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Amorphous hydrogenated carbon films treated by SF$_6$ plasma

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Abstract. This work was performed to verify the chemical structure, mechanical and hydrophilic properties of amorphous hydrogenated carbon films prepared by plasma enhanced chemical vapor deposition, using acetylene/argon mixture as monomer. Films were prepared in a cylindrical quartz reactor, fed by 13.56 MHz radiofrequency. The films were grown during 5 min, for power varying from 25 to 125 W at a fixed pressure of 9.5 Pa. After deposition, all samples were treated by SF$_6$ plasma with the aim of changing their hydrophilic character. Film chemical structure investigated by Raman spectroscopy, revealed the increase of sp$^3$ hybridized carbon bonds as the plasma power increases. Hardness measurements performed by the nanoindentation technique showed an improvement from 5 GPa to 14 GPa following the increase discharge power. The untreated films presented a hydrophilic character, which slightly diminished after SF$_6$ plasma treatment.

1. Introduction

Amorphous hydrogenated carbon (a-C:H) films have attracted great interest due to their promising properties, such as high hardness, wear resistance, low friction coefficient, chemical inertness and biocompatibility [1-6]. They are usually applied as protective coating for optical windows, hard disk and fibers [7], magnetic media [8], machine parts [9], biomedical coating and biosensors [10]. These films are usually synthesized by glow discharge techniques as Plasma Enhanced Chemical Vapor Deposition (PECVD), and their properties depend on the conditions of the process such as discharge power, excitation frequency, deposition time, monomer kind and pressure, among others. The combination of these parameters determines the chemical structure of the films, whose sp$^3$/sp$^2$ proportion rate is responsible for their mechanical, chemical and tribological properties [11,12]. Plasma treatments are interesting because they alter the surface properties and preserve the bulk ones. Fluorine-containing gases are widely used for etching processes and plasma treatments to modify the conventional polymer surfaces [13,14], for instance, to produce hydrophobic polymers used in packing and non-sticking applications [15,16]. This work aimed to verify the hardness and wettability of a-C:H films prepared from acetylene/argon mixture plasma at different radiofrequency (RF) power. Following the deposition, the films were submitted to SF$_6$ plasma with the purpose of modifying their hydrophilic character.
2. Materials and Methods
Films were prepared in a cylindrical quartz reactor, fitted with two parallel plate electrodes. In this equipment, the upper electrode is connected to 13.56 MHz RF power supply and the lower one is grounded. Plasmas were established in a mixture of acetylene and argon, respectively in the proportion of 30% and 70% related to the total gas pressure fixed at 9.5 Pa. Deposition time was 5 min and the excitation power varied from 25 to 125 W. Films were deposited onto glass and silicon substrates, placed on the lower electrode. The substrates temperature was kept fixed at 25 °C during the deposition process. After the deposition, the samples were treated with SF$_6$ radiofrequency plasmas (13.56 MHz) for 5 min. This treatment was performed in a stainless steel cylindrical vessel, fitted with two plate electrodes, using 70 W of power and 13.3 Pa of pressure. Film chemical structure and composition were investigated by Raman spectroscopy in a Renishaw Micro-Raman Spectrometer, with argon-ion laser excitation wavelength at 514 nm. Thickness measurements were carried out by Alpha-Step Tencor profilometer, and hardness was evaluated by a Nanoindenter Hysitron Tribolindenter. Film wettability was evaluated by contact angle technique, using a Ramé-Hart 100-00 Goniometer. Such analysis was performed before and after the SF$_6$ plasma treatment.

3. Results and discussions
Figure 1 shows Raman spectra of the a-C:H films deposited at discharge power ranging from 25 W to 125 W. As can be seen, the two bands at approximately 1350 cm$^{-1}$ and 1570 cm$^{-1}$ fitted with Gaussian curves correspond to D and G peaks, respectively. The D peak is associated with sp$^3$ hybridized carbon bond and G peak is related to sp$^2$ state. This figure indicates that a-C:H films is predominantly formed by sp$^2$ bonding. Both peak positions shift towards lower wavenumbers as the power increased, which suggests an increase in the sp$^3$ bonding [17]. In this sense, we calculated the ratio of D and G peak areas, I$_D$/I$_G$, which is depicted in figure 2. As can be seen in this figure, the I$_D$/I$_G$ intensity ratio improved from 0.25 to 0.55 as the power increased. This finding confirms the rise in the sp$^3$ states and can be explained by processes involved in plasma polymerization. It is known that higher discharge power induces a greater molecular fragmentation of the precursor mixture (acetylene and argon), and the film grows through diverse recombination between dangling bonds and free radicals. The probability of C-H bond breakage is higher than C-C ones and it leads to loss of hydrogen atoms and consequently film carbonization. Besides, during the deposition, the film is also bombarded by all species presented in the discharge, promoting recombination via chain crosslinking. All these processes are intensified by heavy species as argon ions, which is abundant into the discharge [17].

