Diagnosis of carbon laser produced plasma by using an electrostatic energy analyzer

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Using an electrostatic energy analyzer in both, time-of-flight (TOF) and retarding field analyzer (RFA) modes, respectively, some laser produced plasma parameters are derived from monitoring the positive particles. In TOF mode, the plasma temperature and centre of mass velocity evolutions as a function of laser fluence have been derived. In RFA mode, a charge separation phenomenon was evidenced. TOF spectra recorded for different applied retarding voltage present two separated peaks whose corresponding time values increase with the applied voltage. Moreover, a reheating effect of the plasma was evidenced as a consequence of reflected ions.

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1. Introduction

Carbon laser produced plasma has been extensively studied due to its large potential applicability showed for the carbon allotropes (nanotubes [1], fullerenes [2] and graphene [3,4] that can be obtained in a pulsed laser deposition (PLD) system. For physical vapour deposition methods (that include PLD), the properties of the resulted thin films depend on the plasma parameters. The monitoring of plasma characteristics could bring additional information on the thin film growing mechanism [5].

Despite of the various investigation methods applied for the characterisation of laser produced plasmas, the comprehension of the complete panel of phenomena involved in laser ablation process are not yet satisfactorily explained. Primary, there is a call for further improvement of existing techniques or to develop new ones giving the transitory nature of plasma whose parameters rapidly evolve in space and time. Secondly, the large palette of materials for which it may be applied and the various experimental parameters which may be varied (laser wavelength, laser focalization spot size, etc.) makes further problems for a rapid and compreenhesive description of laser ablation process. The developed optical investigation methods (e.g., time and space resolved optical emission spectroscopy, laser induced fluorescence, ICCD fast imaging, shadowgraphy, etc.) have the advantage of to be non-invasive, offering the possibility to follow the plasma parameters in space and time describing the excited part of the ablated particles. The positively and negatively charged particles are monitored regardless their energy state by using complementary diagnosis techniques, such as Langmuir probes [6] and electrostatic energy analyzer [7].

By using an electrostatic energy analyzer for laser produced plasma characterization, the energy distribution of the ionic species can be obtained. This is generally a determining factor for low roughness and the grain size of the deposited films [8,9]. In the present paper, using an electrostatic analyzer in TOF operational mode, plasma temperature and centre of mass velocity as a function of laser fluence have been derived. We also investigate the possibility of monitoring the positively charged species in RFA mode.

2. Experimental

Carbon laser produced plasma has been generated by the laser ablation of high purity (99.99%) pyrolytic graphite disc (1 mm thickness) placed in an evacuated chamber (10^{-6} mbar). The energy source for ablation was a KrF excimer laser (248 nm, 20 ns, 5 Hz), directed on the target surface at 45° incidence with respect to the normal and focalized by a 500 mm focal lens. The laser fluence was varied in a low laser fluence regime, below 5 J/cm^2, by changing the distance between the focalization lens and the target surface.

The electrostatic energy analyzer is composed by a Faraday cup and three metallic grids (Figure 1), electrically isolated by ceramic inners of 1 mm in thickness. The collector was placed at a distance of 17.5 cm from the target surface on the axis symmetry of the ablation plume. The entrance grid to electrical device is provided with an aperture Φ_1 (5 mm) while a second aperture Φ_2 (9.5 mm) is placed at the access point in the Faraday cage. The last one must be larger than the former because the beam is more divergent in the decelerating region [10]. By the fact that the length of the device is much shorter than the distance to the target surface, one can consider a one-dimensional expansion model of laser produced plasma.

The first grid, exposed directly to plasma, is connected to the ground potential to ensure in the measurement vicinity a minimal electrical perturbation of the plasma. The second, suppression grid (SG) and the third, retarding grid (RG) are electrically biased, as follows: SG – negatively for repelling the primary electrons derived from the plasma and RG – positively for ions repelling, respectively. For a good signal to noise ratio electric batteries were used in order to ensure the bias voltage for collector and GS. For GR, the applied voltage was varied in the range of 0÷120 V by using two stabilized power supplies (HM8143). The electrical signals were recorded by using the 50 Ω terminal impedance of 2 GHz oscilloscope (LeCroy), external triggered by a fast response signal photodiode (2 ns rise time). Each recorded TOF spectra is an average of ten laser shots directed on fresh surface by using an automated target carousel control system.

