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Thin films generated by plasma immersion ion implantation and deposition of hexamethyldisilazane mixed with nitrogen in different proportions

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Abstract. In this work, it was used a plasma system composed of a cylindrical stainless steel reactor, a radio-frequency (13.56MHz) power source fixed at either 25 W or 70 W, a power source with a negative bias of 10kV and a 100Hz pulse. The system worked at an operational pressure of 80mTorr which consisted of varying concentrations of the monomer HMDSN and gaseous nitrogen in ratios: HMDSN (mTorr)/nitrogen (mTorr) from 70/10 to 20/60 in terms of operational pressure. The structural characterization of the films was done by FTIR spectroscopy. Absorptions were observed between 3500 cm⁻¹ to 3200 cm⁻¹, 3000 cm⁻¹ to 2900 cm⁻¹, 2500 cm⁻¹ to 2000 cm⁻¹, 1500 cm⁻¹ to 700 cm⁻¹, corresponding, respectively, to OH radicals, C-H stretching bonds in CH₂ and CH₃ molecules, C-N bonds, and finally, strain C-H bonds, Si-CH₃ and Si-N groups, for both the 70 W and the 25 W. The contact angle for water was approximately 100° and the surface energy is near 25mJ/m² which represents a hydrophobic surface, measured by goniometric method. The aging of the film was also analyzed by measuring the contact angle over a period of time. The stabilization was observed after 4 weeks. The refractive index of these materials presents values from 1.73 to 1.65 measured by ultraviolet-visible technique.

1. Introduction

Material processing using low-temperature, low-pressure RF excited plasmas is essential in many current scientific and technological issues encompassing microelectronics, optical, electrical, biomaterial and others industries [1-12]. This feature of such plasmas gives rise to a very reactive chemistry in a relative cold environment whose kinetics is not easily controlled [13]. Plasma Immersion Ion Implantation & Deposition (PIIID) is a highly efficient technique for surface modification and thin film deposition. It can produce or modify metals, semiconductors and polymeric materials [14-18]. In this case, the materials are produced in a gas or vapor discharge and it is polarized simultaneously with high voltage pulses. Plasma ions are accelerated toward the films and implanted into their surfaces while the films are deposited.

In this work, PIIID process is used to obtain thin films from mixtures in various proportions of hexamethyldisilazane (HMDSN) and nitrogen at two power conditions, 25 and 70 Watts excited by

13.56 MHz and polarized by pulses of negative 10 KV in 100 Hz. The samples were analyzed by infrared, uv-visible and goniometric techniques.

2. Experimental setup

The PIIID occurs inside a cylindrical stainless steel reactor 21.5 cm in diameter and 24.5 cm in height, with pipes to evacuation, controlled gas admission, and optical observation. Inside the reactor, there are two parallel stainless steel discs shaped plain electrodes with a gap of 3cm between them. The upper electrode is powered by a 13.56 MHz radiofrequency power source for the deposition; the lower one is fed by a 100 Hz and 10 kV high voltage power source for the ion implantation. In this lower electrode is where the glass and aluminum substrates are placed.

The system is initially evacuated by mechanical and turbomolecular vacuum pump, reaching the pressure of 10^{-5} Torr, cleaning the system. After that, the turbomolecular pump is switched off and the mechanical pump keeps the system at 10^{-3} Torr. Then the HMDSN enters the reactor by a precise needle valve until it reaches the required pressure, so the nitrogen enters the same way and completes the pressure. The aim is to vary the proportion of the HMDSN and the nitrogen from 10mTorr to 10 mTorr so that the sum of them both is equal 80 mTorr in each deposition and try them all in both 25 W and 70 W of RF power for 20 minutes. The molecular structure of the samples was investigated by FTIR analysis using a Perkin Elmer Spectrum 100. The refractive index was measured by a Perkin Elmer Lambda 25 UV/VIS Spectrometer. The contact angle, surface energy and aging of the films were analyzed by a Hamé-Hart 300 – F1 equipment. The aging of the film was also analyzed in a period of 4 weeks.

3. Results and discussions

Figures 1 and 2 illustrate the infrared spectra of PIIID – HMDSN/Nitrogen films deposited at 70 W and 25 W radiofrequency power supply respectively. However, the HMDSN and nitrogen concentration was modified in each implantation/deposition process. The most important vibration modes of the molecular structure of these thin films are presented in table 1.

Table 1. PIIID – HMDSN/nitrogen film infrared spectra vibration modes.

