Effect of substrate bias on the properties of plasma deposited organosilicone (pp-HMDSN) thin films

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Organosilicone thin films have been deposited by plasma polymerization (pp) in a plasma enhanced chemical vapor deposition (PECVD) system using hexamethyldisilazane (HMDSN: $C_6H_{19}Si_2N$) as a monomer precursor, at different biases of the stainless-steel substrate holder. The substrate bias affected film thickness, surface morphology, chemical composition and photoluminescence (PL) emission. For a negatively biased substrate, it is found that the film thickness is the minimum, while the porosity and PL emission are the maximum. For a positively biased substrate, the thickness and the ratio of Si/N are the maximum which correspond to a blue shift of the PL emission in comparison with the case of non-biased grounded substrate. In addition, the characterization of the plasma using a single cylindrical Langmuir probe has been performed to obtain information about both the electron density and the positive ion energy, where it can be concluded that the ion energy plays a major role in determining film thickness.
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Organosilicone thin films deposited can be obtained in plasma enhanced chemical vapor deposition (PECVD) systems, from liquid precursors such as hexamethyldisiloxane ($C_6H_{18}Si_2O$: HMDSO) and hexamethyldisilazane ($C_6H_{19}Si_2N$: HMDSN) through the plasma polymerization (pp) process. These deposited materials are well-known for their use in various technological and industrial applications, such as photoluminescence (PL) in silicon based light materials[1], hard coatings[2], gas sensing devices[3], hydrophobic surfaces[4], barrier layers[5], corrosion protection[6] and insulation layers[7]. These thin films properties can be altered according to different operations' conditions, such as plasma source type and reactor configuration, gas mixture, plasma parameters (applied power, filling pressure) and substrate conditions (temperature, applied bias). In general, the deposition process in the plasma environment involves chemical complex occurring in the gas phase and on the substrate surface. TRUNEC et al[2] studied the effect of substrate temperature on deposited pp-HMDSO thin films properties and found that increasing the substrate temperature leads to an increase in film hardness. SCHMIDT-SZALOWSKI et al[8] and SAHLI et al[9] found that the organosilicone thin film growth rate decreased with the substrate temperature increase. LI et al[10] showed that applying a negative bias to the substrate causes a decrease in the deposition rate of pp-HMDSO thin films.

In the present work, the effect of applying an external bias to the stainless steel substrate holder on the properties of pp-HMDSN amorphous thin films, which are deposited in a remote radio frequency (RF) plasma system, has been investigated. Thin films properties' study will focus on film thickness, chemical composition analysis, surface morphology and PL property.

The used remote plasma system for the deposition of pp-HMDSN thin films is described in previous works[3,6], where the used plasma source is a hollow cathode discharge (HCD) configuration (Fig.1), which is constituted of two coaxial tubes with 300 mm length and 80 mm diameter as two electrodes. The inner tube forms the RF-biased electrode and the outer one forms the grounded electrode. Both tubes are supplied with two rows of coaxial holes (hole diameter equals 3 mm) aligned to each other providing 30 plasma jets. To form the primary plasma, the supply gas is injected into the inner electrode at both ends to maintain a constant pressure along the entire electrode. Deposition has been performed in argon plasma (Ar flow rate equals 16 sccm) at 100 W applied RF power, for 12 sccm HMDSN flow rate, for 20 min deposition time and at 8 Pa total pressure. The substrate holder, which is made of stainless-steel, has been biased negatively (V_s=−10 V), positively (V_s=+10 V) and without bias (grounded, V_s=0). So the samples will be given the labels S_{10n}, S_{10p} and S_0, respectively. The deposition has been carried out on silicon substrates for studying the properties of thickness, surface morphology and PL emission, and on aluminum substrates for the study of the elemental composition of deposited thin films.

The thicknesses of the deposited thin films have been measured using cross-sectional method in scanning electron microscope (SEM-TSCAN VEGA\\XMU). The surface morphology of deposited thin has been studied

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using atomic force microscope (AFM-Park Scientific Instruments AP-0100) and the obtained images have been analyzed using Gwyddion free software. The chemical composition has been obtained using an SEM-energy dispersive X-ray spectroscopy (EDS). The PL spectra were measured at room temperature (RT) in a SPEX monochromator having a He-Cd laser as an excitation source with 325 nm excitation wavelength.

