

# Effect of Ion Irradiation on the Structural Properties and Hardness of a-C:H:Si:O:F Films

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**Abstract.** Amorphous carbon-based thin films, a-C:H:Si:O:F, were obtained by plasma immersion ion implantation and deposition (PIIID) from mixtures of hexamethyldisiloxane, sulfur hexafluoride and argon. For PIIID the sample holder was biased with negative 25 kV pulses at 60 Hz. The main system parameter was the proportion of SF<sub>6</sub> in the reactor feed, R<sub>SF</sub>. To allow comparison to growth without intentional ion implantation, some films were also grown by plasma enhanced chemical vapor deposition (PECVD). The objectives were to investigate the effects of fluorine incorporation and ion implantation on the film's chemical structure, and principally on the surface contact angle, hardness and friction coefficient. Infra-red and X-ray photo-electron spectroscopic analyses revealed that the films are essentially amorphous and polymer-like, and that fluorine is incorporated for any non-zero value of R<sub>SF</sub>. Choice of R<sub>SF</sub> influences film composition and structure but ion implantation also plays a role. Depending on R<sub>SF</sub>, hydrophilic or hydrophobic films may be produced. Ion implantation is beneficial while fluorine incorporation is detrimental to hardness. For ion implanted films the friction coefficient falls about one third as R<sub>SF</sub> is increased from 0 to 60%. Films prepared by PIIID without fluorine incorporation present fairly low friction coefficients and hardnesses greater than those of conventional polymers.

## 1. Introduction

There is at present a growing need for the development of nanoscale devices. The electronics industry fabricates miniaturized components from materials that match thin structures with specific electrical properties [1-3]. The production of microscopic three-dimensional structures, such as pistons, capacitors, transformers and gears, is another promising area with selected material requirements [4-7]. The production of thin films of a specific material is, therefore, a first requisite for such technologies. Despite this, such films or layers are not only used for these ends. Indeed the greatest spectrum of studies in this area deals with surface modification of materials by coating [8-11] Thus the surface properties of the material are modified while the bulk properties remain essentially unchanged.



The coating of computer hard discs is an application for which an extremely fine film is necessary to protect the device against wear but without changing its storage capacity [12, 13]. Another example of applications involves coatings that accelerate/inhibit cellular metabolism and the activity of fungi, which have a decisive role in the development of biomaterials [14-16]. Coating technology continues to be a growth area [17].

Plasma enhanced chemical vapor deposition (PECVD) is a versatile technique for the production of thin films [18]. A key advantage is its ability to produce films simply and cheaply at ambient temperatures. Owing to its low energy consumption and production of clean by-products, the technique is considered environmentally friendly. By altering the chemical composition of the plasma, the applied power or its frequency, or the reactor geometry or substrate temperature, films with a wide range of properties may be produced [18].

A hybrid plasma deposition technique, which permits *in situ* alteration of the film properties is plasma immersion ion implantation and deposition PIIID [19]. In this method, simultaneously with plasma ignition, negative high voltage pulses are applied to the samples, thus attracting high energy positive ions from the discharge. The impacting ions induce a number of effects, including the scission of chemical bonds, thus producing unsaturated groups, the release of volatile group, such as  $\text{CH}_x$  ( $x$  of 1 to 3), and film compaction. Film stoichiometry may also be altered. In addition, the PIIID technique permits adjustment of the bombarding ion intensity during film deposition.

The aims of this work were to determine the effect of ion bombardment during film growth as well as that of fluorine incorporation on the properties of the films produced by PIIID. To allow comparison with the PIIID films, some films were also produced by PECVD. Although the methods are distinct, variation of the system parameters often produces identical tendencies in the behavior of the material properties. The optimization of the treatment parameters is obtained through the analysis of the influence of each parameter on the performance of the material.

## 2. Experimental

The films were deposited in the system shown schematically in Figure 1. A cylindrical stainless steel vacuum chamber is connected to a pumping system capable of reducing the chamber pressure to about  $10^{-3}$  Pa. Gases are admitted via steel tubing through flowmeters and needle valves. Liquid monomers are retained in glass evaporation cells which are connected to the chamber via needle valves.

A Tokyo Hy-Power radiofrequency (13.56 MHz) power supply (maximum power 300 W) allows the excitation of a discharge between internal, horizontal, circular, stainless-steel electrodes. To produce bombardment by positive ions from the plasma, the lower electrode is connected to a Carl Zeiss UBI2 supply, which produces negative pulses (25 kV, 60 Hz). Greater details of this system are given elsewhere [20].

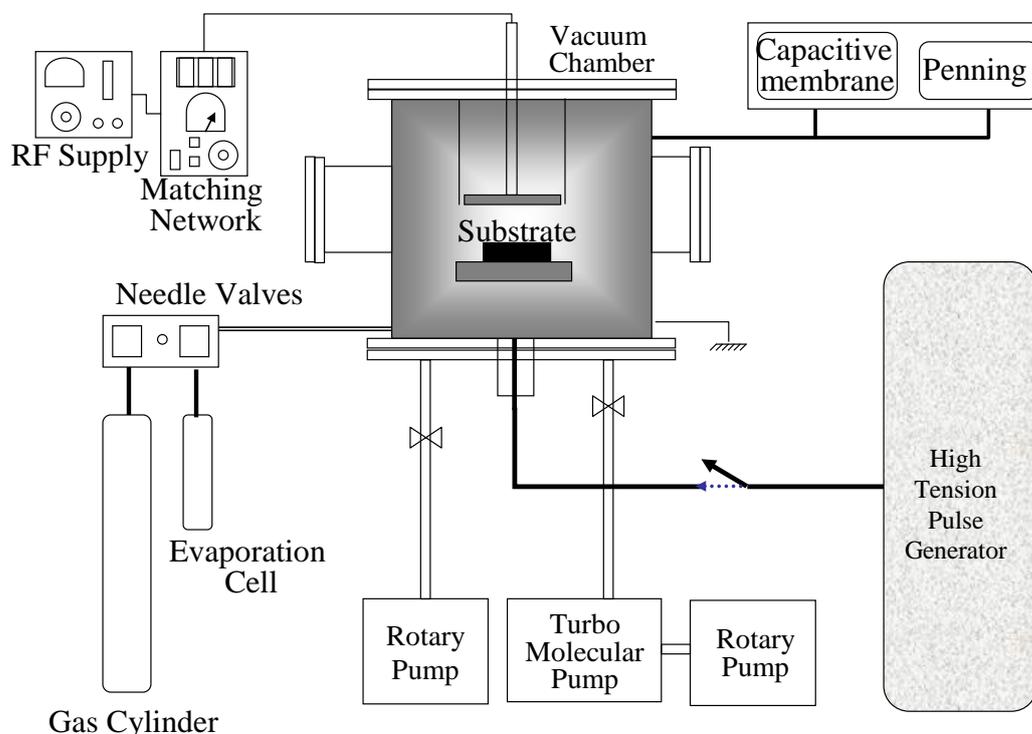


Figure 1 – Details of the deposition system.