Vibration modes	Absorption peak (cm^{-1})
O-H stretching	3400
N-H stretching	3350
C-H stretching in CH_3 groups	2960
C-H stretching in CH_2 groups	2900
Si-H stretching	2130
C=O stretching	1700
N-H bending in NH_2 groups / C=C stretching	1650
C=N / C=O bending	1600
CH_3 bending in $\text{Si}-(\text{CH}_3)_x$ groups	1230
Si-O stretching	1050
Si-N stretching	940
$\text{Si}-(\text{CH}_3)_x$ rocking – stretching	850
Si-C stretching	800

For 70 W or 25 W PIIID, the same vibrational modes were observed in the samples, independently of the HMDSN-nitrogen concentration in the plasma, as shown in the figures 1 and 2. On the other hand, the intensity of the same bands like $\text{Si}-(\text{CH}_3)_x$, Si-O, Si-N in the range $1500\text{-}900\text{ cm}^{-1}$ was changed. This implies that the chemical structure of the films was modified by PIIID process. Although the HMDSN does not contain oxygen, it was observed in the molecular structure of the films. It can be attributed to the atmospheric or residual oxygen present inside the reactor during PIIID process that reacts with the free radicals in the samples structure. Si-O and Si-H vibration modes in the

films are due to three concomitant effects of ion implantation processing: chain breakage, unsaturation and crosslinking. It is known that the impact of energetic ions with a target material causes chemical bond breakages and promotes emission of atomic and molecular species [19].

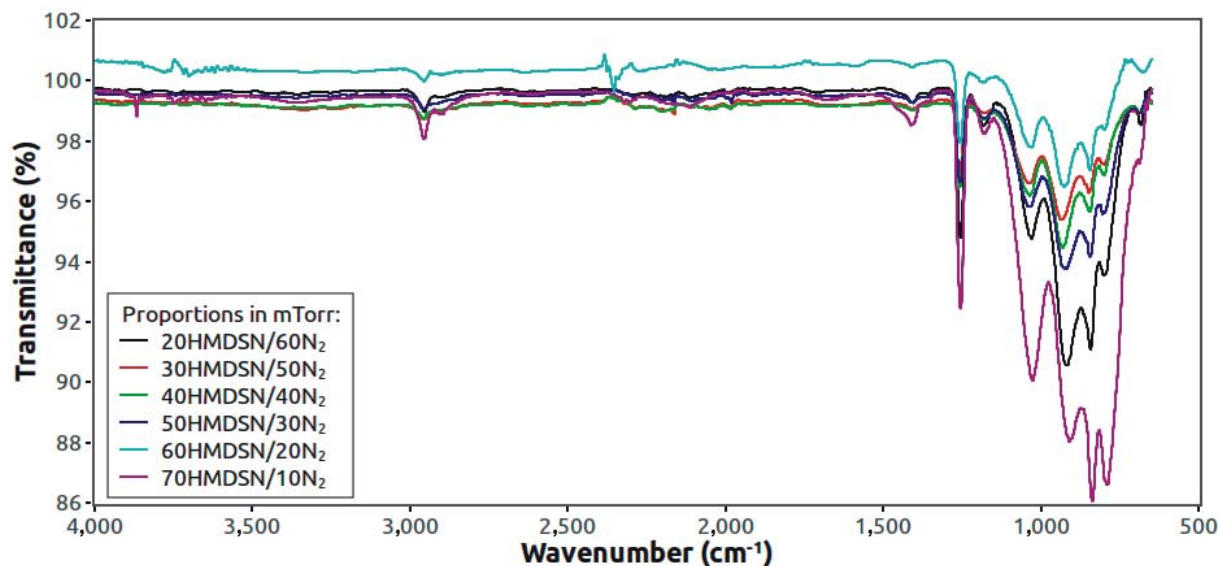


Figure 1. IR spectra of HMDS/Nitrogen PIID films at 70 W.

