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Interaction of two laser ablation plasmas

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The interaction of two plasmas generated by laser ablation (Nd:YAG at λ = 1064 nm) from two perpendicular carbon targets was studied by optical emission spectroscopy. The experiments were carried out in high vacuum (8 x 10^{-6} Torr). Spatial and temporal measurements were performed. The covered spectral range was from 280 nm to 740 nm. It was found that the emission intensity of the excited species decreased significantly, when the plasmas were interacting. The remaining emission corresponds to CII (426.7 nm) and CIII (406.8 nm), with $I_{CII} >> I_{CIII}$. Time of flight measurements showed that the interaction of the plasmas produced more energetic species, with values as high as 10 keV for the CII specie, however, their life times were shorter. Carbon thin films were deposited at different positions relative to the plasmas and subsequently characterized by scanning electron microscopy and Raman spectroscopy.

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1. Introduction

Thin film synthesis by pulsed laser deposition has been widely investigated in the past years. In this method the material is evaporated from a target and transferred to the substrate in the form of a plasma consisting of various species. Particularly neutrals, ions and clusters have been detected by different techniques. A serious drawback inherent to the evaporation of many materials is that very small liquid droplets are expelled together with the vapor and the resulting film is splashed by these particles [1]. This problem has been the object of several studies and many solutions have been suggested. Some of them are related to the characteristics of the target, such as high homogeneity and high density together with a periodically polished surface tend to minimize the production of particulates. Another kind of solution is the use of different filters such as velocity filters, grids or diaphragms. An interesting approach to remove particulates has been the so called cross-beam pulsed laser deposition CBPLD [2]. In this technique laser plumes from two different targets ablated by two synchronized lasers intersect in the vicinity of the targets and form one plume in a direction different from the directions of the original plumes. Gas-dynamic interaction of two plumes does not affect the relatively slow movement of droplets, and the substrate can be readily shadowed from the droplets by a diaphragm placed in the direction of the resulting plume. It is also clear that complex gas dynamic processes taking place in the colliding plasma plumes can change energetic characteristics of the erosion jet. Taking into account that at the front of the plume the laser plasma is rarefied, one can expect that the most energetic particles of the plasma are filtered from the resulting plume. Previous work [2] was focused on the characteristics of the crossed beam pulsed laser deposition plasma recorded by a Langmuir probe. In the present work a similar study is performed using optical spectroscopy at several points within the two colliding plasmas.

2. Experimental set-up

The plasmas were produced using a Q-switched Nd:YAG laser (Lumonics HY1200) at 1064 nm (10 ns pulse duration at 10 Hz) as energy source. The laser was divided into two beams of approximately equal optical path, these two beams were both focused on two carbon targets, at 90° one with respect to the other, forming two perpendicular plasma plumes, as it is schematically shown in figure 1. The experiments were performed at a base pressure of 8 x 10^{-6} Torr. The total energy density was of the order of 10^8 W/cm^2, and the energy density of each beam could be varied. During irradiation the targets were rotated in order to avoid crater formation.

The plasma emission spectra were recorded using a 0.75 m spectrometer (Spex model 1702/04) equipped with a fast intensified charge coupled device (ICCD) (Princeton Instruments model 1024E) with a 150 ns gate for photon detection. The light was collected by a UV-Vis fiber bundle placed at the side window of the vacuum chamber, approximately 20 cm apart from the plasmas. Delay times from 100 to 1500 ns were used to follow the temporal evolution of the emission. At delay times greater than 1500 ns typically no signal emission was detected. Synchronization between laser pulse and ICCD was ensured using an electro-optical detector. In this configuration a spectral window of 20 nm could be observed.

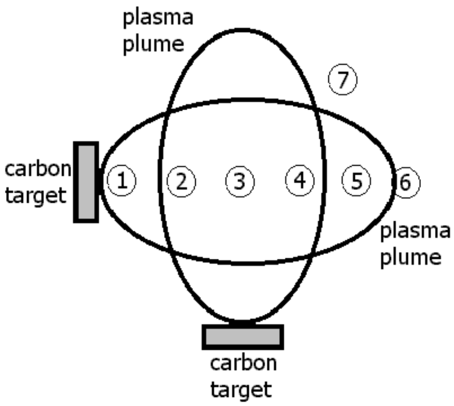


Figure 1. Schematic drawing of the geometry used to study the interaction of the two plasmas.

