PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. 4 No 2, 02NNSA15(3pp) (2015)

Electrical Properties of Hybrid Composites Based on Poly(3,4-ethylenedioxythiophene) with ZnO and Porous Silicon Nanoparticles

I.B. Olenych*, O.I. Aksimentyeva, Yu.Yu. Horbenko

Ivan Franko National University of Lviv, 50, Dragomanov Str., 79005 Lviv, Ukraine

(Received 02 June; published online 29 August 2015)

The electrical properties of hybrid nanosystem based on poly(3,4-ethylenedioxythiophene) with ZnO and porous silicon nanoparticles were studied by the methods of current-voltage characteristics and thermally stimulated conductivity. The dependence of electrical parameters of hybrid films on their composition has been found. The analysis of the temperature dependences of the composites conductivity in the temperature range of 80–330 K indicates the activation character of charge transfer and presence the trapping of unequilibrium carriers at the porous silicon and ZnO nanoparticle – polymer interface.

Keywords: Nanocomposite, Conjunction Polymer, Porous Silicon, Zinc Oxide, Conductivity.

PACS numbers: 73.61.Ph, 73.63.Fg, 78.30.Jw

1. INTRODUCTION

The progress in nanoelectronics determines the demand for novel low-dimensional materials, which have specific physical properties due to quantum confinement effect. It is known that conducting polymers with conjugated backbone and controlled electron characteristics represent promising components of organic-inorganic composites [1,2]. The conducting polymers manifest electron delocalization arising from conjugated double bonds in a polymer backbone. They reveal electrical conductivity in the doped states (p- or n-doping) though remain insulators when undoped. Among the variety of conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is of particular interest due to relatively low resistivity and remarkable optical and electrochemical properties [3-5]. Recently, hybrid nanosystems on the base of conductive polymers reinforced with inorganic nanoparticles of different nature are in the focus of increased attention [6-8]. Incorporation of low-dimension components such as silica and ZnO nanoparticles give a possibility to use redox-activity of conjugated polymers, size effects and large area surface of nanostructures [9-12].

Silicon nanoclusters can be prepared using a straightforward procedure of electrochemical etching of single-crystalline silicon, with further formation of a layer of 'porous silicon' (PS). Ever since the intense visible photoluminescence of the PS has been detected at the room temperature by Canham in 1990 [13], the PS is regarded as a promising active element for optoelectronics [14,15]. Zinc oxide is also promising functional wide-band semiconductor, which has attractive optical (high transparency, intense photoluminescence) and electrical (high electron mobility) properties. Materials based on it are widely used for making optoelectronic converters, transparent electrodes, thin film transistors, gas sensors [16-18]. An interaction between nanoparticles in the hybrid composites can lead to significant differences in their properties compared to those of the individual components – strengthening some of these properties or forming new ones [19-21].

Therefore, the aim of the present work was to create the hybrid systems PEDOT–PS–ZnO and studying the electrical properties of hybrid films based on such composites.

2. EXPERIMENTAL PROCEDURE

The hybrid composite was prepared on 3,4-ethylenedioxythiophene in the form of aqueous suspension 1.5 % of main substance stabilized by polystyrene sulphonic acid (PSS) as surfactant and doping agent. The other components of hybrid composite were PS and ZnO nanoparticles.

The PS was manufactured by means of photoelectrochemical etching performed in galvanostatic mode on single-crystalline silicon substrates, which had the typical thicknesses of 400 μm and the crystallographic orientation (100). The silicon substrates had the *n*-type conductivity, with the specific resistance of 4.5 Ohm cm. Ethanol solution of hydrofluoric acid (the volume ratio of the components HF: C_2H_5OH = 1:1) was used as an electrolyte. The anodic current (the density of 30 mA/cm^2) passed during all the etching time (about 20 min). After cleaning of our samples with distilled water and drying in air, a resulting porous layer has been taken off from the surface of the plate. It had the shape of a finely-dispersed powder. The sizes of silicon particle ranged from a few tens of nanometers to several microns.

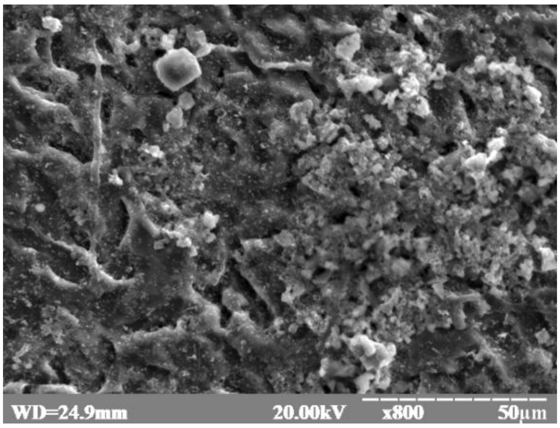
The resulting powder of PS was mixed with ZnO nanoparticles at a volume ratio of 2:1, 1:1, 1:2 to create three series of experimental samples of nanocomposite with different content. The mixture was mixed with 0.75 ml PEDOT suspension and exposed to ultrasonic treatment for 8 hours. After this suspension was applied to a glass substrate and dried at room temperature for 72 hours. Eventually, the monolithic film of hybrid PEDOT–PS–ZnO nanocomposite was obtained.

