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Abstract. Amorphous silicon carbonitride (a-SiCN:H) films were synthesized by radiofrequency (RF) Plasma Enhanced Vapor Chemical Deposition (PECVD) using hexamethyldisilazane (HMDSN) as precursor compound. Then, the films were post-treated by Plasma Immersion Ion Implantation (PIII) in argon atmosphere from 15 to 60 min. The hardness of the film enhanced after ion implantation, and the sample treated at 45 min process showed hardness greater than sixfold that of the untreated sample. This result is explained by the crosslinking and densification of the structure. Films were exposed to oxygen plasma for determining of the etching rate. It decreased monotonically from 33 Å/min to 19 Å/min for the range of process time, confirming structural alterations. Hydrophobic character of the a-SiCN:H films were modified immediately after ion bombardment, due to incorporation of polar groups. However, the high wettability of the films acquired by the ion implantation was diminished after aging in air. Therefore, argon PIII made a-SiCN:H films mechanically more resistant and altered their hydrophobic character.

1. Introduction

Plasma-polymerized HMDSN films are widely employed in different applications due to attractive properties, such as transparency, biocompatibility, chemical inertness and electrical resistance, among others. However, for applications in sliding conditions, they cannot provide mechanical resistance to wear. In this sense, post-treatment such as plasma immersion ion implantation (PIII) is an advisable process, due to its operational and economical viability [1-3]. PIII is a known technique for surface treatment of metal, semiconductor and polymeric materials, but few works report its application to treatment of plasma-polymerized films. PIII process is performed in the same plasma system used to deposit plasma polymers, being the samples biased with high negative voltage pulses. Plasma ions attracted by target potential are driven to polymeric surface, and the interactions between ions and polymeric structure may be more intense than those induced on other kind of material [1-3]. Consequently, the surface properties of plasma-polymerized films may be completely altered. It knows that the degree of the modifications depends on the plasma parameters (power, pressure, ion specie, etc.) and pulse characteristics (shape, length, magnitude, frequency) [1-3]. In this work, it was investigated the effect of argon PIII on wettability, mechanical properties and oxidation resistance of the plasma-polymerized HMDSN. The surface properties alterations were correlated with the modifications in the chemical structure promoted by the ion implantation.

2. Materials and Methods

PECVD was performed in a cylindrical stainless chamber with two horizontal plate electrodes adjusted capacitively. The upper electrode is connected to RF power supply (13.56 MHz), and the lower one is ground and used as substrate holder. Power, pressure and time adjusted for the deposition of the plasma-polymerized HMDSN films were respectively of 80 W, 40 mTorr and 30 min. PIII was performed in the same reactor using a power of 50 W, argon pressure of 40 mTorr and sawtooth-like pulses of 30 kV-100 Hz. PIII treatment ranged from 15 to 60 min. After ion implantation, as-deposited and treated samples were exposure to oxygen discharges (50 W, 40 mTorr, and 30 min) to determination of the etching rate. Alpha-Step Tencor profilemeter was used to evaluate the thickness of the films after all the processes. Atomic chemical structure of the film surfaces was investigated by X-ray photoelectron spectroscopy (XPS), and molecular structure was estimated via deconvolution of XPS high resolution spectra. Hardness of the samples was evaluated by a Hysitron Triboindenter.