![Figure 1. Raman spectra of samples deposited at different applied powers, prior to SF$_6$ treatment.](image1.png)

![Figure 2. I$_D$/I$_G$ ratio of the films as a function of the deposition power.](image2.png)
In figure 3 the hardness of the films is plotted as a function of the discharge power. The hardness of the a-C:H film deposited at 75 W is about the same (within the error bar) as the hardness of the films deposited at 25 W (5 GPa), and attains larger values at 100 W (14 GPa) and 125 W (12 GPa). This is related to $I_D/I_G$ ratio of the films, which is the same at lower powers, however increases for power above 75 W. As explained before, $I_D/I_G$ rate is related to sp$^3$ groups, which control the mechanical properties, therefore the increase of power promoted the hardness improvement. It is believe that long deposition time as well as high discharge power cause increase of the substrate temperature and consequently, the structure hardness is reduced. It is important to note that a-C:H films present hardness values ranging from 9 to 16 GPa [18] and the hardness of the polymer films deposited from acetylene-argon mixtures achieves 14 GPa.

**Figure 3.** Film hardness as a function of the discharge power.

Figure 4 shows the thickness of the a-C:H films treated and untreated by SF$_6$ plasma, as a function of the discharge power. The thickness of untreated sample diminished from 74 to 24 nm with increasing the power, probably due to sputtering processes caused by argon ions. During the collisions, these heavy ions can transfer enough energy to remove a portion of the film surface increasing the sputtering effect. After SF$_6$ treatment, the thickness present the same tendency as the power increases, however their values are slightly lower than the untreated sample thickness. In this case, the highly reactive fluoride atoms are responsible for etching process. Ablation processes due to creation of volatile groups which are taken to the plasma also contribute for thickness reduction. The etching effect is more intense for soft films, as can be observed in the case of the sample deposited at 25 W.

**Figure 4.** Film thickness as a function of the RF power.

**Figure 5.** Contact angle of the untreated and treated films as a function of the RF power

**Figure 6.** Surface Energy of the untreated and treated films as a function of the power.
Figure 5 shows the contact angle measurements of the untreated and SF$_6$ treated films. As can be seen, the contact angle measurements of the as-deposited films kept the same value around 73° independently on the deposition power. This result is consistent with surface energy measurements which present a constant value of 58 Erg, as can be seen in the figure 6. Although the film chemical structure was altered by different RF power, the hydrophilic character of the untreated films was preserved. After SF$_6$ treatment, there was an increase of the contact angles, mainly for the sample deposited at the lower power (94°). Probably, the fluorine atoms removed hydrogen atoms from the polymeric chain and recombine with dangling bonds. Besides, the fluorine atoms can be linked to free radicals trapped in the film structure. These processes promoted the loss of some polar groups and the film acquired a slightly hydrophobic character. The quantity of free radicals of plasma polymerized films depends on the chain mobility. Thus, the samples deposited at higher power may not have enough mobility to allow recombination with free radicals, therefore their contact angle was around 84°. In figure 6 it can be seen that the surface energy of the films decreased from approximately 54 Erg to 36 Erg after the treatment, but they are practically the same for the films deposited at different RF powers, in spite of the structural differences among them.

4. Conclusions
The plasma polymerized films deposited from acetylene-argon mixture presented a structure predominantly containing sp$^2$ hybridized bonds, but the sp$^3$ groups tend to rise as the discharge power increases from 75 to 125 W. This alteration of the chemical structure promoted the hardness improvement from 5 GPa to 14 GPa, which characterize these polymers as a-C:H films. The thickness of the untreated films decreased with the deposition time, probably due to sputtering and substrate heating. The SF$_6$ treatment also diminished the thickness, probably due to etching effect, and the films become less hydrophilic than the untreated film.

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