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Plasma-Assisted Deposition of Dielectric Conformal Coating Using Hexamethyldisiloxane as Precursor

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***Abstract*—Plasma polymerization is a rapidly growing field of plasma technology. Using this method, it is possible to solve applied problems, for example, the deposition of conformal dielectric coatings to protect electrical circuit boards operating in outer space. In this paper, we study the vapor deposition of hexamethyldisiloxane using low-pressure plasma. The morphology, dielectric strength under plasma, and chemical composition of the deposited coating are studied. It was established that the coating has a lamellar structure, which, together with the data of IR spectroscopy, indirectly prove the formation of a polymer coating. The dielectric strength of the coating under plasma was 650 V.**

Keywords—plasma polymerization, conformal coating.

I. Introduction

At present, the deposition of polymer coatings from reactive plasma is widely studied [1, 2], since there is great practical interest in plasma polymerized coatings. For example, there is a need for electrical insulating coatings to protect the printed circuit boards of electronic devices operating in outer space from environmental influences [3, 4]. In the research [3] authors shows, that a different breakdown voltage under plasma is observed depending on the size of the defects, but the authors emphasize that the defect independently of its size should be considered as a risk of the development of a secondary arc. In this investigation an assessment of the electric strength of the deposited coating was made by contact scanning with an electrode containing rolling ball at a voltage of 400 V. The experiment showed that the coating deposited by this method is able to withstand such voltage, but due to the weak interaction at the metal / deposited coating interface and the low degree of polymerization, satisfactory mechanical properties of the film have not achieved. In another study [5], the authors used plasma to deposit polycyanurates-like polymers and investigated the dielectric properties of the resulting films, in particular the dielectric constant and dielectric loss, but there are no data on dielectric strength.

To solve this problem, organosilicon coatings can be used as protective layers for electrical insulation [7, 8]. Hexamethyldisiloxane is one of the options that can be used as a precursor for a plasma polymerization process [6–8].

II. Experimental Setup and Methods

The experiments on plasma-chemical coating deposition were carried out on the setup, the scheme of which is shown in Fig. 1. The setup was adapted specifically for local deposition of coatings.

In this study, a hollow cathode plasmatron was used to generate a glow discharge. The plasma volume was limited by the walls of the glass tube, at the exit of which there was a stainless steel anode. A flow of argon working gas was supplied through the electrode system, perpendicular to the substrate, with a flow rate of 216 sccm. Precursor vapors (hexamethyldisiloxane, 99.5%) were mixed with argon, passed through the discharge zone, and deposited on a cooled substrate (-20°C). The discharge power during the deposition process was 5 W; the pressure in the chamber was kept constant at the level of 3–4 Pa. The deposition time was 20 minutes.

The substrate material varied depending on the objectives of the study, silicon substrates were used to study the thickness, morphology and chemical composition, and copper substrates were used to study the dielectric strength.

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The film thickness was studied using an interference microscope profilometer "MNP". To accurately measure the thickness of the coating, the silicon substrate was coated with a silicon wafer plane-to-plane, so that after removing the silicon wafer, a wafer-coating step was formed. The coating thickness was recorded as the height of this step. The morphology of the coating and the substrate – coating interface were analyzed using an ALTAMI MET 1T optical metallographic microscope. The chemical structure was studied using a Nikolet 5700 IR Fourier spectrometer. Pure silicon was used as the zero sample. The spectra were deciphered from reference data [9] and from previous works on the deposition of hexamethyldisiloxane [6,8]. The dielectric strength of plasma-polymerized coatings was estimated by the contact method with an electrode in the form of a rolling ball with a radius of 2 mm at applied voltages of 100, 200, and 400 V. The measurements were carried out at a temperature of 21°C. The scan area was approximately 1 cm^2. In outer space, a spacecraft is electrified, which is associated with the action of electron and ion plasma flows. Therefore, a breakdown of the dielectric coating occurs. Thus, in addition to scanning, it is necessary to evaluate the dielectric strength of the coating under plasma. The measurement scheme is shown in Fig. 2. The gradually increasing voltage of negative polarity was applied to the copper substrate until an electrical breakdown of the coating occurs. An electrical breakdown of the dielectric coating was indicated by a voltage drop and current flow in the measuring circuit.

