

## Plasma-polymerized hexamethyldisilazane treated by nitrogen plasma immersion ion implantation technique

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Conf. Ser. 167 012055

(<http://iopscience.iop.org/1742-6596/167/1/012055>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 200.145.3.40

The article was downloaded on 18/07/2013 at 21:40

Please note that [terms and conditions apply](#).

## Plasma-polymerized hexamethyldisilazane treated by nitrogen plasma immersion ion implantation technique

**R Y Honda<sup>1</sup>, R P Mota<sup>1</sup>, R G S Batocki<sup>1</sup>, D C R Santos<sup>1</sup>, T Nicoleti<sup>1</sup>, K G Kostov<sup>1</sup>, M E Kayama<sup>1</sup>, M A Algatti<sup>1</sup>, N C Cruz<sup>2</sup>, L Ruggiero<sup>3</sup>**

<sup>1</sup> Laboratório de Plasma, Faculdade de Engenharia, UNESP, Av. Dr Ariberto Pereira da Cunha-333, 12516-410, Guaratinguetá, SP, Brazil.

<sup>2</sup> Laboratório de Plasmas Tecnológicos, Unidade Diferenciada, UNESP, Av. Três de Março-511, 18085-180, Sorocaba, SP, Brazil.

<sup>3</sup> Faculdade de Ciências, UNESP, Av. Luis E. Carrijo Coube 14-1, 17033-360, Bauru, SP, Brazil.

E-mail: honda@feg.unesp.br

**Abstract.** This paper describes the effect of nitrogen Plasma Immersion Ion Implantation (PIII) on chemical structure, refraction index and surface hardness of plasma-polymerized hexamethyldisilazane (PPHMDSN) thin films. Firstly, polymeric films were deposited at 13.56 MHz radiofrequency (RF) Plasma Enhanced Chemical Vapour Deposition (PECVD) and then, were treated by nitrogen PIII from 15 to 60 min. Fourier Transformed Infrared (FTIR) spectroscopy was employed to analyse the molecular structure of the samples, and it revealed that vibrations modes at 3350 cm<sup>-1</sup>, 2960 cm<sup>-1</sup>, 1650 cm<sup>-1</sup>, 1250 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> were altered by nitrogen PIII. Visible-ultraviolet (vis-UV) spectroscopy was used to evaluate film refractive index and the results showed a slight increase from 1.6 to 1.8 following the implantation time. Nanoindentation revealed a surface hardness rise from 0.5 to 2.3 GPa as PIII treatment time increased. These results indicate nitrogen PIII is very promising in improving optical and mechanical properties of PPHMDSN films.

### 1. Introduction

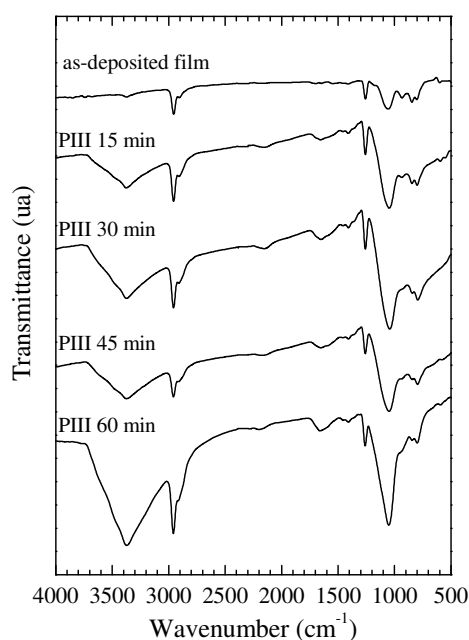
PIII is a highly efficient technique for surface modification of metal, semiconductor and polymeric materials [1,2,3,4,5] and, it has been applied in different areas, such as aeronautic, electronic, optical and biomedical. In this implantation process, the samples are immersed in gas discharge and are polarized with high negative voltage pulses. Plasma ions are accelerated toward the samples and implanted into their surfaces. This bombardment promotes bond breakage and recombination processes on chemical structure of the target surface and consequently, it causes modifications in its chemical, optical, electrical, biological, mechanical and tribological properties [6,7,8]. However, the degree of these modifications is strongly dependent on plasma parameters (frequency, discharge power, gas pressure, gas specie), pulse characteristics (amplitude, repetition rate and work time) and target material [8]. In this work, plasma-polymerized HMDSN were used as target, because they are interesting to many applications, such as optical, protective and biocompatible coatings [9,10,11,12]. Refractive index and surface hardness of HMDSN films treated by nitrogen ions were correlated to molecular chemical modification induced by PIII technique.

