The Curious Case of Transient Plasma Generated by ns-laser Ablation of Ag in Ar Gas

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Research Article

Keywords: Langmuir probe, optical emission spectroscopy, perturbative probe, plasma dynamics, thickness profile, laser ablation

Posted Date: December 17th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-126802/v1>

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Abstract

The continuous effort for transitioning pulsed laser deposition technique from an experimental tool into an industrial one is sustained by the use of complex technologies for in situ real-time monitoring of the deposition process. Floating Langmuir Probe (LP) and optical emission spectroscopy (OES) measurements were used for plasma monitoring during the pulsed laser deposition of Ag films under various Ar pressure conditions. The electrical measurements revealed a complex multi-structured distribution of the ions, which was strongly influenced by the increase of Ar pressure. The generation of highly energetic ions with the addition of Ar and the degree of Ar gas ionization was also explored. OES measurements confirmed the presence of highly ionized Ar species in the plasma. A peculiar effect was seen under pressures higher than 10 Pa, where the presence of high electronic charges lead to a perturbative behavior of plasma in the vicinity of the LP. The effect of these complex dynamics on the structure and quality of the deposited thin film was also investigated revealing a strong correlation between the electronic distribution in plasma and thin film thickness profile.

Introduction

Understanding the fundamentals of well-established techniques like the pulsed laser deposition (PLD), has been the core driving force behind transitioning them from laboratory to industry¹. The road to achieve this task has been arduous so far as there is a strong multi-component dependence (laser-target-gas-substrate)² that requires tailoring through empirical trial and error approaches for each material³⁻⁵, every desired properties, or applications. The complexities of the fundamental processes during PLD are well known. Our group in a recent series of papers discussed the plasma plume splitting⁶, ionic oscillations⁷ or gas effect on metallic plasma dynamics⁸, complementing other groups results on phenomena like plasma flip-over effect⁹, plasma rebound¹⁰ and complex structures formation¹¹. The main approach for highlighting these processes has been the implementation of a wide range of diagnostic tools such as optical emission spectroscopy (OES)¹², mass spectrometry¹³, laser-induced fluorescence¹⁴, or Langmuir Probe (LP) method¹⁵. All of these methods, previously established for low or high temperature plasmas generated using different *sources*, were successfully adapted for the particularities of ns-laser produced plasmas¹⁶: rapid space and time evolution, local partial thermodynamic equilibrium, heterogenous composition – photons, electrons, ions, molecules, clusters, nanostructures, etc..

A particular interest has been given to laser-produced Ag plasma as Ag has shown promising results in a wide range of applications spanning from plasmonic resonance¹⁷, flexible conductive electrodes¹⁸ or even medical and biological applications¹⁹. From a diagnostic perspective several papers have reported on the behavior of LP in transient plasma generated by short or ultrashort laser ablation of Ag in various configurations in terms of laser properties^{20,21}, gas nature²²⁻²⁶ and LP geometries^{8,23,27,28}. The general consensus is that during the ablation process there are generated high energy multiple charged ions^{9,14,20} (up to 100 eV), and complex nanostructures^{20,22} that can affect the properties of the thin films. Several

studies have been focused on the angular distribution of Ag ions and the deposited material showing the dependence on the laser fluence and gas nature with a widening of the ionic distribution seen with the increase of the background pressure²⁹. However, the majority of the reported results only took into account the ionic saturation current as a measure of the ablation process³⁰ and used specific flat squared geometries placed against the expansion direction of the plasma. The range of measurements spanned from a few mm to tens of mm and often gave conflicting results. Baraldi et al.³¹ reported Ag ions with a kinetic energy of 50 eV measured at 4 cm in low vacuum 10^{-3} Pa on a wide range of laser fluences 2.5–15 J/cm², Amoruso et al.²⁹ report of 50 eV Ag ions recorded at 8 cm from the target generated by ablation with a laser fluence of 2.4 J/cm² and a pressure of 10^{-6} Pa and Kang et al.³² found at 4 cm 50 eV Ag ions generated with a 1.9 J/cm² fluence at 10^{-4} Pa. These can be seen as limitation of using the saturation current regime of the probe as the LP does not differentiate between multiple charged ions or even different ionic species as the theory assumes only single ionized species in homogenous plasmas, which is unquestionably not true for ns-laser produced plasmas. We recently reported on an alternative approach for plasma monitoring⁸ using floating probe measurements in connection with complementary OES investigations as an alternative to the classical approach for a more accurate tool to describe the kinetics of the ejected particles.

