2018 IEEE 8th International Conference on Nanomaterials: Applications & Properties (NAP – 2018)
September 9-14, 2018, Zatoka, Odesa Region, Ukraine

Ministry of Education and Science of Ukraine
Sumy State University

Proceedings of the 2018 IEEE 8th International Conference on Nanomaterials: Applications & Properties (NAP-2018)

NANOmaterials:
Applications &
Properties-2018

2018, Part 1

ISBN 978-1-5386-5333-3

www.nap.sumdu.edu.ua

Sumy
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2018

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Founded in 2011

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Low Temperature Electrical Behavior of CNT-based Nanocomposites

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***Abstract*— Electrical properties of single- and multi-walled carbon nanotubes composites were investigated in the range of 50 to 200 K. It is established that composite films with multi-walled nanotubes loading show lower resistances as compared to their single-walled counterpart.**

Keywords—nanotube; electrical properties; low temperature; composite; polymer

I. Introduction

One can define carbon nanotubes as cylindrical objects that are formed as the result of envelopment of the graphene layer. In the case of one graphene layer, the resulting structures are called single-walled carbon nanotubes. Since its inception in [1-3], tremendous efforts have been put into the study of the properties of carbon nanotubes, which in many respects are unique. Composites based on nanotubes and having good homogeneity are of considerable interest for a wide range of applications, from simple protection from electromagnetic interference to complex optical devices [4-7]. Speaking of polymer-based nanocomposites, increased attention is recently paid to poly(3,4-ethylenedioxythiophene) - PEDOT host matrices doped by poly(styrene sulfonate) (PSS) [8,9] and reinforced with carbon nanotubes.

Many works focus on the interaction of external fields with PEDOT structures [10-12], as well as the recently widely studied behavior of electrical properties of nanocomposites as a function of frequency [13,14]. However, not very much is known about the change in the conductivity or dielectric properties of such composites in the region of low temperatures. That said, information about nanofiller's influence on composite parameters such as loss tangent or dielectric permeability is crucial as far as functional applications are considered [15-17].

Therefore, the aim of this work is to study the electrical properties of single-walled and multi-walled carbon nanotubes composites at low temperatures in the range from 50 to 200 K.

II. Experimental

Composite films were obtained with water suspension (1%) of poly-3,4,-ethyldioxythiophene, stabilized with a surface-active anionic substance. Single-walled carbon nanotubes (SWCNTs) with 90 wt.% and average diameter near 1 nm and multi-walled carbon nanotubes (MWNTs) with 95 wt% with mean outside diameter of 65 nm and mean inside diameter near 10 nm were used as nanofillers.

Suspension described above was compounded with PEDOT:PSS polymer solution and ultrasonically processed during 4 h. After processing, mixture was deposited on glass substrate by drop-casting liquid on the substrate and centrifugation. After drying at room temperature for 48 h, composite films of PEDOT:PSS/nanotubes were shaped on the glass. Thicknesses of obtained films were near 20 μm. By varying the ratio between PEDOT:PSS solution and suspension of nanotubes, films with different concentration of nanotubes (12 wt% and 16 wt%) were fabricated.

Electrical contacts were deposited on the film surface with conductive paint at the opposite side of the sample (coplanar, or lateral geometry), the distance between the contacts being set to 3 mm.

Electrical tests were carried out exploiting E7-20 RLC meter capable of measuring impedances in the range of 10^{-5} to 10^{9} Ohms using 1 V excitation signal from 40 mV to 1 V at frequencies ranging from 25 Hz up to 1 MHz. Temperature experiments were carried out utilizing custom cryostat equipped with the DE-202A closed cycle cryocooler. Temperature control functions were conducted by Cryocon 32 temperature regulator.

III. Results and Discussion

Aiming to get an idea of the conductivity mechanisms, samples of PEDOT:PSS/CNTs films were exposed to impedance measurements at low temperature. Temperature dependencies of the measured sheet resistance of composite films reinforced with SWCNT and MWCNT measured at 100 kHz in the range from 50 to 200 K are shown in Fig. 1 for PEDOT:PSS/SWNT films with 12 wt% and 16 wt% and Fig. 2 for PEDOT:PSS/MWNT films with 12 wt% and 16 wt%, respectively.

