ISSN 1330–0008
CODEN FIZAE4

INTERACTION OF POLYETHER SULPHONE WITH OXYGEN PLASMA

LIDIJA I. BELIČ, MIRAN MOZETIČ and KAROL POŽUN

Institute of Electronic and Vacuum Technique, Teslova 30, 61000 Ljubljana, Slovenia

Received 7 September 1995

UDC 538.971

PACS 68.35.-p

Polyether sulphone was found to be a useful material for production of high reliability humidity sensors. In order to obtain best properties of the sensors, the polymer surface should be activated before a thin layer of metal is deposited. A way to do it is exposition of the polymer to oxygen plasma. In order to prevent destructive action of the plasma, a very mild inductively coupled RF oxygen plasma was created in a vacuum system. The plasma density was of the order of 10^{16} m^{-3}, and the electron temperature 4 eV. Active particles produced in plasma interact with the polymer causing oxidation of the surface layer and a continuous thinning of the polymer foil. In our case the rate of thinning was 25 μm per hour.

1. *Introduction*

Polyether sulphone is a chemical compound which exhibits high ability of water consumption. Since the concentration of water molecules in the polymer depends on the relative humidity of the atmosphere, it is often used in humidity sensors [1,2]. This type of humidity sensor is made of a thin polymer foil mounted on metal electrode and covered with very thin layer of metal [3,4]. Both metal electrodes represent a parallel plate capacitor. The layer of metal at the upper electrode should be porous in order to transmit water molecules. The sensitivity of the device depends on various parameters including the foil thickness. In this paper we describe a method for reducing the thickness of polymer foils.

Polyether sulphone is a high temperature engineering thermoplastics with an outstanding long term resistance to creep at temperatures up to 150 °C [5]. The structure is amorphous polymer which possesses only bonds of particularly high thermal and oxidative stability. Since the foil becomes soft at the temperature of 220 °C it cannot be thinned by temper oxidation. In spite of this, we tried to reduce the foil thickness by exposure to oxidizing atmosphere. Since the material is resistant to oxygen molecules, we used more reactive oxygen particles, like free oxygen atoms, vibrationally excited molecules, and ionized atoms and molecules. All these particles were produced in low pressure oxygen plasma.

2. *Erosion of polymer in oxygen plasma*

Polymer foil was cut to pieces 20 mm $\times$ 60 mm, placed onto glass substrates, and mounted into a discharge vessel of a vacuum system. The system was pumped with a rotary pump with the pumping speed of 2.2 l/s with the base pressure of 1×10^{-3} mbar. In order to prevent aggressive gases entering the pump, a trap filled with zeolite was mounted between the pump and the discharge vessel. The discharge vessel was a glass cylindrical tube with the diameter of 40 mm and the length of 800 mm. At one side it was pumped, and on the other side oxygen leaked through a needle valve. The base pressure in the discharge vessel was 2×10^{-2} mbar and the effective pumping speed 2 l/s. Low pressure weakly ionized plasma was created in the discharge vessel by the use of inductively coupled RF generator with the frequency of 27.12 MHz and the output power of approx. 150 W. Plasma parameters were measured with a double electrical probe [6]. A typical probe characteristic is plotted in Fig. 1. The electron temperature in plasma was 3–5 eV, Debye length of the order of 10^{-4} m, while plasma density was found to depend substantially on the pressure in the discharge vessel and is plotted in Fig. 2.

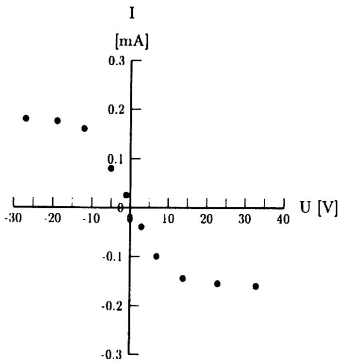

Fig. 1. Double probe characteristics at the pressure of 60 Pa. *Plasma parameters calculated from this curve are as follows: Electron temperature* 4.5 eV, *plasma density* 1.5×10^{16} m^{-3}, *Debye length* 1.3×10^{-4} m.

Oxygen molecules entering the discharge suffer inelastic collisions with energetic electrons, leading to dissociation, excitation and ionization. The degree of ionization of molecules in the discharge is rather low (less than 10^{-6}), but since the recombination coefficient for the reaction $O + O \rightarrow O_2$ of glass is as low as 10^{-4} [7], the degree of dissociation is much higher. Oxygen atoms readily react with polymer molecules on the sample surface leading to oxidation. The oxidation of polymer in oxygen plasma takes place even at room temperature though the polymer itself is not flammable. Heating the foil in oxygen atmosphere in the absence of plasma leads to melting rather than oxidation.