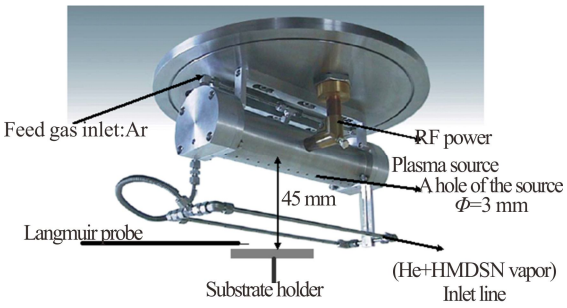


Fig.1 Image of the HCD source inside the plasma chamber, the positions of feed gas and HMDSN vapor lines, the substrate holder and Langmuir probe

Fig.2 gives the cross-sectional SEM images of the studied pp-HMDSN thin films, accompanied with the evolution of film thickness as a function of the substrate bias. One can observe a clear effect of the substrate bias on the film thickness, which are the maximum for positively biased substrate and the minimum for the negatively biased one. Film thickness equals 68 nm, 85 nm and 107 nm for the samples of S_{10n}, S_0 and S_{10p}, respectively. To explain this great influence of substrate bias on film thickness, we refer to the plasma parameters, namely electron density (n_e) and ion energy (E_i), where these two parameters can be determined by using single cylindrical Langmuir probe measurements which provide the current-voltage (I-V) characteristics of the plasma as described in details in Ref.[11]. The probe has been located just above the substrate holder. The positive ion energy in the plasma is given by the relation[12]

$$E_i=e(V_p-V_s), \quad (1)$$

where e is the electron elementary charge, V_p is the plasma potential and V_s is the substrate bias. The values of the measured V_p were 28 V, 30 V and 35 V for the samples of S_{10n}, S_0 and S_{10p}, respectively. Fig.3 illustrates the Langmuir probe characteristics (I-V) with the inset giving both the resulted electron density (n_e) and the ion energy (E_i), where it can be seen that both of them decrease with substrate bias increase. It was reported that the thin film surface bombardment by positive ions (here, argon ions: Ar^+) coming from the plasma causes a physical sputtering of the thin film during deposition[10,12]. PRSKALO et al[13] reported that the physical sputtering of the silicon nitride thin film occurs when argon ion energy is higher than its physical sputtering threshold (≈20 eV). Our deposited material is silicon nitride-like thin film[1], and the obtained ion energy is higher than 20 eV (as seen from the inset of Fig.3), thus the physical sputtering of the deposited thin films occurs for all samples. Comparing the behavior of film thickness (inset of Fig.2) with that of ion energy (inset of Fig.3) as a function of substrate bias, one can conclude that the films thickness is inversely proportional to ion energy. Although the decrease of electron density (n_e) induces less fragmentation of the precursor in the discharge plasma and consequently a lower expected film thickness, it seems that the ion energy plays a predominant role in determining the film thickness due to the sputtering effect of the deposited material.

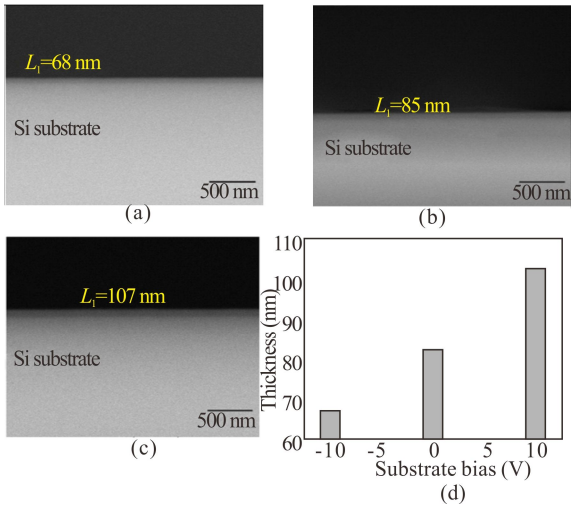


Fig.2 SEM images with a cross-section method for studied samples of (a) S_{10n}, (b) S_0 and (c) S_{10p} accompanied with (d) deduced film thickness

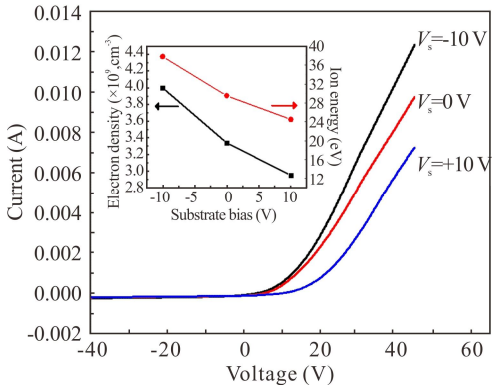


Fig.3 *I-V* characteristics of Langmuir probe for different substrate biases (-10 V, 0 V and +10 V) (The inset shows the deduced ion energy and electron density)

Fig.4 exhibits the EDS spectra of the prepared samples of S_{10n}, S_0 and S_{10p}, and the spectra are shifted for clarity. The formation of deposited pp-HMDSN thin film on Al substrate is established through the detection of the elements of C, N, and Si, in addition to Al which comes from the substrate. The apparition of oxygen in the spectra indicates the absorption of ambient oxygen and humidity in the film structure soon after its preparation[14]. The atomic concentrations (at%) of the

detected elements in the film structure (C, O, N and Si) have been evaluated after the deduction of the substrate contribution, and the results are given in Tab.1, where one can observe an increase of the concentrations of the elements C, N and Si, which are originated for the precursor (HMDSN), probably due to the decrease of the energy of ions that bombards the thin film surface, and a decrease of the concentration of incorporated atmospheric oxygen into the film structure with the substrate bias increase.