## 2. Materials and Methods

PPHMDSN films, with 295 nm average thickness, were prepared by PECVD in a cylindrical stainless steel reactor fitted with two parallel plate electrodes. RF power supply (13.56 MHz, 50 W) was connected to upper electrode and the lower one, used as substrate holder, was grounded. HMDSN vapour pressure was 40 mTorr and deposition time was 30 min. PIII was performed in the same reactor, fixed at the lower electrode to a high voltage pulser. Nitrogen plasma of 50 W power and 40 mTorr pressure was established while negative pulses of 30 kV amplitude and 100 Hz repetition rate were applied. PIII treatment time varied from 15 to 60 min. Thickness measurements were carried out by Alpha-Step Tencor profilometer. Molecular chemical structure of the film surfaces was investigated by Fourier Transformed Infrared (FTIR), using a Perkin Elmer FTIR 1600 spectrometer. Refractive index was analysed by visible-ultraviolet (vis-UV) using a Hitachi U-3501 spectrometer and hardness was evaluated by a nanoindenter Hysitron Triboindenter.

## 3. Results and discussions

Figure 1 shows the IR spectra of PPHMDSN films submitted to different time of nitrogen PIII. As can be noticed, as-deposited film spectrum is characterized by C–H stretching at  $2960\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$ , Si–CH<sub>3</sub> stretching at  $1250\text{ cm}^{-1}$ , Si–O stretching at  $1050\text{ cm}^{-1}$ , Si–N stretching at  $940\text{ cm}^{-1}$ , Si–(CH<sub>3</sub>)<sub>x</sub> stretching at  $840\text{ cm}^{-1}$  and Si–C stretching at  $800\text{ cm}^{-1}$ . Although HMDSN monomer contains no oxygen (O), free radicals trapped in PPHMDSN film structure react with atmosphere O during the deposition process or when the samples are removed from the reactor [3,7]. Therefore, O-containing groups usually appear into PP film molecular chain. Observing IR spectra of the implanted films, it can be seen that some of the original PPHMDSN bands were intensified with the rise of nitrogen PIII treatment time. Besides, there was the appearance of three new absorption bands: O–H stretching at  $3400\text{ cm}^{-1}$ , Si–H stretching at  $2130\text{ cm}^{-1}$  and the band centered around at  $1650\text{ cm}^{-1}$ . The later is attributed to unsaturated carbon bonds, such as C=O and C=N. It is possible that N–H stretching at  $3350\text{ cm}^{-1}$  and N–H bending at  $1650\text{ cm}^{-1}$  are overlapped by large bands, because N ions are highly reactive and are introduced into the polymeric structure. Chemical bonds and their related absorption peaks are shown in Table 1.

