Journal of Optoelectronics and Advanced Materials Vol. 6, No. 2, June 2004, p. 477 - 479

SHORT COMMUNICATION

NANOSTRUCTURED "BRUSH-TYPE" THIN-FILM COVERED WITH A SILVER LAYER

S. Dreve[*], E. Indrea, I. Bratu, M. Bako[a], Gh. Mihailescu, L. Olenic, S. Pruneanu, V. Znamirovschi[a]

National R&D Institute of Isotopic and Molecular Technologies, P.O. Box 700, R-3400 Cluj-Napoca 5, Romania
[a]'Babes-Bolyai' University, Faculty of Physics, 1 Kogalniceanu st., 3400 Cluj-Napoca, Romania

It was demonstrated the feasibility of a polyvinylformaldehyde nanostructured "brush-type" thin-film covered with a silver layer. The poly-vinyl-formaldehyde nanostructured thin-film was prepared using the template deposition technique on anodic aluminium oxide film, which allowed the control of the thickness and the structure of the polymeric film. By chemical and evaporation techniques a silver thin layer was deposited on the film surface. The determination of the optical properties in correlation with the thickness was done. X-ray and electronic microscopy microstructural investigations were performed for the plastic thin-film with and without silver thin layer. The data were correlated with the specimen preparation methods.

(Received January 29, 2004; accepted June 3, 2004)

Keywords: Polyvinylformaldehide thin-film, Porous alumina membrane, UV/VIS, Infrared (IR); X-ray diffraction, Electronic microscopy (SEM)

One application which is frequently mentioned for nanometer-sized semiconductor crystals is the conversion of the optical into electric signals. At the basis of such transducers is the nanostructured thin layer of polymer, having deposited on it different doped films, following the application purpose.

Polymeric thin films, as polypyrrole, polyaniline, polyvinylformaldehyde, polythiophene (and their derivatives) are explored as promising basis-materials for the fabrication of microsensors, or to immobilise chemosensitive compounds [1].

The principles for the synthesis and preparation of polymeric nanostructured thin films generally follow specific techniques, upon the final purpose of sensing and ability to transfer the information. It is reported that [2,3] the microstructure can be achieved and controlled by various fabrication techniques, such as the use of thin film preparation technique on a template support.

For experimental purposes all the used reagents were A. R. grade. A solution with the specific mass of 1.230 g/cm^3 of polyvinylformaldehyde, $C_{10}H_{18}O_{12}$, (Merck quality) in dichlorethane was prepared. Separately, a pure alumina nanostructured membrane, (disk shape with 3 cm diameter) was prepared via the anodisation of aluminium metal in acidic solution [4]. This membrane contains cylindrical pores of uniform diameter of 50 *nm*. On the top of the alumina nanostructured support the chemical deposition of a thin silver film was performed, in order to realise the conductive layer of the assembly [5].

A separation funnel, consisting in a reservoir and a capillary separated by a valve, was filled with the solution of known concentration. A cleaned piece of thin glass having fixed on it the alumina nanostructured silvered face up was mounted under the capillary of the separation funnel. The solution is allowed to escape at a controlled flow rate. The solvent readily evaporates from the solution and a thin polyvinylformaldehyde layer of high homogeneity sticks to the alumina disk. The alumina template membrane was removed and the resulting material of polyvinylformaldehyde covered with silver were washed with double distilled water and dried in normal conditions.

[*] Corresponding author: simina@s3.itim-cj.ro

The preparation of the polyvinylformaldehyde-silver (PVF-silver) assembly using different parameters of deposition allowed identifying the several types of nanostructured polymeric films that were characterised:

PVF1-Ag particles of 80-130 nm deposited on a smooth surface of polymer;

PVF2-„brush-type" structure 50-70 nm fibrils covered with silver thin layer;

PVF3-ordered structure with pores of 0,5-2μm;

PVF4-disordered structure with pores of 1-2 μm.

Optical characterisation. The UV/VIS and IR measurements (Carl-Zeiss Jena spectrophotometer) revealed the variation of thickness of the assembly between 0.35-3.0 μm. The assemblies having a total thickness of 2.5 *nm* show a larger optical absorption the blue wavelength region. The variation of the reflection coefficient in IR domain was determined, and it was evidenced that its values decrease with the roughness of the assembly. The chemical tests, the determination of dielectric characteristics, and the optical properties in correlation with the thickness will be detailed elsewhere [6].

Structural characterisation. The X-ray diffraction patterns of the polymeric film without the silver deposited layer indicate a disordered structure of the polymeric chains. For the nanostructured PVF-silver assembly the X-ray diffraction analysis revealed, Fig. 1, the characteristic cubic structure of the Ag layer. The maximum intensity of the corresponding maxim is for the (111) structure, indicating that the Ag crystals have the tendency to develop on the normal crystallographic direction of the (111) plane.