We analyzed by means of LP and OES the dynamics of a laser produced Ag plasma in Ar gas at different pressures. The main focus was to accurately characterize the laser produced plasma plume from both ionic and electronic points of view and to understand the role of Ar gas pressure in the PLD process. The LP and OES measurements were correlated with the properties of the Ag thin films resulted from the PLD process, determined by surface analysis techniques.

Results And Discussion

The *classical* approach in LP measurements of metallic plasmas consists of recording the ion saturation current evolution in time. Although its benefits are well known, it has one major disadvantage: when using the saturation current, all the sub-structuring of the ionic cloud is mediated and integrated under the envelope of the current, offering little information on the inner structuring of the plasma. We have recently shown⁸ the advantages of using the floating current approach for Ag expansion in N₂. In Fig. 1 it is represented the floating probe measurements at 0° recorded for all the expansion conditions investigated. For 0.05 Pa and 0.5 Pa, a three-peak structure of the ionic and electronic regions can be observed, similar to the distribution seen for Ag plasma expansion in N₂⁸. The structuring of the plasma has been investigated before and it is accepted that different groups of particles can be ejected through different ablation mechanisms^{29,33}. Electrons and fast ions will be firstly ejected through Coulomb explosion mechanism³⁴, which subsequently will induce a transient double layer at the edge of the plasma leading to a differential acceleration of single and multiply-charged ions forming the outer-edge of the plasma, while slow atoms clusters or nanoparticles will expand with a significant lower velocity forming the core of the plasma. With the increase of the Ar gas pressure (from 0.05 Pa to 10 Pa) we observed that the two

peak structure seen for the early stage ($t < 2\mu\text{s}$ time region) merged into a single one at 2 Pa and exhibited an overall increase in ion density by a factor of 3.3. A closer look into the evolution of the floating electronic current revealed an unexpected dynamic. The transition from 0.05 Pa to 0.5 Pa was followed by a decrease in floating electron current by 50% and by a steep increase of the same current with the pressure. However, it is worth discerning that although the electron density decreases, the average velocity, estimated through the arrival time of the maximum electronic density, increases for pressures below 2 Pa being followed by a decrease for subsequent higher pressures. This rather peculiar effect that showcases an interesting dynamic of electrons during expansion could strongly impact the overall deposition process especially with the increasing Ar pressure in the reaction chamber.