3. Results and discussions

Fig. 1 (a) shows the atomic concentration of chemical species identified in C 1s spectrum of the as-deposited and treated films. As can be seen, carbon concentration drops while oxygen concentration increases with process time. It means that ion bombardment induced C – C bond scission and C atom desorption. Besides, C – H bonds may be broken because hydrogen is light and weakly bound [4,5]. As result, free radicals or pendant bonds left in the polymeric structure are passivated by reactions with oxygen from environment. However at longer treatment time both carbon and oxygen atomic concentration trend to saturation. Moreover, silicon concentration was not altered during the bombardment, which indicates that silicon atoms are strongly bound in the polymeric chain. Nitrogen concentration is lower than others and diminishes after the implantation. It is likely that volatile nitrogen compounds were formed and etched from the surface during the bombardment [6].
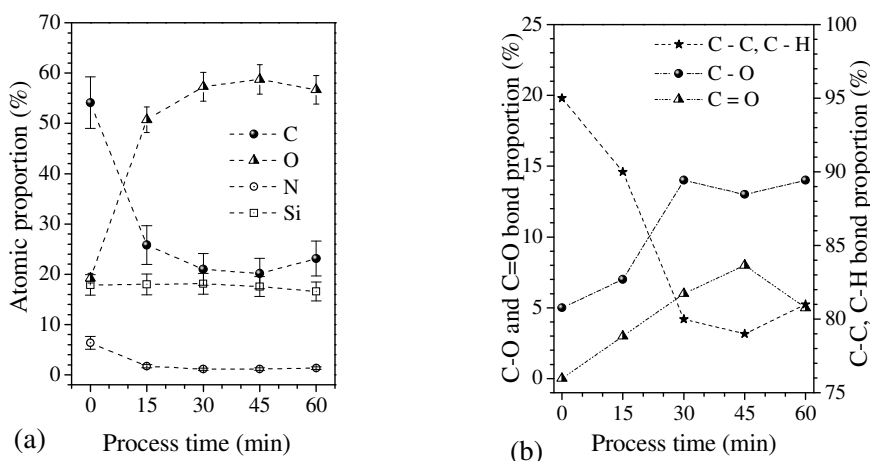

Fig. 1. C, O, N, Si atomic concentrations (a) and chemical bond concentration (b) of the plasma polymerized HMDSN films. As-deposited sample is shown in *t = 0*.

Recombination processes are confirmed in Fig. 1 (b), in which are depicted the chemical bond concentration. As can be observed, C – C or C – H bonds decreased with treatment time, as discussed above. Saturation behaviour is perceived after 30 min of process, indicating the stabilization of the chemical structure. During the implantation, interactions between ions and solid promote electronic and nuclear collisions. The former is responsible for crosslink and the later causes bond breakage or

polymeric degradation [4]. In the beginning of implantation, free radicals are spaced from each other and the scissions are predominant. Increasing the time of process, free radical recombinations become more intense, leading to crosslink of the chains. At longer treatment, however, scissions restarts and the polymer degradation is inevitable [5]. Thus, it is believed that treatments longer than 15 min favour the structure strength, while treatment longer than 60 min may not contribute to enhancement of any surface property. Oxygen-containing groups, $C-O$ and $C=O$, increases with treatment time. $C-O$ species are sp^3 hybrid states and are related to crosslink of the chain [6]. As can be seen, such species also trend to saturation after 30 min of process. $C=O$ bonds, on the other hand, decrease in 60 min of process. Although the bombardment favours unsaturated processes, the decrease of $C=O$ bonds may be an indication about the beginning of degradation of plasma-polymer films. Thus, it is expected the improvement of the structure rigidity at treatment time shorter than 60 min.
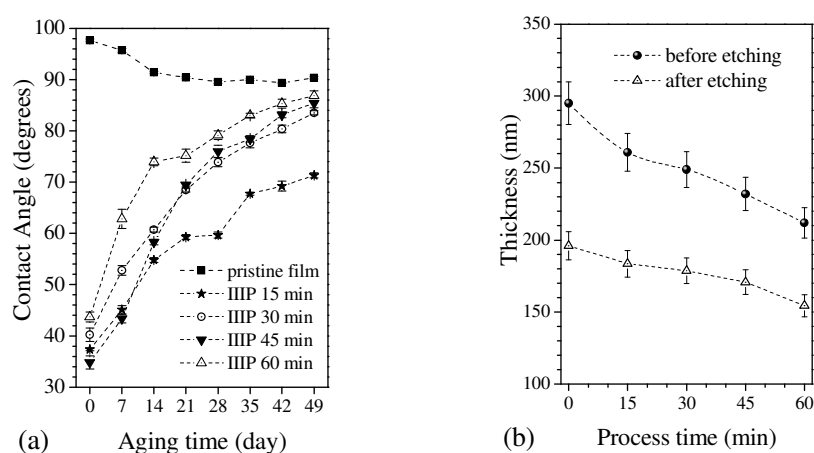

Fig. 2. Temporal evolution of contact angles (a) and thickness of the pristine ($t=0$) and PIII-treated plasma-polymerized HMDSN films (b).