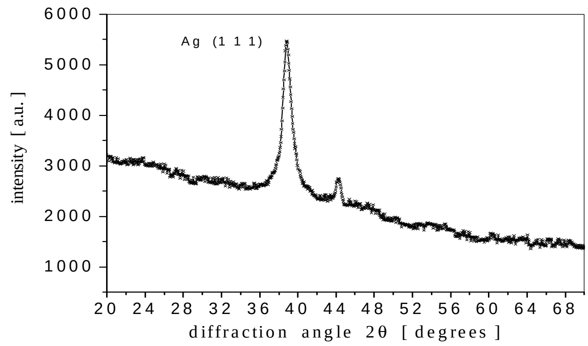

Fig. 1. The X-ray diffraction pattern of the PVF-Ag nanostructured thin film.

The Fourier analysis of the Ag (111) and (200) X-ray diffraction lines indicated small size Ag microcrystals (D_m ~100 Å) covering the polyvinylformaldehyde "brush-type" thin film.

Electronic microscopy. The four different types of nanostructured polymer-silver assemblies were investigated and the SEM images are presented in the Fig. 2-5. The images show that there is a good correlation between the preparation parameters of the assembly and the shape and dimensions of the nanostructures.

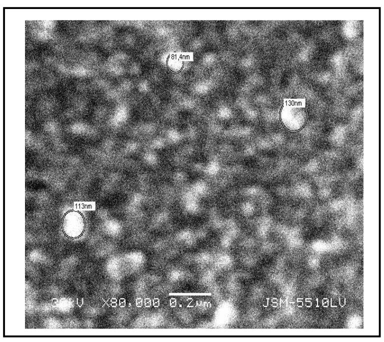

Fig. 2. SEM image of the PVF1 assembly Ag particles of 80-130 nm.

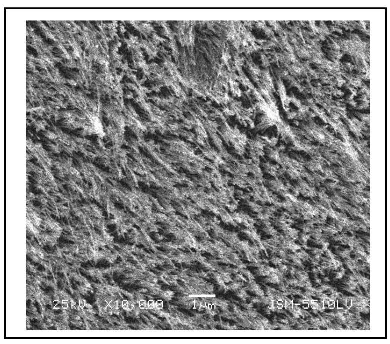

Fig. 3. SEM image of the PVF2 assembly-„brush-type" structure with 50-70 nm fibrils covered with silver thin layer.

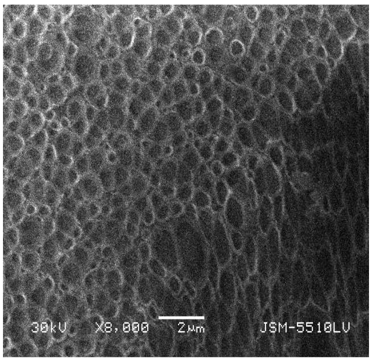

Fig. 4. SEM image of the PVF3 assembly ordered structure with pores of 0.5-2 μm.

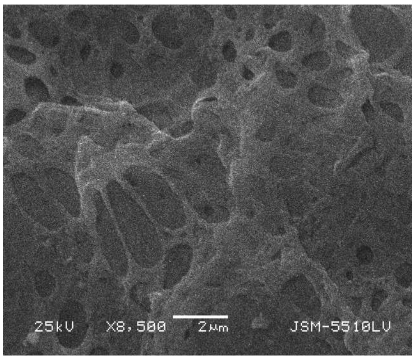

Fig. 5. SEM image of the PVF1 assembly disordered structure with pores of 1-2 μm.

The results are in good agreement with the literature data [7] and the new "brush-type" polyvinylformaldehyde-silver nanostructured thin-film assembly can be used as basis for the fabrication of sensing multilayer device [8].

References

[1] M. Nishizawa, K. Mukai, S. Kuwabata, C. R. Martin, H. Yoneyama, J. Electrochem. Soc. **144**(6), 1923 (1997).

[2] H. T. Sun, M. T. Wu, P. Li, X. Yao, Sensors and Actuators **19**, 61 (1989).

[3] I. Shimizu, H. Arai, T. Seiyama, Sensors and Actuators, **7**, 11 (1985).

[4] Evelina Palibroda, A. Lupsan, Stela Pruneanu, M. Savos, Thin Solid Films **256**, 101 (1995).

[5] Stela Pruneanu, Liliana Olenic, G. Borodi, G. Sigartau, G. Mihailescu, Proceeding of International Semiconductor Conference, Sinaia, Roumania, 2002.

[6] Simina Dreve, Emil Indrea, "Nanostructured "brush"-shape Ag deposited on submicronic resin film", in press.

[7] H. Schmidt, M. Mennig, Institut für Neue Materialen Report, Saarbrucken, Germany.

[8] F. Faupel, R. Wilecke, A. Tran, Materials Science and Engineering: R: Reports **22**(1), 1-55 (1998).