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Characterization of the laser ablation plasma used for the deposition of amorphous carbon

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Abstract

The plasma produced by laser ablation of a graphite target was studied by means of optical emission spectroscopy and a Langmuir planar probe. Laser ablation was performed using a Nd:YAG laser with emission at the fundamental line with pulse length of 28 ns. In this work, we report the behavior of the mean kinetic energy of plasma ions and the plasma density, as a function of the laser fluence (J/cm^2), and the target to probe (substrate) distance. The characterized regimes were employed to deposit amorphous carbon at different values of kinetic energy of the ions and plasma density. The mean kinetic energy of the ions could be changed from 40 to 300 eV, and the plasma density could be varied from 1×10^{12} to 7×10^{13} cm^{-3}. The main emitting species were C$^+$ (283.66, 290.6, 299.2 and 426.65 nm) and C^{++} (406.89 and 418.66 nm) with the C$^+$ (426.65 nm) being the most intense and that which persisted for the longest times. Different combinations of the plasma parameters yield amorphous carbon with different structures. Low levels (about 40 eV) of ion energy produce graphitic materials, while medium levels (about 200 eV) required the highest plasma densities in order to increase the C–C sp^3 bonding content and therefore the hardness of the films. The structure of the material was studied by means of Raman spectroscopy, and the hardness and elastic modulus by depth sensitive nanoindentation.

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Keywords: Amorphous carbon; Laser ablation

1. Introduction

Amorphous carbon (a-C) thin films with properties close to those of diamond (high C–C sp^3 content) have been the subject of many studies due to their potential applications. However, films with properties close to those of a graphitic-like material (i.e. high C–C sp^2 content) are also of interest for biological applications [1], or doped with nitrogen for the formation of hard and very elastic materials [2]. In summary, different values of the sp^2/sp^3 ratios yields materials that can have different applications; therefore, a good control of the deposition process is required for a given application. The most commonly used methods to create these types of films involve the use of plasmas and the properties of the deposited films are closely related to the plasma parameters used during deposition. In the present work, pulsed laser deposition technique was used for the formation of amorphous carbon thin films. The plasma produced when the target is ablated can have parameters (mainly ion mean kinetic energy and plasma density) that can be varied in a very wide range, depending of the experimental conditions [3,4]. In order to identify the possible working regimes, the plasma produced during ablation of a carbon target was characterized by means of optical emission spectroscopy and a planar Langmuir probe. In this work, it is shown that plasma diagnostics is a useful tool for controlling the microstructure (the sp^2/sp^3 ratio) and therefore the properties (in this case, the hardness) of the deposited films.

2. Experimental setup

Laser ablation was performed using a Q-switched Nd:YAG laser with emission at the fundamental line ($\lambda = 1064$ nm) with

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a 28 ns pulse duration. The energy density (fluence) delivered to the target could be varied from 6 up to 38 J/cm^2. The laser beam was focused on a rotating high purity graphite target at an incidence angle of 45°. The vacuum chamber was evacuated to a base pressure of 7×10^{-6} Torr. All the experiments reported in this paper were performed at this base pressure. The amorphous carbon films were deposited on silicon substrates previously cleaned in ultrasonic bath of methanol. The distance between substrate and target was varied from 4 to 12 cm.

Optical emission spectroscopy was carried out using a gated intensified CCD, which allowed time resolved measurements for the different distances from the target up to approximately 4 cm, where the plasma emission becomes so weak, that it is undetectable. The light from the plasma was collected by a system of lenses, focused on a UV-vis optical fiber bundle and transported to a 0.5 m spectrograph. A 40 μm slit and a 1200 l/mm grating were used throughout. With this arrangement, a 40 nm spectral window with a 2 Å resolution was obtained.

A Langmuir planar probe that could be displaced along the propagation axis of the plasma plume (at the same distances used for deposition on the substrates) was used to study the time of flight curves of plasma ions and for determination of the plasma density. The probe consisted of a 6-mm diameter stainless steel disk, and was biased at a fixed voltage (−30 V), where saturation of the ion current was evident. The signal from the probe was monitored through a 15 Ω load resistor and recorded on a fast (500 MHz) digital oscilloscope.

The Raman spectra were recorded with a high-resolution micro-Raman system (LabRam HR 800) using the 632 nm line of a He–Ne laser in a backscattering configuration, attenuated 100 times on a 2 μm spot. For each Raman measurement, the sample was exposed to the laser light for 5 s and 100 acquisitions were performed in order to improve the signal to noise ratio.

Nanoindentation testing on the deposited samples was carried out using a CSM nanohardness tester with a Berkovich diamond tip with maximum loads in the range of 1.5–3 mN, so that there is no influence of the substrate on the results. The thickness of the samples used for the nanoindentation tests were in the range of 200 ± 50 nm, with a roughness of less than 4 nm.