For a more in-depth analysis of this electron depletion of the plasma on the main expansion axis (0°), we performed angular measurements at each Ar pressure (Fig. 2a-d). As the Ag angular density distribution is relatively known and has been thoroughly investigated for a wide range of background gasses and irradiation conditions³⁵⁻³⁷, the natural choice is to change the approach towards a kinetic one and thus we represented the expansion velocity angular distribution for each of the three ionic structures and the main electronic one. For an Ar pressure of 5×10^{-2} Pa three ionic structures (Fig. 2-b) were seen expanding with different velocities (tens of km/s for the 1st and a few km/s for the latter two). This result is in good agreement with data recently reported^{24,38}. The width of the angular distribution is also strongly dependent on the range of kinetic energies describing each of the three ionic structures. The 2nd and 3rd structures exhibited a wider angular distribution, which can be correlated with the Ag-Ar collisions, confirmed by data from Fig. 2 (d) where the results from 5 Pa are represented. There it can be seen that each of the distributions widens with the increase of the Ar pressure while the expansion velocities decrease. These results confirm the report from Amoruso et al.³⁹ concerning Ag expansion in Ar in a $10^{-3} - 40$ Pa range. When considering the angular distribution of electron velocity (Fig. 3a and 3-c) we observed an unexpected evolution. For low Ar pressures, the main expansion direction (a cone of $\pm 15^\circ$ around the main $- 0^\circ$ axis) the emitted electrons presented a lower expansion velocity, ranging from 70 km/s for 5×10^{-4} Pa and 90 km/s for 10^{-2} Pa, compared to the one seen at the edge of the plasma where we find energetic electrons expanding with 250 km/s for 10^{-3} Pa and 270 km/s at 10^{-2} Pa. This can be explained if we consider the effect of the transient double layer at the front of the plasma. The spatial and angular distribution of the charge densities^{34,40} suggests that the electrical field will be stronger closer to 0° axis and will be weaker towards the edges of the plasma. Therefore, in front of the plume there will be a strong oscillatory movement (as seen in Fig. 1 inset) of the electron cloud leading to a loss in their kinetic energy. As the Ar pressure was increased, the thermalization of the electronic structure was observed (Fig. 3-c), with the front of the plasma showing a wide angular distribution and a quasi-constant distribution in the $\pm 40^\circ$ cone with velocities ranging from 140 to 120 km/s. Similar behavior was found for 10 Pa with a wide angular distribution of the velocity centered around 140 km/s.

Further exploration into the Ar pressure effect on the ionic and electronic charge distribution involves the analysis of charge density distribution with the expansion velocity. This particular analysis consists of

transforming the electronic or ionic time-of-flight signal into energy distribution. There are two approaches reported: the first one reported by Krassa et al.⁴¹ and Toftmann et al.⁴² where the ionic saturation current is transformed into a charge yield distribution on their respective kinetic energy and the second one based on revising the LP classical approach for flowing plasmas^{15,16}. Both techniques involve the value of the ionic current in the saturation region of the I-V characteristic. It is worth noting that these techniques work well for pure, single-element plasmas with mostly single ionized species present, which is a well-known limitation of the technique. To overcome this, we used the floating current as a reference and implemented the approach from our previous report⁸. Selected charge distributions with velocities are presented in Fig. 4a. In these charge distributions there are three ionic structures and a major electronic one. An increase by a factor of 4 and a convolution of the first and second ionic structures are the main features seen as a result of Ar pressure increase. At 5×10^{-1} Pa, there is a supplementary peak characterized by a considerably higher kinetic energy. This is an atypical behavior of the ions as it is expected that the ejected particles will lose energy by thermalization. Our data reveals the generation of a new high energetic ion bunch having at 5×10^{-1} Pa kinetic energies of 90 eV, almost double the values of the high Ag energetic structure (54 eV) (Fig. 3-b). The energies of the ablated particles are still high, even at 10 Pa, which disagrees with the report from Fazio et al.²², who implemented OES measurements and reported a stopping distance of the plasma at 25 mm for Ag expanding in 10 Pa Ar with 11 km/s. We report here the presence of high energetic ions (I – 2.9 eV, II – 13.5 eV and III/I* – 22 eV) at 37 mm from the target accompanied by electrons with energies of 40 eV. These differences could arise from the limitation of the spectroscopy measurements, which only observe the excited states from the plasma. Geohegan group⁴³ eloquently showcased this behavior by successfully depositing complex carbon structures under conditions when the emission of the plasma has reportedly stopped a few cm in front of the substrate. The generation of high energetic ions during laser ablation of metals was previously observed by Hansen³⁵, who reported groups of ions with 50 eV and 100 eV, and by Anoop⁴⁴ reporting energies of 100 and 331 eV for Cu plasma. However, Lunney et al.²⁷ reported average values of 31 eV for Ag ions. There are no other reports regarding the enhancement of the ionic energy by the increase of background gas, on which we reported here for the first time. In Fig. 3b we can see the kinetic energy of electrons decreased from 180 eV to 40 eV in the widespan of 10 Pa while the energies of the 2nd and 3rd ionic structures decreased from 26 eV to 14 eV from 13.6 eV to 2.9 eV, respectively. For the 1st ionic structure, we noticed a quasi-stationary behavior for low pressures ($< 5 \times 10^{-1}$ Pa) followed by a steep increase and subsequent decrease ranging from 88 eV to 18 eV.