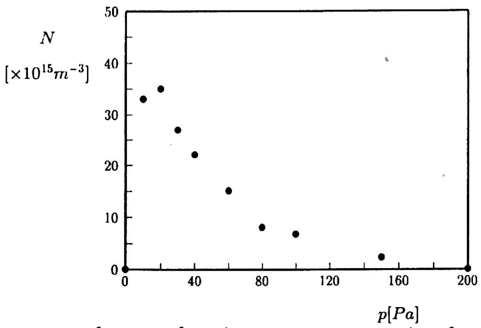

Fig. 2. Oxygen plasma density vs. pressure in the discharge vessel.

When a sample was exposed to plasma with a rather high density of 3×10^{16} m^{-3}, rapid oxidation took place and the temperature raised over the melting point of 220 °C. The oxidation was so effective that the energy dissipated on the surface was large enough to cause thermal decomposition of the polymer and the foil became black. To avoid this effect, further experiments were carried out in a weaker plasma with the density of 5×10^{15} m^{-3}. Samples were exposed to plasma for 10, 30 and 60 minutes. After the exposure, the thickness of the foil was measured with mechanical surface profile analyzer. The result is plotted in Fig. 3. The thickness of the foil was found to decrease with increasing duration of plasma processing. The curve is rather linear with the slope of 25 μm/h. The erosion was fairly homogeneous so that the thickness did not vary for more than 4 μm.

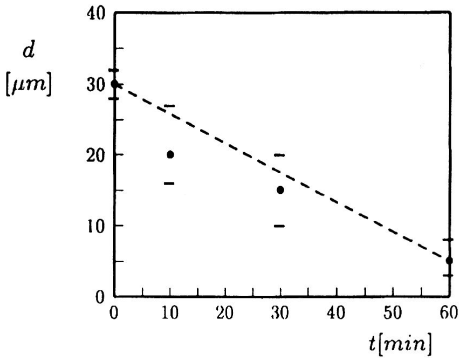

Fig. 3. Polymer foil thickness vs. duration of plasma treatment.

3. Conclusion

Polyether sulphone foils were treated in low pressure weakly ionized oxygen plasma. Plasma density was varied between 1×10^{15} and 3.5×10^{16} m^{-3}. At rather high plasma density the foil melted and thermal decomposition of polymer took place. Therefore, most of experiments were performed at low plasma density of the order of 10^{15} m^{-3}. In this condition the foil is continuously oxidizing due to exposure of its surface to a rather large flux of very reactive oxygen particles. During the treatment, the foil thickness was reduced as surface oxidation was in progress. The rate of thinning was about 25 μm per hour. Exposure of the samples to oxygen plasma also led to activation of its surface so that the adhesion of deposited metal was much better than for untreated samples.

Acknowledgement

The work was financially supported by the Slovenian Ministry of Science and Technology (project J2 – 7641).

References

1) S. Takeda, J. Appl. Phys. **47** (1976) 5480;
2) S. Takeda, Vacuum **41** (1990) 1769;
3) S. Takeda, Jap. J. Appl. Phys. **20** (1981) 1219;
4) M. Matsugutchi, Y. Sadaoka, M. Shinmoto and Y. Sakai, Bull. Chem. Soc. Jpn. **67** (1994) 46;
5) C. A. Harper, *Handbook of Plastics and Elastomers,* Mc Graw - Hill, New York (1975);
6) J. D. Swift and M. J. R. Schwar, *Electrical Probes for Plasma Diagnostics,* Iliffe Books, London (1969);
7) H. Wise and B. J. Wood, in *Advances of Atomic and Molecular Physics,* (Edited by D. R. Bates and I. Estermann), Vol. 3, p 322. Academic Press, New York (1967).

DJELOVANJE KISIKOVE PLAZME NA POLIETERSULFON

Polietersulfon je pogodan materijal za osjetljive slojeve vrlo pouzdanih proba za vlažnost. Radi postizanja dobrih svojstava, površina polimera mora se aktivirati prije naparavanja metalne elektrode. Jedna od metoda je izlaganje polimera blagoj, induktivno proizvedenoj kisikovoj plazmi. Aktivirane čestice u plazmi uzrokuju oksidaciju površine polimera i njegovo stanjivanje. Primjenjivali smo stanjivanje brzinom 25 μm na sat.