Films were deposited from mixtures of hexamethyldisiloxane (HMDSO), sulfur hexafluoride ( $\text{SF}_6$ ) and argon (Ar). Before depositions the system was pumped to the base pressure and HMDSO introduced to produce a pressure of 0.26 Pa, which was maintained constant for all the depositions. The proportion of  $\text{SF}_6$  ( $R_{\text{SF}}$ ) in the feed was increased from 0 to 80% while that of Ar was correspondingly decreased, maintaining the total gas pressure at 1.3 Pa. The discharge was excited by the application of rf power to the upper electrode while the substrate holder was polarized with high voltage negative pulses (25 kV, 60 Hz). Deposition times of one hour were used and following each deposition the chamber was filled with nitrogen until atmospheric pressure was reached. The effects of these deposition conditions on the film properties were examined.

Film thickness was measured from well-defined step-heights using a Veeco Dektak 150 profilometer. The molecular structure of films was analyzed by Infra Red Reflectance Absorbance Spectroscopy (IRRAS) using a Bomem MB-101 FT-IR spectrometer. The spectra were taken from samples prepared on aluminum-coated glass slides. X-ray Photoelectron Spectroscopy (XPS) was used to study the chemical composition of the surface of the films deposited onto stainless-steel substrates. The spectra were obtained with a SVW HA100 spectrometer using procedures described previously [21].

The affinity of the films for water was evaluated via measurement of the contact angle,  $\theta$ , using a Ramé-Hart 100-00 goniometer. Substrates for these films were polished silicon wafers. At least three drops of deionized water of about 2  $\mu\text{l}$  volume were placed on different regions of the sample. The contact angle was measured at ambient temperature on each side of the drop (as seen in front elevation) ten times. The results presented are the arithmetic mean of these measurements ( $n = 60$ ).

Nanoindentation tests [22] using a Hysitron Triboindenter on films deposited onto polished silicon substrates were undertaken to determine film hardness. The indentation was measured as a function of the normal load applied to the diamond probe in the range from 800 to 10.000  $\mu\text{N}$ . At least eight

indentations per load were made. The hardness was calculated from curves of the indentation versus the applied force, according to the method developed by Oliver and Pharr [23]. Mean values and standard deviations are presented.

Using the nanoindenter's lateral-force device, scratch tests were undertaken on the same samples. At least five scans of 20  $\mu\text{m}$  were taken in different regions of the sample. A constant applied load of 300  $\mu\text{N}$  and a velocity of 1.0  $\mu\text{m s}^{-1}$  were used. The tests were made without lubrication using as a tribological pair the sample and the diamond tip of the indenter, which has a diameter of about 100 nm. Among other parameters, the lateral and normal forces on the tip were determined, permitting calculation of the friction coefficient of the samples.

Topographic images of the sample surfaces were obtained using Scanning Atomic Force Microscopy (SAFM) in the image acquisition mode of the nanoindenter, employing the same samples as those submitted to nanoindentation and hardness tests. A constant force of 2.0  $\mu\text{N}$  was applied to the indenter tip and a scan undertaken over an area of 50 x 50  $\mu\text{m}^2$ . From the images, it was possible to determine the mean roughness [24] ( $R_a$ ) in regions established as representative of the samples.

### 3. Results and Discussion

#### 3.1 Thickness, Molecular Structure and Chemical Composition

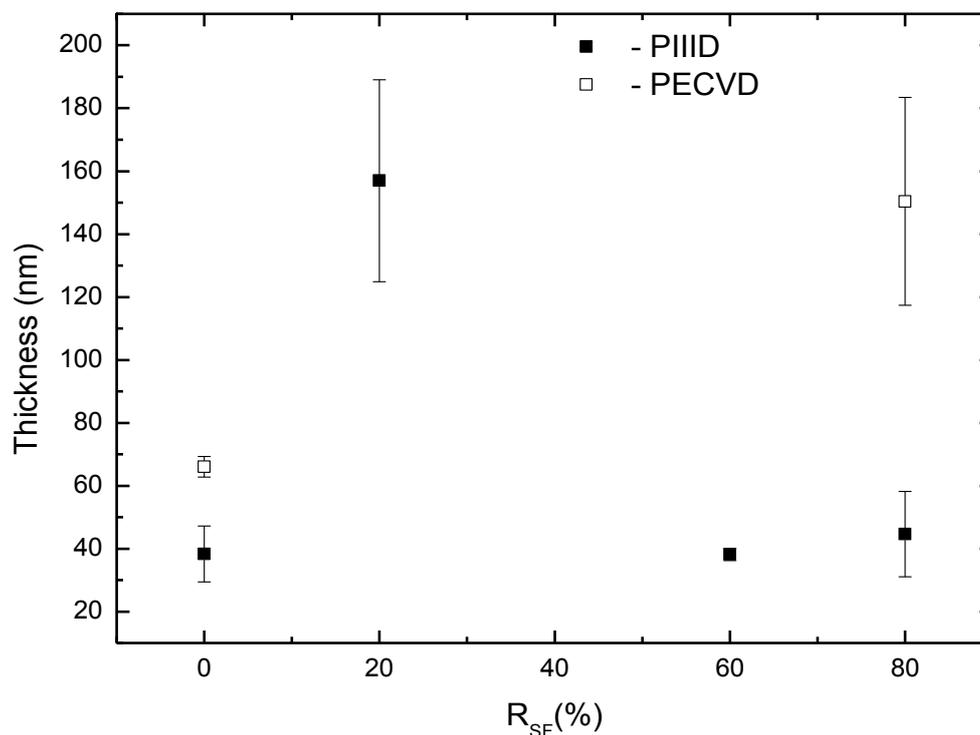


Figure 2 – The film thickness as a function of  $R_{SF}$

Figure 2 shows the thicknesses of the films, which fall in the range 40 to 160 nm. Figure 3 shows the infrared spectra obtained from films deposited at different proportions of  $\text{SF}_6$  in the feed to the

chamber,  $R_{SF}$ , during ionic bombardment and of those produced at  $R_{SF}$  of 0 and 80% by conventional PECVD.

