

DEPOSITION OF ADHERENT DLC FILMS USING A LOW-COST ENHANCED PULSED-DC PECVD METHOD

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ABSTRACT

DLC films are usually obtained by plasma decomposition of a hydrocarbon-rich atmosphere using PECVD technique. PECVD of insulating films requires the substrates to be powered with an alternating pulse. A summary of the degree of hardness, friction coefficient, deposition rate, total stress, adherence, and structural properties as a function of pulsed-DC voltage are presented. Si(100), Ti6Al4V alloy, and stainless steel were used as substrates. Microindentation was used to measure the hardness on thin DLC films. The friction coefficient and critical load were determined by using a tribometer. A conventional profilometry technique was used to measure the total stress and thickness. The film microstructure was studied by means of Raman scattering spectroscopy. The results obtained show that the DLC films deposited using a low-cost EP-DC PECVD method provided the best overall results, presenting a very high adherence with different substrates, a low friction coefficient, low total stress, and a high hardness, over a large deposition area at a reasonable growth rate.

1. INTRODUCTION

Diamond-like carbon (DLC) films have attracted significant attention recently due to their properties of high degree of hardness, chemical inertness, low friction coefficient, and high wear resistance. DLC film may be produced by a great number of deposition techniques such as plasma enhanced chemical vapor deposition (PECVD) through a hydrocarbon discharge, sputtering of a graphite target, arc-discharge, pulsed laser deposition (PLD), and ion-beam assisted deposition (IBAD) [1-3]. The properties of DLC films have been shown to vary according to growth conditions. In particular, the self-bias voltages applied to the substrate holder during DLC film deposition in the r.f. PECVD affect the microstructures and mechanical properties of the films [4,5]. The right choice of these parameters leads to films with diamond-like properties and suggests their performance in a great number of applications, making DLC films attractive for materials engineering and for their production at industrial scale.

DLC films are usually obtained by plasma decomposition of a hydrocarbon-rich atmosphere using r.f. PECVD techniques. PECVD of insulating films requires the substrates to be powered with an alternating pulse. For DLC film deposition, the cathode pulse is usually driven by a radiofrequency source (13.56 MHz). High-power pulsed-DC sources [6-8] may use as an alternative of r.f. PECVD method. Pulsed-DC PECVD technologies provide higher deposition rates, DLC films with high adherence, and do not require matching networks, resulting in a reduction of production cost.

To overcome the low adhesion problems of hard DLC films, different coating concepts have been proposed, such as: deposition of a thin metal interlayer [9,10]; surface implantation [11]; chemical interlayer gradients or a multilayer coating [12]; variation of the self-bias voltage in the beginning of the deposition [13]; and use of surface thermal treatments [14]. The interlayers, specially the multilayers, cause a continual change in the thermal expansion coefficient and help to reduce stress in the DLC films. The r.f. PECVD technique, using silane as silicon precursors, has been applied to deposit a thin amorphous silicon interlayer between metallic substrates and DLC films in order to increase the coatings' adherence [15].

In this study, adherent DLC films were deposited using a low-cost enhanced pulsed-DC PECVD (EP-DC PECVD) method. The DLC films were analyzed according to their microstructure, mechanical, and tribological properties as a function of pulsed-DC voltage. Si(100), Ti6Al4V alloy, and stainless steel substrates were used. A thin amorphous silicon interlayer was used to improve the DLC films' adhesion on the substrates, using silane as the precursor.

2. EXPERIMENTAL PROCEDURES

DLC films were deposited using a low-cost EP-DC PECVD technique, employing an asymmetrical capacitively-coupled deposition system [1]. For tribological properties determinations, DLC films were deposited up to a thickness of approximately 2 μm on polished Ti6Al4V alloy and stainless steel 304 substrates, using methane as hydrocarbon source. Si(100) substrates were used in order to measure the deposition rates, Raman scattering spectra, the total stresses, and the hardness degrees of the DLC films. The substrates were

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cleaned ultrasonically in an acetone bath before putting them into the vacuum chamber and they were additionally cleaned in an argon discharge prior to deposition. Thin amorphous silicon interlayers (~ 100 nm) were deposited using silane as the precursor to improve the film's adhesion.