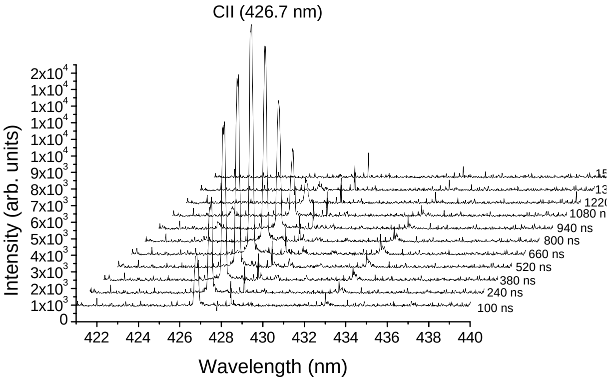


Figure 2. Typical emission spectrum of the ablated carbon targe showing the behavior of the most intense line as a function of time.

The Optical Emission Spectroscopy (OES) measurements were performed along the axis of one of the plasmas, at the points indicated in figure 1 and separated 1 cm from each other, and at a point outside the superposition of the plasmas, indicated also in figure 1 by number 7, which is located at approximately 8.5 cm from the targets.

Carbon thin films were deposited at room temperature and 8 x 10^{-6} Torr, using one and two interacting plasmas on pieces of silicon (100) wafers placed at points 3 and 7 shown in figure 1. The obtained thin films were characterized by Raman spectroscopy and scanning electron microscopy. Raman spectroscopy measurements were performed at room temperature in air with a Spex 1403 double monochromator using the 514.5 nm line of an Argon laser (Laser Ionics) at a power level of 100 mW in a backscattering configuration. The signal was detected with a photomultiplier and a standard photon counting system. The surface morphology of the films was observed with a scanning electron microscope (Phillips XL30).

3. Results and discussion

a) Time of flight measurements

Optical emission spectroscopy (280-740 nm) of the carbon plasmas reveals the presence of several species; CI (462.19, 476.7 nm), CII (426.7, 430.7, 463.91, 464.7 nm) and CIII (406.8, 418.6 nm). The more intense emissions correspond to CII and CIII species. A typical spectrum for a single carbon plasma is presented in figure 2. In order to perform the spectral analysis the CII line was used, because this line is the more intense. The other emission lines, though less intense have a similar behavior.

In figure 3 the emission intensity of the CII line (426.7 nm), taken at point 3 (see fig 1), as a function of time is presented for each individual plasma and when both plasmas are present. The emission intensity of each one of the plasmas can be varied by varying the power in each of the beams, into which the main beam is divided. The overall behavior discussed below, does not depend on the concrete value of power present in each of the beams. The effect on the energy of the CII species in the plasma is striking; when the individual plasmas are considered the corresponding energies determined from time of flight measurements (this procedure was explained in detail elsewhere, [3,4]) are 0.76 keV and 0.4 keV respectively. When both plasmas are present the energy of the CII species increases to 1.9 keV. However in this particular position the intensity of this line is significantly lower and its lifetime also decreases. This can be explained considering that at this point, where the plasmas cross each other, the corresponding plasma density is higher than in the individual case, therefore the excited specie has a higher probability to be recombined. The reason for the increase of the energy of this specie in this case is difficult to find. Furthermore this effect can be analyzed in detail by plotting the velocity of the specie CII in the case of the individual plasma and in the case of colliding plasmas as shown in figure 4. In this figure one observes that for an individual plasma the velocity associated to CII is approximately constant as opposed to the case of colliding plasmas where the acceleration of the specie strongly increases and subsequently decreases.

In figure 5 the spatial behavior of the maximum intensity of the CII line when the plasmas are colliding is presented. One observes that the intensity of the emission reaches a maximum value peaking near the target. Moreover the energy of this specie in the position where the intensity is maximum is of the order of 10 keV.

An interesting point to analyze is the one labeled 7 in figure 1, since it is in this particular position the pulsed laser deposition experiments by CBPLD have been performed [2,5]. These authors have reported that the splashing effect is significantly reduced when the substrate is placed in this position. The corresponding analysis of the optical spectra showed that as expected, the maximum emission intensity, corresponding to the individual plasmas occur at higher times with higher intensities, than in the case when the plasmas are colliding. The specie under consideration, at this point, achieves energy values of 0.5 keV approximately, when only one of the plasmas is

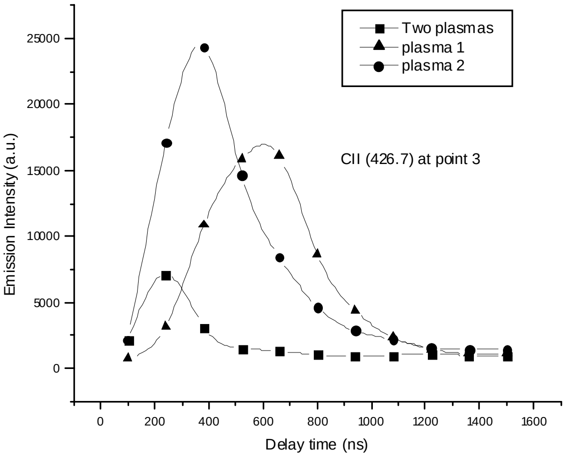


Figure 3. Emission intensity of the CII line taken at point 4, as a function of time for each individual plasma and when both plasmas are present.