Fig.5 exhibits the two-dimensional (2D) AFM images (scan area: 0.95 μm×0.95 μm) of the prepared samples of S_{10n}, S_0 and S_{10p}, at different substrate biases of −10 V, 0 V and +10 V, respectively. The images are accompanied with their related height distribution histograms which reveal, to a certain degree, that an uniformity (a quasi symmetric Gaussian height distribution) of the deposited film surface exists for all the samples, where the related kurtosis (R_{Ku}: characteristic of surface sharpness) and skewness (R_{Sk}: characteristic of profile symmetry) were found to have values close to 3 and 0, respectively, which reveals the quasi uniformity of deposited pp-HMDSN thin film, for sample S_{10n}, R_{Ku}~3.1 and R_{Sk}~0.2, for sample S_0, R_{Ku}~2.9 and R_{Sk}~−0.1, and for sample S_{10p}, R_{Ku}~3.0 and R_{Sk}~0.2. It is well known that when the height distribution is Gaussian, we have R_{Ku}=3, and when it is symmetrical, we have R_{Sk}=0[15]. Tab.2 summarizes the AFM analysis which involves the surface root-mean-roughness (*RMS*), the mean grain size and the surface porosity (the ratio between the area of pores to the total analyzed surface area). The AFM images and height distribution histograms reveal the formation of nanostructured deposited thin films, where the grain size varies between 8 nm and 10 nm and the height of grains varies between 2.7 nm and 5 nm. One can notice that there isn't a significant effect of the substrate bias on grain size. Generally, the substrate bias enlarges the grains due to the increase of surface mobility caused by the enhancement of the particles' kinetic energy which impacts the thin film surface[16], this isn't confirmed in our study, which maybe because the applied substrate bias isn't high enough, where this bias seems to affect more the kinetics of electrons and ions rather than the neutral particles involved in the film growth.

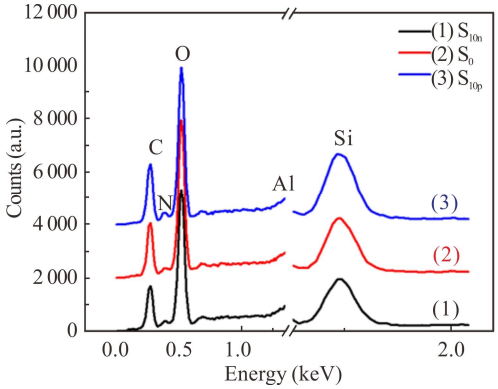
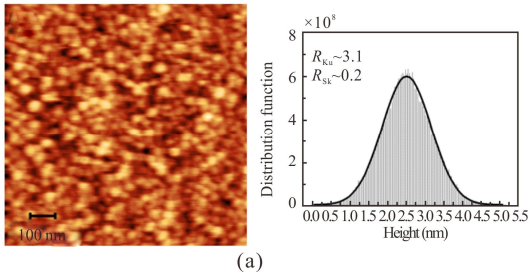


Fig.4 EDS spectra of the prepared samples of S_{10n}, S_0 and S_{10p}

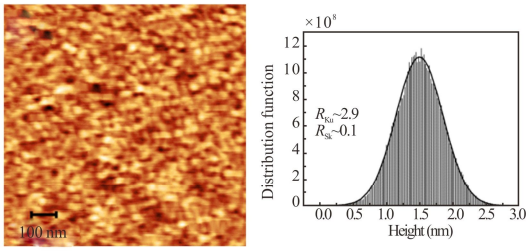
Tab.1 Atomic percentages of the detected elements in the deposited pp-HMDSN thin film as a function of substrate bias

Sample	C (at%)	N (at%)	O (at%)	Si (at%)	Si/N
S_{10n}	62.0±0.5	5.7±0.2	25.3±0.3	7.0±0.2	1.23
S_0	62.5±0.5	6.0±0.2	24.3±0.3	7.2±0.2	1.20
S_{10p}	63.0±0.5	6.2±0.2	22.8±0.3	8.0±0.2	1.29

The deposited pp-HMDSN thin films are relatively smooth (low roughness, *RMS*<1 nm). The deposited pp-HMDSN thin film at a negative substrate bias (S_{10n}), which corresponds to the highest ion energy bombarding the substrate (Fig.3), exhibits the most porous (6%) and rough (*RMS*=0.7 nm) nanostructure due to the attack of surface by argon ions. The porosity of sample S_{10p} is greater than that of S_0, which isn't expected because the ion energy for S_0 is greater than that for S_{10p}, which can be understood through the existing competition between film deposition (precursor fragmentation by electrons) and film etching (surface attack by energetic ions).



