Published by IOP Publishing for Sissa Medialab

Received: *December 13, 2019*
Accepted: *January 20, 2020*
Published: *February 20, 2020*

Plasma Physics by Laser and Applications (PPLA 2019)
Physics Department, University of Pisa, Pisa, Italy
29–31 October, 2019

EUV induced, low temperature plasmas, produced in an aerosol target

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Abstract: In this work spectral investigations of low temperature plasmas, created by photoionization of aerosol targets, were performed. A laser produced plasma (LPP) source of extreme ultraviolet (EUV) was used as a source of ionizing radiation. The source was driven by a 10 Hz Nd:YAG laser system, delivering pulses of energy up to 10 J with a time duration of approximately 10 ns. The aerosol target was formed using a specially prepared system composed a mist ultrasonic generator and a solenoid valve. The mist was created inside a small cell containing a small portion of methanol and filled with a He gas. The valve coupled to this cell allowed to inject the aerosol into a vacuum chamber synchronously with the EUV pulse. Low temperature plasmas created by the EUV irradiation of the aerosol target were investigated mainly by spectral measurements. The spectra, acquired in the UV/VIS range, were composed of lines corresponding to radiative transitions in atoms and singly charged ions originating from the He gas and dissociation products of the methanol. Spectral measurements were performed also for aerosol targets created from solutions of various inorganic salts in the methanol. In this case, additional lines corresponding to decomposition products of these salts were detected.

Keywords: Plasma diagnostics - interferometry, spectroscopy and imaging; Plasma generation (laser-produced, RF, x ray-produced)

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https://doi.org/10.1088/1748-0221/15/02/C02035

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1 Introduction

Low temperature plasmas are widely used in various technologies especially in microelectronics industry for deposition of thin films, plasma etching, implantation of dopant atoms into silicon, selective removal of silicon, photoresist or polymer films [1, 2]. Plasma treatment can be employed for surface activation or functionalization [3]. Fluorination can improve properties of thin carbon layers by increase of the film roughness and hydrophobicity [4]. Low temperature plasmas are also utilized for spectrochemical analysis. In particular it was shown by various authors that the excitation of atomic or molecular species in cold plasmas is a powerful method for such analysis. The method was used for a large variety of analytical tasks such as detection of noble metals [5], rare earth elements [6], iron in industrial silicon [7] or the determination of Hg with the aid of continuous cold vapor generation [8]. In these cases the analyzed sample in a form of aerosol was introduced into the low temperature plasma and the emission spectra of the excited species were recorded.

For such analysis a microwave plasma torch (MPT) as the low temperature plasma generator is usually employed. The low temperature plasma in this case is sustained in a dielectric tube inserted into the microwave field applicator. Plasmas in such generators can be created in a gas flowing through the tube under atmospheric pressure. The plasma is partially formed outside the tube forming a plasma beam [9]. Liquid samples to be investigated using spectroscopic methods, are dispersed by pneumatic nebulization. The electron density is in this case at a level of 10^{13} cm^{-3} [10].

Much higher electron density can be obtained in low temperature plasmas, created by the method based on photoionization of gases using intense pulses of extreme ultraviolet (EUV). Such plasmas can be induced in gases with the near-atmospheric density. It was reported in our previous papers that the electron density in plasmas created this way can exceed a value of 10^{17} cm^{-3} using a table top, commercially available laser [11]. In experiments performed using a high power laser system PALS in Prague, Czech Republic, delivering pulses with energy up to 600 J the density reached even $2 \cdot 10^{18}$ cm^{-3} [12]. In this paper results of experiments concerning the EUV induced low temperature plasmas, created in aerosols, are presented. Aerosols were initially produced using a specially prepared nebulization system and delivered into the irradiation area synchronously with

the driving EUV pulses. Various inorganic chemical compounds were dissolved in methanol and used for creation of aerosols. To limit unwanted spectral lines emitted from the EUV induced plasmas, aerosols were formed in a He gas. The most intense emission from plasmas created in aerosols could be expected in UV-VIS spectral range, hence, measurements in this range were performed. Spectral lines corresponding to dissociation products of the methanol molecules or the dissolved salts were detected. The most intense lines originated from radiative transitions in atoms or single charged ions.

