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ADHERENT a-C:H FILMS DEPOSITED BY IBAD METHOD

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ABSTRACT

Adherent and low-stress a-C:H films were deposited on Ti6Al4V and stainless steel substrates using ion beam assisted deposition (IBAD) technique. An amorphous silicon interlayer was applied to improve the adhesion of the a-C:H films on the metal substrates. The elemental composition and atomic density of the films were determined by ion beam analysis. The film microstructure was studied by means of Raman scattering spectroscopy. The mechanical properties were determined by means of stress and hardness measurements. The friction coefficient and critical load were evaluated by using a tribometer. The tests showed that the composition, the microstructure, and the mechanical properties of the films depend on the intensity of the ion current. The tribological analyses showed high a-C:H film adhesion on metallic substrates. These results confirmed the advantages of the IBAD technique for a-C:H film deposition for industrial applications.

1. INTRODUCTION

Different types of wear-resistant thin films have been used successfully in many fields, such as cutting tools, microelectronic systems, to reduce costs and improve performance. The amorphous hydrogenated carbon (a-C:H) films have much great potential as protective coatings because of their high degree of hardness, chemical inertness, low friction, and high-wear resistance.

The major disadvantage of super hard diamond-like carbon (DLC) film deposition and, therefore, their technical applications is that there is often a relatively low adhesion of these films on metallic substrates caused by very high total compressive stress on these coatings. To overcome the low adhesion problems of these films on metallic substrates, different coating concepts have been proposed by many research groups [1-6]. The interlayers, especially the multilayers, cause a continual change in the thermal expansion coefficient and help to reduce stress in the a-C:H films.

Several techniques have been used to synthetize DLC films, including plasma enhanced chemical vapor deposition (PECVD) [7,8], sputtering [9,10], laser deposition [11,12], and IBAD [13,14]. The IBAD is a low temperature process and can be used to make a coating with good adhesion to a substrate because the film is formed by simultaneous deposition with ion implantation. The IBAD process offers the possibility to deposit DLC films onto steels and others metal substrates with particularly good interface adhesion.

In this study, the IBAD system was used to deposit adherent and low-stress a-C:H films on Ti6Al4V and stainless steel substrates. A thin amorphous silicon interlayer was used to improve the a-C:H films' adhesion. The films were analyzed according to their microstructure, mechanical and tribological properties as a function of ion current.

2. EXPERIMENTAL PROCEDURES

The a-C:H films were deposited by IBAD methods, employing an end-Hall ion source [15] (see Figure 1). The end-Hall ion source was mounted into the 1 m^3 cylindrical stainless steel deposition chamber, shown in the Figure 2. The thin amorphous silicon interlayers (~100 nm) were deposited by the r.f. PECVD technique to improve the film's adhesion, using silane as the precursor gas [16]. Ti6Al4V alloy and stainless steel 304 substrates were polished by using diamond powder (1 μm) and were cleaned ultrasonically in an acetone bath before putting into the vacuum chamber. The substrates were additionally cleaned in argon discharge prior to deposition. In addition, Si (100) substrates were used in order to measure the total stress of the a-C:H films.

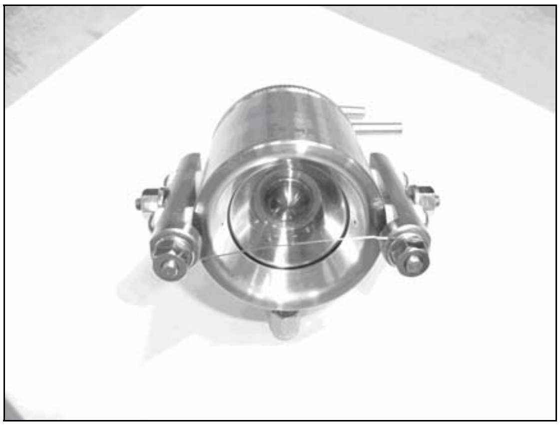

Figure 1 – End-Hall ion source.

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Argon was used as the bombardment gas, while methane was used as a precursor. The argon/methane rate was kept constant at 1/4, while the ion energy was maintained constant at 150 eV. The base and operating pressure in the chamber were approximately $3x10^{-4}$ Pa and $1x10^{-2}$ Pa, respectively. A series of DLC films were deposited by changing the total ion current from 2 up to 4.5 A. The DLC film's thicknesses of approximately 2 μm were determined by stylus profilometry.

