



Properties of corona charged plasma vapour deposited PTFE film

R. Kacprzyk, J. Ziąja

Institute of Electrical Engineering (I-7), Technical University of Wrocław,
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Properties characterising charge storage in submicron polytetrafluoroethylene (PTFE) layer deposited by evaporation in a radio-frequency (RF) plasma are described in this paper. X-ray diffraction (XRD) and scanning electron microscopy (SEM) investigations have shown that the method allows to deposit amorphous and uniform dielectric layers exhibiting resistivity at room temperature in the order of 10^{14} Ωm . Electrical conductivity and thermostimulated discharge current (TSD) results were measured in the temperature range 300-450K while an isothermal discharge characteristic was examined at room temperature.

1. INTRODUCTION

The fluoroderivative polymers were applied more widely at the end of the 40's. Polytetrafluoroethylene is one of the plastics belonging to this group. Good dielectric properties and hydrophobicity of the PTFE [1] permit its application as an electret material [2,3]. The other problem is PTFE processing especially in case of foils or thin dielectric layers. One of the methods of thin (submicron) layer preparation, which potentially can be applied to the PTFE seems to be polymerisation [4] or evaporation [5] in a plasma (PVD). Superiority of the second above-mentioned method was proved by better uniformity of deposited layers.

2. SAMPLE PREPARATION

The samples were evaporated in a vacuum chamber equipped with a flat and parallel electrode system securing a strong electrical field necessary for plasma creation. The chamber was also equipped with the system of a polymer vapour as well as auxiliary gas (argon) dosage. The Tarflen® SM1 in the form of a powder with nonregular and polycrystalline grains was used as a parent material. The polymer vapours were obtained by a controlled heating of the powder in the evacuated quartz bulb connected to the vacuum chamber. Glass plates covered with an Al layer deposited by application of a magnetron sputtering were used as substrates. The Al layer ca 100 nm thick was used as a polarising electrode in the conductivity measurements. The substrates were placed on one of the discharge electrodes and the chamber was evacuated to 10^{-4} mm Hg. Evaporation of the layers was carried out in the following conditions: PTFE vapour pressure 0.1 - 0.2 mm Hg (with or without argon additive), the average discharge power 100 - 500 W, polarising voltage frequency 200 kHz. The deposition time was changed in the range 1 - 10 min. Discharge power was regulated by pulse length

changing in the range 50 - 500 μs . The electrode diameter was 90 mm and the distance between them was 50 mm. None of the electrodes was cooled during the process. The procedure described above makes it possible to obtain layers with thicknesses ranged from about 200 up to 1000 nm. Finally 40 nm thick Al electrodes (if necessary) were deposited on the layer by Al evaporation in a vacuum. Results presented below were given for the sample with the electrode surface 3.2 cm^2 and thickness ca 650 nm. The sample thickness was determined on the base of capacitance measurements and assumption of the layer dielectric permittivity equal to that of the thick Tarflen samples ($\epsilon_r = 2.0$). Correctness of a such estimation was confirmed by investigation of sample's fracture using scanning electron microscope.

3. MEASUREMENTS

XRD investigations and microscope observations were carried out on the additional samples prepared under identical conditions as the samples for other investigations. Measurements of TSD currents were carried out on the samples polarised within a period 3600s, at the temperature 423K by application to the electrodes voltage equal 10V. TSD discharge was carried out directly after polarisation process, with the rate of temperature increase equal 2 K/min. The sample was heated by the flat copper heater to which the sample was pressed. Sample's temperature was measured with a Cu-Konst thermocouple pressed to the sample surface (on the other side than the heated one) by a small teflon insulator. Capacitance of the samples was measured at the frequency 1 kHz with a typical digital differential bridge (E315-Meratronik) in a three electrode system. Surface potential of the samples was measured by compensation method with application of the vibrating head working as a zero detector [6].