2 Experiment

In our experiments, a laser produced plasma (LPP) EUV source based on a double-stream gas-puff target, irradiated with laser pulses of energy 5.7 J and pulse duration of approximately 10 ns. A commercial Nd:YAG laser (NL 129, EXPLA, Lithuania) operating with 10 Hz repetition rate was employed. The double-stream gas-puff target was formed by pulsed injection of a Xe into a hollow stream of He gas, synchronously with laser pulses. For creation of the target a solenoid valve system, equipped with a double nozzle set-up, was employed. The laser beam, having a diameter of approximately 25 mm, was focused onto the target, such as, to obtain maximum intensity in the EUV spectral region. The focal spot diameter was approximately 100 µm. The most intense emission was in the spectral region centred at $\lambda = 11$ nm, however, the EUV radiation was emitted in a spectral range much broader, $\lambda \sim 1$–20 nm. More details concerning the LPP EUV source can be found elsewhere [11].

The aerosol target was created using a specially prepared system composed of two sub-systems: a mist ultrasonic generator and a solenoid valve. The mist is created inside a small cell filled with a gas under a pressure of 0.5–6 bar and containing approximately 20 ml of a liquid to be atomized. The valve allows to inject the aerosol into a vacuum chamber synchronously with creation of the LPP. Parameters of the resulting aerosol target depend on the liquid properties, the gas backing pressure and the piezo disc resonant frequency. The piezoelectric disc having a 20 mm diameter is mounted at a bottom of the mist cell. Its resonant frequency determines a diameter of the created droplets. In our system a 2.45 MHz piezoelectric disc was employed. According to the US patent, US 7,129,619 B2, it should allow to produce droplets with a mean diameter of approximately 1.5–1.7 µm. According to our measurements [13] based on the laser light scattering, the averaged diameter was a little bit larger, of approximately 2 µm. Increase of the resonant frequency would result in decrease of their mean diameter. The aerosol target is created in two steps. In the first step, a saturated aerosol is being formed inside the mist cell, in the second one the aerosol is injected into the vacuum chamber by opening of the valve. Its opening time is approximately 1 ms. Minimum time required to produce the saturated aerosol inside the mist cell is 15 seconds. This time depends on a power of a RF generator and the liquid properties. In our experiment, we used the 9W RF generator. The valve system can work in a single pulse regime or with a repetition rate up to 10 Hz. The aerosol is injected into the vacuum chamber by a tube nozzle with a 1.6 mm inner diameter. Optimal value of the gas pressure in our experiments was 2 bar. A schematic view of the aerosol target system together with the experimental arrangement and a spectrum of the EUV radiation, delivered by the LPP source is presented in figure 1. As can be noticed the aerosol was injected into a vicinity of the laser produced plasma. The distance between the LPP and the outlet of the nozzle

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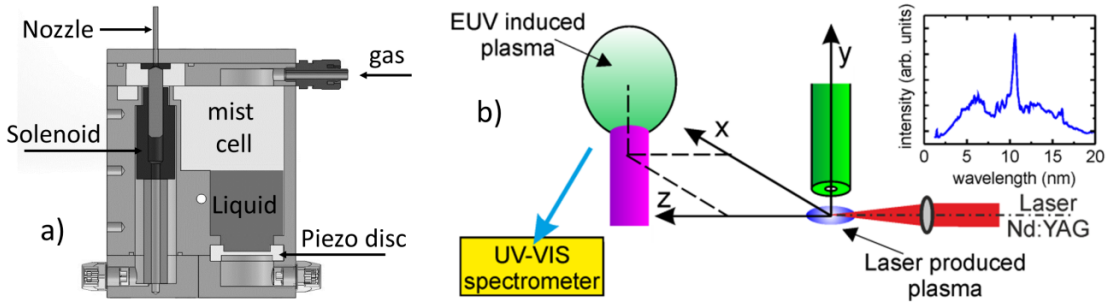

Figure 1. Experimental set-up: a) aerosol target system, b) experimental arrangement together with the LPP EUV emission spectrum.

for the aerosol injection was approximately 8 mm. The EUV fluence at this distance, measured in the wide range, exceeded 100 mJ/cm^2.