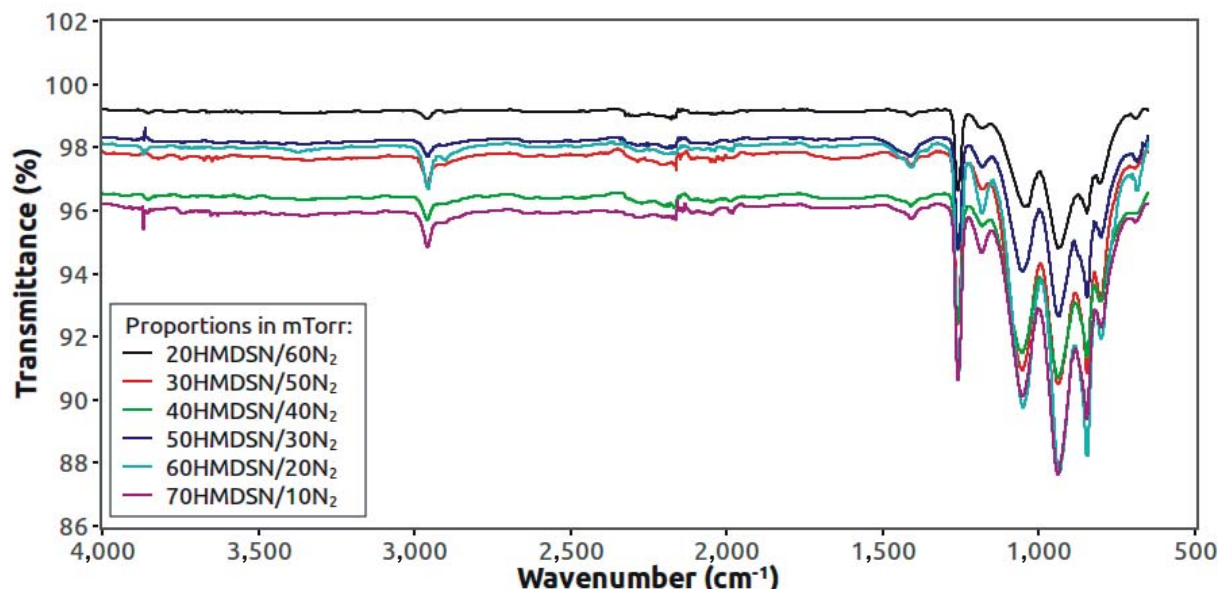


Figure 2. IR spectra of HMDS/Nitrogen PIID films at 25 W.

In polymeric materials, hydrogen bonds are preferentially lost because they belong to chain termination and hydrogen atom progressive emission induces the appearance of dangling bonds. The dangling bonds can recombine through unsaturation process such as double bond between carbon atoms or between carbon atoms and other species present in the polymeric structure.

Figure 3 shows the behavior of the refractive index of the films obtained at 70 W and 25 W. At 70 W the refractive index decreases from 1.73 to 1.70 while it decreases from 1.69 to 1.65 for the samples obtained at 25 W.

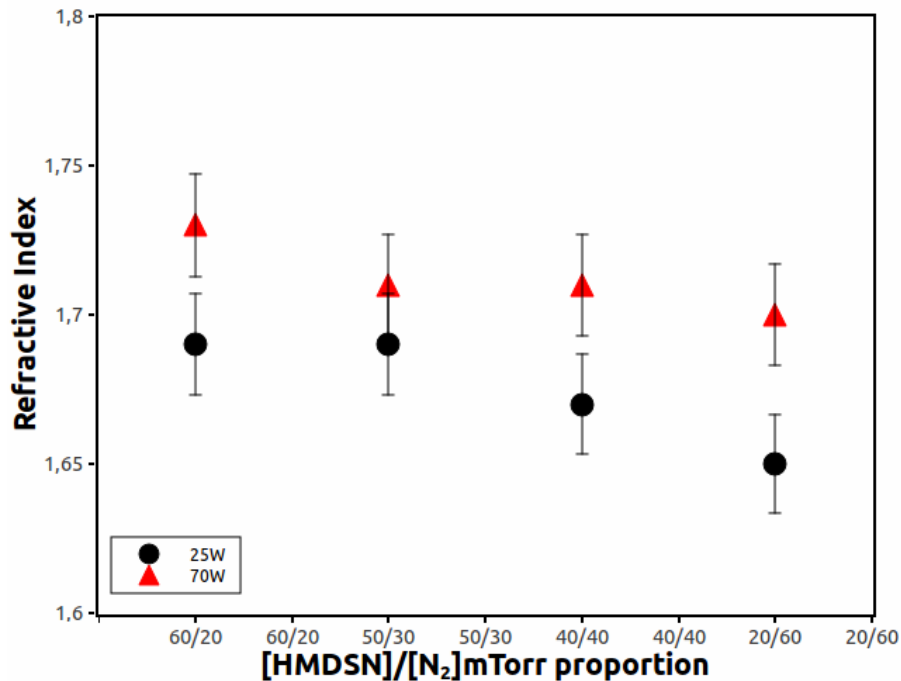


Figure 3. The refractive Index of the films obtained by PIID at 70 W and 25 W in some different proportions of HMDS/Nitrogen.