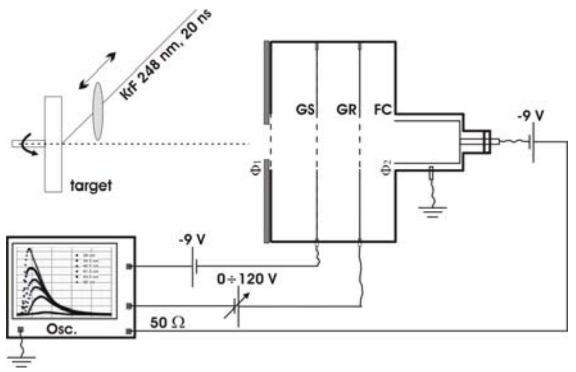

Fig. 1. Experimental set-up scheme (the bias voltage for GS and FC were assured by 9 V electric batteries in order to avoid unwanted electrical signal influences).

The metallic grids used in the experiment were 200 μm spacing. Care should be taken when the grid type is chosen. When a negative voltage is applied, the incident electrons are repelled from a region comparable with the Debye length, which is a function of plasma electron density and temperature. Therefore, the plasma must not be able to shield the electrical potential into the grid spacing. In our case, assuming that the working laser fluence range is below 5 J/cm^2, and by using for temperature and density the results from [7], the estimated Debye length is of the order of our grid spacing. Moreover, the value of the negative electrical potential applied to GS (-9 V) was proved to be sufficient for electron repelling in order to separate the ion from the electron contribution to the signal.

3. Results and discussion

The electrostatic energy analyzer was initially used in time of flight mode for measuring the transitory signal corresponding to positive ions. By varying the bias voltage on GS it was found that for -9 V, the ion contribution to the signal is not influenced by the primary electron influences. A supplementary negative voltage applied to collector of -9 V was necessary to block eventually escaped primary electrons and the secondary electrons emitted by the interaction of plasma particles and metallic grids. Thus, in this configuration for fixed laser pulse energy of 320 mJ the TOF spectra were recorded for different focalization spot sizes (Fig. 2 (a)).

The classical approach in TOF mode supposes that the laser produced plasma can be considered as an instantaneous point source of plasma [11]. For that, it is required to be accomplished two minimal conditions: one, characteristic emission time to be smaller that the ion flight time and, second, the dimension of the ion source is much smaller than the expanding distance to the collection point. Laser ablation can be generally described as the evaporation of a fraction of the target material directly exposed to a focalized laser beam. Near the target surface is thus created a very dense and hot cloud of particles, called Knudsen layer (KL), whose dimensions are much shorter than the analyzing distance (17.5 cm). For low vacuum laser produced plasma, the emitted particles (with a characteristic time of few nanoseconds) expand freely with a constant velocity v_X. In these assumptions, the most probable expansion velocity (v_P) can be calculated by simply measuring the flight time (t_P) required for particles expansion from the target to the collector in order to attain their maximum. As can be seen in Fig. 3 (a) the most probable time of flight t_P have a shift to earlier times with respect to the laser pulse. Thus, a rapid estimation for v_P gives a variation domain of 1x10^4÷2 x 10^4 m/s for the investigated fluence range.