The substrates were mounted on a water-cooled 6 cm diameter cathode supplied by an asymmetrical bipolar pulsed-DC source, developed in our laboratory (see Figures 1 and 2). The voltage waveform consisted of a fixed positive pulse amplitude of 30 V followed by a variable negative pulse whose peak amplitude varied from -250 to -700 V. A pulse frequency of 20 kHz was used, resulting in duty cycles of 50%. The films were deposited with a total gas pressure of 10 Pa at 10 sccm gas flow for methane.

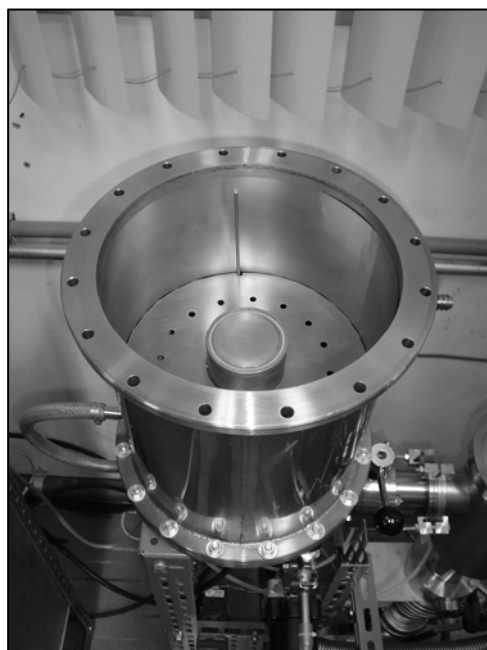


Figure 1 – Deposition chamber with the water-cooled cathode.

The film's atomic arrangements were analyzed by Raman scattering spectroscopy. The spectroscopy was performed with a Renishaw 2000 system using an Ar^+ -ion laser ($\lambda=514$ nm) in backscattering geometry. The laser power on the sample was approximately 0.6 mW and the laser spot had a 2.5 μm diameter. The Raman shift was calibrated in relation to the diamond pick at 1332 cm^{-1} . All measurements were carried out in air at room temperature.

Total stress was determined by measuring the radius of curvature of the substrates before and after the DLC film deposition by means of stylus profilometry and by applying Stoney's equation, as described in detail in the literature [16,17]. The hardness of the films was measured by employing a Fisherscope micro-indenter, applying a load of 10 mN. The values presented in this study correspond to the average of 13 indentations carried out in different spots for penetration depths that were shallower than 10% of the thickness of the films.

The friction coefficients and critical loads were determined using a CETR pin-on-disk tribometer under ambient conditions (20 °C, 55% RH). In the pin-on-disk tribometer, a pin is mounted on a stiff lever and pressed onto the test sample (in the form of a disk) with a precisely known weight. As the sample is rotated, the resulting frictional force acting between the pin and the sample is measured from the small lateral deflection of the lever. The load at which the coating is stripped from the substrate is deemed the critical load. A 20 mm high Ti6Al4V pin with a 6 mm diameter and a 3 mm thickness Ti6Al4V disk with a 51.4 mm diameter and machined finishing ($R_a=0.3\text{ }\mu\text{m}$) were used. The DLC film were deposited on Ti6Al4V and stainless steel disks, using amorphous silicon interlayer, with a thickness of approximately 2 μm . Friction coefficients measurements were carried out keeping the load constant at 5 N, while for the critical load measurements the load were varied from 0.2 to 20 N.



Figure 2 – The asymmetrical bipolar pulsed-DC source.