4. RESULTS

XRD investigations carried out on samples deposited from evaporated PTFE only as well as from the PTFE vapour-Ar mixture showed, in both cases, the amorphous character of obtained layers. Similar measurements carried out on the parent material showed its semicrystalline structure. Figures 1 and 2 show the sample surface structure and layer fracture, investigated using SEM. The surface as well as bulk of the sample exhibit no substantial defects and irregularities. Layers with thicknesses in the range 200-1000 nm were semitransparent and showed good adherence to the substrate. Although IR investigations confirmed appearance of three- and tetra- fluoroethylene groups in the layer material, the spectrum exhibits rather more complex nature. Isothermal discharge measurements were carried out on samples polarised by a corona discharge in air by application of a point-plane electrodes system. The point electrode (curvature radius ca. 20 μm) was polarised with a voltage (-)8 kV and a sample to point electrode distance was 50 mm. Polarisation was carried out at room temperature and within a period of 100s. Directly after polarisation the sample was subjected to the surface potential measurements. A typical isothermal discharge curve obtained for the polarised layer and PTFE foil was shown in Fig. 3. It is clearly seen that the charge decay process occurring on the PVD-PTFE layer did not show saturation symptoms and was found to be incomparably faster than that on PTFE foil. An example of TSD curve obtained for electrets polarized at elevated temperatures (thermoelectrets) and analysed in a short-circuit with application of Al electrodes

is shown in Fig. 4. TSD curve for PVD-PTFE layer exhibits appearance of a relaxation process characterised by a single current peak in the temperature 325 K.

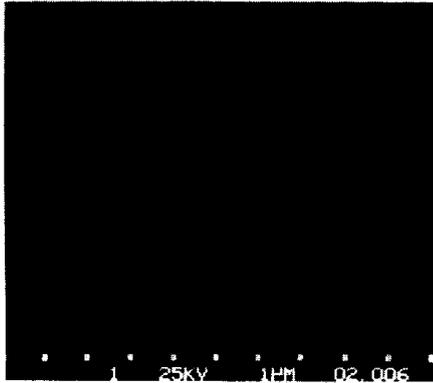


Fig. 1. SEM picture of the PVD-PTFE layer surface. Magnification 10 000 x.

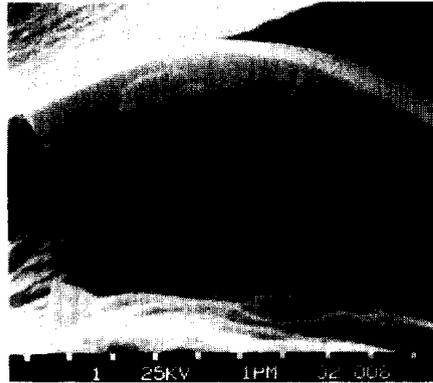


Fig. 2. SEM picture of the PVD-PTFE layer break. Magnification 10 000 x

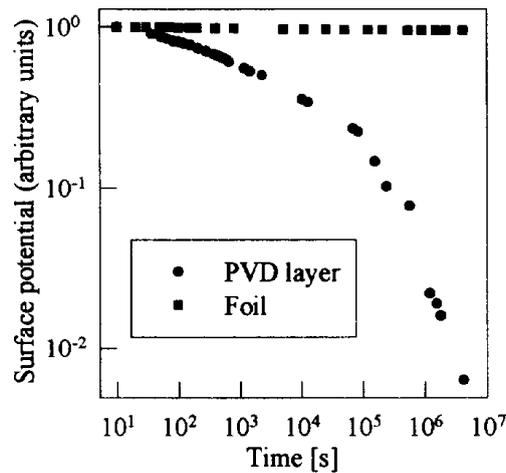


Fig. 3. Isothermal discharge curves for PTFE samples polarised by a corona discharge (point electrode polarised with - 8 kV, 100 s) obtained for electrets stored in air at the temperature $T=293\text{K}$ and relative humidity $h=60\%$ and in open circuit conditions.

A permanent current increase observed in the range of temperatures above 350K can not be associated with the pyroelectric effect which was confirmed experimentally. The true nature of the observed phenomenon is not known. Investigations of TSD current carried out on samples of PTFE foil equipped with Al electrodes and polarized in similar conditions exhibited only one

peak at the temperature ca 500K [7]. Temperature dependence of conduction currents for PVD-PTFE layer polarized with 10V and obtained in nonequilibrium conditions was shown in Arrhenius coordinates in Fig. 5. The upper plot which was obtained for the layer heated at the rate of 3 K/min. exhibited a “hump” with a maximum in the temperature ca 320-330K. The lower plot, obtained for the cooled layer, could be approximated by a straight line describing activation process with one activation energy of 0.83 eV in the whole considered temperature range considered (300-450 K). Similar measurements carried out on samples of PTFE foil gave the activation energy of 0.37eV [7]. A lack of the “hump” in the last case may result from a total polarisation of the layer within the heating period. The resistivity estimated at the room temperature from the current measurements (for cooled samples) was found to be level $2 \times 10^{14} \Omega\text{m}$ i.e. 4-5 orders of magnitude lower in comparison to that for PTFE foil.