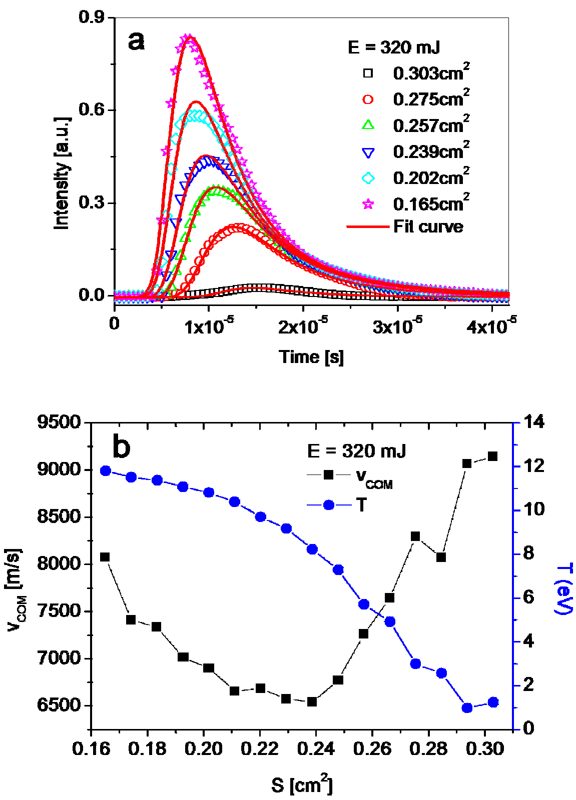

Fig. 2. Electrostatic energy analyzer in TOF mode: (a) TOF spectra and (b) derived temperature and v_{COM} variation for different laser spot size.

The velocity distribution of the expanding species can be expressed by a Maxwellian function, $f(v_X)$ [12]. In particular, considering the main contribution to the signal being done by the single charge ions, the first derivate of the current density expressed as $j = ev_X f(v_X)$ (where e is the elementary electron charge), gives the ion signal variation as a function of time:

$$I(t) = \frac{c}{t^3}\exp\left[-\frac{m}{2k_BT}\left(\frac{x_P}{t} - v_{COM}\right)^2\right] \qquad (1)$$

where c, k_B, T and v_{COM} are an arbitrary constant, Boltzmann constant, plasma temperature and the centre of mass velocity, respectively (x_P denotes the collector position and t the time). Using this function the TOF spectra were well fitted, the fitting curves being represented in Fig. 2 (a) by solid lines. From the fitting data, plasma temperature and centre-of-mass velocity have been derived (Fig. 2 (b)) as a function of laser spot size. It results that plasma temperature decreases with the laser spot size while the centre of mass velocity has a peculiar variation, after an initial slow decreasing region (until the value of 6500 m/s is reached) it is followed a faster increasing section.

In RFA mode, by applying on GR a positive voltage V_R, ions that have the kinetic energies below eV_R are repelled towards the opposite direction of the collector. This time the velocity distribution can be deduced from the height of a potential barrier that they can overcome [13]. The velocity distribution is determined by the momentum in the direction perpendicular to the equipotential lines (preponderant direction of plasma expansion). The velocity distributions thus derived are not presented here; this will make the object of a future paper.

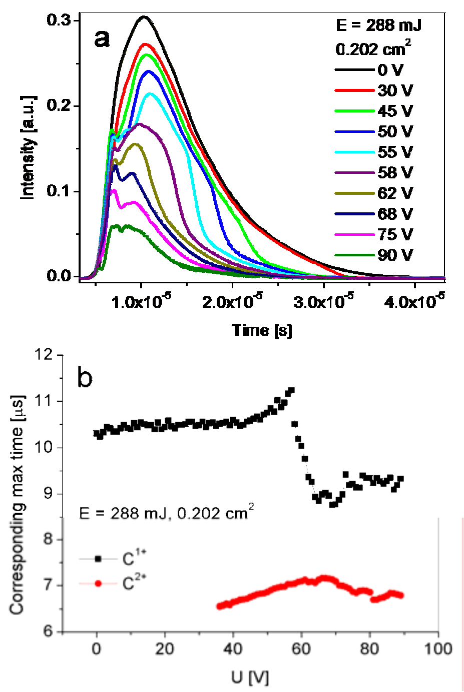

Fig. 3. Electrostatic energy analyzer in RFA mode: (a) TOF signals and (b) corresponding maximum time for C^{2+} and C^{1+} as a function of retarding voltage.