The plasma density was 10^{-8} cm^3; the pressure in the vacuum chamber was maintained at 1 Pa.

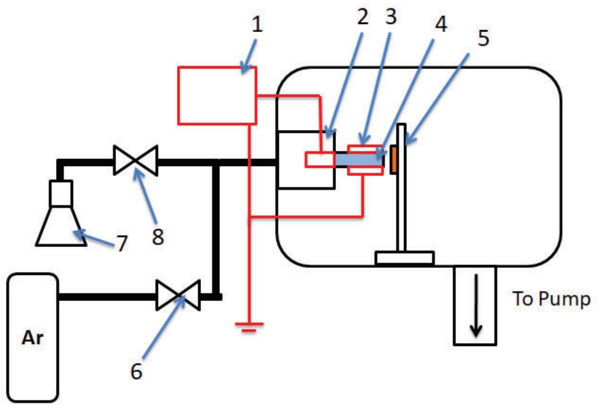


Fig. 1. Scheme of setup; 1 – power source, 2 – hollow cathode plasma torch, 3 – anode, 4 – plasma chemical reactor, 5 – cooled substrate holder, 6 – argon flowmeter, 7 – precursor flask, 8 – precursor flow controller.

III. Results

Using optical interferometry, it was found that the thickness of the resulting coating is 20 μm, which indicates a high film growth rate compared to other studies [5–7].

Fig. 3 shows a micrograph of the surface of the deposited coating, the interface between the substrate and the coating and a pure silicon substrate, obtained using an optical microscope. The micrograph shows a clear interface between the initial silicon substrate and the deposited film. The coating has a homogeneous close-packed lamellar structure. This indicates the formation of a partially crystalline amount of polymer (not more than 60% crystallinity). The study of the interface shows that ordered fibers are formed in the coating volume, oriented perpendicular to the substrate, which can indicate a strong chemical integration of the coating.

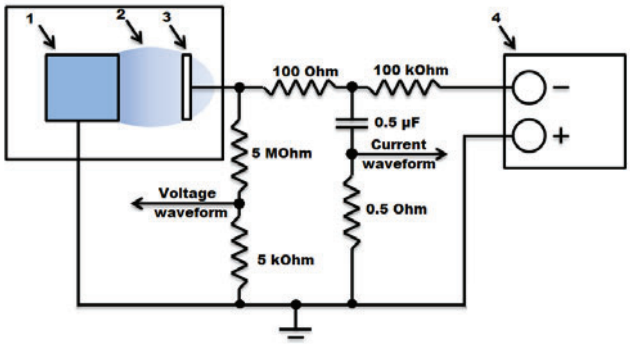


Fig. 2. The scheme for measuring dielectric strenght under plasma; 1 – plasma source, 2 – plasma, 3 – sample, 4 – power source.

Data on the chemical structure of the coatings obtained using infrared spectroscopy are shown in Fig. 4 and Table I. The results showed the presence of bands, characteristic bond vibrations in hexamethyldisiloxane. Vibrations corresponding to 2960 cm^{-1} and 2900 cm^{-1} relate to vibrations of the C-H bond in the methyl group CH_3. In the 1657 cm^{-1} region, a wide low-intensity peak is observed, which most likely refers to adsorbed water. Further, 1403 cm^{-1} is correlated with deformation vibrations of the methyl group in Si-(CH_3). Further, in the region of 1100–930 cm^{-1} with a maximum at 1020 cm^{-1}, there is a wide and intense peak, which characterizes the vibrations of the Si-O-Si and Si-O-C bonds. The maxima of 834 and 785 cm^{-1} indicate Si-C stretching vibrations in the structures of Si-$(CH_3)_3$ and Si-$(CH_3)_2$. A maximum of 752 cm^{-1} characterizes the deformation vibrations of C-H.