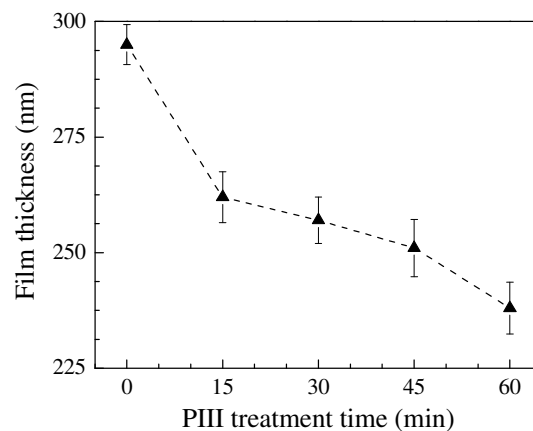


**Figure 1.** IR spectra of PPHMDSN films treated by nitrogen PIII for different time.

**Table 1.** PPHMDSN film infrared spectra vibration modes.

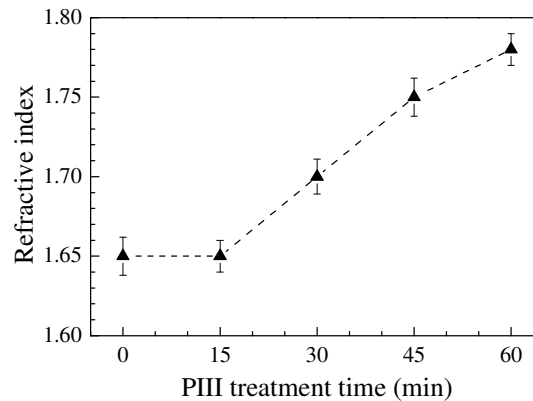
Vibration modes	Absorption peak ( $\text{cm}^{-1}$ )
O–H stretching	3400
N–H stretching	3350
C–H stretching in $\text{CH}_3$ groups	2960
C–H stretching in $\text{CH}_2$ groups	2900
Si–H stretching	2130
C=O stretching	1700
N–H bending in $\text{NH}_2$ groups / C=C stretching	1650
C=N /C=O bending	1600
$\text{CH}_3$ 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

These molecular chemical modifications are attributed to three concomitants 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 [8]. In polymeric material, hydrogen (H) bonds are preferentially lost because they belong to chain termination, and H atom progressive emission induces the appearance of dangling bonds. These dangling bonds can recombine through unsaturation processes such as double bond between carbon atoms or between carbon atoms and other species present in the polymeric structure. The presence of C=C, C=O and C=N bonds is suggested around  $1650 \text{ cm}^{-1}$  band, although it is difficult to distinguish them in the spectra. Chain crosslinking can also occur due to dangling bonds, and it is responsible for the chain mobility decrease and, consequently, for the structure stiffness. These factors increase the density of the samples while their thicknesses diminish. Figure 2 shows PPHMDSN film thickness measurements after and before ( $t=0$ ) PIII treatments.

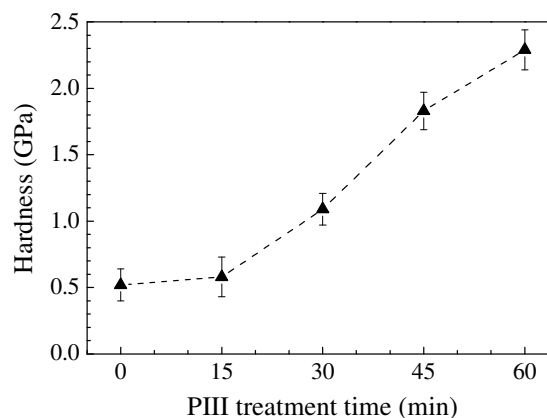


**Figure 2.** Thickness of PPHMDSN films as a function of implantation time.

As can be seen in figure 2, the thickness of the films diminished from 295 nm to 238 nm as the treatment time increased. This can confirm the density rise of the samples, although the thickness decrease can be also related to sputtering processes frequently observed in ion implantation treatments [8]. The density increase promotes alterations in the optical properties of the samples, which was evaluated through refractive index measurements show in figure 3. In that figure, it can be noticed a slight refractive index enhancement from 1.65 to 1.78. Moreover, the density rise is directly related to hardness improvement. Figure 4 shows the hardness measurements performed at 70 nm depth, as a function of treatment time. As can be seen, the PPHMDSN film hardness rose from 0.5 to 2.3 GPa as nitrogen PIII treatment time increased. It corroborates the unsaturated and crosslinking process enhancement suggested before. In this sense, it is necessary to emphasize that ion implantation usually promotes modifications into the film surface, however IR and vis-UV analyses were performed in the film bulk. Therefore, any alteration in these analyses shows that PIII is an effective technique for surface modifications.



