ICREN-01/2013 February 16-17, 2013 Constantine, Algeria
First International Conference on Renewable Energies and Nanotechnology impact on Medicine and Ecology

Polyimide surface treatment by plasma deposition of organosilcon nano-thin layers

I. Nouicer[a*], S.Sahli[a**], Z.Ziari[a], A. Bellel[b].

[a]*Université Mentouri de Constantine, Laboratoire Microsystèmes et Instrumentation (LMI), Faculté des Science de l'Ingénieur, Constantine 25017, Algeria*
[b]*Laboratoire díEtude des Matériaux Electroniques pour Applications Médicales (LEMEAMED), Faculté des Sciences de l'Ingénieur, Constantine, Algérie*

Corresponding author : * ilyes.nouicer@gmail.com, ** sahli50@hotmail.com

Abstract

Plasma enhanced chemical vapor deposition (PECVD) technique has been used to deposit organosilicon nano-thin layers on polyimide (PI) films substrates from hexamethyldisiloxane (HMDSO) precursor. The nano-thin layers chemical structure was analyzed using Fourier Transform InfraRed (FTIR) spectroscopy and the surface wettability was characterized by contact angle measurements. FTIR analysis showed that the chemical formula of all deposited nano-thin layers were $SiO_xC_yH_z$-like. Increasing deposition time leads firstly to the increase of the treated PI films hydrophobicity and then to a quasi-saturation of the contact angle value when the discharge time increases beyond 2 min. Ellipsometry measurements showed that the refractive index measured on nano-thin layers elaborated from pure HMDSO with a discharge time of 30 s was found higher than that measured on films deposited with discharge time of about 420 s. Increasing time deposition leads to the decrease in the porosity of the nano-structure coating, leading to denser structure.

Keyword : Plasma polymérisation, organosilicon, nano-thin layers, wettability, FTIR, refractive index;

1. Introduction

Because of their excellent mechanical strength, low dielectric constant and high chemical and thermal resistance. Polyimides (PIs) have been widely used in many applications: microelectronics (flexible chip carriers), biomedical (tubing) and aerospace technologies [1-2]. However, PI has poor hydrophilic character and low hydrophobic properties (the surface energy value of this material is about 104.71 mj/m^2 [5]). Many research works have been developed to modify the PI surface properties. For this purpose, several treatment techniques have been used such as plasma glow discharge, corona discharge and ion

beam [5]. Among these methods, plasma glow discharge is ecological and economical method used for deposition of thin layers on a wide variety of substrates, it has the advantage of keeping bulk properties unchanged [1].

Introducing an organic monomer precursors in plasma deposition reactor, leads to deposit a thin layer because of a molecules precursor fragmentations and a recombination process on the polyimide substrate surface [13, 14]. In recent works, we have studied the potential decay phenomena at the polyimide surface [4] and the improvement of its wettability by the use of SiO_x-like films elaborated by plasmas [1][5]. Using AFM analysis, we have showed that the wettability of the polyimide coated SiO_x-like films is partially monitored by the surface nanostructure.

In the present work, we have carried out some investigations on the improvement of polyimide films hydrophobic character using plasma polymerized hexamethyldisiloxane (PPHMDSO) thin layer elaborated in a capacitively coupled plasma reactor. The composition of the coatings has been investigated by Fourier-transform infrared spectroscopy (FTIR) and the results have been correlated with water contact angle measurements.