The sample produced at 0%  $SF_6$  by PECVD presents absorption bands due to OH (3400 and 957  $cm^{-1}$ ), C-H (2870 and 2920  $cm^{-1}$ ), C=O and C=C (1600-1700  $cm^{-1}$ ) and Si-O-Si (1100-1200  $cm^{-1}$ ) groups. The latter peak may also contain a contribution from SiCH<sub>2</sub>Si groups, which are readily formed via plasma reactions of methylsilyl groups [25-27]. A weak absorption at about 1270  $cm^{-1}$ , related to C-H in CH<sub>3</sub>Si groups, is also detected, demonstrating that the HMDSO molecule - (CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub> - is partially preserved.

The presence of O-H in the structure may be attributed to the oxygen bound in the HMDSO molecule. As oxygen is not linked to hydrogen in this molecule, however, multiple-stage reactions must occur in the plasma phase to form O-H and, therefore, this mechanism is not considered the most important. Residual oxygen in the chamber may contribute more effectively to oxygen incorporation during deposition. In addition, post-deposition reactions between free radicals trapped from the plasma and water vapor and atmospheric oxygen are known to produce hydroxyl groups in the deposited material [28].

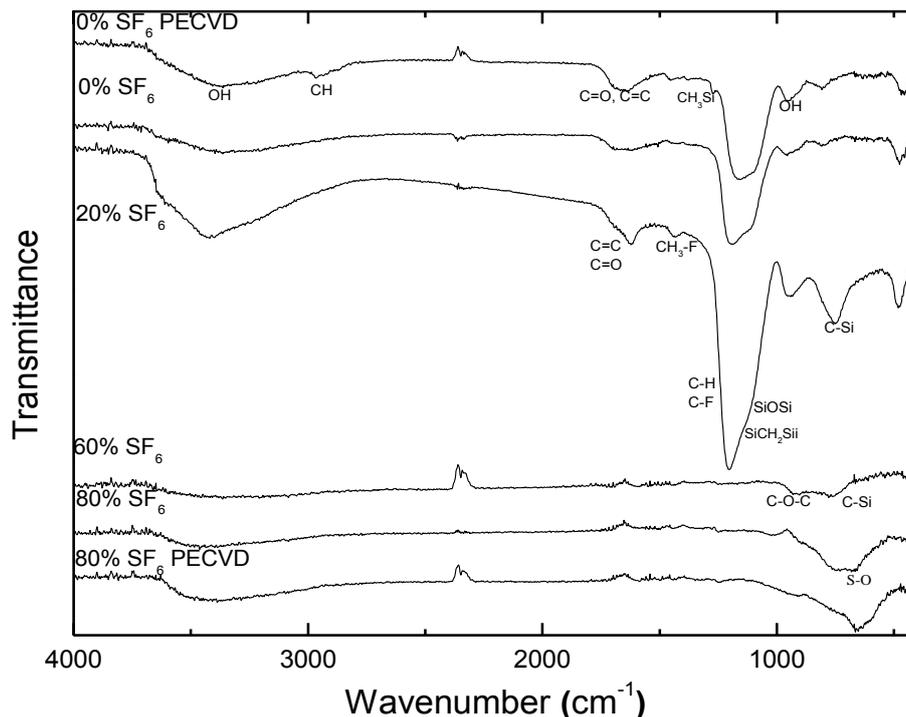


Figure 3 – Transmittance infrared spectra of films produced by PECVD and by PIID at different  $R_{SF}$ .

The detection of absorptions due to C=C and C=O groups is interesting since neither is present in the monomer. These bonds are formed via reactions either in the plasma phase or on the film surface or both, but the constituents are derived from the fragmentation of the monomer molecule. Post-deposition reactions between free radicals and atmospheric oxygen also contribute to the production of C=O.

The spectrum of the film prepared with  $R_{SF} = 0\%$  by PIID presents the same absorptions as already mentioned, but with lower intensities in some cases. This effect may be observed by comparing the absorptions at 2970 and 3400  $\text{cm}^{-1}$  (due to C-H and O-H, respectively). The fall in the intensity of these absorptions is associated with the different ion bombardment fluences produced in the two methods. In PIID, the transfer of energy to surface species by collision with fast ions produces, among other effects, the fragmentation of chemical bonds. Species weakly bound to the solid, such as H, are preferentially emitted [29, 30], reducing the concentration of C-H and O-H groups. Additional evidence for this effect is the behavior of the absorption at 1270  $\text{cm}^{-1}$ , which derives from vibrations in C-H groups in  $\text{CH}_3\text{Si}$ . When films are prepared by PIID this band disappears, confirming the greater degree of molecular fragmentation in this process.

Contrary to what is expected for films produced by plasma polymerization of HMDSO without  $\text{SF}_6$  in the feed [25-27], no absorbance peaked at around 2100  $\text{cm}^{-1}$  and attributable to SiH is seen in the spectrum (film produced by PECVD without  $\text{SF}_6$  in the feed). Thus, under the conditions used here, hydrogen is preferentially bound to carbon or lost from the film or both. As already mentioned, the absence of strong absorptions owing to CH groups from all of the spectra, and the tendency of the films grown at high  $R_{SF}$  to become 'inorganic', indicate a loss of hydrogen.

The band between 1100 and 1200  $\text{cm}^{-1}$ , which appears in the spectra of both films deposited at  $R_{SF} = 0\%$ , is attributed to the superposition of the absorptions due to CH and SiOSi. The process of dehydrogenation, however, does not affect the intensity of this band as occurs with the absorptions at 2920 and 2870  $\text{cm}^{-1}$ , indicating that the contribution of C-H groups to this absorption is negligible.

For  $R_{SF} = 20\%$ , absorptions in the film spectra appear due to fluorine-containing groups, such as  $\text{CH}_3\text{-F}$  (1436  $\text{cm}^{-1}$ ) and C-F (1000-1400  $\text{cm}^{-1}$ ). Atomic fluorine and  $\text{CF}_x$  ( $x = 1$  to 3) radicals are frequently observed in plasmas containing fluorinated gases [31-33] and are considered film precursors. As the chamber feed does not usually contain compounds in which carbon is bound to fluorine, multiple-stage plasma reactions or plasma/surface reactions or both are necessary to produce these species.

