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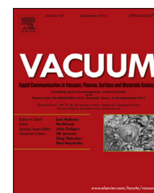

Amorphous silicon carbonitride films modified by plasma immersion ion implantation

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ABSTRACT

Amorphous silicon carbonitride (a-SiCN:H) films were deposited from hexamethyldisilazane (HMDSN) organic compounds via radio-frequency (RF) glow discharges. Afterwards the films were bombarded, from 15 to 60 min, with nitrogen ions using Plasma Immersion Ion Implantation (PIII) technique. X-ray photoelectron spectroscopy (XPS) showed that O–containing groups increased, while C–C and/or C–H groups decreased with treatment time. This result indicates chemical alterations of the polymeric films with the introduction of polar groups on the surface, which changes the surface wettability. In fact, the hydrophobic nature of a-SiCN:H films (contact angle of 100°) was changed by nitrogen ion implantation and, and after aging in atmosphere air, all samples preserved the hydrophilic character (contact angle $<80°$) independently of treatment time. The exposure of the films to oxygen plasma was performed to evaluate the etching rate, which dropped from 24% to 6% while the implantation time increased from 15 to 60 min. This data suggests that PIII increased the film structure strength, probably due to crosslinking enhancement of polymeric chains. Therefore, the treatment with nitrogen ions via PIII process was effective to modify the wettability and oxidation resistance of a-SiCN:H films.

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1. Introduction

Plasma Process is a well established technique to synthesize solid materials as powders or thin films from organic compounds, and is performed using electrical discharges at low or high pressures, as well as at the atmospheric pressure [1–4]. Plasma polymerization is a nonequilibrium process and consequently, the different temperature of the electrons and ions influence the polymerization mechanism. Therefore, molecular structure and chemical composition of plasma-polymerized (PP) films can be completely different compared with those of conventional polymers synthesized by chemical processes. PP films present an amorphous structure, their chains are highly branched and cross-linked, and present good adhesion on different substrates, such as metal, polymer, ceramic and wood [1,2]. All these features make the PP films highly attractive for many technological applications, such as protective coatings, optoelectronic devices, and biomedical coatings, among others [5–9]. However, PP films can present poor mechanical and tribological properties, mainly during operations of sliding conditions against harder materials, which limit their application. In this sense, surface modification processes can be used to improve their mechanical and wear properties, such as ion implantation using high energy ion beam [10,11]. In this technique, the bombardment alters the chemical composition and molecular structure of the target surface, as well as the shelter layers, altering its surface properties. However, this is an expensive technique because the equipment is a line-of-sight ion gun, which treat the surface locally and demands time and energy to treat large surfaces or complex shape components [12,13]. An alternative technique is Plasma Immersion Ion Implantation (PIII), in which the samples biased periodically with higher negative pulses are bombarded by plasma ions. This is a clean and dry process, which can carry out one-step treatments at lower time and with higher ion implantation rate [12,13]. In this technique, the pulse characteristics (amplitude, frequency, duration), the discharge parameters (chemical specie, pressure, power, etc.) and the type of target material determine the final surface properties of the treated materials [12,13]. PIII has been applied for surface modification of metals, semiconductors and conventional polymers, but it is an innovative technique for treatment of PP films. For that reason, this work investigated the chemical structure and surface properties of the PP HMDSN films treated by PIII using nitrogen ions.

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2. Experimental

The films investigated in this work were deposited on glass and polished silicon substrates, both previously cleaned in ultrasonic baths. Initially, the substrates were washed in a mixture of deionized water and detergent, and then rinsed in tap water. After this stage, the substrates were washed in petrol ether to remove any organic contamination from their surface, and finally they dried in an oven.

Thin films were produced via Plasma Enhanced Chemical Vapor Deposition (PECVD). In order to do that, it was adjusted the gas pressure in the chamber. A turbomolecular pump was used to evacuate the reactor to the base pressure of 1.0×10^{-3} Pa. Then, argon gas was introduced into the reactor to reach the minimum operating pressure of rotary pump around 4.0×10^{-1} Pa. Finally, HMDSN vapor was added to reach the working pressure of 5.3 Pa. The system employed to perform both PECVD and PIII treatments present parallel-plate electrodes capacitively connected to RF power supply of 13.56 MHz, as described elsewhere [14]. The deposition discharge was established at 50 W of power applied to the upper electrode, while the lower electrode (substrate holder) was grounded. PECVD process lasted 30 min.

After the deposition, the samples were submitted to PIII treatment. In this case, after the procedure to achieve the base pressure as described above, nitrogen was introduced into the chamber until reaching the working pressure of 5.3 Pa. The bombardment discharge was established at 50 W of RF power, while the substrate holder was connected to pulse supply. The pulse parameters were: 30 KV amplitude, 100 Hz of frequency, and 5 ms of duration. The PIII treatment ranged from 15 to 60 min.

