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NANOPARTICLES GROWTH IN DUSTY PLASMAS FROM ORGANOSILICON PRECURSOR

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ABSTRACT

In this work, plasma discharge has been generated from pure HMDSO precursor in low frequency reactor. It has been observed that a cloud of Nanoparticles could be formed in a plasma discharge for some deposition parameters such as discharge power, time and pressure. Discharge signal analysis have been used in order to investigate the effect of deposition parameters on the nanoparticles growth. The study of discharge signal analysis shows that the pulse frequency is strongly related to plasma composition. Their value shifted from about 170 Hz to 250 Hz according to deposited parameters. This shift has been attributed to the nanoparticles formation in the plasma reactor. On the other hand, Nanoparticles embedded in thin films have been characterized by EDX and FTIR spectroscopy in order to reveal the NP's composition.

Key Words: *Nanopowders, Dust, growth mechanism, PECVD*

NOMENCLATURE

Symbols :

F_p Pulse Frequency, Hz

P pressure, mbarr

Abbreviations:

HMDSO Hexamethylidisiloxane

NPs Nanoparticles

1. INTRODUCTION

Since the first observation of Nanoparticles, they were considered as harmful or impurities in microelectronics technology. In previous works¹, Nanoparticles (NPs) have been observed encapsulated in thin layers, the chemically active species allow to grow particles or to modify their surface properties², which leads to form new materials. However, the fact that plasma process mechanism leads to powder formation in plasma discharge is not yet fully investigated. Many studies were made in order to better understand the mechanism of nanoparticles formation in plasma discharge. In this paper, a study based on plasma enhanced chemical vapor deposition (PECVD) as a deposition technique and Hexamethylidisiloxane (HMDSO)as precursor is conducted using discharge signal analysis in order to find the best conditions to create NPs. To gain more information about the composition of new material (NPs) an Energy Dispersive X-ray spectroscopy analysis were made.

2. EXPERIMENTAL METHOD

2.1 Creation of particles in dusty plasma:

The plasma discharge was generated using a pulsed wave generator that has a power range from [6 – 26] W and a wave frequency of 33 KHz. The pressure of HMDSO vapor has been varied in the range of [0.2 - 1] mbar. Moreover, deposited time has been varied from 2 to20 min. The plasma polymerized thin layers were

deposited on intrinsic silicon. Fig.1 presents the PECVD reactor used in this study. it is described in a more detailed way elsewhere ¹.

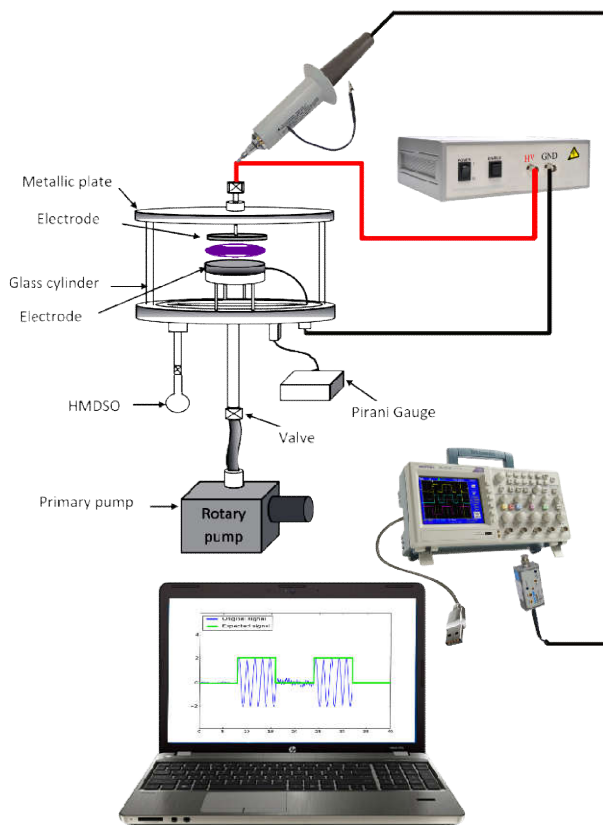


FIGURE 1: DESCRIPTION SCHEMATIC OF THE EXPERIMENT

2.2 Film Characterization

The pulse frequency is monitoring using Tektronix TDS2024C and a high voltage probe (P6015A). The variation of this parameter is used in order to investigate the discharge signal analysis during plasma discharge. Chemical structure and composition of deposited thin layers were characterized by means of FTIR spectroscopy using a Thermo Nicolet Avatar 360 spectrometer. To characterize the evolution of the surface morphological feature of the coated film, scanning electron microscopy (JEOL JMS-7800F) has been used.

