Journal of Optoelectronics and Advanced Materials Vol. 7, No. 4, August 2005, p. 2159 - 2164

Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

SIO_2 - LIKE THIN FILMS GENERATION IN CORONA DISCHARGES IN AIR AT ATMOSPHERIC PRESSURE: IR SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY INVESTIGATIONS

A. Groza, A. Surmeian*, M. Ganciu, R. Medianu, I. I. Popescu

Institute of Atomic Physics-INFLPR, P.O.Box MG 36, Bucharest 077125, Romania

This paper demonstrates that the coupling between negative and positive corona discharges in air at atmospheric pressure can be used as a physical method for SiO_2 thin films generation, having an organo-silicon compound (silicone oil) as precursor.

(Received July 4, 2005; accepted July 21, 2005)

Keywords: Infrared spectroscopy, Corona discharge, Plasma applications

1. Introduction

In air at atmospheric pressure, the negative and positive corona charge injection at the free surfaces of different dielectric fluids introduced in the discharge, attack their chemical structure inducing new solid compound formation [1].

This paper demonstrates that by alternating the injection of positive and negative ions on the free surface of a silicone oil drop introduced in the positive and respectively negative corona discharge in air at atmospheric pressure and ambient temperature, amorphous SiO_2 thin films are generated. The influence of the charge type and density of the injected ions on the chemical structure and surface topography of the organosilicon compound has been studied by IR spectrometry and atomic force microscopy (AFM).

In the last years, the interest on the chemical and physical methods for SiO_2 thin films generation has notably increased, such films being used for insulation, anti-refection, corrosion resistant, self-lubricant or tightening coating. Compared with the chemical methods the main advantage of the physical method presented in this paper is that the SiO_2 films obtained from silicone oils precursors under positive and negative corona charge injection may uniformly coat any polished and unpolished complex metallic surfaces by penetrating the electrode surface pores.

2. Experimental conditions

The experimental set-up used is presented in Fig. 1.

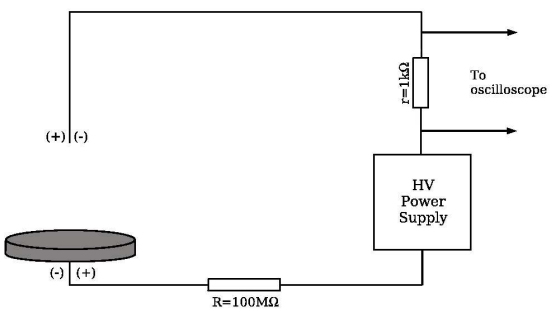


Fig. 1. Experimental set-up.

* Corresponding author: surmeian@infim.ro

The electrode discharge configuration was of wire-to-plane type. The copper wire electrode of 40 mm length was situated in air at atmospheric pressure perpendicular to the center of a germanium disk electrode of 22 mm diameter. The interelectrodic gap was 8 mm. In order to avoid any environmental air movement in the interelectrodic gap, the electrodes were introduced in a glass cage. A DC high voltage of 24 kV was applied through a resistor R = 100 MΩ.

The temporal evolution of the current discharge in both negative and positive corona discharge was visualized on a Tektronics 320 oscilloscope. The discharge current in a Trichel pulsed regime of the negative corona discharge, measured across a resistor r = 1 kΩ (the Trichel pulses being accompanied by a DC permanent current), is presented in Fig. 2. The pulsating nature of the current is due to phenomena involved in charged-particles movement. When a high DC negative voltage is applied to the sharp electrode, the surrounding air becomes ionized. The charged particles created in this way form a cloud drifting along the field lines. Due to both geometric effect and local presence of these clouds, the electric field between electrodes is strongly nonuniform and varies with time as successive clouds drift from one electrode to the other. Unlike the negative corona discharge, the current of the positive corona discharge consists only in a DC component having the same value as that of the permanent current of the negative corona discharge in the given electrical and geometrical conditions.