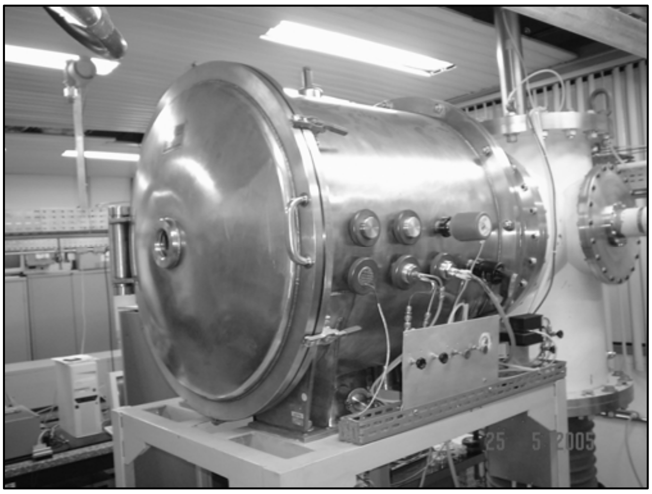

Figure 2 – The cylindrical stainless steel deposition chamber.

The elemental composition was determined by ion beam analysis (IBA), using Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA), employed a 1.6-MV Pelletron electrostatic accelerator 5SDH from the National Electrostatic Corporation. For the measurements, a 2.2-MeV He^+ beam was used. The atomic density was inferred by combining the atomic density of the area provided by IBA and the film thickness.

The film's atomic arrangement was analyzed by Raman scattering spectroscopy. The spectroscopy was performed with a Renishaw 2000 system using an Ar^+-ion laser (λ = 514 nm) in backscattering geometry. The laser power on the sample was ~ 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 film curvature by means of stylus profilometry and by applying Stoney's equation [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.

Friction coefficient and critical load were determined using a CETR pin-on-disk tribometer under ambient conditions (20 ºC, 55% RH). A 20 mm high Ti6Al4V pin with a 6 mm diameter and the 3 mm thickness Ti6Al4V and stainless steel disks with a 51.4 mm diameter and machined finishing (Ra=0.3 μm) were used. The a-C:H films were deposited on the disks, using amorphous silicon interlayer, with a thickness of approximately 2 μm. The critical load was defined as load at which the coating was stripped from the substrate.

3. RESULTS AND DISCUSSION

Figure 3 shows the deposition rate as a function of the ion current for films deposited by IBAD method. An increase in the deposition rates was observed. This behavior can be explained because of the higher methane flow needed to obtain higher values of ion current. Also, the contribution to a higher generation rate of nucleation sites on the film surface due to the more energetic ion bombardment should be taken into account.

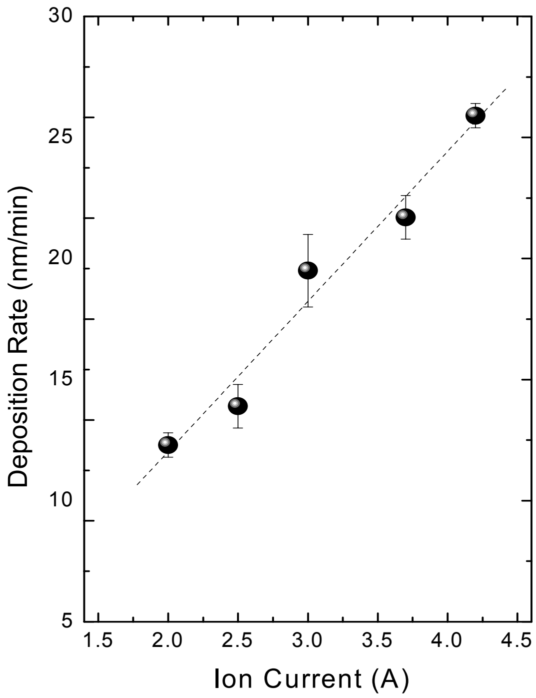

Figure 3 – Deposition rate as a function of the ion current.

The hydrogen content and atomic density of the a-C:H films as a function of the ion current were presented in Figure 4. Films deposited at low ion current presented higher hydrogen contents and lower atomic densities, while for higher ion current values, the density increased and hydrogen content decreased. The hydrogen content reduction is due to a more effective ion bombardment leading to preferential hydrogen sputtering that occurs because of the weaker strength of C-H bonds when compared to the C-C bonds. The film density behavior with the increase of the ion current clearly shows that the increase ion flux and the energy of the ionic species induce a higher density of nucleation sites on the film surface, resulting in a denser film microstructure. The hydrogen content and the atomic density kept approximately constant values (20 at.% and $1.3x10^{23}$ atoms/cm^3, respectively) for the higher ion current values. These values correspond to what are typically reported in the literature for a-C:H films [18]. Moreover, greater CH_4 molecule fragmentation in the plasma as the power was increased may have contributed to the decrease of the incorporation of hydrogen content.