This slight tendency in the behavior of the refractive index is the same in these cases, 70 W or 25 W. The PIID process at 25 W produces films more colorless than at 70 W, which are slightly yellow. These alterations in the optical properties of the samples can be due to the random structure of the chains in a plasma polymer. Because the structures are random it makes theoretical interpretation of the experimental results rather difficult. However, it seems reasonable to suppose that some trends in the physical behavior of a “conventional” polymer must be followed by a HMDSN-Nitrogen PIID polymer film. For example, the density of π bonds is influenced by the degree of hydrogenation that depends in turn on the applied power and different concentration of HMDSN and nitrogen in the PIID process. The detachment of hydrogen, for example, from the polymer also affects bond lengths, thus changing the refractive index. In both cases (70 and 25 W) the films thicknesses decrease from 100 to 55nm while the concentration of nitrogen was higher than HMDSN. In the PIID process nitrogen can contribute to make chemical bonds to form the film and it can promote ablation to destroy the polymer and so to reduce the film thickness.

Figures 4 and 5 present the contact angle and surface energy as a function of HMDSN and nitrogen concentrations at 70 and 25 W PIID process respectively.

Independently of the HMDSN and Nitrogen concentration, in both cases of the PIID process at 70 or 25 W, the contact angle and surface energy presented the same behavior with very close values. As the contact angle is near 100 degree, the samples present hydrophobic character and it was not changed after aging effect over the films. A representative aging effect can be observed in the figure 6. The films obtained in this work result of a competitive process of polymerization and ablation. As was discussed first, these films are formed mainly by free radicals within their structures and surfaces. So, rapid recombination of atoms and molecules involving oxygen contributed to create polar groups and

to saturate the surface bounds responsible for the hydrophobic character of the samples for a long time.

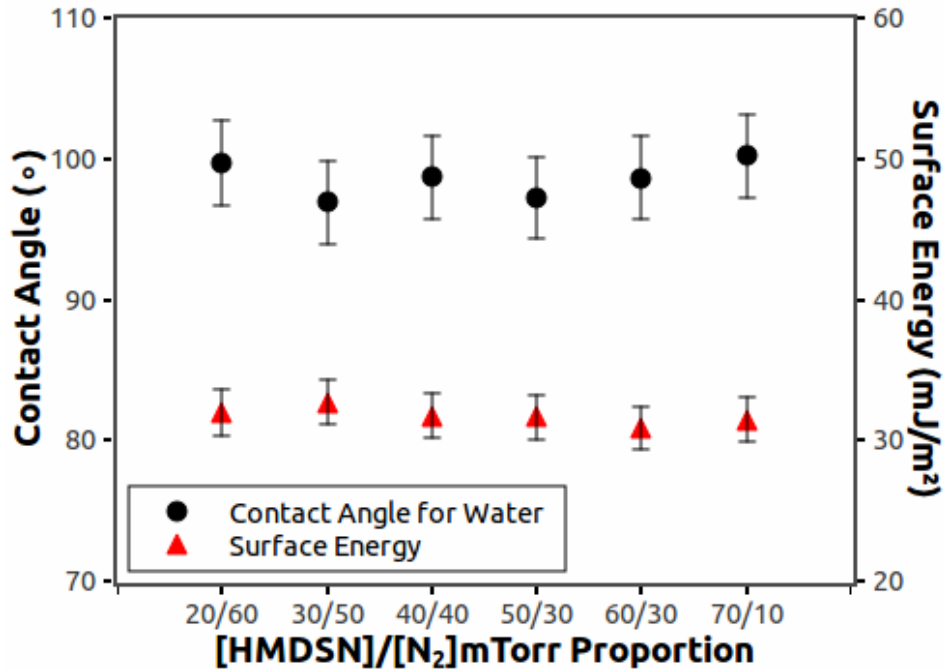


Figure 4. Contact angle and surface energy as a function of HMDSN and nitrogen concentration at 70 W PIID process.