3. RESULTS AND DISCUSSION

Figure 3 shows the deposition rate as a function of the pulsed-DC voltage. DLC films were deposited on Si(100) substrates for these measurements. The first observed increase in the deposition rate may be attributed to the increase on the arrival rate of reactive neutral radicals and/or fast ion species on the film's growing surface [18]. The deposition rate presented a maximum values at pulsed-DC voltage values around -400 V. The observed decrease of the deposition rate for higher negative pulsed-DC values suggested the presence of an erosion process when the film surface had been bombarded with more energetic ions. This suggestion was reinforced with the observation of a progressive graphitization and hardness decrease of the DLC films upon negative pulsed-DC values increases (see Figs. 4 and 6).

Raman spectra for DLC films present two overlapping bands known as the *D* and *G* bands. While the *D* band, that appears approximately at 1360 cm^{-1} , is derived from the relaxation of the D_{6h} point group symmetry of finite graphite crystallites, which allows forbidden modes to show Raman activity, the *G* band, that appears approximately at 1550 cm^{-1} , is associated with the optically allowed E_{2g} mode zone center of crystalline graphite [19]. The spectra were fitted using two Gaussian lines. The intensity ratio of the *D* and *G* peaks, I_D/I_G , *G* band peak position (ω_G), and the full width

at half maximum (FWHM) of the G peak (Γ_G) as a function of the pulsed-DC voltage, obtained from the fitted parameters, are plotted in Figure 4. The increase of the I_D/I_G ratio, together with the shift of the G band's peak position towards higher frequencies, accompanied by a reduction of the FWHM of the G peak, is usually interpreted in terms of an increase of graphitic domains, either in number or in size [20]. These results suggested a progressive graphitization of the DLC films upon negative pulsed-DC values increases. These DLC films have low H content (less than 20 at.%) and they have a high sp^2 content [21].

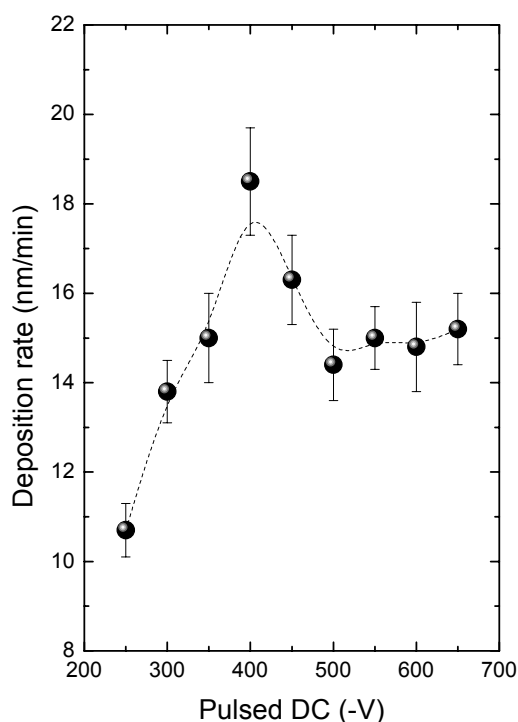


Figure 3 – Deposition rate as a function of the pulsed-DC voltage. DLC films were deposited on Si(100) substrates.

Figure 5 shows the total compressive stress measurements as a function of the pulsed-DC voltage. The low stress values between 0.6 – 1.1 GPa were determined, when the thin amorphous silicon interlayer was used. A significant decrease of the stress values was observed in relation to the DLC films deposited using r.f. PECVD technique (2.2 – 3.3 GPa), when the thin amorphous silicon interlayer were not used [5]. The stress reduction, together with the formation of the SiC interface suggested an increase in the DLC films adherence [15]. The SiC interface was formed due to the reaction of the carbon species with silicon atoms in the beginning of the DLC deposition. A significant amount of metallic silicon (~55%) was determined from X-ray photoelectron spectroscopy (XPS) spectra [15]. The high quantity of metallic silicon suggested that this form was probably responsible for the silicon binding in the metallic substrates (Si(100), titanium alloy, and stainless steel). The presence of a maximum value was observed for the film deposited at pulsed-DC voltage values around -400 V.