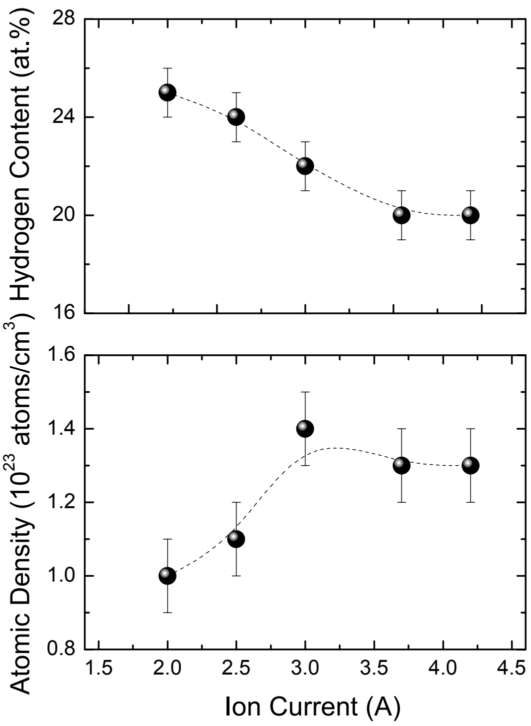

Figure 4 – The hydrogen content and atomic density as a function of the ion current.

Raman spectra for a-C:H films presented two overlapping bands known as *D* and *G* bands, which appear approximately at 1390 cm^{-1} and at 1545 cm^{-1}, respectively. The spectra can be fitted using two Gaussian lines. The I_D/I_G intensity ratio, *G* band peak position (ω_G) and *G* bandwidth (Γ_G) as a function of the ion current, obtained from the fitted parameters, for films deposited by IBAD technique were plotted in Figure 5. The observed 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 bandwidth, is usually interpreted in terms of an increase of graphitic domains, either in number or in size [19]. The results suggest a progressive graphitization of the a-C:H films upon ion current increase.

Figures 6 and 7 presented the total compressive stress and the hardness values as functions of the ion current. A significant decrease of the stress values was observed in relation to the a-C:H films deposited using r.f. PECVD technique [16]. The observed reduction of the stress values of the a-C:H films deposited by IBAD was explained by the use of a thin amorphous silicon interlayer. The films deposited at low ion current presented higher stress and hardness, while for higher ion current values, the compressive stress and hardness decreased. These results suggested that internal stress reduction was responsible for the increase of a-C:H film adherence on metallic substrates. Both the internal stress and hardness values reached a maximum at 2.5 A. The existence of this maximum in the measured mechanical properties of a-C:H films has been explained by the subplantation model [20,21]. The stress and hardness reduction in the films deposited with higher ion current suggested a progressive graphitization, as had been observed in the Raman results.

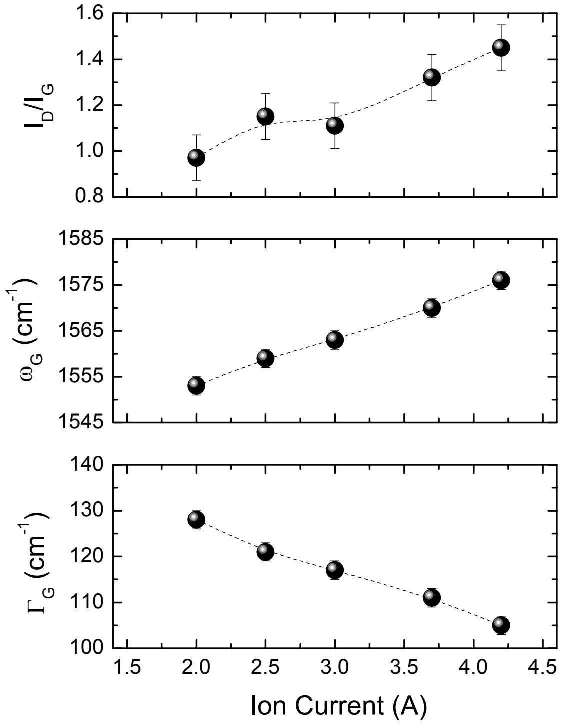

Figure 5 – I_D/I_G intensity ratio, G band peak position (ω_G) and G bandwidth (Γ_G) as a function of the ion current.

Figure 8 shows the friction coefficient values between the Ti6Al4V pin and the disks with a-C:H film deposited using the IBAD technique. The a-C:H film were deposited using an ion current of 2.5 A. The disk rotation velocity was kept constant at 0.1 m/sec. The mean friction coefficient value was approximately 0.12. The similar results were measured for all films deposited using different ion current values. These results confirmed the advantages of the a-C:H deposited by IBAD method for tribological applications.