Furthermore, the data can be analyzed in the framework of the two expansion regimes for laser-produced plasmas²⁶: free expansion regime (collision-less) and the collisional regime. Given the wide range of Ar pressures used in this work we were able to capture dynamics without collisions ($10^{-5} - 10^{-2}$ Pa) and collisional regimes (for Ar pressure $10^{-1} - 10$ Pa). The transition collision-less/collisional occurs around 10^{-1} Pa where it appears a high energy ionic peak, therefore we can conclude that the interaction of high energetic plasma front with the Ar gas leads to the ionization of the gas and subsequent acceleration of the Ar ions. In the framework of our expansion scenario the ionization is an energetically favorable

process as both electrons (127.3 eV @ 5×10^{-1} Pa) and ions (I – 38 eV, II – 20.5 eV @ 5×10^{-1} Pa) have enough kinetic energy to generate 1st and 2nd ionization states for Ar. The possibility of the background gas ionization scenario has been previously reported by Amoruso et al.²⁶ when investigating the laser ablation of MgB₂ in 10 Pa of Ar gas. Isaac et al.³⁷ even reported the full ionization of 27 Pa of Ar gas in the vicinity (0.6–1 mm) of the Ag target, both reports being supported by OES investigations.

The Ar gas ionization by the plasma front influences beside the ionic distribution, the overall density of electrons which are *secondary* products to the ionization processes. In order to analyze electron dynamics in high-pressure regime, the saturation electronic current ($V_{\text{probe}} = +20$ V) evolution in time under various Ar pressures and the angular evolution of the I_{esat} at 10 Pa are represented in Fig. 4. In a consistently changing collisional regime ($> 5 \times 10^{-1}$ Pa) the overall electronic density is defined by a wider angular distribution shown in Fig. 5-b where the saturation current does not vary significantly with the angle. The electrons are described by a considerably lower kinetic energy seen through the increase in time of flight signal of the current explained by the presence of low energy groups of electrons (Fig. 4-a). Arrival times of the order of a few *ms* are attributed to electrons traveling with velocities of a few *m/s* and even lower in the case of Ag expansion in 10 Pa of Ar. We can notice that the arrival time of the electrons changes considerably with the addition of Ar. In the free expansion pressure regime, we observe *life-times* of about 150–300 μs while for the collisional regimes we determine values two order of magnitude higher. The longer life-time is correlated with the lower mass of the electrons and with their significant scattering during expansion while the increased current density amplitude is related to the additional electron changes resulted from Ar ionization processes.

At higher pressures (5 Pa and 10 Pa) we observed a peculiar electron dynamics. In a time-span starting from 300 μs up to 3 ms, a modulated oscillatory regime was seen, with the effect being present for all measuring angles. This *strange* behavior has been previously reported for positively biased electrodes immersed in Ar plasma under similar pressures (> 2 Pa). It represents, according to the report of Dimitriu et al.⁴⁵ that a self-organized structure called plasma fireball appeared on the surface of the electrode. The oscillations are induced by the disruption of the double layer formed around the fireball and the ionic core being expelled in the plasma. The data presented here in Fig. 5 is of paramount importance for LP measurements and their limitation as real-time monitoring technique of PLD process, considering the relatively large measuring distance, 37 mm, the low voltage applied on the probe (4–20 V) and the PLD conditions (5–10 Pa – Ar gas). It means that in high Ar pressure conditions, for biases higher than 4 V a fireball-like structure is formed on the probe surface, and thus LP is becoming perturbative for the deposition process. This is the first report of a perturbative working regime for LP in PLD systems, offering a quantitative limitation in terms of pressure, gas nature and deposition geometries.