3. RESULTS

3.1 Discharge Signal Analysis:

The applied signal used to generate plasma discharge is composed of two types of signals; pulse signal and wave signal. it is more described in Fig2a). This figure shows theoretical signal delivered by pulsed wave generator. The pulse frequency is considered as the envelope frequency (it is represented by green line) and the wave frequency is the applied signal frequency (it is represented in a blue line).

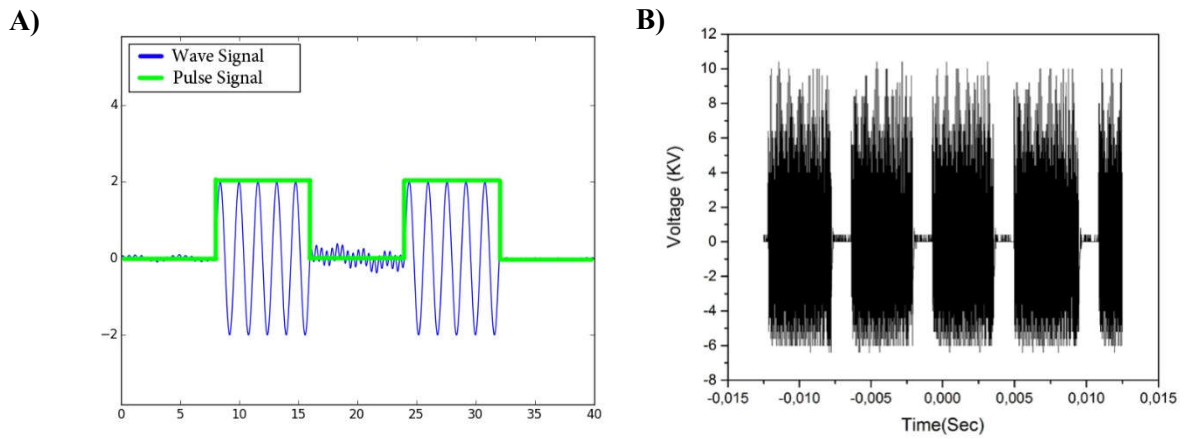


FIGURE 2: A)THEORETICAL PULSED WAVE SIGNAL, B)EXPERIMENTAL PULSED WAVE APPLIED SIGNAL.

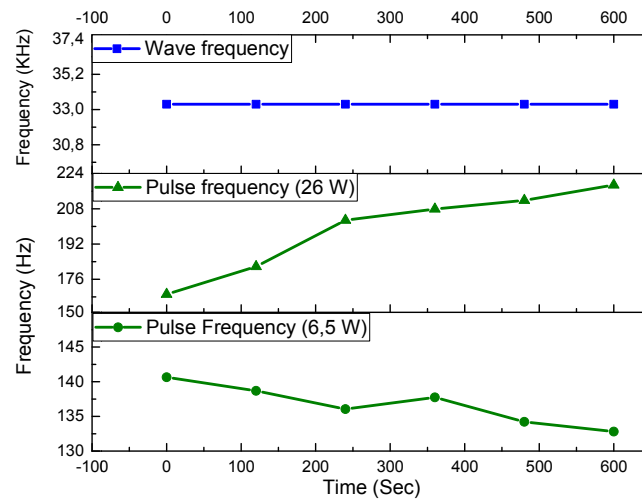


FIGURE 3: PULSE FREQUENCY VARIATION DURING DEPOSITION OF THIN FILM (0.4 MBAR, 10 MIN)