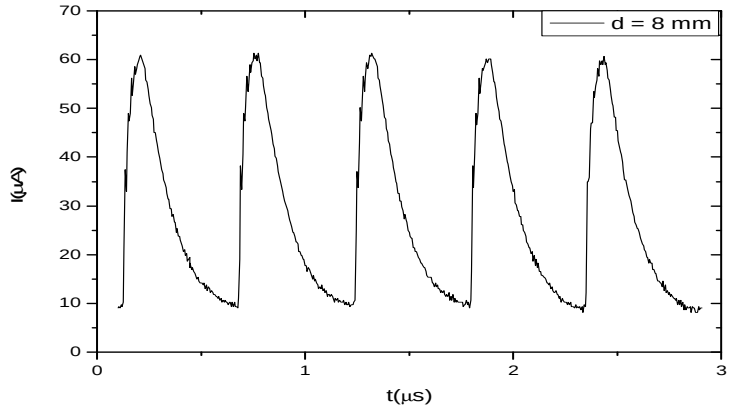


Fig. 2. The waveform of the negative corona discharge current.

By introducing a dielectric fluid in a corona discharge, the negative and positive ions injection on the free surface of the liquid induces electrohydrodynamic instabilities associated to high electric fields. As a result, the convective currents generated in the liquid bulk provide the charged particles transport to the plane electrode [2, 3].

The effect of positive and negative ions on the structure and surface topography of the organosilicon compound was investigated by transmission IR spectrometry using an IR spectrophotometer Specord IR 75 (Carl Zeiss Jena), and atomic force microscopy (AFM) using a Nomad Microscope (Quesant Instrument Corporation) operating in a contact mode.

3. Results and discussions

A silicone oil drop (1μl) was stretched in a thin layer on a germanium support under positive and respectively negative corona charge injection.

The IR spectra of the organosilicon compound irradiated at different time intervals indicate the processes induced by the corona charge injection in the compound bulk which lead to an amorphous SiO_2 cross-linked network formation. The IR spectrum [4] of the silicone oil used in this experiment is presented in Fig. 3.

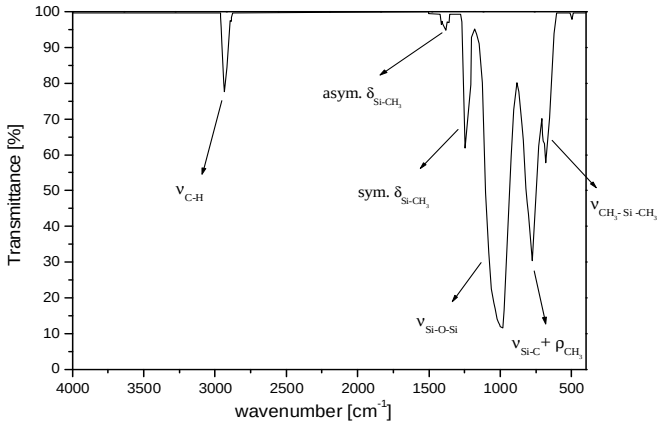
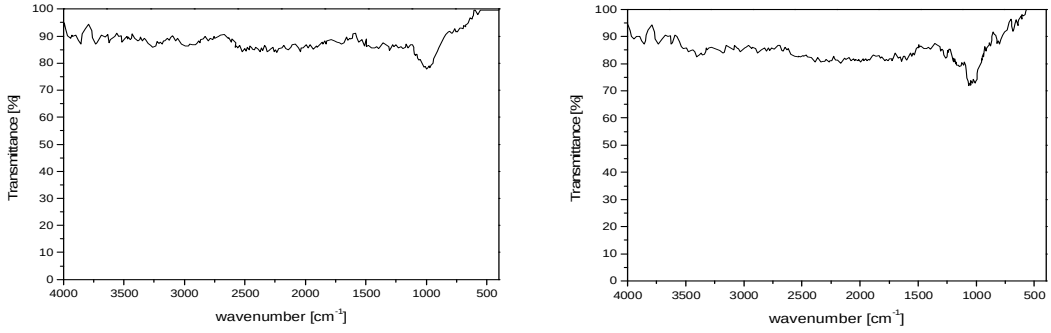


Fig. 3. The IR spectrum of the silicone oil.