For  $R_{SF} > 20\%$ , there is a high proportion of atomic fluorine in the plasma which, together with ionic bombardment, contributes to the erosion of the film by etching. Therefore the deposition rate is determined by the balance between film growth and ablation. In PECVD the deposition rate tends to decrease (that is the film thickness decreases for a fixed deposition time) with increasing  $R_{SF}$ , which accounts for the absence of absorptions in the spectra of films produced under these conditions. It is worthwhile observing the absorption at 650  $\text{cm}^{-1}$  in the two spectra of samples prepared at  $R_{SF} = 80\%$ , which indicates the presence of sulfur.

Table 1 shows the atomic ratios F/C, O/C and Si/C, determined from XPS spectra of the films deposited with ionic bombardment. The F/C ratio grows with increasing  $R_{SF}$ , reaching a maximum of 0.19 at  $R_{SF} = 80\%$  of  $\text{SF}_6$ . This result may be the consequence of a decrease in the proportion of carbon, of the increase in the incorporation of fluorine or, more probably, both.

**Table 1.** Atomic ratios F/C, O/C and Si/C in the PIID films as a function of the proportion of  $\text{SF}_6$  in the feed,  $R_{SF}$ .

$R_{SF}(\%)$	F/C	O/C	Si/C
0	-	2.05	-
20	0.02	0.35	0.10
60	0.07	0.23	0.12
80	0.19	0.81	0.04

To clarify this problem, high resolution F1s spectra were deconvoluted, revealing a component at 687.0 eV associated with C-F bonds, and a contribution at 684.0 eV, identified as ionic fluorine in

carbon structures [34], that is, free fluorine. The relative contribution (by area) of each component was calculated and the results are presented in Figure 4.

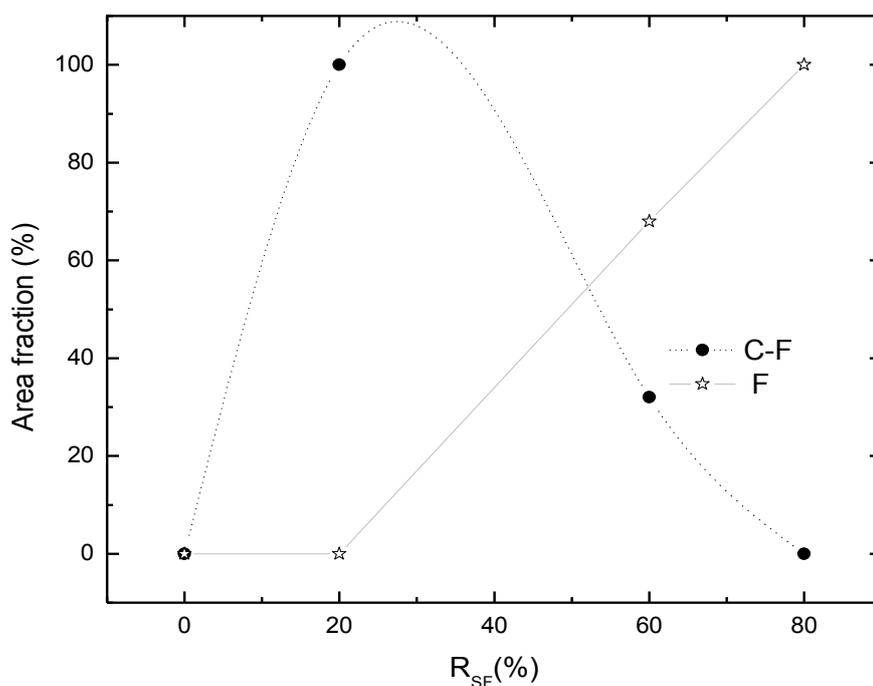


Figure 4 – Contribution of each component of the high resolution F1s peak as a function of  $R_{SF}$ .

The proportion of C-F groups is high in the sample prepared at  $R_{SF} = 20\%$  as shown by some bands in the infrared spectrum of this film. Despite this, when  $R_{SF}$  increases, the proportion of C-F decreases in opposition to the increase in the proportion of free fluorine.

The reduction in the quantity of C-F species is explained by the ablation of the film when the proportion of  $SF_6$  is increased, which leads to the removal of carbon and an increase in free fluorine, resulting in an increase in F/C.

The O/C data, also represented in Table 1, reveal the incorporation of oxygen in the deposited material. It is known that when films are produced by PECVD from monomers that do not contain oxygen, some incorporation of oxygen is still observed. The ratio O/C is substantially reduced when  $R_{SF}$  is increased from 0 to 20%, but the influence of greater  $R_{SF}$  values is less pronounced. This result is attributed to a fall in the concentration of residual free radicals in the films at higher  $R_{SF}$ . The intensity of ion bombardment is reduced with the reduced concentration of Ar in the plasma, thus reducing the absorption of oxygen-containing groups.

Nitrogen was also detected, but only in the film deposited without  $SF_6$  in the chamber feed. Here it should be remembered that to reach atmospheric pressure following film deposition, the chamber was filled with nitrogen. Generally, the incorporation of nitrogen occurs to a lesser degree than is observed for oxygen, and its apparent absence at  $R_{SF} > 0$  is due to the lower proportion of free radicals in the

samples. As well as the physical effects of ion bombardment, competition between F, H and Si to form bonds with C contributes to a reduction in the concentration of free radicals.

Another interesting behavior is that of Si/C. Silicon was not detected in the film deposited without SF<sub>6</sub> in the feed. This result differs from that obtained by infrared spectroscopy, in which a band arising from SiOSi groups (1100 to 1200 cm<sup>-1</sup>) was detected. In infrared spectroscopy, however, the beam passes completely through the width of the film, while XPS is a surface analysis technique. Thus the surface and bulk of the film may differ in chemical structure and composition, and this may be due to plasma-surface reactions. When the deposition is undertaken in the absence of F, the relatively high ionic bombardment removes species such as H and Si. This process may also induce the production of free radicals, thus contributing to the increased attachment of oxygen. As the proportion of F increases, ionic bombardment is reduced and the proportion of surface Si increases. At R<sub>SF</sub> ≥ 80%, however, etching of Si increases and the proportion of this species tends to decrease, so that Si/C decreases as F:C correspondingly increases. Thus the presence of Si on the surface is strongly dependent on plasma-surface interactions.