2. Experimental details

Polyimide films substrate with a thickness of 50 µm (Kapton ® HN from DuPont Nemour) were cut into rectangular shaped (6.5×1 cm^2). Before any deposition and in order to eliminate any dusts, samples were cleaned with distilled water and then dried using nitrogen gas jet. The plasma polymerized hexamethyldisiloxane nano-thin layers were deposited on PI substrates using a home made low frequency (12.5 kHz) capacitively coupled plasma reactor. The reactor consisted of a cylindrical chamber equipped with two circular electrodes spaced with about 3 cm (figure 1). In each deposition experiment, a high resistively n-type silicon square shape (2x2 cm^2) substrate (used for thickness measurement and FTIR analysis) was placed with PI substrates on the lower electrode. The reactor was pumped down lower than 10^{-2} mbar using Alcatel rotary pump. By the using of monomer inlet system with a needle valve, vapors of HMDSO was introduced without any gas vector. The pressure in the reactor was monitored with a Pirani gauge. During the deposition process, the plasma discharge power and the pressure in the reactor were kept fixed at 40 W and 0.2 mbar, respectively and the deposition time was varied from 30 to 900 seconds in order to obtain film with different thickness. All experiments were performed at room temperature. The coating thickness and refractive index were determined using a profilometer (Alpha step) and microspot beam spectroscopic ellipsometer (Sopra GES5) with an incident angle of 75,6° (silicon Brewster angle).

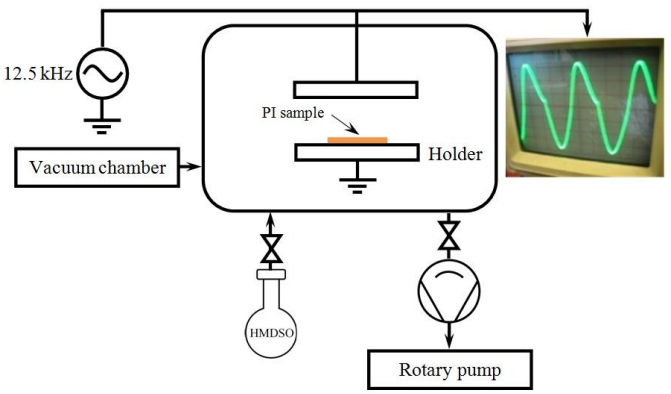

Fig 1: Schematic diagram of the PECVD system.

The wettability of the coating was evaluated by water contact angle measurements using the experiment system set-up represented in figure 2. The image of the liquid drop (5 µl) deposited onto the coated PI substrates was acquired by a numerical camera and transmitted to a computer to calculate the contact angle. All contact measurements angle were performed at atmospheric pressure and room temperature. For more precision, all contact angle data were averaged from five measurements.

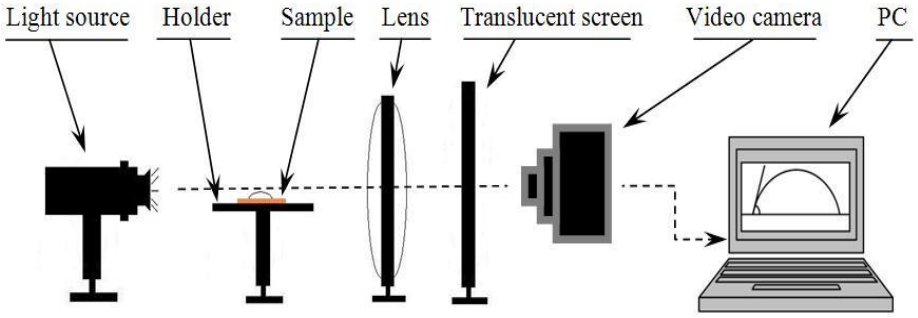

Fig 2 : Experimental set-up for contact angle measurement.

Fourier transform infrared (FTIR) analysis was performed on PPHMDSO nano-thin layers deposited on silicon substrate using Nicolet Avatar 360 spectrometer. All spectra were acquired in absorbance mode in the 400 - 4000 cm^{-1} range with 4 cm^{-1} resolution.

3. Results and discussion

Plasma discharge Time effects on wettability and adhesion work (Wa) of HMDSO nano-thin layer Fig 3 illustrates the variation of the contact angle and adhesion work as a function of discharge time recorded on nano-thin layers deposited on a polyimide substrate. The contact angle increases quickly during the first three minutes of the deposition, passing from 64° for an untreated polyimide to approximately 82° for films treated with a deposition time of about 3 minutes. For deposition time higher than 3 minutes, we reach a steady state value. This saturation is probably related to the variation in the chemical structure. According to reported work, the non-polar (dispersive) groups are responsible for the increase of contact angle [9]. Contrary, the value of adhesion work was about 104,71 mj/m^2 for untreated PI then decreases rapidly to about 82,93 mj/m^2 for films deposited with discharge time less than three minutes. The value of adhesion work did not increase much further beyond 3 minutes.