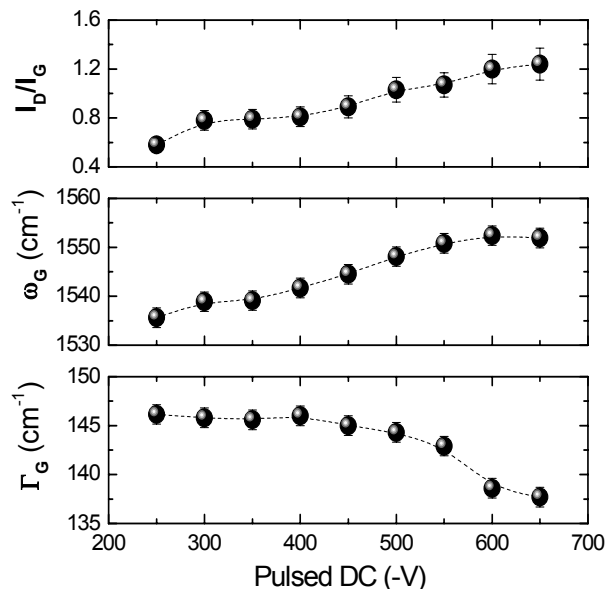


Figure 4 – I_D/I_G intensity ratio, G band peak position (ω_G) and G bandwidth (Γ_G) as a function of the pulsed-DC voltage. DLC films were deposited on Si(100) substrates.

The hardness values as function of the pulsed-DC voltage are shown in Figure 6. High hardness values were obtained for the DLC films deposited by this technique. An increase of the hardness was observed when the negative pulsed-DC voltage increased. This behavior is directly correlated with the increase of the atomic density and the decrease of the hydrogen content in the DLC films [4,22]. Both the total compressive stress and hardness values reached their maximum at pulsed-DC voltage of approximately -400 V. The existence of this maximum in DLC films deposited by PECVD techniques has been explained by the subplantation model [23,24]. The reduction in stress and hardness in the films deposited with higher negative pulsed-DC voltages suggests a progressive graphitization. While low bombardment energies (below 100 eV) could not induce the formation of sp^3 hybridized carbons, bombardment energies typically above 400 eV promoted the generation of too many defects in the carbon matrix and led to a graphite-like material. As a consequence, only a relatively narrow window of energies (~100 eV) promoted the deposition of hard DLC films [23,25].

Figure 7 shows the friction coefficient values between the Ti6Al4V pin and the titanium alloy disk with a DLC film as a function of the cycle number. The DLC thicknesses were approximately 2 μ m and the films were deposited using a pulsed-DC voltage of -400 V. The sliding velocity was kept constant at 0.1 m/sec. The mean friction coefficient value was 0.08. The similar results were measured for all films deposited using different pulsed-DC values. This result confirmed the advantages of the DLC films deposited by this method for tribological applications.

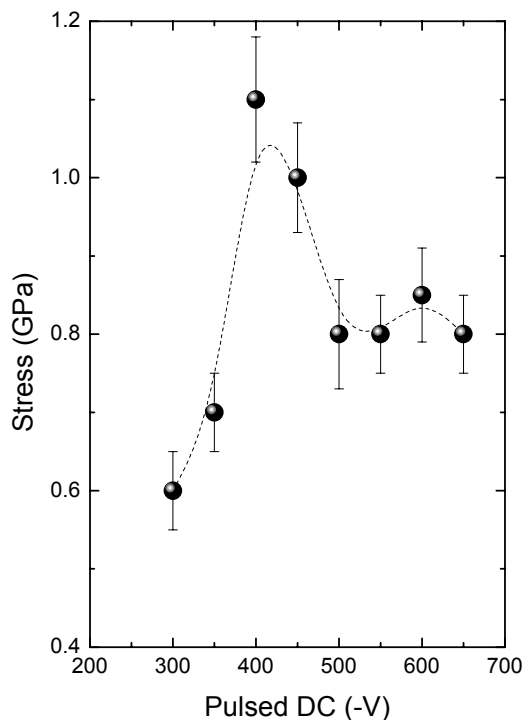


Figure 5 – Total compressive stress as a function of the pulsed-DC voltage. DLC films were deposited on Si(100) substrates, using a thin amorphous silicon interface.