Finally, it is worth noting that sulfur was detected in the samples prepared by PIID with 60% and 80% SF<sub>6</sub> in the feed. Sulfur incorporation is expected in SF<sub>6</sub> plasmas [35] and was confirmed by the infrared spectra.

Considering the complete set of analyses undertaken it is concluded that the films deposited are amorphous carbon polymers. The material is already fluorinated when R<sub>SF</sub> = 20% is employed. At R<sub>SF</sub> greater than 20%, however, little fluorine is incorporated and there is a reduction in the proportions of C, O and Si, reducing the film deposition rate. Deposition together with ionic bombardment results in surfaces with structures and compositions distinct from those obtained with conventional PECVD.

### 3.2 Wettability and Roughness

The affinity of the surface of the films for water is illustrated in Figure 5, where the surface contact angle is shown as a function of R<sub>SF</sub>. The results obtained for films produced by PIID reveal that  $\theta$  increases with increasing R<sub>SF</sub>.

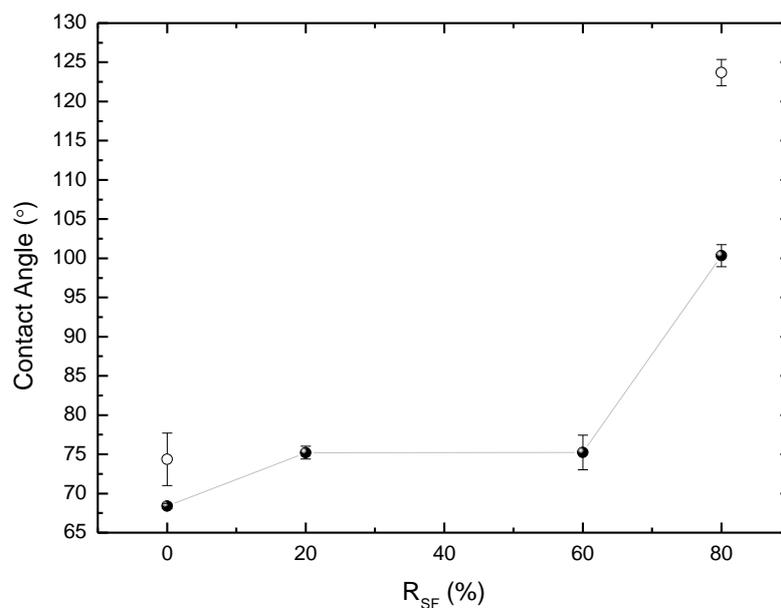


Figure 5 – Surface contact angle of the films produced by PECVD (○) and by PIID (●) as a function of R<sub>SF</sub>.

According to the chemical composition, the surface prepared without the addition of fluorine to the discharge presented the greatest proportion of O and N. Such species, connected to carbon, form polar groups that attract water molecules electrostatically. The absence of Si contributes to the hydrophilic character of this sample (Table 1). On the other hand, when  $R_{SF} = 20\%$ , there is a decrease in the proportion of O that is compensated by the incorporation of F, which in moderate proportions, also contributes to the spread of the drop on the surface. At greater values of  $R_{SF}$ , however, the greater incorporation of F and the presence of Si cause the formation of a hydrophobic film with  $\theta$  of about  $100^\circ$ .

Although the films deposited at  $R_{SF} = 80\%$  using the two techniques originated in plasmas with the same chemical composition, their surface wettabilities are distinct owing to ionic bombardment (or its absence).

To complement the interpretation of the wettability, the mean roughness ( $R_a$ ) of the surfaces was determined, as shown as a function of  $R_{SF}$  in Figure 6. The pristine silicon substrate presented a roughness of 4.6 nm. Comparing this value with those obtained for films produced by PIIID, an increase in surface roughness is observed. There are no significant variations in  $R_a$  when  $R_{SF}$  is increased from 0 to 60%. Only for  $R_{SF} > 60\%$  is there an increase in surface roughness.

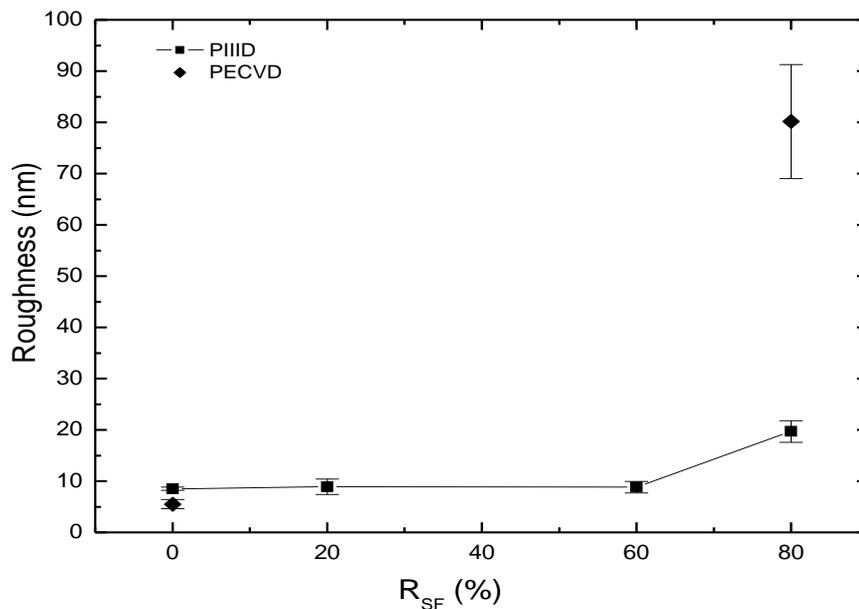
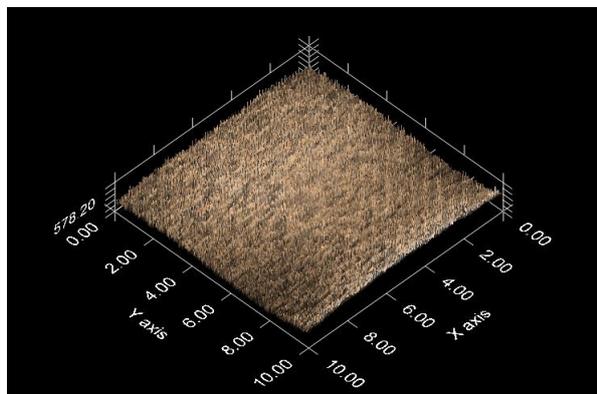
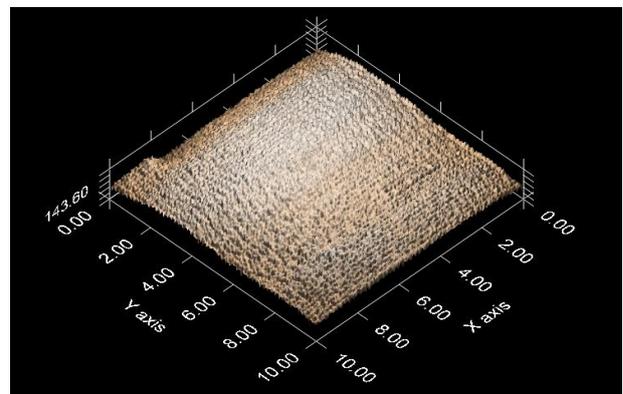