The microstructure of the hybrid film PEDOT–PS–ZnO was investigated by a scanning electron microscope (SEM) Selmi REMMA-102. SEM image of the film surface in the mode of secondary and elastically

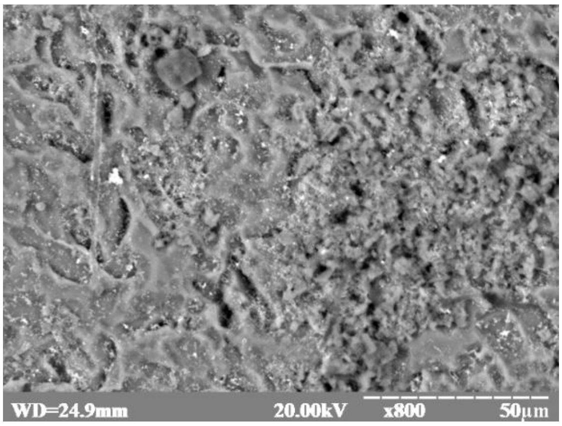
* iolenych@gmail.com

 © 2015 Sumy State University

reflected electrons are shown in Fig. 1. Study of the surfaces exhibit a considerable variation in dispersivity of PS powder, mixed with nanoparticles of ZnO. The SEM images sections of greater brightness were identified as nano ZnO in the mode of elastically reflected electrons. A mixture of semiconductor nanoparticles integrated into the polymer film.



a



b

Fig. 1 – SEM image of the surface of the hybrid composite PEDOT–PS–ZnO in mode of secondary (a) and elastically reflected (b) electrons

In order to study electrical properties of hybrid composite films silver contacts were thermally deposited onto the films surface. The thickness of contacts was about 0.5 microns. The distance between contacts was 4 mm. Inset in Fig. 2 shows the experimental samples. Current-voltage characteristics (CVC) were measured according to standard methods. Voltage range was from -5 Volts to 5 Volts with step 100 mV. Temperature dependences of electric conductivity were measured in vacuum (10^{-3} mm Hg) starting from liquid nitrogen temperature. Polarization voltage was 1 V. Samples were heated linearly at the rate of 0.1 K/sec.

3. RESULTS AND DISCUSSION

Electrical properties of hybrid PEDOT–PS–ZnO films depend on the composition. CVC of experimental samples are shown in Fig. 2. The increase of zinc oxide content in the composite caused a conductivity reduction of hybrid film. This may be caused by a higher resistance of wide band ZnO nanoparticles compared with resistance of PS. At low voltages (below 5 V) current scales is linearly with voltage.

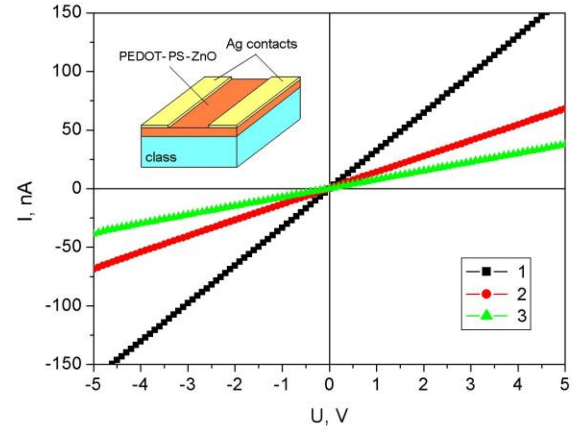


Fig. 2 – CVC of hybrid films PEDOT–PS–ZnO with different composition: 1 – PS:ZnO = 2:1; 2 – PS:ZnO = 1:1; 3 – PS:ZnO = 1:2

Temperature dependence of the conductivity of the hybrid PEDOT–PS–ZnO films in the temperature range of 80–330 K shows the non-monotonic increase of conductivity with temperature (Fig. 3).

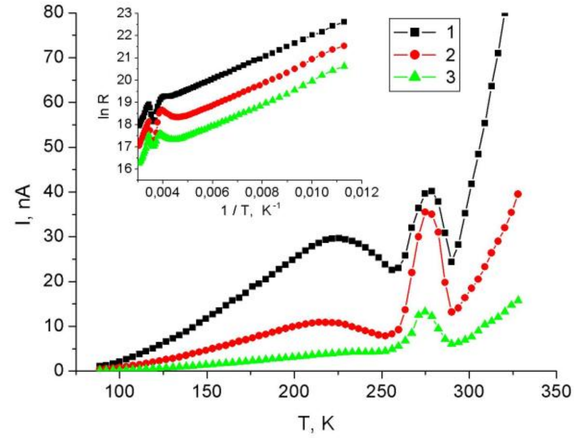


Fig. 3 – The temperature dependence of the electrical conductivity of the hybrid films PEDOT–PS–ZnO with different composition: 1 – PS:ZnO = 2:1; 2 – PS:ZnO = 1:1; 3 – PS:ZnO = 1:2. In the inset: the temperature dependence of the resistance of samples in the coordinates $\ln R - 1/T$

In the low temperature region (80–220 K) one observes exponential increase of the conductivity. This indicates the activation mechanism of charge transfer in structures [22]. Based on the temperature dependence of the resistivity represented in coordinates $\ln R - 1/T$, we can estimate the activation energy of conductivity. An activation energy of conductivity for experimental samples in the low temperature area calculated by angle of graphics $\ln R - (1/T)$ was about 43 meV.