After nitrogen PIII, in the same plasma system, the PP films were exposed to etching discharge. In this process, oxygen was introduced in the reactor to reach the work pressure of 5.3 Pa, the discharge was ignited at 50 W of RF power, and the exposure time was 30 min. The thickness of the etched layer from the samples was measured in a Tencor Alpha-Step 500 profilemeter (INPE-São José dos Campos).

Atomic chemical composition of the film surface was analyzed by X-ray photoelectron spectroscopy (XPS) using an XSAM HS Kratos spectromicroscope (UFSCAR – São Carlos). This analysis was performed in an ultra high vacuum environment, employing Mg Kα radiation fixed at 1253.6 eV of energy and 30 W of power. The spectra were fitted using a Gauss function, and the Shirley background was subtracted before peak fitting. All peak binding energies were referenced to C 1s peak at 284.8 eV related to C–C, C–H carbon bonds.

3. Results and discussion

XPS survey spectra of the PP HMDSN films revealed the presence of four bands of binding energies recognized as carbon (C 1s), oxygen (O 1s), nitrogen (N 1s) and silicon (Si 2p). Their atomic concentrations are shown in Fig. 1 as a function of PIII treatment time. Although the HMDSN, $(CH_3)_3$–Si–NH–Si–$(CH_3)_3$, does not contain O atoms in its structure, and the O_2 gas was not added in the plasma processes, this element appears on the as-deposited HMDSN film (t = 0 s) structure and its concentration increases with PIII treatment time. This is usually observed in plasma processes and it is explained by post-reactions between free radicals trapped in the film structure with oxygen and water vapor from the environment [1–3]. When ions penetrate the polymer, the collisions along the ion tracks induce bond scissions, excitation, and ionization, among other effects [15,16]. Ionizations are responsible for the creation of free radicals, which can readily recombine via chain cross-linking and carbon unsaturated bonds [15,16].

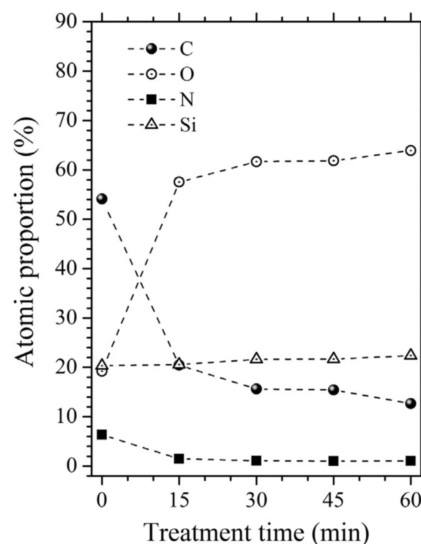

Fig. 1. C, O, Si and N atomic concentration as a function of implantation time.

Incomplete chemical reactions left free radicals in the polymer structure, allowing post-reactions with environment reactive species, such as oxygen and nitrogen. Considering that plasma system consists of a turbomolecular pump, which allows reaching a base pressure of 10^{-4} Pa, and that there is no leak in the system, post-reactions must be occurring when the films are removed from the reactor. As can be observed in Fig. 1, O atomic concentration increases rapidly for 15 min of implantation, while C and N atomic concentration decay at the same time. It is believed that free radicals are sparsely produced at the initial stage of the treatment and the average distance between radicals does not permit the chain cross-linking. Therefore, recombination reactions occur within polymeric chains through unsaturated bonds or, on the other hand, the bonds can be broken [15,16]. The bond breakage usually results in the emission of small molecules, such as CH_x, NO, CO, H_2, C, and H atoms, as verified by many researchers [17]. Consequently, C, H and N atom concentration may be diminished after the implantation. It is important to remember that XPS analysis cannot evaluate the hydrogen concentration, but it is known that these atoms are taken from the polymer surface because they are weakly bonded to polymeric chain termination [15–17]. Therefore, for a shorter treatment time, species are removed from the polymeric film due to bond scissions and free radicals and unsaturated bonds can be created in the polymeric structure, but the cross-linking may not be favored in this initial stage of implantation. Nevertheless, longer treatments allow successive cross-linking, which enhances the structural stiffness of the polymeric films and avoids the creation of free radicals. It is perceived by the saturation behavior observed in O, C and N concentration after 30 min of the process. Si atomic content it seems to increase after implantation but, if Si atoms were not introduced in the process, this amount is statistically constant upon treatment. Therefore, silicon atoms are not removed from PP HMDSN films by the implantation. From literature data [18], according to XPS analysis, HMDSN monomer presents 67% carbon, 22% silicon and 11% nitrogen. In our work, Si concentration in the polymeric film is around 20% and, therefore, it is practically the same proportion reported for the monomer. The deconvolution of C 1s high-resolution spectra resulted in three components located at 284.6 eV, 286.5 eV and 288.4 eV, respectively identified as C–C/C–H, C–O/N–O and C=O bonds. The molecular concentration of these species is depicted in Fig. 2. As can be seen, C–C/C–H bond

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