Figure 6 – The roughness of the surfaces coated with films prepared by PECVD and by PIIID at different proportions of  $SF_6$  in the chamber feed. The roughness of the silicon substrate was 4.6 nm.

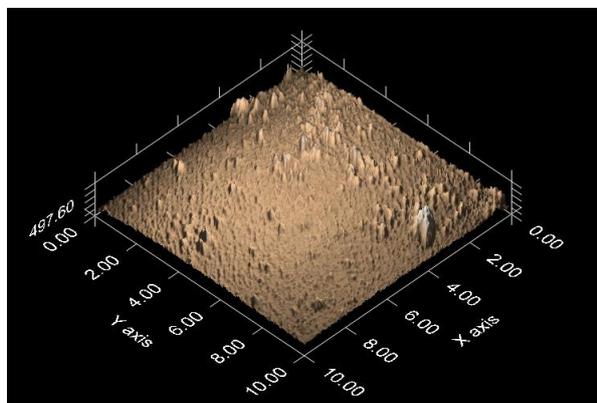
In contrast,  $R_a$  is very similar to that obtained for the silicon substrate when the films are produced without fluorine by PECVD, but increases sharply when  $R_{SF}$  is increased to 80%. Figure 7 shows the topographic images of the samples from which the roughness was determined.



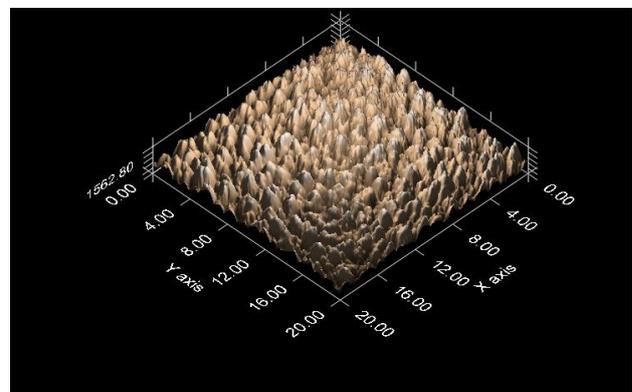
0% SF<sub>6</sub> – PECVD



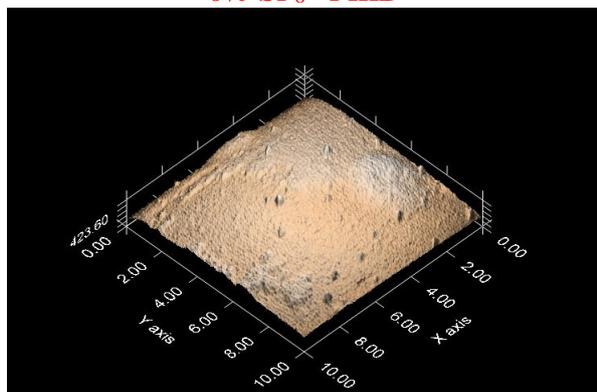
60% SF<sub>6</sub> – PIID



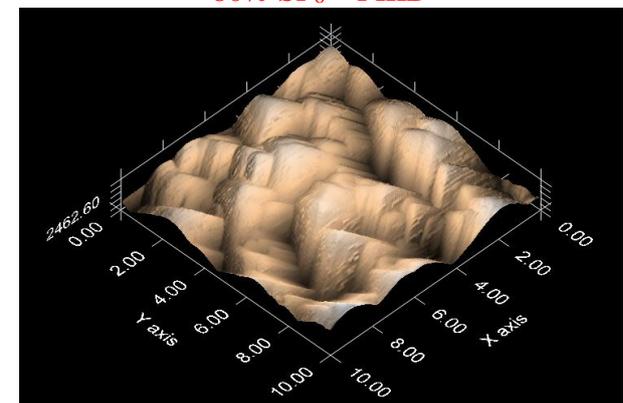
0% SF<sub>6</sub> – PIID



80% SF<sub>6</sub> – PIID



20% SF<sub>6</sub> – PIID



80% SF<sub>6</sub> – PECVD

Figure 7 – Topographic images of the silicon substrates coated with films prepared at different proportions of SF<sub>6</sub> by PECVD and by PIID. The scales are in μm.

Comparing the images of films obtained with  $R_{SF} = 0\%$  and  $R_{SF} = 80\%$  by PECVD, a clear difference is observed. This difference is attributed to the texturization of the silicon surface at the beginning of the deposition by attack by atomic F. Following the deposition of the first few monolayers, this phenomenon ceases and the film follows the topography of the substrate.

On the other hand, when F is present in small proportions in the discharge in depositions with ion bombardment, fluorine ions are formed in the discharge by the rupture of SF<sub>6</sub> molecules, and are also

implanted, decreasing their chemical effect on the surface of the silicon substrate at the beginning of the deposition process. At high  $R_{SF}$  (80%), the abundance of F in the plasma induces both ion implantation and ablation of Si. The surface roughness is modified, but not in the same way as observed in samples prepared at the same  $R_{SF}$ , but without high energy ionic bombardment. These results demonstrate the effect of the incorporation of F in the discharge and of ionic bombardment on the surface topography. In cases where fluorinated films without texturization are required, PIIID is the best choice. It should be remembered, however, that the effect of F on the texturization of the sample depends on the choice of both the plasma and the substrate.

Comparing the results of Fig. 5 and Fig. 6 it is readily noticed that the slight growth in  $\theta$  in the 0 to 60%  $R_{SF}$  range is a chemical effect of fluorine incorporation since roughness remains unchanged in this region. For the highest  $R_{SF}$  value, however, the factor determining  $\theta$  is roughness.