In positive corona discharge, the positive ions (N_2^+, O_2^+) [5], on their way to the negative plane electrode attack the silicone oil chemical structure breaking C-H and Si-C bonds. Fig.4a presents the IR spectrum of the solid compound obtained after 2 hours of positive charge injection. No Si-H, Si-OH, and Si-C vibrational bands are observed. The spectrum is dominated by the vibrational band at 1100 – 1000 cm^{-1} assigned to Si-O-Si asymmetric stretching mode. The band peak position at 1000 cm^{-1} frequency indicates a Si-O-Si bond angle of 123^0 ($\nu = 1134\ cm^{-1} \sin(\theta/2)$, where θ is Si-O-Si bond angle [6]). The broadening of the 1100 – 1000 cm^{-1} vibrational band, which can be observed in the spectrum, demonstrates that bonds rearrangements and cross-linking occur within the compound bulk. For Si-O based compounds the Si-O-Si vibrational band at 1200-900 cm^{-1} is attributed to an amorphous cross-linked SiO_2 network formation [7, 8].

Increasing the irradiation time to 10 hours, further bonds rearrangements generate an ordering of the Si-O bonds in the network observed by the decrease in the half width of Si-O-Si asymmetric stretching vibrational band [9], Fig.4b. In the same time the band peak position is shifted to 1060 cm^{-1} which corresponds to a Si-O-Si bond angle of 138^0. Because in the amorphous network the Si-O-Si bond angle is flexible ($120^0 < \theta < 180^0$) [6,7] and the polarizing effect induced by positive corona electric field favorites the break of C-H and Si-C bonds, the rearrangements and the ordering of $Si^+ - O^-$ bonds could be explained.



a) b)

Fig. 4. IR spectrum of the SiO_2 film obtained after a)2 hours; and b) 10 hours of positive corona charge injection.

The AFM images of the organosilicon compound subject to positive ions injection, Fig. 5, show some irregular structures grown on the SiO_2 layer surface obtained after 2 hours of irradiation, Fig. 5a, which are increasing with the irradiation time, Fig. 5b.

The AFM images and the IR spectra of the SiO_2 compound obtained in the same temporal and type of charge injection conditions, indicate that the irregular structures grown on the SiO_2 layer surface could be associated to the redistribution and ordering of the Si-O bonds in the amorphous SiO_2 network.

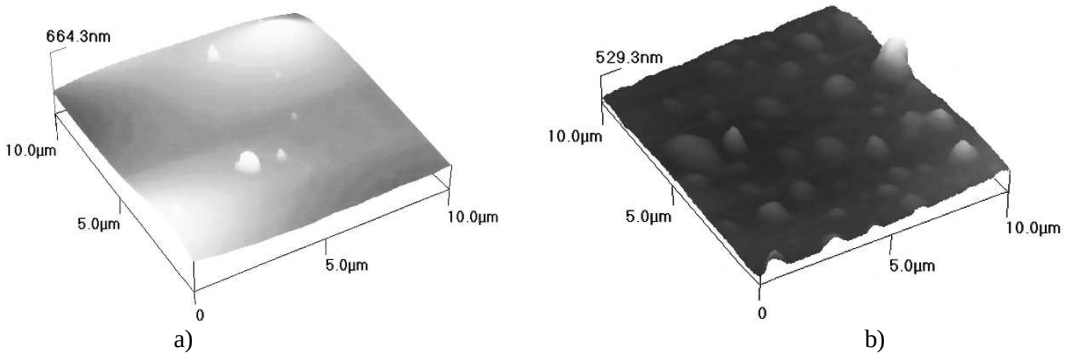


Fig. 5. AFM image of the SiO_2 layer obtained after a) 2 hours; b) 5 hours of positive corona discharge irradiation.

The amorphous SiO_2 compound obtained in positive corona discharge was subjected to negative corona charge injection. The effect of the negative ions , O_2^-, O_3^-, injection consists in the decrease of the C-H and Si-C vibrational bands intensity and in the formation of a new Si-O band at about ~ 800 cm^{-1} [10].

After 2 hours of negative ions injection the IR spectrum, Fig. 6a, presents a new broad Si-O band. The position and the broadening of the vibrational band assigned to the Si-O-Si asymmetric stretching was not altered. These indicate that after 2 hours of negative ions injection, the Si-O bond angle was not changed and consequently the network formed after 2 hours of positive ions injection either.