The EUV induced plasmas were investigated by spectral measurements. The spectrometer was an Echelle Spectra Analyzer ESA 4000, equipped with the ICCD Kodak KAF 1001 camera. The spectrometer system allowed for measurements within the wide spectral range, $\lambda = 200 \div 780$ nm. Its spectral resolution was $\lambda/\Delta\lambda \approx 20000$. To avoid the direct laser light and detection of the Xe plasma visible radiation, an optical axis of the spectrometer was positioned under an angle of approximately 45° in respect to the axis of the laser beam. Apart from that the delay and gate times of acquisition were chosen such as to detect spectra from the EUV induced plasmas, before arrival of the expanding Xe plasma into the spectrometer field of view.

3 Experimental results

Spectral measurements of the EUV induced plasmas were performed for three types of media to be irradiated: a pure He gas, an aerosol formed from pure methanol dispersed in the He gas and the aerosol based on inorganic salts dissolved in methanol. In figure 2 Spectra acquired for

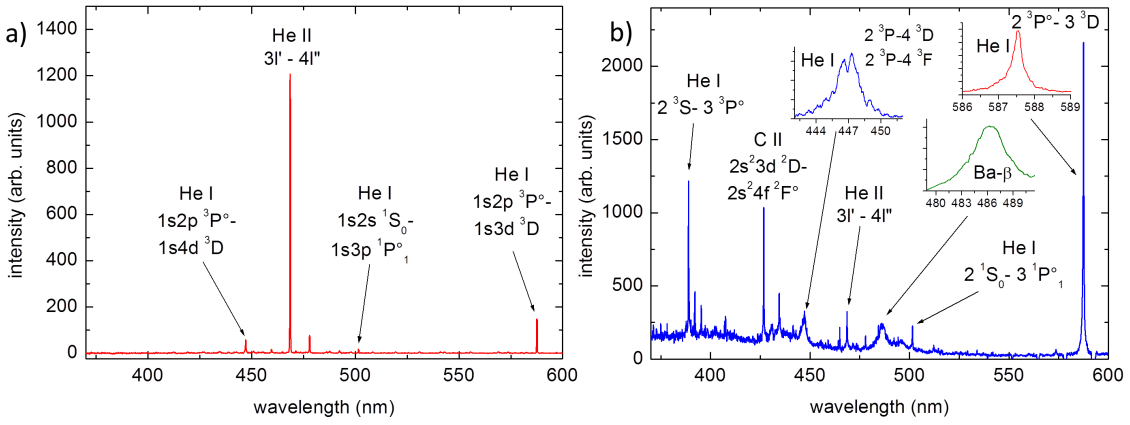

Figure 2. Spectra acquired in the UV/VIS range from the EUV induced plasmas: a) He plasma emission, b) CH_3OH plasma emission, in sub-images selected lines expanded.

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plasmas induced in He gas and in the CH_3OH aerosol are presented. The He spectrum (figure 2a) is composed of multiple emission lines with the most intense one, corresponding to single charged ions, He II. Such lines were recorded also for plasmas created in the CH_3OH aerosol (figure 2b), however, the relative intensities of the lines are significantly different. In particular the 3l′ - 4l′′ He II line is no longer dominating, its relative intensity in respect to He I lines significantly decreased. It should be also pointed out that the He I line corresponding to a 2 ^{3}P-4 ^{3}D (allowed) and 2 ^{3}P-4 ^{3}F (forbidden) transitions is strongly broadened and has a characteristic dip in the central part. Apart from He lines, in figure 2b and figure 3 spectral lines corresponding to dissociation products of CH_3OH molecules are present.