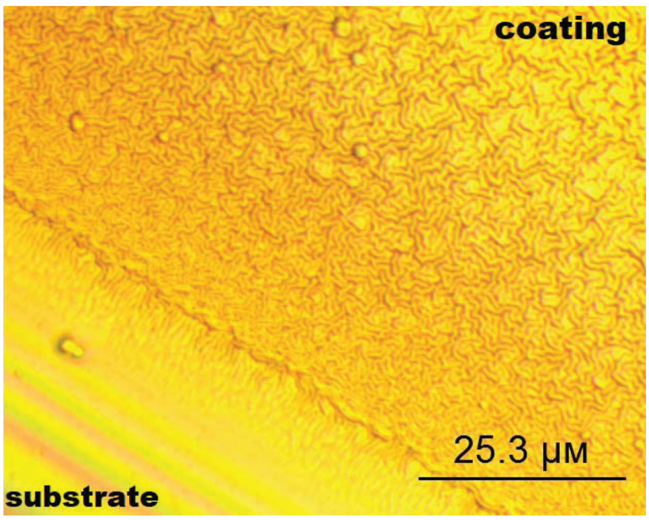


Fig. 3. Morphology of the deposited coating.

The dielectric strength of coatings was measured on samples deposited on copper substrates by contact scanning. The experiment showed that the electric strength of the coatings exceeds 20 MV/m, which corresponds to the fact that this coating with a thickness of 20 μm can withstand a voltage of 400 V.

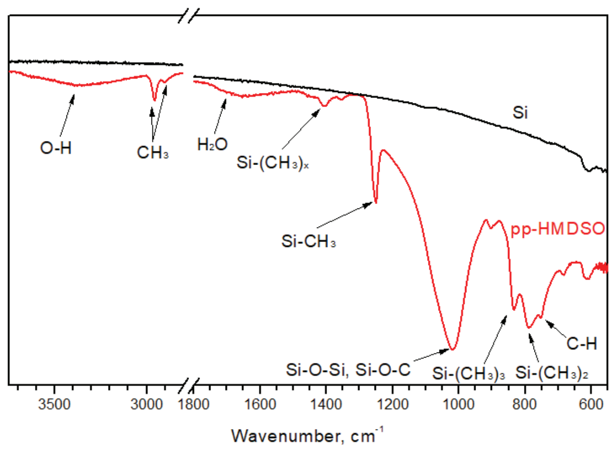


Fig. 4. Infrared spectra of the silicion substrate and the deposited coatings.

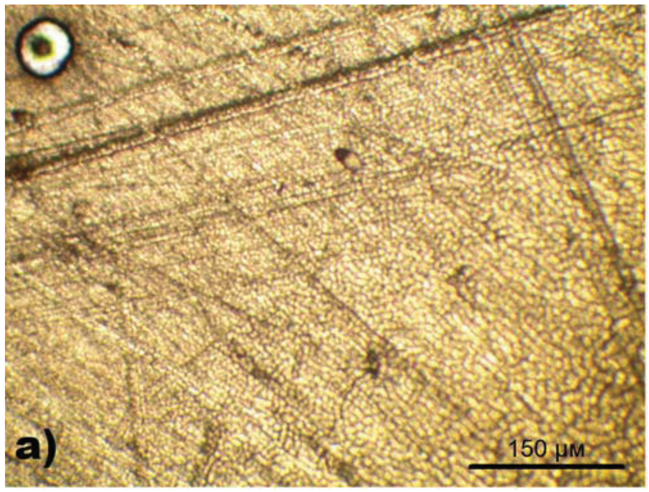
TABLE I. MAXIMUM INTENSITY IN INFRARED SPECTRA OF COATINGS.