Fig. 6b presents the IR spectrum of the amorphous SiO_2 compound obtained after 10 hours of positive ions injection followed by another ten hours of negative ions injection. The increase of the negative ions density at the amorphous SiO_2 layer surface leads to the increase of the new Si-O bonds number and in the same time the Si-O-Si bond angle got altered. The band peak shift from 1060 cm^{-1} back to 1000 cm^{-1} means that the Si-O-Si bond angle decreases to the value it had before than the Si-O bonds ordering has been induced by positive corona long time period irradiation (10 hours). The effect could be explained by the fact that negative corona electric field with the positive polarity on the plane electrode affects the redistribution process favorizing the Si-O bonds network relaxation. Consequently, the processes induced by 10 hours of positive ions injection followed by 10 hours of negative ions injection influence each other and do not cumulate.

The IR spectrum of the SiO_2 compound obtained after 10 hours of negative ions injections, Fig. 6c, coupled with 10 hours of positive ions injection, Fig. 6d, indicates the formation of the new Si-O vibrational band and the shift of the Si-O-Si asymmetric stretching vibrational band peak from 1000 cm^{-1} to 1060 cm^{-1}. Unlike the processes occurring after 10 hours of positive ions injection coupled with 10 hours of negative ions injection, the Si-O bonds generation and arrangements processes involved in the SiO_2 thin film obtained after 10 hours of negative ions injection coupled with 10 hours of positive ions injection are independent and cumulative. The spectrum is similar to the IR spectrum of the SiO_2 film obtained by the method of thermally grown SiO_2 films [11, 12].

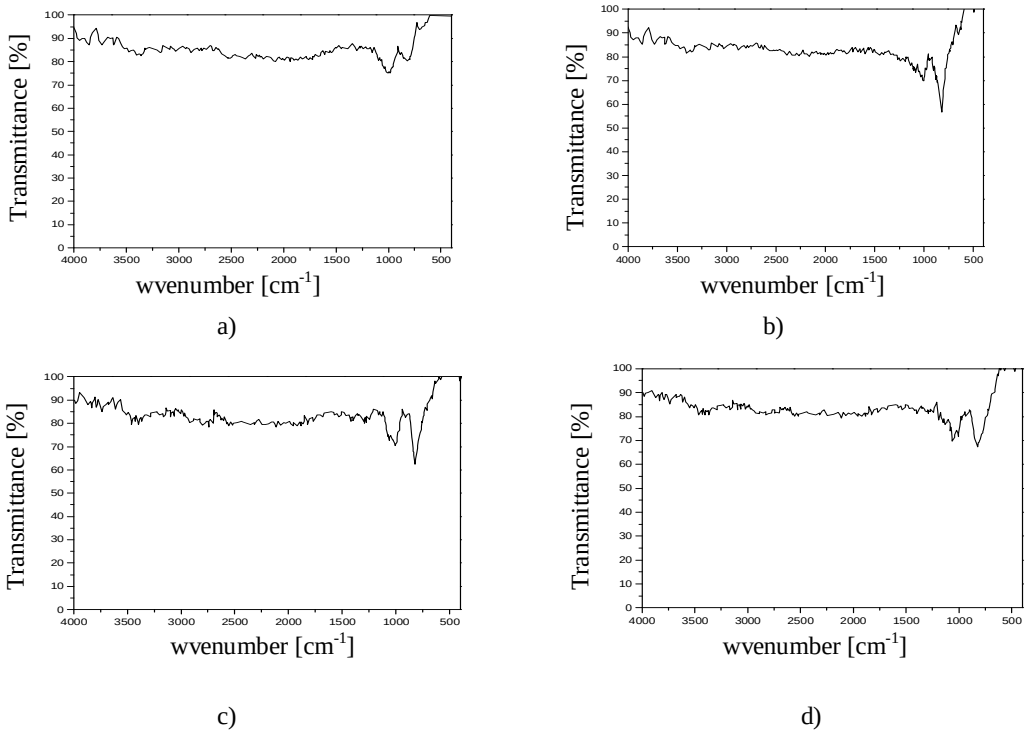


Fig. 6. The IR spectrum of SiO_2 film obtained after: a) 2 hours of positive followed by 2 hours of negative corona charge injection; b) 10 hours of positive followed 10 hours of negative corona charge injection c) 10 hours of negative corona charge injection; d) 10 hours of negative followed by 10 hours of positive corona charge injection.