To confirm the Ar gas ionization scenario alternative, complementary techniques have to be implemented in order to reveal the presence of ionized Ar species in the collisional expansion regime. OES is one of the best techniques to complement the LP analysis as it can show the nature of the plasma species, with many reports in literature for its successful implementation for elemental analysis^{12,46,47} and for

background gas analysis in Ag expanding plasma⁴⁸. The global emission (volume and time-integrated) from the plasma was acquired using an integration time of 100 μ s. The results are presented in Fig. 5a where the overall emission spectra of an Ag plasma expanding in Ar at 10 Pa is represented. We identified using the specialized databases⁴⁹ the presence of atomic and single ionized species of Ag (Ag I – 520.4 nm, Ag II – 531.6 nm) and atomic, single and double ionized species of Ar (Ar I – 455.5 nm, Ar II – 655.8 nm, Ar III – 350.2 nm). The increase in Ar pressure lead to an increase in all emission lines and thus an increase in thermal energy of the electrons consistent with our findings in⁸ where we investigated the effect of N₂ gas on Ag plasma. With the mention that Ar I optical signature in the 300–700 nm spectral range is scarce, we can safely assume that the Ar background gas was partially ionized throughout the plasma volume⁵⁰. Spatially resolved optical emission spectroscopy was implemented to validate the partially ionization scenario. The results, presented in Fig. 5c revealed the excitation of new Ar II and Ar I species in the proximity of the substrate thus confirming that during expansion Ag plasma ionizes the Ar gas generated new species.

Thin film analysis

The *holy grail* of PLD technique is often considered the direct linking of plasma properties and those of the deposited films. With such a complex and layered behavior of Ag plasma generated by ns-laser ablation in Ar gas, as seen through LP and OES, an important question arises, *how do these properties of the plasma affect the deposition of Ag films*. To tackle this, we have produced nanometric Ag thin films in four conditions: 1×10^{-4} Pa, 5×10^{-2} , 2, and at 10 Pa Ar pressure. The chosen pressures are in line with the phenomena observed from LP measurements where different behaviors were seen for low (10^{-5} Pa – 10^{-2} Pa) and high Ar pressures (10^{-1} Pa – 10 Pa), coinciding with the non-collisional/collisional expansion regime of the laser produced plasma. As reported by Scharf⁵¹ the expected effect of the background pressure over the Ag films is reflected by the deposition rate. We confirm the results reported in⁵¹, where the deposition rate increases with the addition of Ar and is followed by a decrease at pressures higher than 4 Pa. The evolution is explained based on the ion thermalization which reduces the thin film sputtering during the deposition process. Results expected as for the conditions used there in terms of laser fluence (6–7 J/cm²) and pulse duration (20 ns). We would like to mention that although the thermalization of the plasma is better reflected by the electrons and Ar ions where we see a decrease in their kinetic energy, for Ar pressure higher than 10^{-1} Pa we see steep increases in the ionic energy of about 50% attributed to the Ar ions generated during expansion. Therefore, the plasma thermalization cannot be the only mechanism influencing the deposition process as their distribution is less affected by the addition of Ar (Fig. 3). Our angular measurements presented unique distributions for both the ionic and electronic particle clouds which will no doubt affect the thickness distribution of the Ag films. To better understand that we performed optical transmission spectroscopy for the estimation of the thin film thickness. The angular distribution of the Ag film growth was analyzed from an experimental deposition on a microscope slide glass substrate 25×75 mm². The images of deposited films are shown in Figure S1 (Supporting Information). The thickness was estimated by fitting an appropriate model to the

obtained transmittance spectra. The model is based on Fresnel equations of a thin, semi-absorbing layer on a thick, non-interference, transparent layer (glass substrate) using the optical functions for Ag from⁵². We included Ag film roughness in this model as an additional layer with optical functions derived from the effective medium approximation of two components: silver and voids (Bruggeman model). The thickness was estimated by fitting an appropriate model to the obtained transmittance spectra. The example of fit for four different Ag layer thicknesses of the Ag layer is shown in Fig. 6a, where the thickness estimated from the fitting is displayed for each of the curves. Here are shown some examples of the spectrum measured for different thicknesses within the same deposited film. The fitted simulation is depicted as a dashed, red curve.