### 3.3 Hardness and Friction Coefficient

Table 2 shows the film hardness estimated from curves of hardness as a function of the penetration depth, and taken at about 15% of the film thickness. As the films were all  $< 200$  nm thick, this is a crude calculation. The implanted films, however, show a tendency to soften with greater fluorine incorporation. Implanted films tend also to be harder than PECVD films grown under otherwise identical conditions. The films produced by PECVD with 0% and 80%  $SF_6$  in the feed were measured with a single load applied to the tip. In both cases, the hardness is a few tenths of a GPa, which is characteristic of polymeric materials. These results agree with literature reports, which demonstrate that the inclusion of fluorine in the structure of carbon films deposited in plasmas [36, 37] reduces their hardness. Owing to the thinness of the film produced by PIIID film at  $R_{SF} = 60\%$  its hardness could not be determined.

**Table 2.** Film hardness of the PECVD and PIIID films as determined by nanoindentation

Method	$R_{SF}(\%)$	H(GPa)
PECVD	0	$0.8 \pm 0.1$
	80	$0.5 \pm 0.5$
PIIID	0	$1.6 \pm 0.3$
	20	$1.5 \pm 0.1$
	60	-
	80	$0.8 \pm 0.4$

The friction coefficient,  $\mu$ , determined by scratch tests using the lateral force device of the nanoindenter, is presented as a function of  $R_{SF}$  in Figure 8. The films produced by PECVD have friction coefficients of less than 0.1 independently of  $R_{SF}$ . From the images of Fig. 7 it may be seen that the topographic differences presented by the samples do not strongly influence  $\mu$ . It should also be remembered that the diamond tip used as a tribological pair for the film has a diameter of about 100 nm, which makes the dimensions and irregularities of the film prepared at  $R_{SF} = 80\%$  irrelevant to the interaction.

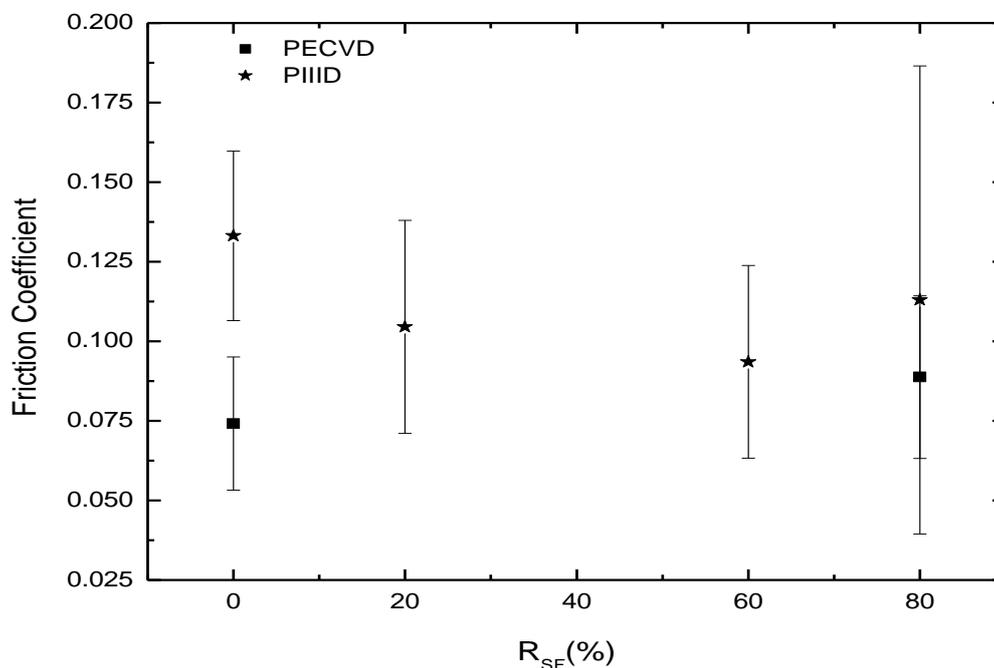


Figure 8 –Friction coefficient of the films produced by PECVD and by PIID at different  $R_{SF}$ . Values obtained with a normal load of 300  $\mu$ N applied to the tip for a 20  $\mu$ m scan.

At  $R_{SF} = 0\%$ , the film deposited with ionic bombardment has a greater value of  $\mu$  than that produced by PECVD. The friction coefficient is reduced by 30% compared to the film without fluorine when  $R_{SF}$  is increased from 0 to 60%. When  $R_{SF}$  is further increased,  $\mu$  tends to increase further.

Comparing the behaviors of the roughnesses (Fig. 6) and of the friction coefficient of the films produced by PIID, it is observed they are similar only in the range of  $R_{SF}$  from 60 to 80%. Otherwise, different tendencies are observed, indicating that the topography is not the dominant factor influencing  $\mu$ . In this study, the incorporation of a highly electronegative species has a greater influence on the tribology than changes in the surface topography. Depending on the morphology and dimensions of the irregularities, they act together with the electronegative effect of fluorine. This may be seen in the sample deposited at the highest value of  $R_{SF}$ , where, despite the increase in the proportion of F incorporated into this sample,  $\mu$  does not decrease. The tribological behavior of this system thus depends on the balance between these processes.

#### 4. Conclusions

The results presented here show that the chemical composition and structure of the films deposited from plasmas of mixtures of hexamethyldisloxane, sulfur hexafluoride and argon depend on the proportion of gases used and the degree of ionic bombardment induced during film growth. Fluorine was incorporated even when only low proportions of  $SF_6$  were present in the discharge. Contamination of the films with oxygen and nitrogen, to degrees which depend on  $R_{SF}$ , was also observed.

Hydrophilic surfaces were obtained by PIID for  $R_{SF} = 0, 20$  and 60%. Increasing  $R_{SF}$  beyond 60%, resulted in hydrophobic films with contact angles of 100°. The same rising tendency was observed in the contact angle of the films prepared by conventional PECVD, but with higher  $\theta$  values than were observed in the film prepared by PIID. Thus the thermodynamic properties of the surface may be

controlled via the chemical composition of the discharge, but ionic bombardment is also of great importance.