3. Results and discussion

The optical emission spectroscopy measurements showed that, for the fluences and distances from the target, used in this experiment, the excited species present in the ablation plasma are atomic species, i.e. no emission from molecular species could be detected. The emitting species are always the same, they only change their intensity as a function of the fluence or distance from the target, and they are C^+ at $\lambda = 283.6$, 290.6, 299.2 and 426.6 nm, and C^{++} at $\lambda = 406.9$, 418.7 nm. Of these, C^+ (426.6) had the highest intensity and emitted light for the longest times after the laser pulse. It can be concluded that the plasma is mainly formed by once ionized carbon, so that the growing film undergoes a continuous bombardment by this specie, and the higher energy and density of this specie, the larger the degree of bombardment.

The values of ion mean kinetic energy and plasma density were obtained from the Langmuir probe measurements. The probe collects the ions from the plasmas and these generate a current pulse that is detected by the oscilloscope. The shape of the curves (the so called time-of-flight (TOF) curves) is shown in Fig. 1, for various experimental conditions. The ion mean kinetic energy was calculated from these curves following the procedure described in [5]. The plasma density was obtained from these curves by taking the maximum value as the ion current for calculation. In fact, this is the maximum plasma density since obviously this varies with time. Changing the fluence and the distance from the target produce a variation on the plasma parameters. The values of ion mean kinetic energy can be varied between 40 and 300 eV, and the plasma density from 1×10^{12} to 6×10^{13} cm^{-3}. The overall behavior of plasma parameters as a function of the laser fluence for different distances from the target is shown in Fig. 2.

The deposition of the thin films was carried out choosing different combinations of ion energies and plasma densities. The first group of samples was deposited using low energy (about 50 eV) and plasma densities from 1 to 3×10^{12} cm^{-3}, so that the growing film undergoes a low degree of bombardment, a second group of samples was prepared using intermediate values of ion energy (between 160 and 200 eV) and plasma densities from 1 to 3×10^{13} cm^{-3}. Finally, a third group was deposited using the maximum obtainable ion energy, about 300 eV, and a plasma density of 7×10^{13} cm^{-3}.

The microstructure of the deposited films was studied by means of visible Raman spectroscopy, in order to study the variation of the characteristic peaks D and G of amorphous carbon as a function of the deposition conditions (i.e. the plasma parameters). For the interpretation of the Raman spectra a Breit–Wigner–Fano + Lorentzian fitting was used to obtain the I_D/I_G ratio and the G peak position. In Fig. 3, the x-axis shows the increase of the degree of bombardment, which is characterized by using the product of the ion energy and the plasma density. From this plot, it can be seen that the I_D/I_G ratio decreases and the G peak moves towards higher values as the

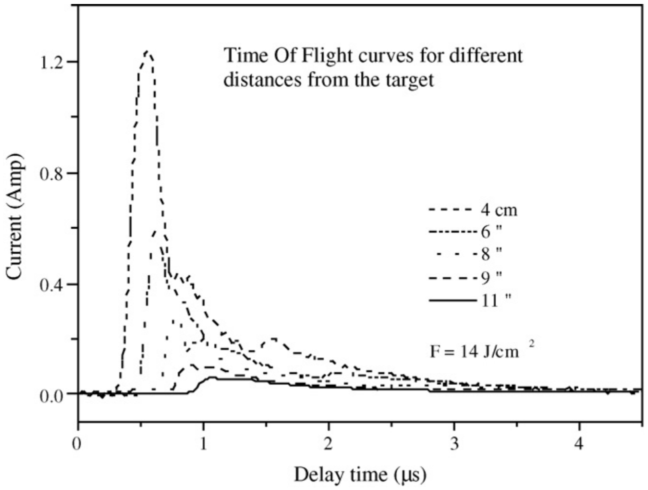

Fig. 1. Time-of-flight curves obtained with the Langmuir probe.

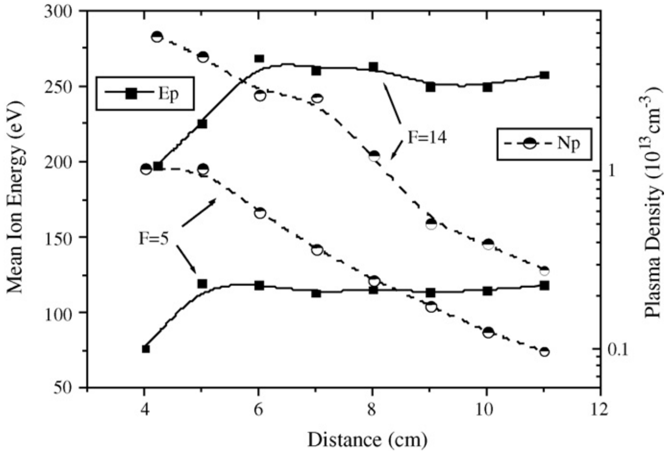

Fig. 2. Mean kinetic energy of ions (Ep) and plasma density (Np), as a function of the distance from the target, for two values of laser fluence (*F*).