The thickness distribution of the thin film (Fig. 6b) resembles the angular distribution of the electron cloud: with energetic minima at low Ar pressure in the central region ($0^\circ \pm 10^\circ$) and higher electron energies towards the edge of the plasma. Thus, we see that there is a more intimate connection between the distribution of electrons and the thickness of the film, which infers that the deposition rate will be influenced by the kinetics of the electrons in the substrate vicinity. When considering the dynamics at the front of the plume where the in the framework of ambipolar diffusion mechanism we can further correlate the deposition scenario with the charged particle dynamics at the front of the plasma plume. The drop in the center of the plume ($0^\circ \pm 10^\circ$) will lead to reduced acceleration and lower oscillatory behavior which will mean that in the central part of the plume the ions are not significantly affected. While at the edge of the plasma ions will suffer a higher acceleration and thus leading to an enhancement of ion density accumulated in the outer regions of the plasma. Results are supported by the floating probe angular measurements where 2nd and 3rd ionic structures have a wider distribution with maxima close to 30° . With the increase of the pressure the scenario changes, the thermalized electronic cloud is now uniformly accelerating the plasma ions and thus the resulting film thickness profile will follow the shape of the ablated ionic cloud (Fig. 2d).

Further investigations on particle kinetic energy at the substrate surface were performed using XRD analysis and AFM measurements. All deposited silver films are polycrystalline (Figure S2 from Supporting Information) and have one phase (FCC structure) with a lattice constant $a = 0.408 \pm 0.001$ nm. The lattice parameter didn't change for silver films deposited at different argon pressure. We observed only that the intensity of reflexes correlated to film thickness. In Fig. 7 we can see the morphology of silver films in the central part of films in the vicinity of 0° . The crystal size for films deposited at 1.1×10^{-4} , 5×10^{-2} , 2 Pa in the range 20–80 nm. The addition of Ar leads to the formation of smaller sized nanoparticles nanocrystals (20–30 nm) and an increase of layer thickness by a factor of 3, result correlated with a uniformization of the electron cloud and the overall plasma thermalization. The subsequent increase of Ar pressure (5–10 Pa) also leads to the generation of a higher density of Ar ionic species which could hinder the deposition process through sputtering processes. The decrease of the thin film thickens previously believed to be driven by the scattering of the Ag species on Ar gas.

Finally, let us address the LP perturbative behavior effect on the deposition process. The thin film analysis did not reveal any impurities nor were the Ag film growth mechanisms affected, since the

perturbative regime appears at a high Ar pressure. To understand these results two important aspects need to be addressed. The first one is related to the perturbation propagation within the plasma volume. Any perturbation will be confined within the plasma Debye sphere. This volume is typically described by a radius larger than the Debye Length by a factor of ten. Our investigations revealed the values for the Debye lengths at high Ar pressure of the order of μm which means that the maximum plasma volume that will be perturbed by the probe will be $4 \times 10^3 \mu\text{m}^3$, a value that decreases with the addition of supplementary Ar gas in the system (confinement of the Ag plasma). The reduced volume and the relatively higher distance between probe and substrate (13 mm) ensure the fact that even when the probe enters a perturbative regime the pulsed laser deposition process is not affected.

Conclusions

Langmuir probe measurements and optical emission spectroscopy were implemented for in-situ measurements of pulsed laser deposition of Ag in various pressures of Ar, from 10^{-5} Pa to 10 Pa. Floating probe regime was used to investigate the Ar pressure effect on the plasma multi - structuring. Three ionic and electronic peaks were observed at low Ar pressures with the addition of Ar leading to the confinement of these multiple structures. Angular distribution of ions and electron revealed a complex transition of the electron kinetic energy. The increase in Ar pressure results in a widening of the ionic angular distribution with a pronounced effect on the low energy ions.