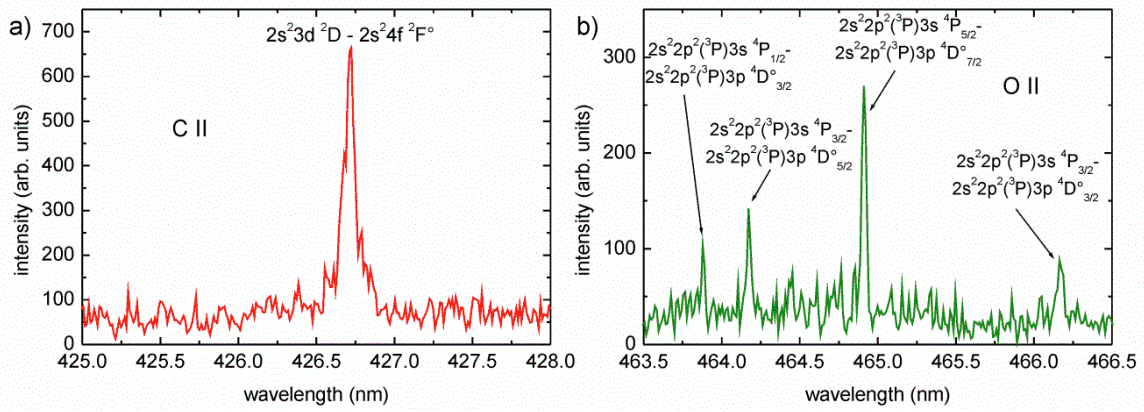

Figure 3. Spectral lines corresponding to single charged ions being dissociation products of CH_3OH molecules: a) C II, b) O II ions

In particular $2s^2 3d\ ^2D$-$2s^2 4f\ ^2F^\circ$ of C II (figure 3a) and $2s^2 2p^2(^3P)3s\ ^4P_{1/2}$-$2s^2 2p^2(^3P)3p\ ^4D^\circ_{3/2}$, $2s^2 2p^2(^3P)3s\ ^4P_{3/2}$-$2s^2 2p^2(^3P)3p\ ^4D^\circ_{5/2}$, $2s^2 2p^2(^3P)3s\ ^4P_{5/2}$-$2s^2 2p^2(^3P)3p\ ^4D^\circ_{7/2}$ of O II (figure 3b) ions, were detected. As could be expected a Balmer β line, strongly broadened due to relatively high electron density, was also recorded. Its spectral width (FWHM) is approximately 4.8 nm, which for low temperature plasmas with $T_e \sim 1$ eV, corresponds to the electron density $n_e \sim 10^{17}$ cm^{-3} [14]. This value was confirmed based on comparison of the 2 ^{3}P-4^{3}L profile with the calculated profiles [15–17] and the Stark broadening of the He I, 2 ^{3}P-3 ^{3}D line [18].

In case of using solutions of various chemical compounds in the methanol, additional lines originating from excited atoms or ions were expected. The inorganic salts used in our experiments (NaCl, NaBr, Na_2WO_4, $CuSO_4$) contained chemical elements of various atomic numbers: Na ($Z = 11$), Cu ($Z = 29$), W ($Z = 74$), S ($Z = 16$), Cl ($Z = 17$) and Br ($Z = 35$). A solubility of the salts in methanol was not high except NaBr [19], hence, the percentage of elements present into the aerosol in most cases did not exceed 1%. Aerosols containing these elements were created and injected into the irradiation region under the conditions corresponding to the pure CH_3OH aerosol. In all cases the emission spectra contained the lines present in plasmas created in this aerosol. Apart from that, additional lines corresponding atoms or ions from the diluted salts, were detected. In figure 4 selected parts of the spectra containing the most intense lines from Na, Cu or W atoms are presented. Some other lines were also detected, but much less pronounced, due to their relatively low intensities. These intensities were comparable to the background formed by

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the scattered light from the LPP and the electronic noise. As could be expected the most intense were two lines of Na I corresponding to transitions $2p^6 3s\ ^2S_{1/2}$-$2p^6 3p\ ^2P_{3/2}$ and $2p^6 3s\ ^2S_{1/2}$-$2p^6 3p\ ^2P_{1/2}$. Two Cu I lines $3d^{10} 4s\ ^2S_{1/2}$-$3d^{10} 4p\ ^2P_{3/2}$, $3d^{10} 4s\ ^2S_{1/2}$-$3d^{10} 4p\ ^2P_{3/2}$ and three W I lines $5d^5(^6S)6s\ ^7S_3$-$5d^5(^6S)6p\ ^7P_4$, $5d^5(^6S)6s\ ^7S_3$-$5d^5(^6S)6p\ ^7P_2$, $5d^5(^6S)6s\ ^7S_3$-$5d^4 6s(^6D)6p\ ^7D_3$ were also well pronounced.

