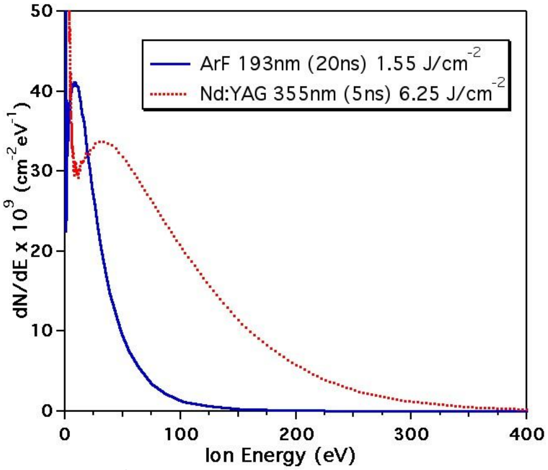

Fig. 4. Ag^{+} ion energy distribution acquired with LP at 6cm from the target at different wavelengths and fluences as indicated in the figure.

The *I-V* characteristic of the Langmuir probe experiments is obtained from the TOF measurement at different voltage biases at a fixed time ($\lambda = 355$nm, $F = 1.6$ Jcm^{-2}.). The electron temperature, $T_{e,}$ is obtained from the slope of the retarding region of the semi-logarithmic *I-V* plot [7]. The T_e calculated from the slope in Fig. 5 is about 0.9 eV. As discussed above, it is also possible to calculate the ion temperature from Eq. (1) using QMS data. An ion temperature of ~ 0.7 eV is obtained from the analysis which is in the same range as the electron temperature from the LP measurements. However, the temperature deduced from these measurements will be an overestimate [8].

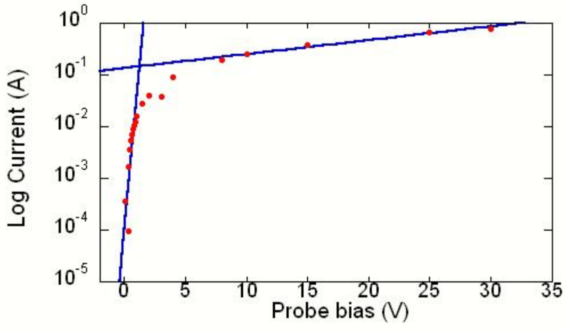

Fig. 5. Semi-logarithmic plot of I-V characteristic where kT_e is obtained from the slope of the linear part.

In Fig. 6 a comparison of the angular distributions of the most probable energy of Ag^{+} ions produced by ablation with different laser wavelengths and fluences (193 nm with 1.6 Jcm^{-2}, and 355nm with 6.25 Jcm^{-2}) as recorded with the two instruments are shown. The shift in the respective peak position measured for 355nm is the result of the geometrical arrangement of the LP and QMS in our set-up which is less than 90° for a perfect peak matching. The plot indicates that the ions expand mainly along the normal to the target surface. The QMS data reveal a strong decrease of the ion signal within ± 20° while the LP measured distribution is somewhat narrower [9, 10]. This difference is probably due to the fact that the MS was operating with a small nozzle aperture of 0.6 mm, whereas the LP has an active area of 7 mm^{2}.

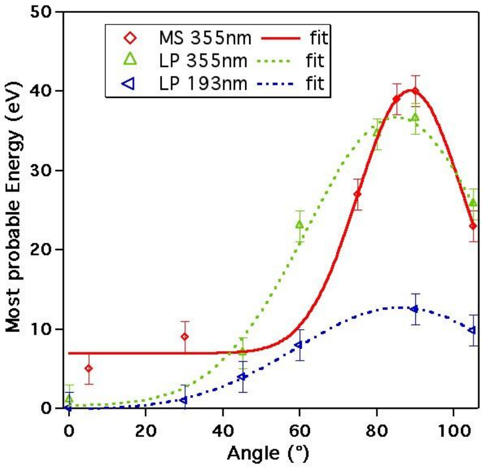

Fig.6. The most probable energy of Ag^{+} ions is measured as a function of the target-probe angle with LP and QMS. A Nd:YAG laser with a wavelength of 355nm and a fluence of 6.25 Jcm^{-2}, and an ArF laser with a wavelength of 193 nm and a fluence of 1.6 Jcm^{-2} is used for Ag ablation.

4. Conclusions

In conclusion we have shown that an ionized plume can be characterized by using a Langmuir probe and a quadrupole mass spectrometer. We have described how the combination of a simple planar Langmuir probe and a complex QMS can be used to measure various aspect of the ablation plume, and we have found good agreement between the results of the two instruments. Furthermore, the plasma temperature T for electron and ions was estimated to be about 0.7 eV. The knowledge of those parameters is of interest for characterization of the laser induced plasma, and for the deposition of thin films using pulsed lasers.

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