**Figure 3.** Refractive index of PPHMDSN films measured at a wavelength of 628.34 nm as a function of nitrogen PIII processing time.



**Figure 4.** Hardness of PPHMDSN treated by nitrogen PIII, measured at 70 nm depth, as a function of implantation time.

#### 4. Conclusions

The results of IR measurements show the O-containing group and unsaturated bond appearance, as well as Si bonds increase, after nitrogen PIII. These molecular chemical modifications induced a rise of the density, refractive index and surface hardness of the PPHMDSN thin films. Nevertheless, the degree of these alterations looks directly dependent on the implantation time. It is attributed to higher amount of insaturation and crosslinking recombination processes at longer treatment time. All analysis performed in this work show nitrogen PIII is efficient to modify the molecular chemical structure of PPHMDSN films and their surface properties.

#### Acknowledgements

Authors thank Instituto Nacional de Pesquisas Espaciais (INPE) for infrared analyses, Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) and FUNDUNESP for financial support.

#### References

- [1] Poon R W Y, Ho J P Y, Liu X, Chung C Y, Chu P Y, Yeung K W K, Lu W W and Cheung M C 2005 Improvements of anti-corrosion and mechanical properties of NITi orthopedic materials by acetylene, nitrogen and oxygen plasma immersion ion implantation *Nucl. Instrum. Meth. B* **237** 411
- [2] Fu R K Y, Cheung I T L, Mei Y F, Shek C H, Siu G G, Chu P K, Yang W M, Leng Y X, Huang Y X, Tian X B and Yang S Q 2005 Surface modification of polymeric materials by plasma immersion ion implantation *Nucl. Instrum. Meth. B* **237** 417
- [3] Gan B K, Bilek M M M, Kondyurin A, Mizuno K and McKenzie D R 2006 Etching and structural changes in nitrogen plasma immersion ion implanted polystyrene films *Nucl. Instrum. Meth. B* **247** 254
- [4] Sui J and Cai W 2006 Mechanical properties and anti-corrosion behaviour of the diamond-like carbon films *Surf. Coat. Tech.* **201** 1323
- [5] Yeung K W K, Chan Y L, Lam K O, Liu X M, Wu S L, Liu K Y, Chung C Y, Lu W W, Chan D, Luk K D K, Chu P. K and Cheung K M C 2008 New plasma surface-treated memory alloys: towards a new generation of “smart” orthopaedic materials *Mat. Sci. Eng. C* **28** 454
- [6] Burakowski T and Wierzchon T 1999 *Surface Engineering of Metals* (Flórida, CRC Press)
- [7] Lawrynowicz Z 1992 *Metallurgy, Heat Treatment, Surface Engineering* 115–117 50
- [8] Santos D C R, Rangel R C C, Mota R P, Cruz N C, Schreiner W H and Rangel E C 2004 Modification of plasma polymer films by ion implantation *Mater. Res.* **7-3** 493
- [9] Chen C-H, Yang M-R and Wu S-K 2008 Polymerized hexamethyldisilazane coated on equiatomic TiNi shape memory alloy using DC-pulsed plasma assisted chemical vapor deposition *Surf. Coat. Tech.* **202** 2709
- [10] Ladwig A, Babayan S, Smith M, Hester M, Highland W, Koch R and Hicks R 2007 Atmospheric plasma deposition of glass coatings on aluminum *Surf. Coat. Tech.* **201** 6460
- [11] Wagner N J, Gerberich W W and Heberlein J V R 2006 Thermal plasma chemical vapor deposition of wear-resistant, hard Si-C-N coatings *Surf. Coat. Tech.* **201** 4168
- [12] Silva M L P, Tan I H, Nascimento A P, Galeazzo and Jesus D P 2003 Use of plasma polymerized highly hydrophobic hexamethyldisilazane films for sensor development *Sens. Act. B* **91** 362