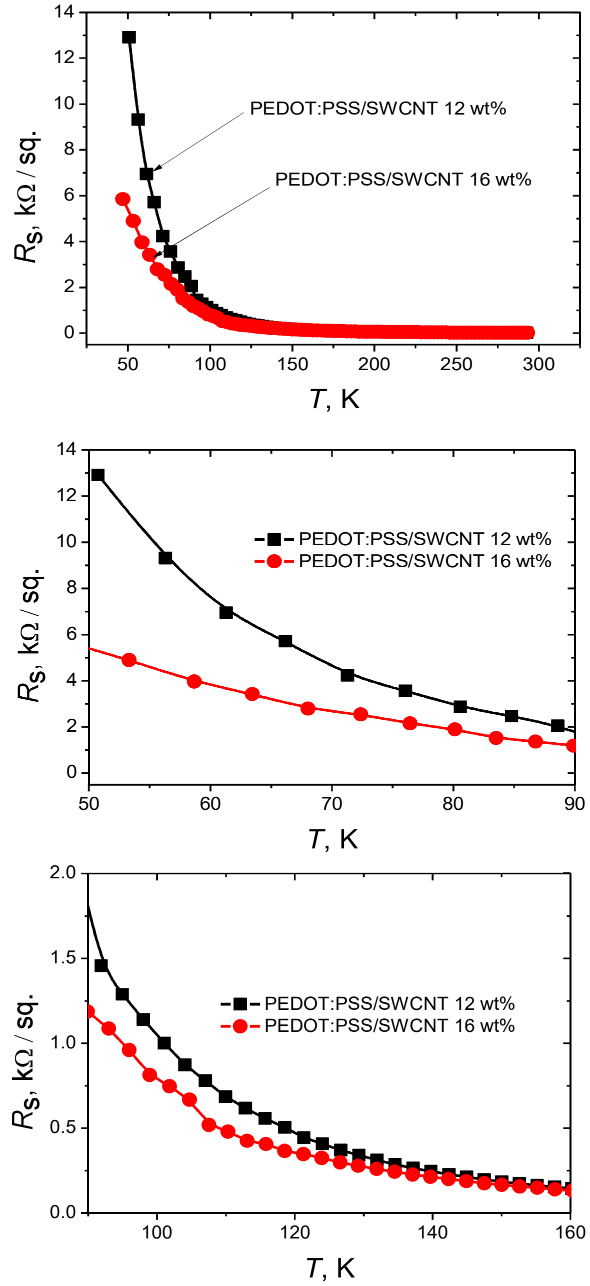


Fig. 1. Dependencies of sheet resistances on temperature for PEDOT:PSS/SWCNT composite films measured in cooling regime