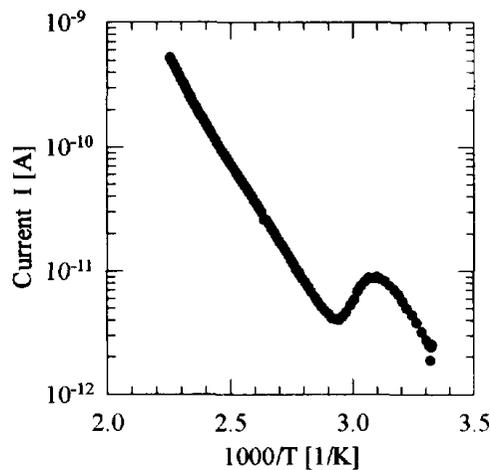


Fig. 4. TSD curves for PTFE shortcircuited thermoelectrets (polarized 10V, 423K, 1h) obtained for temperature rate 2K/min.

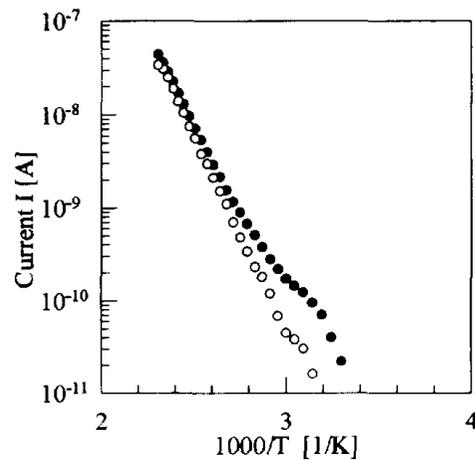


Fig. 5. Current-temperature dependence in Arrhenius coordinates for PVD-PTFE layer. Polarisation voltage 10V = const.

The observed difference between current plots shown in the Fig. 5 describes the polarisation component of the measured current. Comparison of the temperature ranges of TSD peak and the “hump” appearance suggests their similar origin. The observed serious difference in the electrical properties between PTFE foil and PTFE-PVD layer would be difficult to explain by a structural differences only [1]. The basic reason seems to be a foreign molecules (originating from the electrodes e.g.) built-in process occurring during evaporation accompanied by a RF plasma. Such an “additive” introduced or dispersed in the amorphous PTFE lattice could be a reason of additional relaxation process as well as serious changes in conductivity. However the confirmation of the last hypothesis requires additional investigations.

5. CONCLUSIONS

Application of the plasma vapour deposition method allows to obtain of PTFE layers of submicrometer thicknesses. The layers exhibited an amorphous structure, good uniformity and adherence to the substrate and were semitransparent in the range of visible radiation.

Investigations of charge storage properties and electrical conductivity of the obtained layers showed a serious differences in these parameters in comparison to the properties of PTFE foils. The temperature dependence of a conduction current for the PVD-PTFE layer indicated occurrence of only one conduction mechanism in the temperature region 300–450K characterised by an activation energy 0.83 eV. The TSD spectrum revealed additional polarisation process appearing in the region of lower temperatures (below ca 360K) and characterised by an activation energy of 0.8 eV.

Relatively fast charge decay on PVD-PTFE layers confirmed by a small activation energy of the TSD peak and its position on the temperature axis indicates some limits in application of the obtained layers as an effective electret material.

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REFERENCES

1. Tarflen. Otrzymywanie i własności, Biuletyn Zakładów Azotowych S.A. Tarnów, 1990.
2. B. Hilczer, J. Małecki, *Elektrety i piezopolimery*, PWN, Warszawa, 1990.
3. G.M. Sessler, *Elektrety*, Mir, Moskva, 1983.
4. J. Tyczkowski, *Cienkie warstwy polimerów plazmowych*, PWN, Warszawa, 1990.
5. F. Quaranta, A. Valentini, P. Favia, R. Lamendola, R. d'Agostino, *Appl. Phys. Lett.*, 63 (1993) 10.
6. C.W. Reedyk, M.M. Perlman, *J. Electrochem. Soc., Solid State Sci.*, 1 (1968) 49.
7. L. Badian, B. Łowkis, E. Motyl, A. Gubanski, *Badanie elektretowych wkładek mikrofonowych*, Raport I-7/R-211/78, P.Wr., Wrocław, 1978.