Fig.3 shows both frequencies' (pulse and wave frequency) value evolution as a function of different depositions parameters. It can be observed that wave frequency remained constant with $f_w=33$ kHz, which is the set value used in this experiment. Whereas for the measured pulse frequency (f_p) as a function of depositions parameters, it has been observed that f_p value is strongly linked to deposited parameters. We notice that f_p increases for high power discharge 26 W and decreases for low power discharge 6,5 W. The deposited thin layer is represented with a parallel RC, the resonance frequency of such circuit is: $f_r = \frac{1}{2\pi RC}$. So the pulse frequency is the resonance frequency of the discharge. It explains the increase of pulse frequency at high applied power by the decrease of the impedance due to the high fragmentation of the gas in plasma. However, pulse frequency decreases when the impedance increases at low applied power due to the low fragmentation.

At dusty plasma which is related to the presence of nanoparticles, the discharge seems to be more resistive. Also, the primary species of the nanoparticles tend to have negative ion properties because they must be charged in order to accumulate³. This property implicates the use of nanoparticles impedance that is parallel to the plasma impedance. In Fig.4 A), the pulse frequency at 6.5 W seems to be constant during plasma discharge. While it changes with the increase of pressure in the plasma reactor. The rising of pressure leads to high impedance values which cause low pulse frequency.

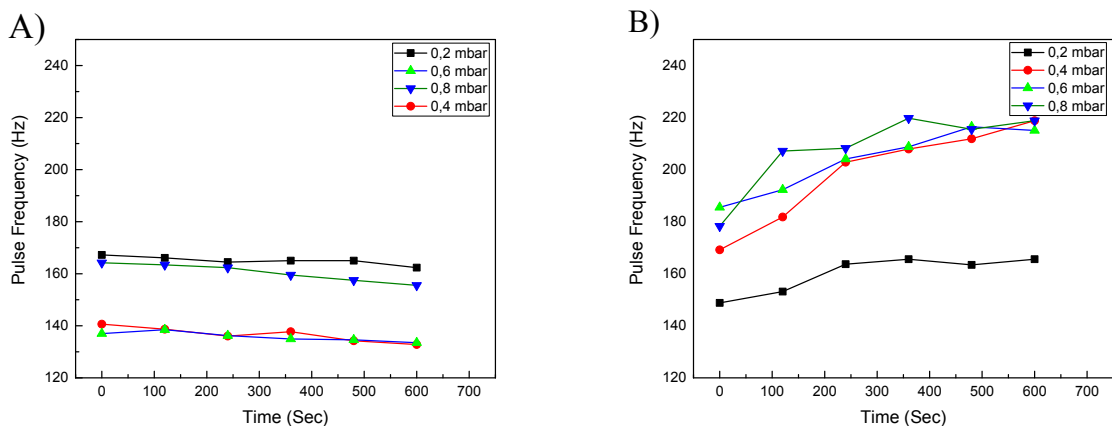


FIGURE 4: PULSE FREQUENCY VARIATION FOR 10 MIN, A) 6.5 W. B) 26W.

On the other hand, following Fig.4B), pulse frequency increases from 175 Hz to 220 Hz beyond pressure of about 0.4 mbar. The shift of pulse frequency towards a value of about 220 Hz is observed for all conditions that Nanoparticles appear in the plasma discharge (dusty plasma). Therefore, from the discharge signal analysis it can be suggested that pulse frequency value variation may indicate the formation of NP's in plasma discharge.