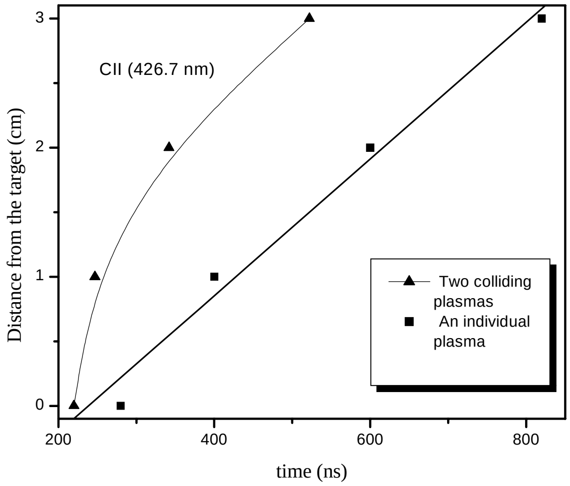


Figure 4. Position of the observed maximum of emission with respect to the target position as a function of time, from this graph the velocity of the maximum can be deduced.

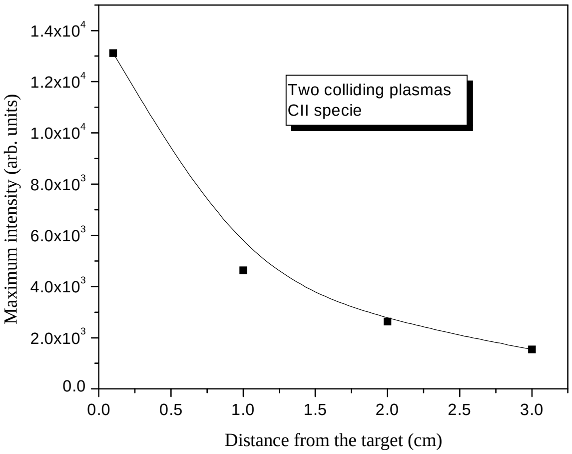
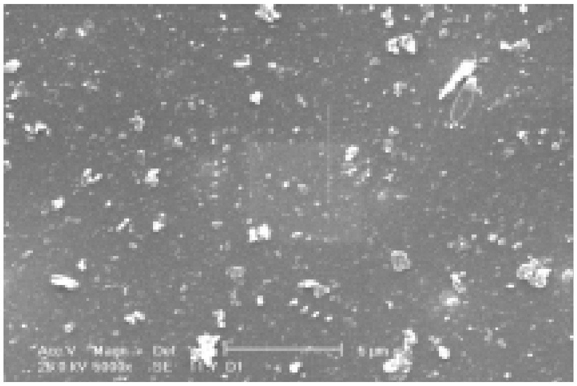


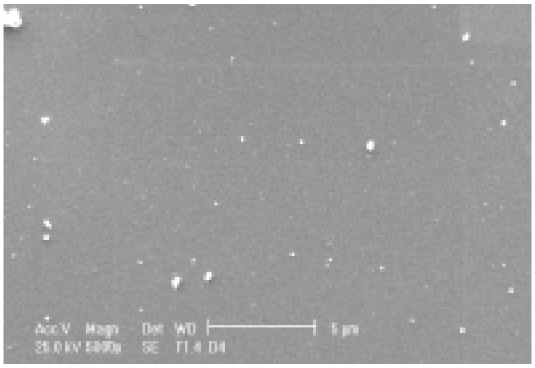
Figure 5. Spatial behavior of the maximum intensity of the CII line.



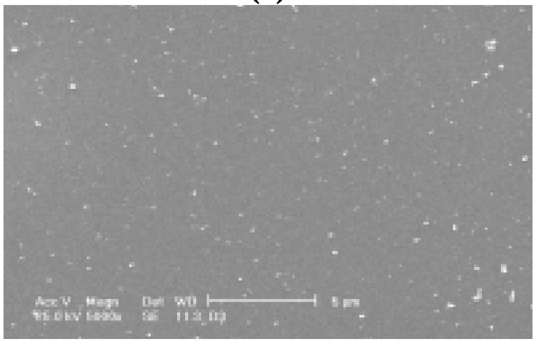
(a)

(b)

Figure 6. SEM images of the film deposited at point 3 with a) the two plasmas present and b) only one plasma present.



(a)



(b)

Figure 7. SEM images of the film deposited at point 7 with a) the two plasmas present and b) only one plasma present.