Wavenumber, cm^{-1}	Vibration
3600–3000	O-H stretch
2957, 2910	symmetric and asymmetric stretching vibration of a CH_3 group.
1660	H_2O
1405	CH_3asymmetric bending
1250	Symmetric deforomation of the Si-CH_3 group
1020	Si-O-Si asymmetric stretching and Si-O-C asymmetric stretching
835	Si-$(CH_3)_3$ stretch
790	Si-$(CH_3)_2$ stretch
752	C-H deformation

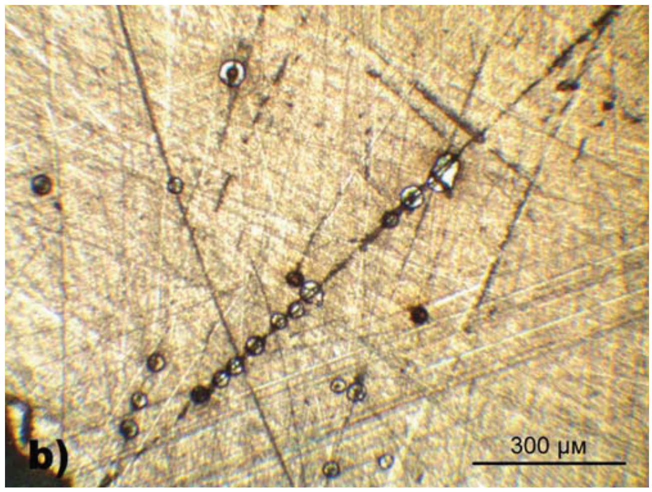
The dielectric strength of the coating under plasma was measured using the measuring circuit shown in Fig. 2. The experimental results showed that the electrical breakdown of the coating occurs when the negative potential on the sample increases to -650 V. Fig. 5a shows a micrograph of the coating surface after the breakdown under the plasma, obtained with using an optical microscope. A crater with a diameter of 50 μm, which was formed as a result of electrical breakdown of the coating, is visible in the image. Fig. 5b demonstrates a case of numerous craters on the substrate surface affected by several breakdowns. It is clearly seen that craters are attached to scratches because of enhancement of electric field at scratch edges.

IV. DISCUSSION

According to the analysis of the morphology of the deposited coating, it can be assumed that a plasma polymer with a crystalline rather than amorphous structure is formed on the surface of the substrate, as indicated by the formation of ordered close-packed lamellas during the deposition process. At the interface, it is seen that a fibrous structure forms in the coating volume. The formation of such a structure is associated with the features of film growth. We assume that nucleation begins in defects in the crystal lattice of the substrate, and then fiber growth occurs. The formation of polymer chains is also indicated by the presence of stretching vibrations of Si-$(CH_3)_2$, which may be inside the polymer chain. The presence of bands characteristic of vibrations of the Si–O–C and O–H bonds indicate fragmentation of the precursor molecules with the formation of new bonds and the formation of new chemical structures.



(a)



(b)

Fig. 5. Micrographs of the surface of the coating deposited on a copper substrate after electrical breakdown.

Often, dielectric strength is highly dependent on the morphology of the coating. For example, the presence of pores or gas bubbles inside a dielectric can greatly reduce breakdown voltage. Therefore, most likely, in this case, high dielectric strength is due to the fact that the coating is a close-packed homogeneous structure.

V. Conclusion

The vapor deposition of hexamethyldisiloxane according to the procedure presented in this work leads to the formation of a homogeneous lamellar structure of the coating with a complex chemical composition. Dielectric strength of the coating exceeds 20 MV / m. An electrical breakdown of the coating under plasma occurs when the negative potential of the substrate increases to -650 V. Thus, in this work it is shown that films deposited from hexamethyldisiloxane vapors can be an alternative to existing methods of electrical isolation of printed circuit board components.

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