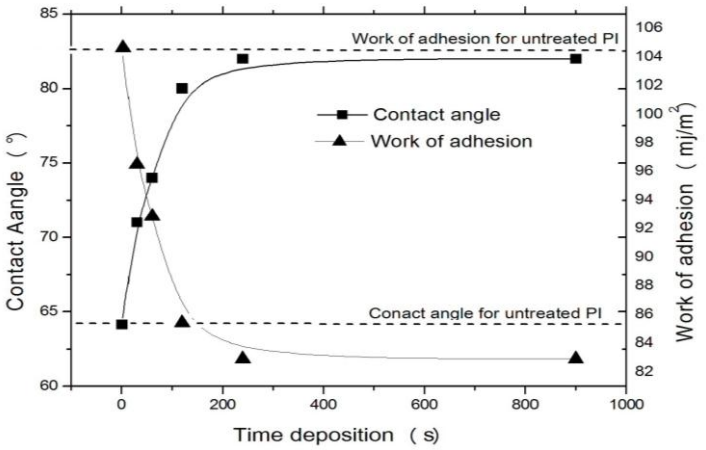

Fig 3: Variation of contact angle and adhesion work as a function of discharge time.

Our results are in the same order of magnitude compared with those found by Mi Ran Moon et al [6] on thin HMDSO deposited on silicon dioxide substrate using radio frequency plasma glow discharge (discharge power of 10 watts under a chamber pressure of 0.5 torr). They have concluded that alkane chains (molecules that contain carbon and hydrogen) found in the HMDSO film have the possibility of modifying the surface property of the substrate from hydrophilic to hydrophobic. In addition, Sanghak Yeo et al have recorded a water contact angle of about 94° on HMDSO thin film deposited on glass substrate using radio frequency plasma glow discharge (pressure of about 0.5 torr and discharge power of 60 W during 10 minutes) [7].

3.1. Physico-chemical characterizations of treated surface films by FTIR spectroscopy

The infrared absorption spectra obtained for nano-thin layers elaborate on high resistively silicon substrates are given in figure 4. The assignment of vibration peaks was made by referring to several works [6, 7, 8]. The most intense absorption peak on these spectra is located around 1000 to 1150 cm^{-1} and is assigned to asymmetric stretching of Si-O-Si. Another peak, with lower intensities associated with the symmetrical stretching of the same vibration Si-O-Si appears around 450 cm^{-1}. The vibration peak situated around 800 cm^{-1} can correspond to the CH_3 mode and/or to Si-C stretching vibration in the Si-$(CH_3)_2$ groups. An absorption peak between 1250 to 1270 cm^{-1} is assigned to the CH_3 vibration in the Si-$(CH_3)_3$ groups. Peaks located in the 2960 - 2900 cm^{-1} range correspond to the symmetrical and asymmetrical stretching vibrations of CH_x (x = 1, 2, 3) groups. Large absorption band between 3200 and 3700 cm^{-1} is related to the Si-OH vibration and the OH vibration. The presence of OH is probably due to air introduction into the reactor chamber. All these FTIR absorption spectra confirm that the elaborate nano-thin layers have a polymeric structure and can be assigned the $SiO_xC_yH_z$ as chemical formula. FTIR results indicated that the increase in deposition time is accompanied with an increase of organic bands (CH_x, Si-CH_3), which can increase the value of the contact angle and reduce the work of adhesion of the coated PI.