3.2 FTIR analysis:

Figure 5 shows the infrared spectra of films for two different deposition time: 2 and 20 minutes. The wavenumber of the main absorption bands were collected and identified in Table 1^{4, 5}. The spectra revealed the presence of asymmetric stretching vibrations (2969 cm^{-1}), groups of Methylsilil at 1515 cm^{-1} (asymmetric deformation of CH_3 in $(\text{Si}(\text{CH}_3)_x)$), around 1268 cm^{-1} (symmetric deformation of CH_3 in $(\text{Si}(\text{CH}_3)_x)$). Presence of Si-O-Si groups around $1080\text{--}1020\text{ cm}^{-1}$ which is characteristic of the original organosilicon compound $((\text{CH}_3)_3\text{-Si-O-Si-(CH}_3)_3)$. The presence of SiH (2238 cm^{-1}) its formation is explained by multiple step reactions in the plasma phase⁴. Small amount of C=O is observed in films with a deposition time of 20 mins, this also explained by the total fragmentation of the original organosilicon molecule. Between the two samples 2 and 20 mins the last have a surface covered with powder, and we have mention in recent work that SiH molecule is a sign of powder creation⁶. The absence of SiH is linked with the absence of powder (nanoparticles or dusty plasma) in samples of deposition time of 2 mins. Next we intend to know the composition of these nanoparticles.

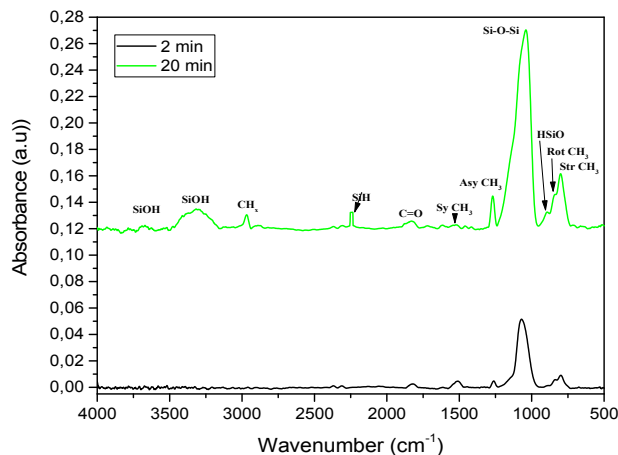


FIGURE 5: INFRARED SPECTRA OF FILMS DEPOSITED IN PLASMAS OF PURE HMDSO

Wavenumber (cm-1)	Mode
3727.7	OH stretching in free SiOH
3315	OH stretching in free SiOH
2969.8	C-H asymmetric stretching in CH ₃
2308.3	C=O
2238.95	Si-H stretching
1828.1	C=O
1515.7	CH ₃ asymmetric deformation in Si(CH ₃) _x
1268.9	CH ₃ symmetric deformation in Si(CH ₃) _x
1080 – 1020	Si-O asymmetric stretching in Si-O-Si
898.66	HSiO hybrid vibrations
846.59	-CH ₃ rotation in Si-(CH ₃) ₃ [Si-C]
798.38	-CH ₃ stretching in Si-(CH ₃) ₂ and Si-O in stretching Si-O-Si