4 Discussion of the results

Irradiation of the aerosol target results in formation of low temperature plasma, having a relatively high electron density of the order of $n_e \sim 10^{17}$ cm^{-3}. As could be expected the spectrum obtained from the aerosol formed from pure CH_3OH dispersed in the He gas contains lines corresponding to excited atoms and singly charged He ions.

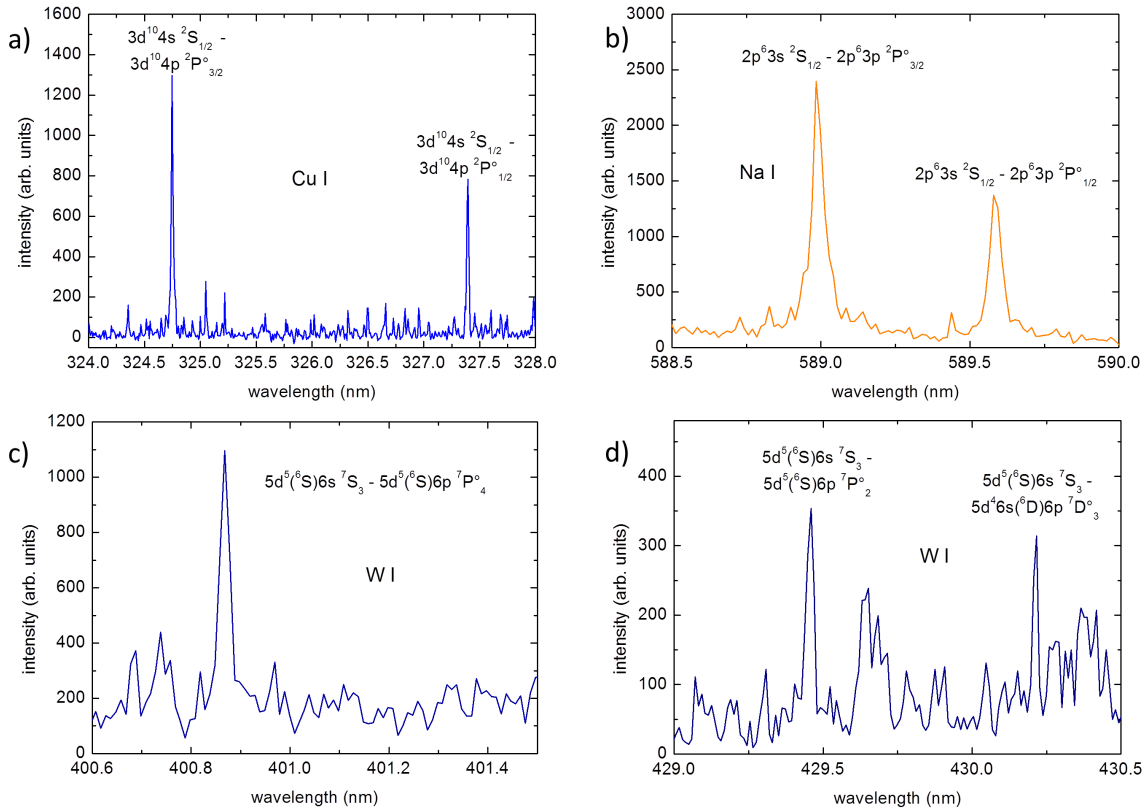

Figure 4. Spectral lines obtained from plasmas induced in aerosols, based on solutions of inorganic chemical compounds (NaCl, NaBr, Na_2WO_4, $CuSO_4$) in methanol. The lines correspond to radiative transitions in: a) Cu I, b) Na I, c,d) W I atoms