Fig. 2 (a) shows the contact angle measurements as function of the aging time in atmosphere air. Plasma-polymerized HMDSN films are typically hydrophobics [7], which is evidenced by contact angle of 98°. Upon bombardment, this measure decreases drastically with treatment time, which is explained by incorporation of oxygen-containing groups, as informed by chemical analysis. After aging, however, the sample treated for 15 min shows the character more hydrophilic than others, presenting a contact angle around 70°, while the reminiscent samples present a contact angle larger than 80°. This behavior is interpreted as a reorganization of the structure after ion implantation. The incorporation of oxygen species in the sample surface generates a gradient of polar group concentration between the surface and the bulk of the polymer film, altering its enthalpy and entropy [8-10]. As result, the mobile polymeric chains tend to bury the polar groups of the surface into the bulk, which diminishes the surface wettability. In this sense, it is believed that hydrophobic recovery depends on the degree of crosslink, which causes the anchoring of the chains and may avoid their movement. But, it does not justify the lower recovery rate for the sample treated at shorter time. This is probably due to chemical and morphological alterations [9,10]. In the Fig. 2(b) is depicted the thickness of the films before and after exposure to oxygen plasma. As can be seen, the thickness of the samples tends to decrease monotonically after ion implantation, which is explained by densification of the samples due to increase of the chain crosslink. Moreover, argon ions usually induce ablation, which also contribute to decrease of the thickness [10]. As can be observed in the same figure, the thickness of the oxygen plasma-exposed films diminished at lower rate, which means that ion implantation enhanced the chemical resistance of the plasma-polymerized films. Fig. 3(a) shows the

etching rate of the samples, indicating the improvement of the chemical resistance up to 57%. This is explained by the rigidity enhancement of the polymeric structure.

Hardness of plasma-polymerized HMDSN films as function of treatment time is depicted in Figure 3 (b). An improvement of sixfold (3.2 GPa) is observed in sample treated within 45 min of processing. It is interpreted as consequence of a highly connected network formed by polymeric chain crosslinking, improving dimensional stability of the structure, as well as mechanical and tribological properties [4-6,9,10]. The crosslink increase was detected by XPS analysis, where $C - O$ bond concentration increased almost threefold within 15 min of implantation, but unsaturated bonds, such $C = O$, also contributes to stability of the chains. However, it is believed that longer treatment time does not favor the improvement of crosslink due to beginning of polymeric degradation[6,10].
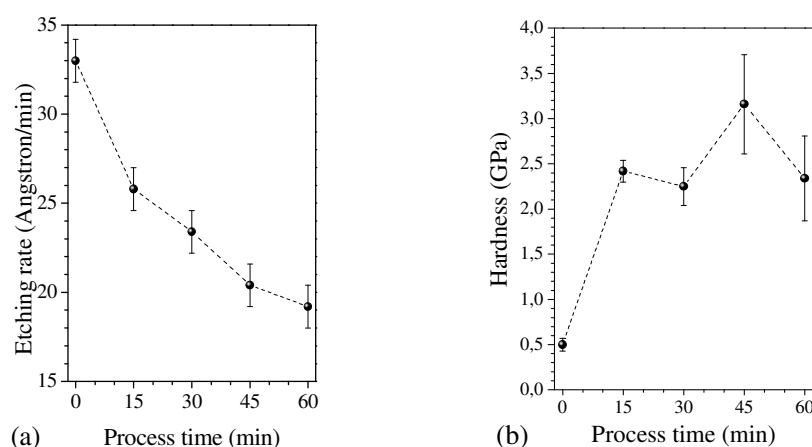

Fig. 3. Etching rate (a) and hardness (b) of the PIII-treated plasma-polymerized HMDSN film

4. Conclusions

Argon PIII is an efficient method to modify the molecular chemical structure of plasma-polymerized HMDSN films and their surface properties. Chemical analysis shows that ion implantation promoted the increase of sp^3 hybrid states and, as consequence, improved the crosslinking of polymer chains. Crosslinking and unsaturated bonds enhanced hardness and oxidation resistance, but they were not enough to avoid the hydrophobic recovery. All of the samples acquired a hydrophilic character upon implantation, but this hydrophilicity diminished after aging in air. In general, the modification induced by argon ion implantation on plasma-polymerized HMDSN films depends on treatment time.

Acknowledgements

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