The hardnesses of non-fluorinated films were increased by ionic bombardment. Moreover, such films possessed hardnesses greater than those typical of similar conventional polymers. While fluorine incorporation (for  $R_{SF}$  up to ~60%) tends to slightly improve tribological performance of the diamond/film pair, ionic bombardment has little effect. The minimal improvement in  $\mu$  due to the incorporation of F does not justify the corresponding loss in mechanical resistance of the material. In summary, ionic bombardment produces some improvement in mechanical resistance of the film while maintaining the friction coefficient at levels acceptable for many applications.

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### References

- [1] Lakin, K M, 2003, *Microwave Magazine*, IEEE, **4** (4), 61.
- [2] Gross, S, Camozzo, D, Di Noto, V, Armelao, and L, Tondello, E, 2007, *European Polymer Journal*, **43** (3), 673.
- [3] Di, C, Yu G, Liu, Y, and Zhu, D, 2007, *J. Phys. Chem. B* **111** (51), 14083.
- [4] Natarajan, S P, 2007, *IEEE Microwave and Wireless Components Letters*, **17** (2), 858.
- [5] Belgacem, B, Calame, F, and Muralt, P, 2007, *J. Electroceram*, **19**,369.
- [6] Kimberley, J, Chasiotis, I, and Lambros, J, 2008, *International Journal of Solids and Structures*, **45**, 497.
- [7] Saul, C K, Lepienski, C M, Cantão, M P, and Schreiner, WH, 2003, *Sensors and Actuators A*, **107**, 80–84.
- [8] Jampala, S N, Sarmadi, M, Manolache, S, and Denes, F S, 2008, *J. Appl. Polym. Sci.*, **107**, 1686.
- [9] Holm, A H, Vase, K H, Winther-Jensen, B, Pedersen, SU, and Daasbjerg, K, 2007, *Electrochimica Acta*, **53**, 1680.
- [10] Tshabalala, M A, and Sung, L P, 2007 *J. Coat. Technol.*, **4**, 483.
- [11] Galkowski, M, Malik, M A, Kulesza, P J, Bala, H, Miecznikowski, K, Wlodarczyk, R, Adamczyk, L, and Chojak, M, 2003, *J. Electrochem. Soc.*, **150** (6) B249.
- [12] Noda, K, Kawanabe, T, and Naoe, M, 1997, *J. Appl. Phys.*, **81**, 5405.
- [13] Kawahara, H, Sakairi, T, Momose, S, Ishihara, Y, and Urai, H, 1996, *Nec Research and Development*, **37** (1), 13.
- [14] Kobayashi, Ohgoe, S Y, Ozeki, K, Hirakuri, K, and Aoki, H, 2007, *J. Mat. Sci. Mat. Medicine*, **18** (12), 2263.
- [15] Blümmel, J, Perschmann, N, Aydin, D, Drinjakovic, J, Surrey, T, Lopez-Garcia, M, Kessler, H, J, and Spatz, J P, 2007, *Biomaterials*, **28** (32), 4739.
- [16] Ai, H, Meng, H, Ichinose, I, Jones, S A, Mills, D K, Lvov, Y M, and Qiao, X, 2003, *Journal of Neuroscience Methods*, **128**, 1.
- [17] Gordillo-Vazquez, F J, Herrero, and V J, Tanarro, I, 2007, *Chemical Vapor Deposition*, **13** (6-7), 267.
- [18] Yasuda H, in *Plasma Polymerization*, (Academic Press, N.Y., 1985).
- [19] Wood, B P, Rej, D J, Anders, A, Brown, I G, Faehl, R J, Malikand, S M, and Munson, C P in *Handbook of Plasma Immersion Ion Implantation and Deposition* edited by Anders, A (John Wiley and Sons, N.Y., 2000) p. 243.
- [20] Rangel, E C, Durrant, S F, Rangel, R C C, Kayama, M E, Landers, R, and Cruz, NC, 2006, *Thin Solid Films*, **515**, 1561.
- [21] Durrant, S F, Landers, R, Kleiman, G G, Castro, S G, and Bica de Moraes, M A, 1996, *Thin Solid Films*, **281/282**, 294.

- [22] Li, X, and Bhushan, B, 2002, *Mat. Characterization*, **48**, 11.
- [23] Oliver W C and Pharr, G M, 1992, *J. Mat. Res.*, **7**(4), 1564.
- [24] Petrik, P, Biró, L P, Fried, M, Lohner, T, Berger, R, Schneider, C, Gyulai J, and Ryssel, H, 1998, *Thin Solid Films*, **315**, 186.
- [25] Wrobel, A M, Wertheimer, MR, Dib, J, and Schreiber, H P, 1980, *J. Macromol. Sci.- Chem.*, **A14**, 321.
- [26] Wrobel, A M, Klemberg, J E, Wertheimer, M R, and Schreiber, H P, 1981, *J. Macromol. Sci. - Chem.*, **A15**, 197.
- [27] Wrobel, A M, Kryszewski, and M, Gazicki, M, 1983, *J. Macromol. Sci. – Chem.*, **A20**, 583.
- [28] Yasuda, H, Bumgarner, M O, Marsh, H C, and Morosoff, N, 1976, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 195.
- [29] Pivin, J C, and Colombo, P, 1997, *J. Mater. Sci.*, **32**, 6163.
- [30] Venkatesan, T, Wolf, T, Allara, D, Wilkens, B J, and Taylor, G N, 1983, *Appl. Phys. Lett.*, **43**, 934.
- [31] Durrant, S F, Mota, R P, and Bica de Moraes, M A, 1992, *J. Appl. Phys.*, **71**(1), 448.
- [32] Durrant, S F, Rangel, E C, Da Cruz, N C, Castro, S G C, and Bica de Moraes, M A, 1996, *Surf. & Coatings Technol.*, **86**(1-3), 443.
- [33] Durrant, S F, Castro, S G C, Bolívar Marinez, L E, Galvão, D S, and Bica de Moraes, M A, 1997, *Thin Solid Films*, **304**(1-2), 149.
- [34] Nansé, G, Papirer, E, Fioux, P, Moguet, F, and Tressaud, A, 1997, *Carbon*, **35**(2), 175.
- [35] Durrant, S F, Mota, R P, and Bica de Moraes, M A, 1992, *Thin Solid Films*, **220**(1-2), 295-302.
- [36] Freire Jr., F L, 2002, *J. Non-Cryst. Sol.*, **304**, 251.
- [37] Yao, Zh Q, Yang, P, Huang, N, Sun, H, and Wang, J, 2004, *Appl. Surf. Sci.*, **230**, 172.