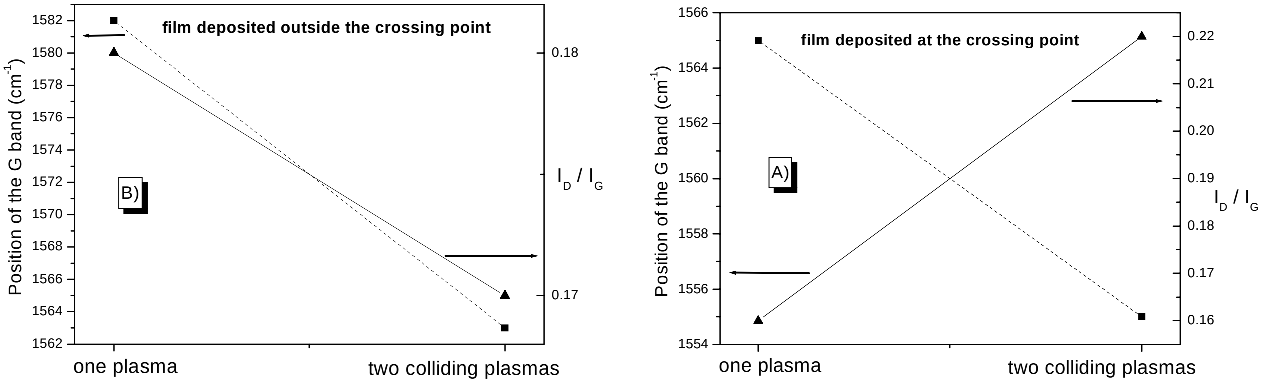


Fig. 8 Position of the Raman G peak and ratio of the intensity of the Raman peaks D and G when one or two plasmas are present at points A) 3 or B) 7.

present. On the other hand, when both plasmas are present the emission intensity of the peak decreases strongly, and its maximum appears at early times, which yields energy values of the order of 3 keV.

b) *Thin film deposition*

Deposition of hydrogen free amorphous carbon (a-C) was carried out at points indicated with numbers 3 and 7 in figure 1. The main idea of these experiments was to study the resultant morphology by SEM and the structure by Raman spectroscopy. Point 3 corresponds to the place where the plasmas cross each other and point 7 is the place outside the crossing point. Figure 6 shows two SEM images of the films deposited in point 3, fig. 6a, shows the morphology of the film deposited when both plasmas are interacting, and fig. 6b, when only one of the plasmas is present. It is clear that the splashing is significantly less when only one of the plasmas is present. When the two plasmas are present the droplets expelled from each of the targets are deposited on the substrate, which results in a higher splashing. Figure 7a shows the morphology of the film deposited in point 7 when both plasmas are interacting, and as it is possible to see, the splashing is reduced in comparison with that obtained in fig. 7b, which shows the morphology of the film in point 7 when only one plasma is present which is in agreement with the results published in [2]. These results show that the higher energy that achieve the species of the plasma, results in a movement of the particles directed along the plasma plume, avoiding the splashing of the substrate in point 7. For the case when only one plasma is present, the plasma particles have less energy and the frequency of collisions can be also greater, resulting this in a more chaotic movement, which deviates the trajectory of some of the particles in the direction of the substrate.

Raman spectroscopy was interpreted in terms of the model proposed by Ferrari and Robertson [6], for this model the BWF + Lorentzian fitting was used to obtain the relation I_D/I_G (as the ratio of the peak heights) and the G – peak position. Figure 8a shows the values of these quantities obtained for the two samples, deposited in point 3. According to the behavior of the ratio I_D/I_G and the G position, these samples are amorphous carbon with an sp^3 content among 20 and 85 %, and this sp^3 content diminishes when the two plasmas are interacting. This is in agreement with the results discussed above, as in the case when the plasmas interact, in point 3 (see fig.1) the energy of the species is greater and more graphite particles are present in the surface. Raman spectroscopy results for the films deposited in point 7, i.e. outside the crossing point of the plasmas, are shown in fig.8b. From these plots it is possible to observe that the sp^3 content in the amorphous films obtained tend to increase when the two plasmas are present, but they are in the region where a 20%, in the sp^3 content is possible as maximum [6]. As discussed above, when only one plasma is present, particles with less energy arrive to the substrate, in this case, i.e. in point 7, we could expect that the film formation is carried out by particles with very low energy, which can be increased when the second plasma is present, this increase of energy yields a higher quantity of sp^3 in the film.

4. Conclusions

Optical emission measurements showed that the interaction of two laser ablation plasmas yield a higher kinetic energy of the excited species in the plasma, however their life time are shorter. At delay times greater than 1 μs no signal emission is detected, for the pressures used in the present experiment (8 x 10^{-6} Torr).

From our experiments we can conclude, that the CBPLD, is capable of producing films with less splashing at certain points, nevertheless as it was shown, in different points the structure of the formed material can be different, due to changes in the energy of the plasma particles.

Acknowledgements

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