TABLE 1: ABSORPTION BANDS DETECTED IN THE INFRARED SPECTRA OF PLASMA-POLYMERIZED FILMS FROM PURE HMDSO

3.3 EDX analysis:

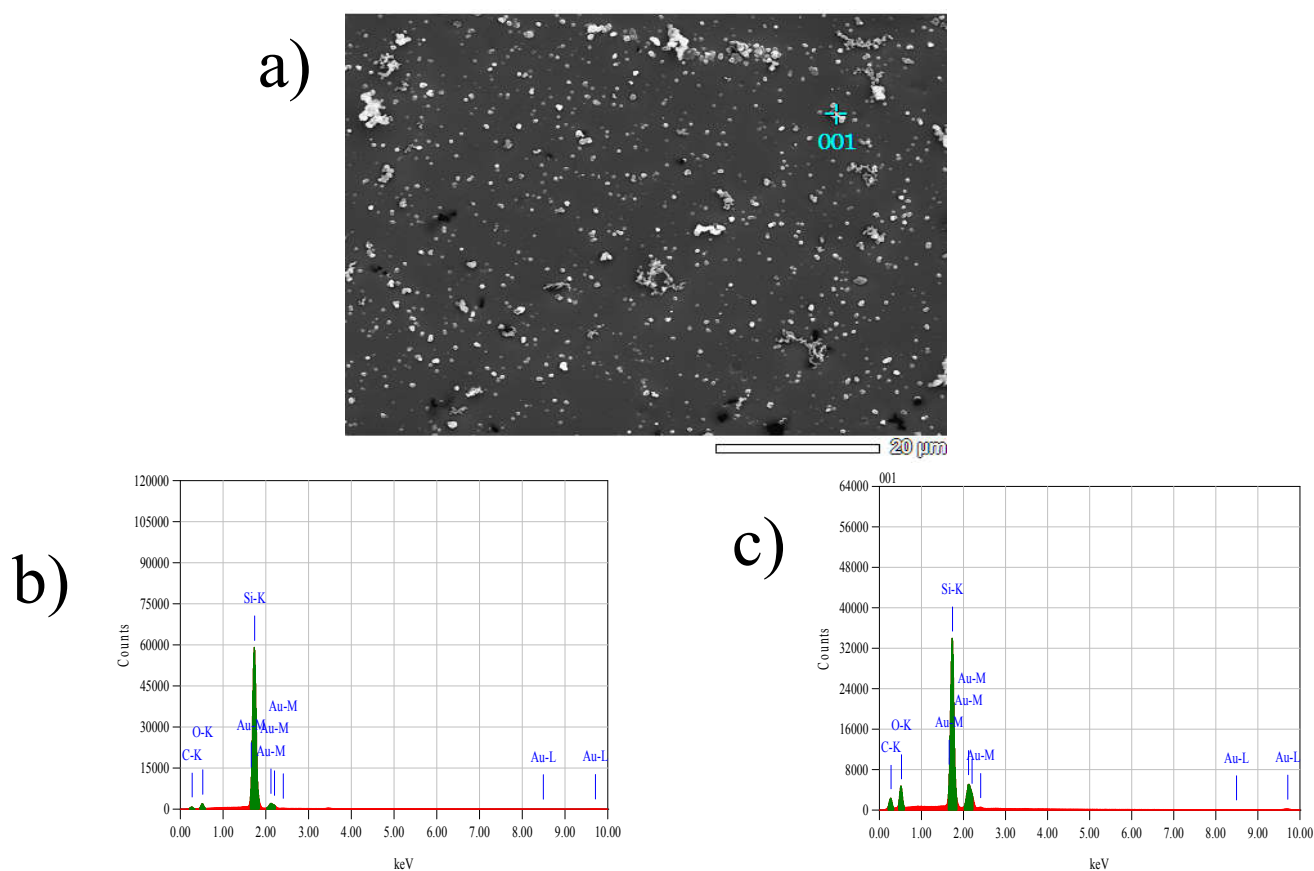


FIGURE 6: A) SEM MICROGRAPH FOR NANOPARTICLES (26 W, 0.2 MBAR, 10 MIN), B) AND C) EDX SPECTRUM OF THE SURFACE AND OF THE NPS RESPECTIVELY.

The composition of the thin layer produced is definitely formed of carbon, Hydrogen, Oxygen and silicon according to the precursor we used (HMDSO); the nanoparticles has the same composition. An EDX analysis was made to confirm the composition of the surface in the presence of NPs and on the NPs themselves, Fig. 6 a) represent the surface with nanoparticles where the first EDX spectrum is made (B) and the point (001) on nanoparticles is where the second EDX spectrum is made (C), the amount of Si decreases in NPs (29.13 %) compared to the amount of Si in all surface (58.58 %), it may be explained by using a silicon substrate. The amount of C (29.81 %) and O (21.76 %) increases in nanoparticles compared to the amount of C (20.02 %) and O (11.10 %) in all surface.

4. CONCLUSIONS

In this work we have investigated the Nanoparticles growth process in the plasma discharge according to some deposition parameters. First we determined the best parameters to create nanoparticles based on the pulsed frequency of the discharge signal. It has been observed that the pulsed frequency is highly linked to plasma composition, also these last is related to plasma impedance. The formation of NP's in the plasma leads to the shift of pulse frequency from 170 Hz to [215 – 235] Hz. Finally, using EDX analysis to know the nanoparticles composition, the results reveal that nanoparticles contain more oxygen and carbon molecules and less silicon molecules compared to the composition of the thin layer.

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