The AFM images and the IR spectrum of the SiO_2 layers obtained after 20 hours of positive and negative corona charge injection (Fig. 7a and Fig. 6b respectively) and after 20 hours of negative and positive corona charge injection (Fig. 7b and Fig. 6d respectively), indicate that the irregular structures grown on the SiO_2 layer are due to the redistribution and ordering of the Si-O bonds in the amorphous network even when new Si-O bonds are generated in the bulk compound.

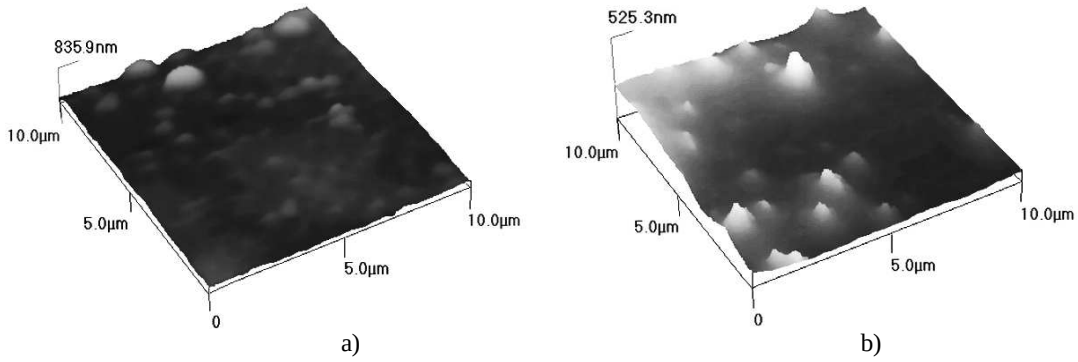


Fig. 7. AFM images of the SiO_2 compounds obtained after: a) 10 hours of positive followed by 10 hours of negative corona charge injection b) 10 hours of negative followed by 10 hours of positive corona charge injection.

4. Conclusions

It was demonstrated by IR spectrometry the effect of the positive charge injection on the organosilicon compound bulk: the SiO_2 cross-linked network formation and the increasing of the rearrangements and ordering of Si-O bonds with irradiation time.
It was emphasized the possibility to increase the oxygen concentration in the compound bulk by negative charge injection.
Using the effects of negative charge injection followed by positive charge injection an ordered Si-O network in SiO_2 thin films was obtained.

Acknowledgements

The authors thank S. Georgescu for technical support.

References

[1] A. Groza, A. Surmeian, M. Ganciu, I. I. Popescu, Europhysics Letters **68**(5), 652 (2004).
[2] M. Ganciu, Romanian Journal of Physics **43**(1-2), 67 (1998).
[3] Andreea Groza, M. Ganciu, Th. Ionescu Bujor, I. I. Popescu, M. Ilies, A. T. Balaban, Proceedings of the International Conference on Phenomena in Ionized Gases, ICPIG XXIV; **2** 127 (1999).
[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", **1**, 3rd Ed., John Wiley &Sons, NY, (1975).
[5] M. Goldman, A. Goldman, Gaseous Electronics, Vol. 1 (Academic Press Inc.) 1978, pp. 21-290.
[6] Y. Park, S. Rhee, Journal of Applied Physics **86**(3), 1346 (1999).
[7] S. M. Iftiquar, High Temperature Material Processes **1**, 36 (2002).
[8] Galikova Anna, Galik Aftanas, Pola Josef, Proceeding of 27th Conference SSCHIE, Tatranske Matliare (SK), 22-26 May 2000.
[9] B. Surma, L. Bryja, A. Misiuk, G. Gawlik, J. Jun, I. V. Antonova, M. Prujszczyk, Crystal Research Technology **36**(8-10) 943 (2001).
[10] A. Groza, A. Surmeian, M. Ganciu, I. I. Popescu, Proceeding of the European Conference on Atomic & Molecular Physics of Ionized Gases, ESCAMPIG XVII, J. Optoelectron. Adv. Mater. **7**(5), (2005).
[11] Koichi Awazu, Hideo Onuki, Applied Physical Letters **69**(4), 482 (1996).
[12] Y. T. Kim, S. M. Cho, Y. G. Seo, H. D. Yoon, Y. M. Im, D. H. Yoon, Crystal Research Technology **37**(12), 1257 (2002).