The critical loads were tested using a Ti6Al4V pin and titanium alloy and stainless steel disks covered with DLC films, deposited using different pulsed-DC voltages and amorphous silicon interlayer. The normal force applied was increased from 0.2 to 20 N (the maximum value for our tribometer) as a function of time. For all measurements and for both of disk, the critical loads were higher than 20 N. These results confirmed that the DLC film adhesion on Ti6Al4V and stainless steel substrates is very high, when an amorphous silicon interlayer was applied. When the 2 μm of thickness DLC films were deposited directly onto the metallic substrates, the films were not adherents. The results obtained demonstrated that the DLC film adhesion on metallic substrates for the films deposited by EP-DC PECVD method is higher than the adhesion on DLC films deposited by r.f. PECVD (critical loads ~ 10 N) and IBAD(critical load ~ 15 N) techniques [26].

4. CONCLUSIONS

The obtained results show that the DLC films deposited using a low-cost EP-DC PECVD method provided the best overall results, presenting a very high adherence with different substrates, a low friction coefficient, low total stress, and a high hardness, over a large deposition area at a reasonable growth rate.

The microstructure and the mechanical properties of these films depended on the intensity of ion bombardment and on the pulsed-DC voltage. The low total compressive stress was responsible for the increase of DLC film adherence on metallic substrates. The hardness values increased for higher negative pulsed-DC voltages and reached their maximum at pulsed-DC voltage of approximately -400 V. The tribological analyses showed strong DLC film adhesion on metallic substrates when the films were deposited using an amorphous silicon interlayer. These results confirmed the advantages of this technique for DLC film deposition for industrial and tribological applications.

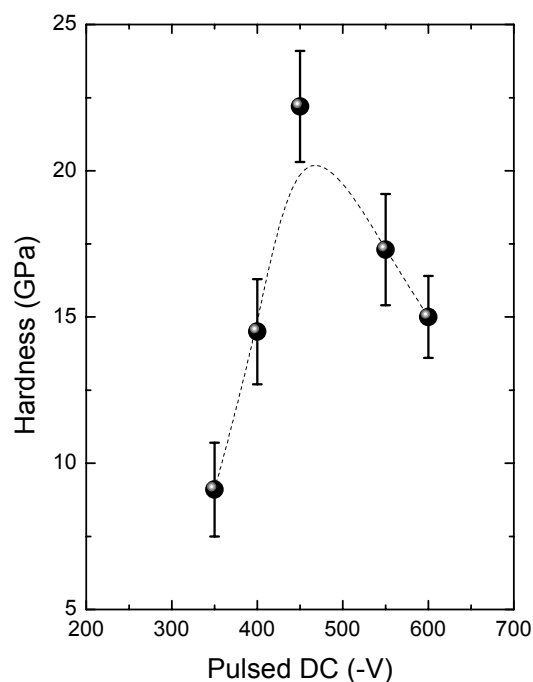


Figure 6 – Hardness as a function of the pulsed-DC voltage. DLC films were deposited on Si(100) substrates.

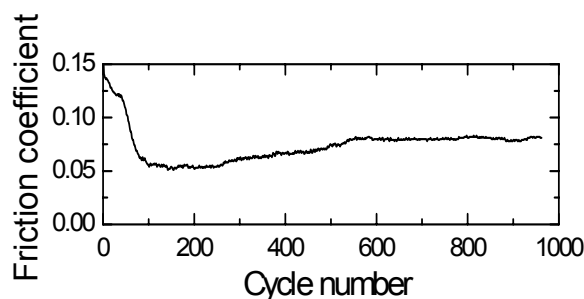


Figure 7 – Friction coefficient values between the Ti6Al4V and DLC film as a function of the cycle number. The DLC thicknesses were approximately 2 μm and the films were deposited using a pulsed-DC voltage of -400 V.

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