Maxima of conductivity of hybrid films PEDOT–PS–ZnO were observed in the range of medium temperature (220–240 K) and at the approach to ambient temperature (270–290 K). This may be connected with the existence of electrically active defects and trapping levels of unequilibrium charge carriers at the nanoparticle–polymer interface. As conductivity in maximum of the temperature range 220–240 K was higher for films with higher content of PS, it is likely that low energy level capture of carriers associated with silicon nanocrystals.

Trapping levels have influence on charge transport in the system of π-electron connections which determines the electrical properties of conductive polymers [4]. In this case the injected as well as thermally stimulated carriers contribute to electrical conductivity processes in PEDOT–PS–ZnO hybrid composites.

4. CONCLUSION

In this work were created the hybrid nanosystems PEDOT–PS–ZnO and studied their microstructure. Based on the analysis of SEM images of the surface of the hybrid composite was revealed a significant variation in dispersivity of PS and ZnO powder, integrated into the polymer film.

It was experimentally proved that the increase of content of ZnO nanoparticle in the composite leads to the decrease in the conductivity of hybrid films. The analysis of the temperature dependences of the composites conductivity in the temperature range of 80–330 K indicates the activation character of charge transfer and presence the trapping of unequilibrium carriers at the porous silicon and ZnO nanoparticle – polymer interface. An activation energy of conductivity for experimental samples in the temperature of 80 – 220 K was about 43 meV.

REFERENCES

1. A.J. Heeger, *Synth. Metals* **123**, 23 (2002).
2. R.S. Kohlman, J. Joo, A.J. Epstein, *Physical properties of polymers handbook* (Ed. J.E. Mark) (New-York: Amer. Inst. Phys. Woodbury, 1996).
3. Ph. Leclere, M. Surin, P. Brocorens, M. Cavallini, F. Biscarini, R. Lazzaroni, *Mater. Sci. Engin. R* **55**, 1 (2006).
4. J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li, J. Shinar, *Polymer* **45**, 8443 (2004).
5. O. Pyshkina, A. Kubarkov, V. Sergeyev, *Mater. Sci. App. Chem.* **21**, 51 (2010).
6. R. Francis, N. Joy, P. Aparna, R. Vijayan, *Polymer Rev.* **54**, 268 (2014).
7. T.K. Das, S. Prusty, *Polym.- Plast. Technol. Eng.* **52**, 319 (2013).
8. S. Kumar, H. Doshi, M. Srinivasarao, J.O. Park, D.A. Schiraldi, *Polymer* **43**, 1701 (2002).
9. T.P. Nguyen, P.Le Rendu, V.H. Tran, *J. Porous Mat.* **7**, 393, (2000).
10. I.B. Olenych, O.I. Aksimentyeva, L.S. Monastyrskii, Yu.Yu. Horbenko, L.I. Yarytska, *Nanoscale Res. Lett.* **10**, 187 (2015).
11. D. Olson, S. Shaheen, R. Collins, D. Ginley, *J. Phys. Chem. C* **111**, 16670 (2007).
12. W. Beek, M. Wienk, R. Janssen, *Adv. Funct. Mater.* **16**, 1112 (2006).
13. L.T. Canham *Appl. Phys. Lett.* **57**, 1046 (1990).
14. O. Bisi, S. Ossicini, L. Pavesi, *Surf. Sci. Rep.* **38**, 1 (2000).
15. I.B. Olenych, *Ukr. J. Phys. Opt.* **12**, 54 (2011).
16. Q. Zhang, T.P. Chou, B. Russo, S.A. Jenekhe, G. Cao, *Adv. Func. Mater.* **18**, 1 (2008).
17. D. Norton, Y. Heo, M. Ivill, K. Ip, S. Pearton, M. Chisholm, T. Steiner, *Mater. Today* **7**, 34 (2004).
18. Y. Cao, P. Hu, W. Pan, Y. Huang, D. Jia, *Sensor Actuat. B-Chem.* **134**, 462 (2008).
19. I.B. Olenych, O.I. Aksimentyeva, L.S. Monastyrskii, M.R. Pavlyk, *J. Appl. Spectrosc.* **79**, 495 (2012).
20. L.S. Monastyrskii, O.I. Aksimentyeva, I.B. Olenych, B.S. Sokolovskii, *Mol. Cryst. Liq. Cryst.* **589**, 124 (2014).
21. A. Aleshin, I. Shcherbakov, E. Alexandrova, E. Lebedev, *Solid State Commun.* **146**, 161 (2008).
22. N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford: Oxford Univ. Press: 1979).