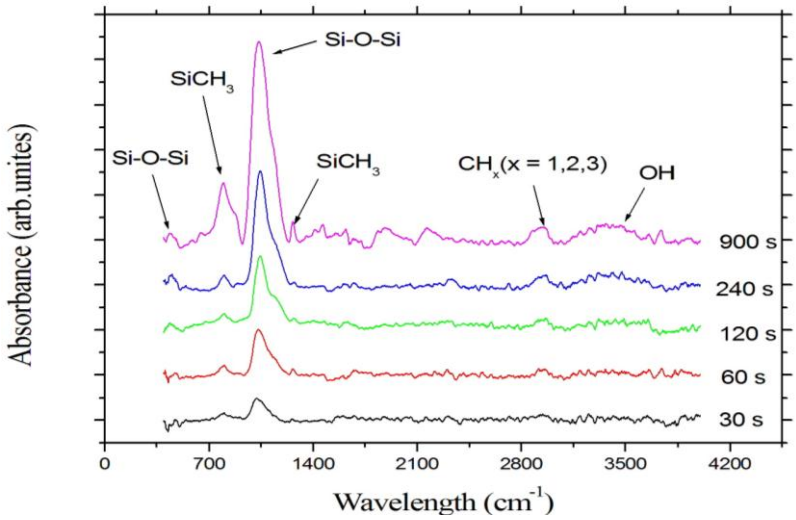

Fig 4: FTIR absorption spectra of nano-thin layers elaborated with different deposition time.

3.2. Refractive index behaviour

The ellipsometric analysis was carried out on nano-thin layers deposited on silicon substrate. Fig 7 shows the variation of the refractive index as a function of plasma discharge time.

It is noticed that the values of refractive index recorded on nano-thin layers are slightly higher than those reported for thermal SiO_2 (n = 1.456). For a wavelength λ = 632 nm, the refractive index was about 1.58 and 1.60 for a layers deposited during t = 30 and 420 s, respectively. These values are close to those found by S.Saloum et al. for thin HMDSO film [10]. In comparison with other works, the values of our refractive indices are higher than that obtained by N. Benissad et al in porous structure [11]. The presence of voids reduces the refractive index. Increasing in deposition time leads to the increase in the number of agglomerates per unit area and the film became denser with low porosity [12], which confirms the hydrophobic character of our nano-thin deposited layers.

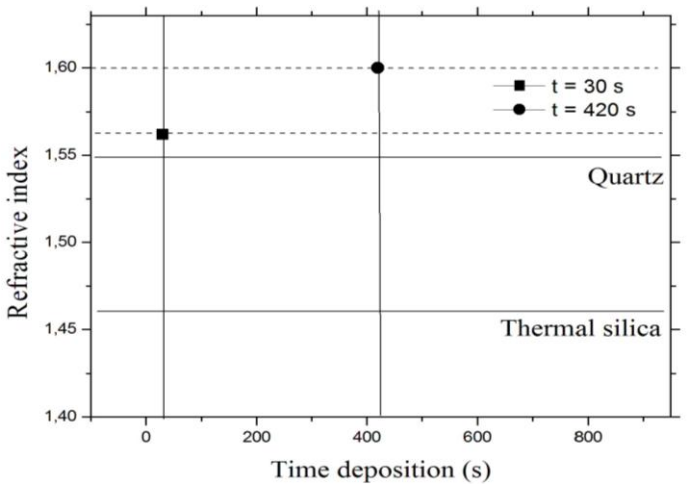

Fig 7 : Refractive index variation as a function of deposition time.

4. Conclusion

Plasma deposition technique has been used to modify the PI surface wettability and adhesion work using HMDSO thin layers. The water contact angle varies from 64° to 82° and adhesion work varies from 104.84 to 82.93 mj/m^2, indicating the organic nature of the coating. FTIR spectra showed a strong dissociation of the monomer molecules and low carbon content in the chemical structure of the deposited nano-thin films. The dispersive groups (or non-polar) such as alkane chains found in chemical structure have been held responsible for the increase of water contact angle that alter the surface state of the PI from hydrophilic to hydrophobic. The ellipsometry spectroscopic analysis showed that as a result of increasing deposition time, there is an incorporation of carbon and hydrogen in the chemical composition of the elaborated layer, which increases the refractive index from 1.58 to 1.60 and explain the decrease in the surface wettability and the work of adhesion (W_a).