The critical loads were tested using a Ti6Al4V pin and titanium alloy and stainless steel disks covered with a-C:H films. a-C:H films were deposited using amorphous silicon interlayer, with a thickness of approximately 2 µm. The normal force applied was increased from 0.2 to 20 N as a function of time. The load at which the friction coefficient increased rapidly was defined as critical load value. In both of used substrates and for all ion current values, the critical loads were evaluated to be approximately 15 N. These results demonstrated that the a-C:H film adhesion on Ti6Al4V and stainless steel substrates is high. The SiC formed in the interface between the amorphous silicon interlayer and a-C:H film, as had been observed in the XPS results [22], was probably responsible for the good a-C:H film adherence on the silicon layer.

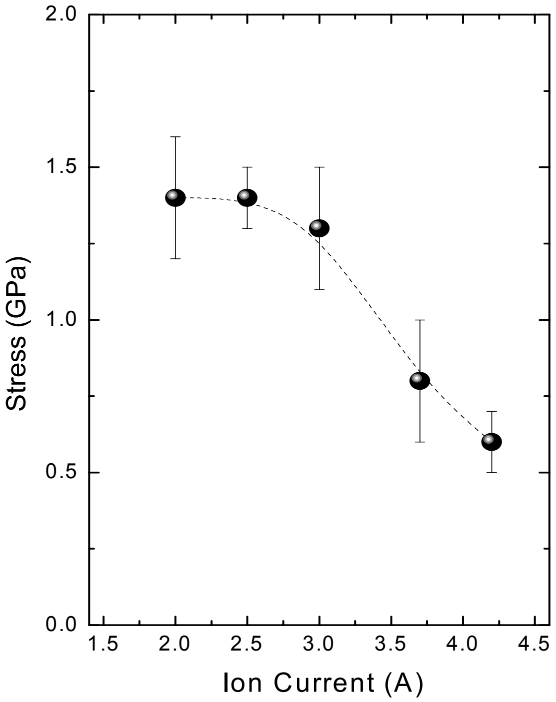

Figure 6 – Total compressive stress as a function of the ion current.

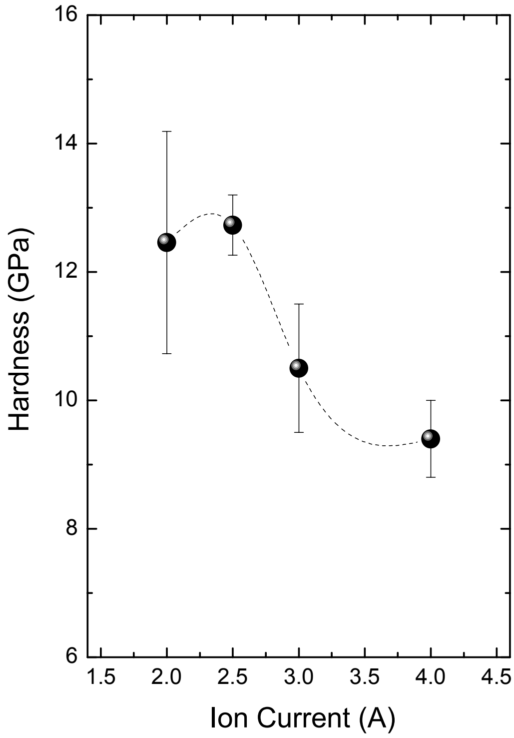

Figure 7 – Hardness as a function of the ion current.

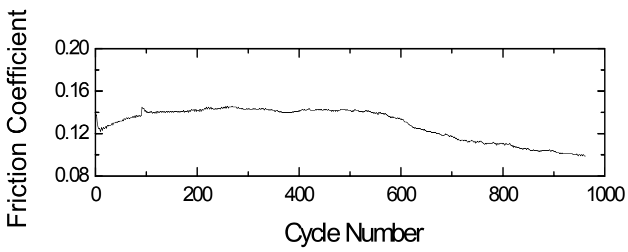

Figure 8 – Friction coefficient of the a-C:H film deposited using an ion current of 2.5 A.

4. CONCLUSIONS

Analysis of the a-C:H films showed that the composition, the microstructure, and the mechanical properties of these films depend on the ion current. The tribological analyses showed a high a-C:H film adhesion on metallic substrates when the films were deposited using an amorphous silicon interlayer. The results obtained show that the a-C:H films present low friction coefficient, low total stress, a high degree of hardness, allowing the deposition over a large area with a reasonable growth rate. These results confirmed the advantages of the IBAD technique for a-C:H film deposition for industrial applications.

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