In Fig. 3 (a) are presented the TOF spectra recorded for different positive bias voltage. The shape of the signal given by the collected ions becomes narrow with the applied voltage. The ions having lower energies than the barrier potential (most probably located in the tail of the TOF spectra) are rejected in a progressive manner by the applied voltage (TOF signal shape becoming narrower). The ions whose energies are grater than eV_R (being located in the maximum signal region), will be decelerated as a function of the ionization state. There is clear evidenced the possibility of tailor the energy distribution function of the plasma charged species by simply using a biased metallic grid. This result is particularly important for thin films deposition process where the energy distribution of plasma particles is generally a determining factor in thin film properties [9].

Increasing the applied voltage, the number of the repelled ions becomes significant (this fact being reflected by a decreasing region in the TOF spectra) and, as well as, the influence on those decelerated will be more pronounced. Thus, beyond a threshold voltage depending on the laser fluence (35 V for a laser fluence of 1.4 J/cm^2, as is presented in Figure 3a), there is a shoulder which appears in the early times of the pulsed signal. We have attributed this to the ions having the charge state +2, C^{+2} (firstly ejected from the laser-target interaction) and the larger and more intense peak to the ions having the charge state +1, C^{+1} appearing at longer times (slower and denser in the ablation plume [14]). Thus, we can assume that in the retarding field applied on GR, the ion signal presents a splitting process into two separated peaks. In Figure 3b is shown the corresponding time for maximum current values *vs.* retarding voltage of both carbon species. It is evidenced different evolutions with the applied voltage. The corresponding maximum time values for C^{1+} ions present a slower increase for initial voltage interval, followed by a faster one until ~58 V value is reached. After this value, the position of the maximum becomes largely affected by the ions rejection from the maximum signal region. The corresponding time of maximum current value for the faster ions, C^{+2} present a constant increase until the bias voltage of ~60 V, after which the position being affected by the ions rejection. It appears that for laser produced plasma, the application of the electrostatic energy analyzer in RFA operation mode have some particularities with respect to the conventional stationary plasmas.

By fitting the first TOF signal with the same Eq. (1), it was obtained the plasma temperature and the centre of mass velocity dependences as a function of the retarding applied voltage (Figure 4). It results that the plasma temperature increases with the applied voltage while the centre of mass velocity has a mirror evolution. For a low temperature, the plasma expansion is faster while for high temperature the process deployment is inverse. Thus, a reheating effect of the plasma is evidenced. When a retarding voltage is applied, the positively charged species are decelerated and repelled back to the plasma. This process was already observed in literature for the case when a tamper is placed in front of the expanding plasma, resulting in an increasing of radiation emission process as consequence of the excitation temperature increasing [15].

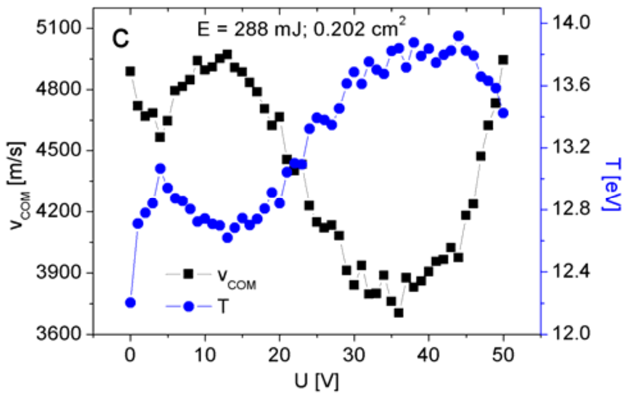

Fig. 4. Temperature and centre of mass velocity variation as a function of retarding voltage.

4. Conclusions

Carbon laser produced plasma has been studied by using an electrostatic energy analyzer in both operation modes, TOF and RFA, respectively. Plasma temperature and centre of mass velocity were obtained as a function of laser fluence, in the case of the former functional mode. Beside, the most probable velocity variation interval was estimated for the investigated fluence range. Attempts were made in RFA mode. The variation of plasma temperature and centre of mass velocity was obtained as a function of retarding applied voltage. Back repelling of the ions explains a reheating effect of the plasma. Further investigations are needed at various distances in respect to the target surface to completely describe this process.

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