An energy depletion was observed for the free expansion conditions across the main expansion axis followed by thermalization of the electrons in the collisional regime. The increase of the Ar pressure resulted in the appearance of a new high energetic ion structure induced from the ionization of the Ar gas by the Ag plasma front. Optical emission spectroscopy measurements confirmed the complete ionization of the gas through spectral signatures of Ar single and multiple ionized ions during pulsed laser deposition. Thin films deposited under identical conditions revealed that the thickness of the Ag films mirrors the electron angular distribution revealing the influence of an electrostatic mechanism over the thin film growth. The thermalization of the Ag plasma also leads to enhancement of film thickness up to an optimum of 2 Pa. The subsequent increase in Ar pressure leads to sputtering of the film by the ionized Ar species. Positive biasing of the probe in Ag plasma expanding in 10 Pa of Ar lead to the formation of a fireball like structure on the probe surface, which induced an oscillatory regime in the 300 μs – 3 ms time-span. This is a novel perturbative regime of the Langmuir probe, which potentially can affect the deposition process. In our irradiation conditions and Ar gas pressures there are no significant influences of this perturbative regime onto the PLD process.

Methods

A YAG Laser ($\lambda = 266$ nm, Energy = 81 mJ) at 10 Hz repetition rate was focused on a silver target (99.99% purity) at a fluence of 3.8 J/cm^2 . The 6 mm thick silver target was continuously rotated to provide a fresh surface per each shot and avoid the local heating and crater formation. The target to substrate and to LP distances were 50 mm and 37 mm, respectively. The plasma investigations were performed under a

residual vacuum of 5×10^{-5} Pa, and at 5×10^{-2} , 5×10^{-1} , 2, 5, and 10 Pa Ar pressure. Each experiment was preceded by a cleaning procedure during which the LP was shielded from the incoming transient plasma while the rotating silver target was laser irradiated with 1200 pulses (for other details on the set-up geometry please see⁸). The signal from tungsten LP (diameter – 0.2 mm and exposed length – 2 mm) was measured by collecting the voltage signal across a load resistor with a Tektronix DPO 4140 oscilloscope. All the performed investigations were time-synchronized by a fast silicon photodiode (Thorlabs FDS100) establishing the initial measuring moment as the moment when the laser was fired.

The light emitted from plasma was transmitted through a linear bundle of 19 channel optical fibers, which simultaneously record the optical emission from a 40 mm length strip oriented parallel to the plasma expansion axis. Optical spectra were collected by an iHR550 Imaging Spectrometer (Horiba) using a 2400 mm^{-1} grating. Plasma image was recorded with a LN_2 cooled Symphony CCD camera (Horiba) having 2048×512 pixels in a wavelength range of 200–900 nm.

Ag thin films were deposited on glass and Si substrates positioned at 50 mm from the target using 5000 consecutive pulses without substrate heating in identical irradiation conditions selected values of Ar pressures (in vacuum at 1×10^{-4} Pa and in Ar at 5×10^{-2} , 2 and 10 Pa). The lateral distribution of the Ag film growth was analyzed from an experimental deposition on a glass substrate $25 \times 75 \text{ mm}^2$. The measurement setup was arranged from a light source, light-collecting optics, and a mini-spectrophotometer. The transmittance spectra were measured by a spectrometer USB4000, Ocean Optics, in the spectral range from 300 to 890 nm. The light source, DT-mini-2-GS – Ocean Optics, was coupled with a focusing lens by an optical fiber with a 200 μm core diameter. Light spot diameter on the sample was about 2 mm, which determined the lateral resolution of the transmittance measurement. Atomic force microscopy (AFM Dimension ICON, Bruker) was used to investigate the surface morphology, roughness and thin film thickness. The measurements were performed under ambient conditions and images were obtained by the Peak Force Tapping mode using ScanAsystAir tips with scan areas of $1 \times 1 \mu\text{m}^2$.

XRD measurements were carried out using the X-ray diffractometer (Empyrean, Malvern Panalytical) with a monochromated Cu K_{α} radiation (photon energy $E = 8.04 \text{ keV}$, wavelength $\lambda = 1.54151 \text{ \AA}$, $U = 45 \text{ kV}$, $I = 30 \text{ mA}$) in grazing incidence X-ray diffraction mode. The incident angle was 0.85° that corresponds to $\sim 10 \text{ mm}$ of sample irradiation. The XRD measurements were made from a central part of deposited film with an area of $10 \times 10 \text{ mm}^2$.