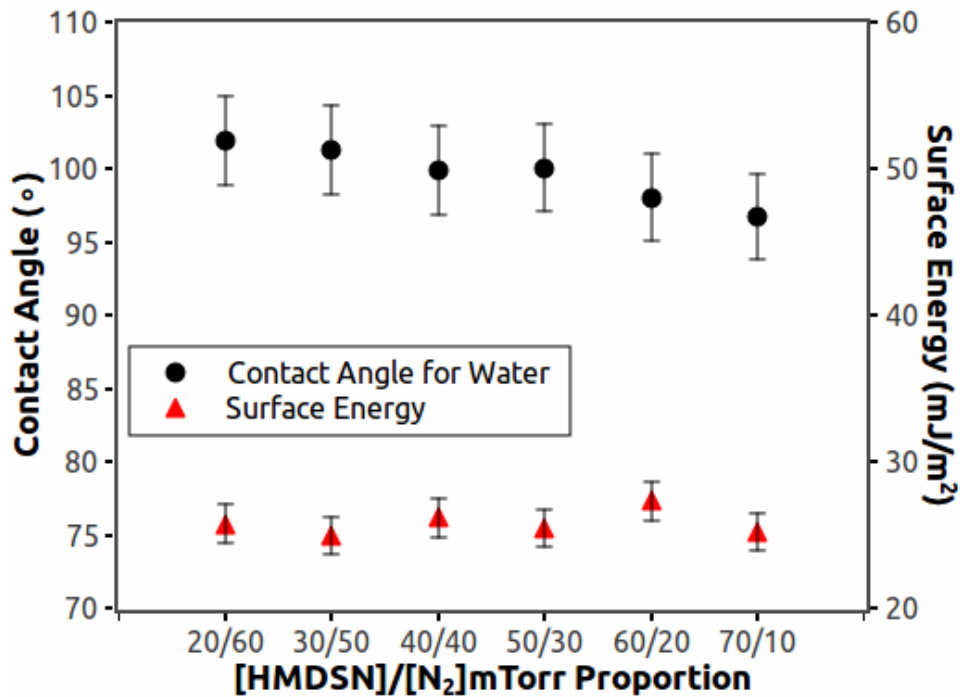


Figure 5. Contact angle and surface energy as a function of HMDSN and nitrogen concentration at 70 W PIID process.

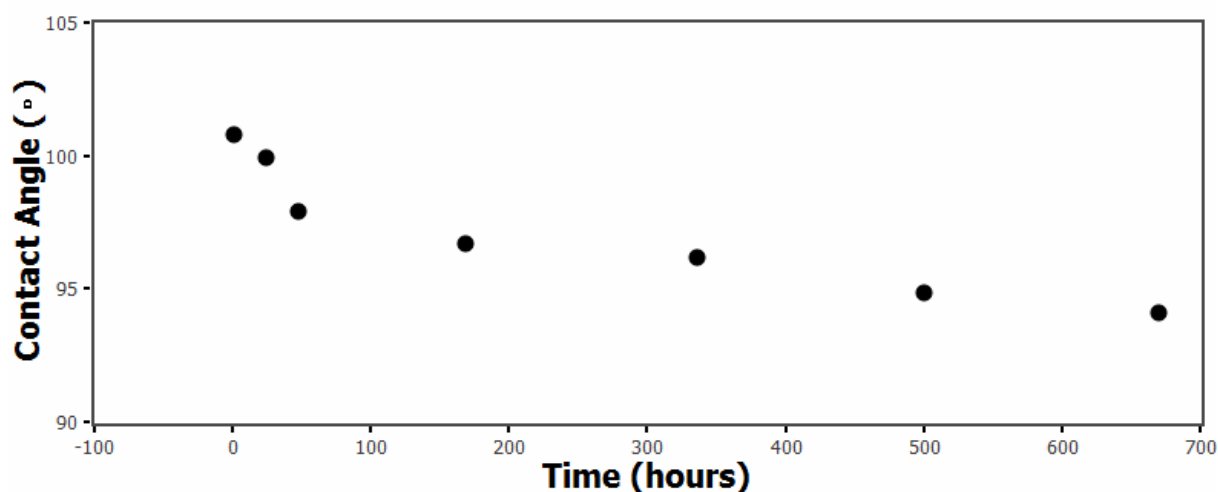


Figure 6. Aging effect represented by sample deposited at 60/20mTorr HMDSN/Nitrogen concentration at 25 W radiofrequency power.

4. Conclusions

The results of infrared measurements show groups not present in the mixture HMDSN-Nitrogen, but present in the films as a consequence of the PIID to produce films with crosslinking structure and formed by free radicals.

The PIID process is a competitive one characterized by polymerization and ablation simultaneously responsible of the formation of nanofilms that present hydrophobic character.

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