(a)



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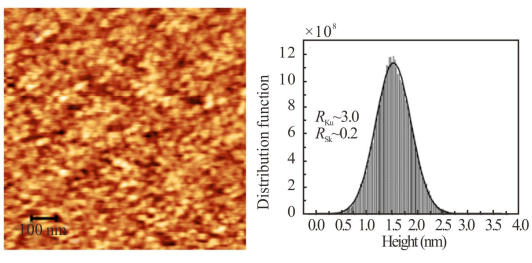

(c)

Fig.5 2D AFM images (0.95 μm×0.95 μm) of prepared samples of (a) S_{10n}, (b) S_0 and (c) S_{10p} (left) accompanied with their histograms of height distribution (right)

Tab.2 Surface morphology parameters of the deposited pp-HMDSN thin films as a function of substrate bias

Sample	*RMS* roughness (nm)	Surface porosity (%)	Mean grain size (nm)
S_{10n}	0.7±0.02	6.0±0.2	12.0±1.0
S_0	0.5±0.02	2.0±0.1	8.0±1.0
S_{10p}	0.5±0.02	4.0±0.2	10.0±1.0

Fig.6 gives the PL spectra at RT of the prepared samples of S_{10n}, S_0 and S_{10p}, which exhibit a broad band centered at 574 nm, 592 nm and 544 nm, respectively, in addition another peak appears at 485 nm in all samples, which can be interpreted by the excess of carbon content[17-19] in the films structure as revealed by EDS analysis (Tab.1). The inset of the figure shows the evolution of both the energy gap (1 239.7/λ) of the central peak and the peak intensity as a function of substrate bias. The existed blue shift of the PL emission can't be attributed to quantum confinement effect (the blue shift follows the reduction of the grain size)[20], because there isn't a grain size effect (Tab.2). Therefore, this PL emission can be attributed to the luminescent defect centers in the structure and to the chemical complexes existing within the film matrix[17-19]. AUGUSTINE et al[19] reported that the evolution of the energy band gap can be correlated to silicon content (ratio Si/N), which is the case in our samples by referring to Tab.1. Regarding the evolution of the PL peak intensity, it doesn't have a clear dependence on film thickness, but it seems to be correlated to the film porosity (Tab.2). Indeed, the porosity enhances the surface area, which is exposed to surface chemistry modifications due to interactions of thin film nanostructures with the atmospheric air enhancing the formation of PL centers. In particular, those are originated from oxygen-related PL mechanisms[21].

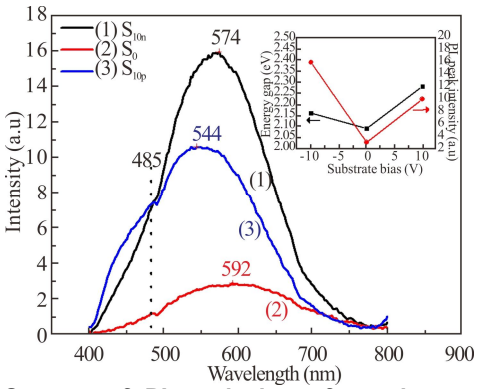

Fig.6 Spectra of PL emissions from the prepared samples of (a) S_{10n}, (b) S_0 and (c) S_{10p} (Inset shows the variation of energy gap and PL peak intensity as a function of substrate bias)

Organosilicone pp-HMDSN thin films were deposited in RF remote PECVD system, using argon as a feed gas and HMDSN as a precursor. The effect of substrate bias on the properties of the deposited thin films has been investigated. It was found that the ion energy bombarding the substrate plays a key role in the deposition process. The film thickness decreases with substrate bias decrease, it is the minimum for negatively biased substrate. The concentrations of C, N and Si elements in the deposited material increase with substrate bias increase. The porosity of film surface is affected by the substrate bias variation and it is the maximum for negatively biased substrate. The PL emission of the deposited films has been interpreted through the chemical composition and the surface morphology, where it was found that the energy gap of the central peak emission follows the variation of ratio Si/N, while the PL intensity is correlated to the surface porosity.

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Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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