Declarations

Acknowledgement

This work was supported by Czech Science Foundation (GAČR) by project No. 20-21069S and by Romanian Ministry of Education and Research, under Romanian National Nucleu Program LAPLAS VI –

contract n. 16N/2019, ELI-RO_2020_12 and Postdoctoral Project PD 145 / 2020. We acknowledge the Operational Program Research, Development and Education financed by European Structural and Investment Funds and the Czech Ministry of Education, Youth and Sports SOLID21 CZ.02.1.01/0.0/0.0/16_019/0000760.

Author contributions

SAI and SC developed and implemented the LP systems and performed the experimental investigations; MN was responsible for the OES measurements and data interpretation; LF was responsible for the AFM measurements and interpretation; JB was responsible for optical characterization of the films and modeling of the data; VC and JL supervised the project and were responsible for the surface analysis. All authors contributed to writing the and reviewing the manuscript

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Figures

Figure 1

Floating probe current collected along the main expansion axis (0°) at 37 mm from the target for different Ar pressures

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Floating probe current collected along the main expansion axis (0°) at 37 mm from the target for different Ar pressures

Figure 2

Angular distribution of ion and electron expansion velocity at 5×10^{-1} Pa (a-b) and 5 Pa (c-d) Ar pressures (lines are guides to the eye)

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Angular distribution of ion and electron expansion velocity at 5×10^{-1} Pa (a-b) and 5 Pa (c-d) Ar pressures (lines are guides to the eye)

Figure 3

Charge density distribution with the velocity at $5 \times 10^{-5} \text{ Pa}$, $5 \times 10^{-1} \text{ Pa}$ and 10 Pa (a) and Ar pressure effect on the kinetic energies of all plasma structures (b)

Figure 4

Electronic current temporal evolution for various pressures (a) and measuring angles (b).

Figure 4

Charge density distribution with the velocity at $5 \times 10^{-5} \text{ Pa}$, $5 \times 10^{-1} \text{ Pa}$ and 10 Pa (a) and Ar pressure effect on the kinetic energies of all plasma structures (b)

Figure 5

Electronic current temporal evolution for various pressures (a) and measuring angles (b).

Figure 5

Optical emissions spectra of the Ag plasma at 10 Pa Ar pressure (a), the impact on the line emission intensity of the Ag I (520.4 nm), Ag II (531.6 nm), Ar II (655.8 nm), Ar III (350.2 nm) (b) and the proof of Ar gas ionization in the proximity of the substrate (c)

Figure 6

Transmittance spectra of Ag film deposited at 10 Pa Ar pressure (blue, solid curves), fitted simulation (red, dashed curves) (a) and angle distribution of thin film thickness for selected Ar pressures 1.1×10^{-4} , 5×10^{-2} , 2, 10 Pa (b).

Figure 6

Optical emissions spectra of the Ag plasma at 10 Pa Ar pressure (a), the impact on the line emission intensity of the Ag I (520.4 nm), Ag II (531.6 nm), Ar II (655.8 nm), Ar III (350.2 nm) (b) and the proof of Ar gas ionization in the proximity of the substrate (c)

Figure 7

Transmittance spectra of Ag film deposited at 10 Pa Ar pressure (blue, solid curves), fitted simulation (red, dashed curves) (a) and angle distribution of thin film thickness for selected Ar pressures 1.1×10^{-4} , 5×10^{-2} , 2, 10 Pa (b).

Figure 7

AFM images of Ag thin films in the 0° region deposited at 1×10^{-4} Pa, 5×10^{-2} , 2, and at 10 Pa Ar pressure. The size of each image is $1 \times 1 \mu\text{m}^2$.

Figure 8

AFM images of Ag thin films in the 0° region deposited at 1×10^{-4} Pa, 5×10^{-2} , 2, and at 10 Pa Ar pressure. The size of each image is $1 \times 1 \mu\text{m}^2$.

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