Acknowledgements

The authors are grateful to Dr P. Raynaud from Joseph Fourier University of Grenoble France for his help with thickness and optical measurements.

References

[1] A. Bellel, S. Sahli, P. Raynaud, Y. Segui, Z. Ziari, D. Eschaich, G. Dennler. Improvement of the Polyimide Surface Wettability Using SiOx Films Deposited in a DECR Reactor from HMDSO/O_2 Mixtures. *Plasma Process and Polym* 2005., 2, 586-594.

[2] S.C. Cho, Y.C. Hong, S.G. Cho, Y.Y. Ji, C.S. Han, H.S. Uhm. Surface modification of polyimide films, filter papers, and cotton clothes by HMDSO/toluene plasma at low pressure and its wettability. *Current Applied Physics* 2009, 9, 1223-1226.

[3] S.J. Park, H.Y. Lee. Effect of atmospheric-pressure plasma on adhesion characteristics of polyimide film. *Journal of Colloid and Interface Science* 2005, 285, 267-272.

[4] Z.Ziari , S.Sahli , A. Bellel, Y. Segui, P. Raynaud. Simulation of Surface Potential Decay of Corona Charged Polyimide. *IEEE Transactions on Dielectrics and Electrical Insulation* 2011, 18 (5), 1408-1415.

[5] Z. Ziari, A. Bellel, S. Sahli, Y. Segui , P. Raynaud. A comparative study on the effect of VUV radiation in plasma SiO_x coated polyimide and polypropylene films. *Progress in Organic Coatings* 2008, 61, 326-332.

[6] Mi Ran Moon a, Eunkyoung Nama, Jihyung Woo, Sungwoo Lee, Kyung Park , Donggeun Jung, Hyoungsub Kimb, Hoo-Jeong Lee. Effects of surface treatments using PECVD grown hexamethyldisiloxane on the performance of organic thin-film transistor. *Thin Solid Films* 2009, 517, 4161–4164.

[7] Sanghak Yeo a, Taeheon Kwon, Changrok Choi, Heonyong Park,June Won Hyun, Donggeun Jung. The patterned hydrophilic surfaces of glass slides to be applicable for the construction of protein chips. *Current Applied Physics* 2006. 6, 267–270.

[8] S. H. Yeo, C. R. Choi and D. Jung. Investigation of Protein Adsorption Using Plasma Treatment for Protein Chips. *Journal of the Korean Physical Society* 2006.6, pp. 1325-1328.

[9] Soon Cheon Cho, Yong Cheol Hong, Soon Gook Cho. Surface modification of polyimide films, filter papers, and cotton clothes by HMDSO/toluene plasma at low pressure and its wettability. *Current Applied Physics* 2009. 9 ,1223–1226.

[10] S. Saloum, M. Naddaf, B. Alkhaled. Properties of thin films deposited from HMDSO/O_2 induced remote plasma: Effect of oxygen fraction'. *Vacuum* 2008, 82, 742–747.

[11] N. Benissad, K. Aumaille, A. Granier, A. Goullet. Structure and properties of silicon oxide films deposited in a dual microwave-rf plasma reactor. *Thin Solid Films* 2001, 384,230-235.

[12] N. Guermat, A. Bellel , S. Sahli, Y. Segui, P. Raynaud. Thin plasma-polymerized layers of hexamethyldisiloxane for humidity sensor development. *Thin Solid Films* 2008, 517, 4455-4460.

[13] Rino Morent, Nathalie De Geyter, SandraVanVlierberghe, PeterDubruel, Christophe Leys, Etienne Schacht. Organic–inorganic behaviour of HMDSO films plasma-polymerized at atmospheric pressure. *Surface & Coatings Technology* 2009, 203, 1366–1372.

[14] Matthias Wolter, Morten Hundt, Holger Kersten. Measurement of CH_4-concentration in HMDSO-containing process plasmas by quantum cascade laser absorption spectroscopy. *Vacuum* 2010, 85, 482-485.