Except these lines there are also emission lines originating from decomposition products of the CH_3OH molecules. It should be pointed out that relative intensities of the He I and He II lines are significantly different comparing to the spectrum obtained for pure, EUV induced He plasma. In particular, a relative intensity of the He II line 3l′-4l″ is much smaller comparing to the He I lines. Apart from that the He I line at the wavelength 447.15 nm is strongly broadened in contrast to

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the corresponding line in the pure He plasma spectrum. It is connected with significantly different conditions of the EUV interaction with the He gas and the aerosol target. The EUV absorption in the He gas with a 10% of the atmospheric density, at a distance of 1 mm in the wavelength range 5 nm $< \lambda <$ 10 nm is very small $\sim$ 1–5%. Hence, the electron density of the resulting plasma is low and the Stark broadening of the He, 447.15 nm line is negligible comparing to the instrumental broadening. In case of the aerosol target, the absorption of the EUV radiation is much higher due to a presence of the methanol microdroplets dispersed in the He gas. A single droplet with a 1 μm diameter is fully opaque for the EUV radiation. It results in increase of a number of the ionization events and in effect high electron density. What is interesting, no molecular spectra were detected. The most intense lines originating from the decomposition products of CH_3OH correspond to singly charged ions O II and C II. For obvious reasons it does not concern the H atoms. It would suggest that the molecules or radicals emitting radiation in the measured range are not formed or their contribution is too low, below the detection limit.

Concerning plasmas induced in solutions of inorganic salts dissolved in the methanol, the interaction conditions are similar to the interaction with the pure CH_3OH aerosol. In this case the spectra are very similar to the spectrum obtained for the CH_3OH aerosol. The difference concerns a presence of lines corresponding to elements from chemical compounds diluted in the methanol. Also in this case any molecular spectra were not detected. In all cases, the most intense lines with intensities comparable to the other lines, originated from excited atoms. Some spectral lines corresponding to single charged ions were also detected but their intensities were very low. What was also interesting non-metal elements contained in the chemical compounds gave no spectra in the measured range. In principle they could react with other species forming molecules that give no spectra or very weak spectra within the measured wavelength range.

5 Summary

In this paper, the LPP EUV source was employed for creation of low temperature plasmas, induced in an aerosol target. In our earlier experiments, the EUV induced plasmas were created by photoionization of atomic or molecular gases. Unfortunately most of the elements do not form volatile chemical compounds under normal conditions. This is a significant limitation for production of plasmas based on desired atomic or molecular species. A possible solution is to use the aerosol target. Such targets can be formed from solutions of various chemical compounds. Plasmas formed by photoionization of these targets can contain atomic or molecular species not encountered in the gaseous form under normal conditions. The target used in this experiment was created by the pulsed injection of a small portion of an aerosol, produced using a specially prepared system, into the vacuum chamber. The EUV irradiation resulted in dissociation and ionization of molecules contained in the aerosol target. The resulting plasmas were investigated by spectral measurements in the UV/VIS range. Some spectral lines were strongly broadened due to a Stark effect. Based on this broadening the electron density could be estimated. In case of aerosols based on a methanol dispersed in the He gas, the density reached the value $n_e \approx 10^{17}$ cm^{-3}. In case of plasmas produced in the pure CH_3OH aerosol, the most intense spectral lines corresponded to radiative transitions in H I, He I, He II, C II and O II species. In case of aerosols based on solutions of inorganic salts, additional lines corresponding to atoms or ions, being products of dissociation of these salts, were detected.

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The EUV induced plasmas based on aerosols can be used for basic studies concerning interaction of intense EUV pulses with matter or spectral analysis of soluble materials. The corresponding investigations based on spectral measurements in a wide spectral range (EUV, VUV, UV, VIS) are planned.

Acknowledgments

This work was supported by the National Science Centre, Poland, grant agreement no. UMO-2016/23/B/ST7/00949, and partially by European Union's Horizon 2020 Programme (LASERLAB-EUROPE) grant agreement no. 654148.

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