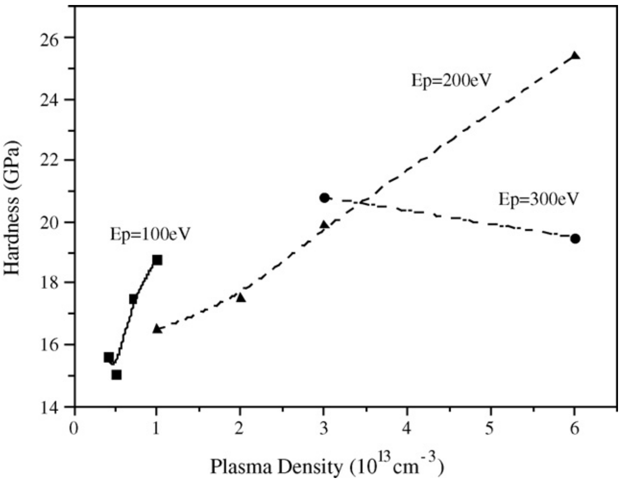

Fig. 4. Hardness of films as a function of the plasma density (Np). Each curve corresponds to different values of ion energy (Ep).

degree of bombardment is increased. This probably means that the number of C–C sp^3 bonds also increases [6]. Probably, this tendency decreases slightly when the ion energy is increased up to 300 eV and the plasma density used is of the order of $7 \times 10^{13}\ cm^{-3}$.

The hardness of the deposited films was measured by nanoindentation and for each sample an average of at least 20 measurements was used. The results are shown in Fig. 4 as a function of plasma parameters; for sake of clarity, the error bars have not been included in the plot but the standard deviation was less than or equal to the 5%. The highest values of hardness (25.4 ± 0.8 GPa) were obtained at a medium level of ion energy (about 200 eV) and a high plasma density of $6 \times 10^{13} cm^{-3}$, while the lowest hardness was obtained with low values of ion energy (about 50 eV) and plasma density ($2 \times 10^{12}\ cm^{-3}$). According to the subplantation model [7], when a low degree of bombardment is used to deposit the films, just a few of the ions (at the beginning of the TOF) have enough energy to implant in the growing film and to produce a change in hybridization, most of the particles in this case have very low energies and they are deposited on the film with a C–C sp^2 hybridization. When the degree of bombardment is increased, a higher quantity of ions have enough energy to implant and to produce a change of hybridization to C–C sp^3. A further increase in the degree of bombardment involves a very high quantity of carbon ions, with such a high energy that an excessive local heating can take place, and with this, a relaxation of the excessive density, gives place to the formation of mostly C–C sp^2 bonds again; and this is observed in the films as a lower value of their hardness (see Fig. 4).

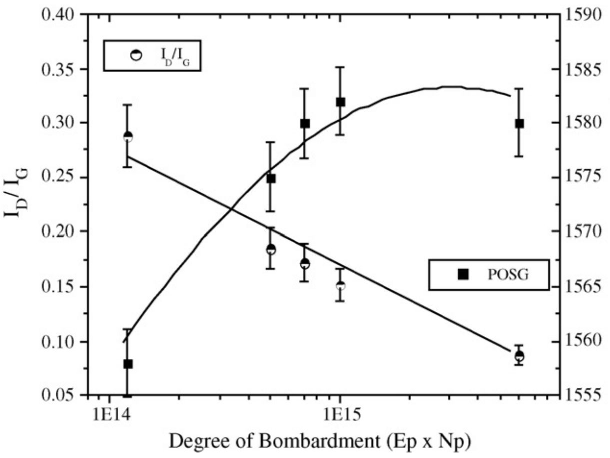

Fig. 3. Raman I_D/I_G ratio and position of peak G as a function of the degree of bombardment (Ep × Np) of the growing film.

4. Conclusions

The optical characterization of the plasma indicated that for all conditions used in this study, the principal species present in the plasma are C^+ ions. It has been shown that the plasma produced by the pulsed laser ablation of a carbon target has an ion mean kinetic energy and plasma density that can be varied over a very wide range. The characteristics of the amorphous carbon thin films produced with this plasma can be controlled through a control of the ion energy and plasma density, since this defines the degree of bombardment of the growing film. The measurement of the plasma parameters can be easily performed using a Langmuir probe. A low degree of bombardment produces films with a high quantity of C–C sp^2 bonds, a higher degree of bombardment probably causes a transformation of some of the C–C bonds to sp^3 configuration. However, a further increase of the degree of bombardment seems to reverse this trend, as the hardness of the material is slightly reduced when ion energies of 300 eV and plasma densities of the order of $7 \times 10^{13}\ cm^{-3}$ are used. The results agree well with the subplantation model proposed by Robertson [7].

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