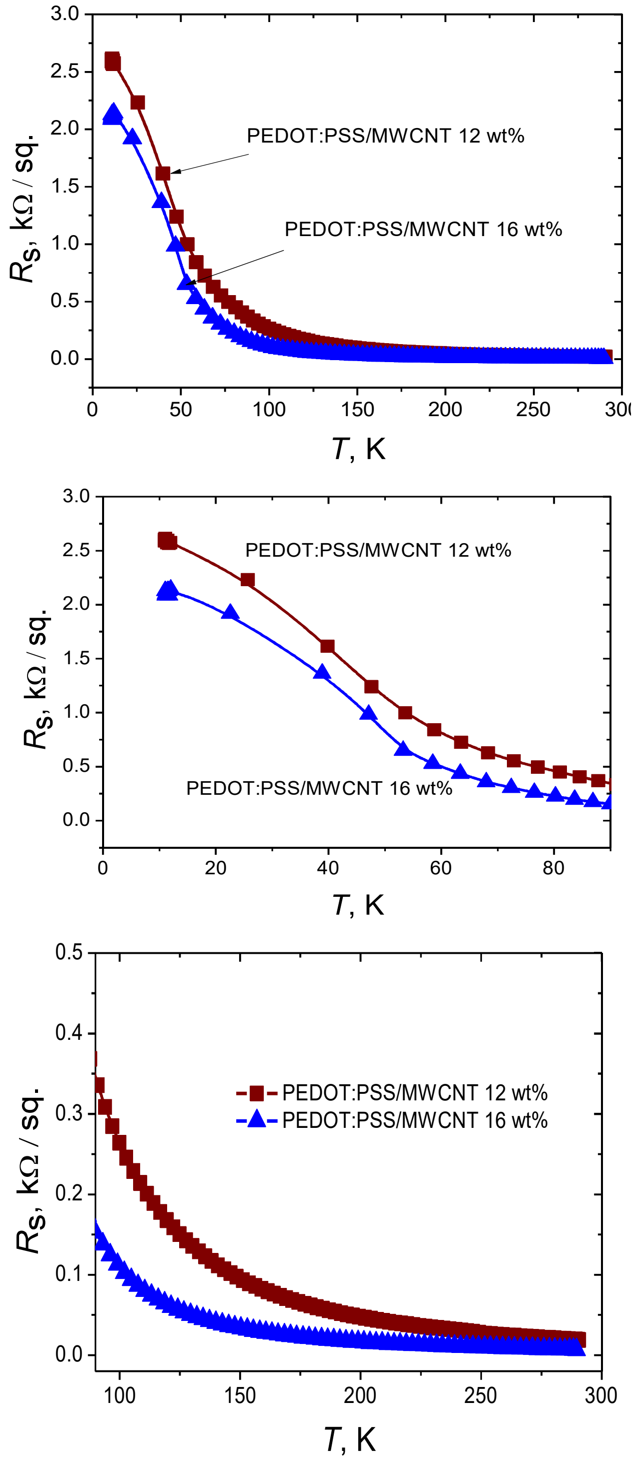


Fig. 2. Dependencies of sheet resistances on temperature for PEDOT:PSS/MWCNT composite films measured in cooling regime

The selection of such temperature range was related with small fluctuations of resistance from 200 K to room temperature and rise in the resistance for SCWNT composites at temperatures below 50 K (most likely due to the limitation of measurement ranges for the RLC meter used) [13,18].

In general, lateral resistance of PEDOT:PSS/CNTs composite films behaves non-linearly upon cooling. The dependencies in Fig. 1 and Fig. 2 are split in two sub-ranges, since there are possibly different mechanisms involved below and above 90 K. As far as different loadings of nanofiller are considered, sheet resistances decrease with nanotube concentration for SWCNTs and MWCNTs polymers. Films with multi-walled nanotube loading show lower resistances as compared to their single-walled composites.

The low-temperature conduction mechanisms follow the activation-type formula, that in terms of resistances can be expressed as

$$R_s \approx T \cdot \exp\left(\frac{eE_a}{kT}\right), \tag{1}$$

where e is the elementary charge, k is Boltzmann's constant. The plot of $\ln(R_s/T)$ as the function of the reciprocal temperature and the least-squares approximation procedure allows to find the activation energy from the inclinations of the fitting lines. Results of such procedure for SWCNTs and MWCNTs composite films are shown in Fig. 3 and Fig. 4.

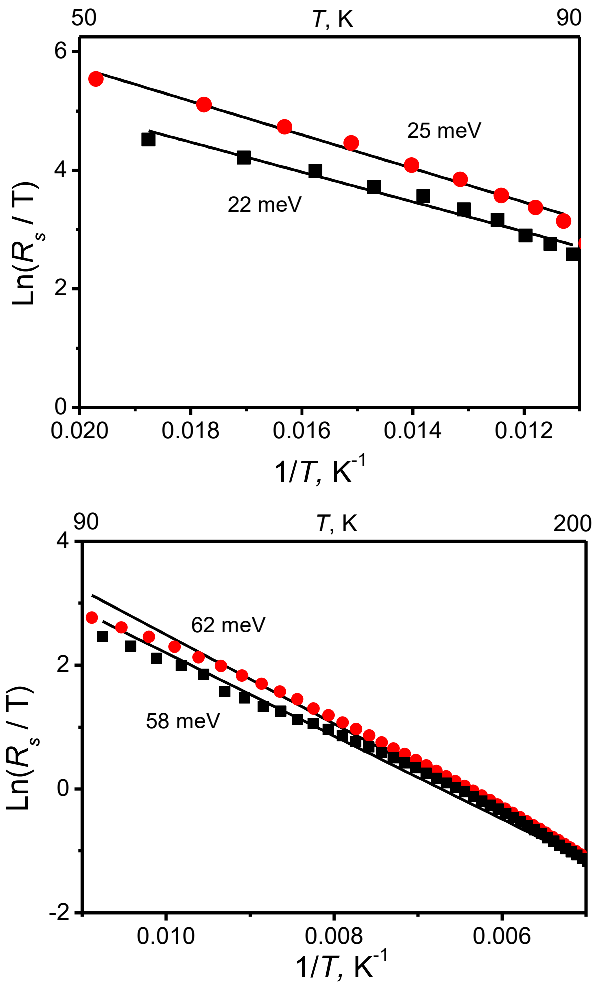


Fig. 3. Arrhenius plots for PEDOT:PSS/SWCNT composite films. Circles denote experimental points for 12 wt% SWCNT loading; squares denote experimental points for 16 wt% SWCNT loading. Solid lines represent linear fitting

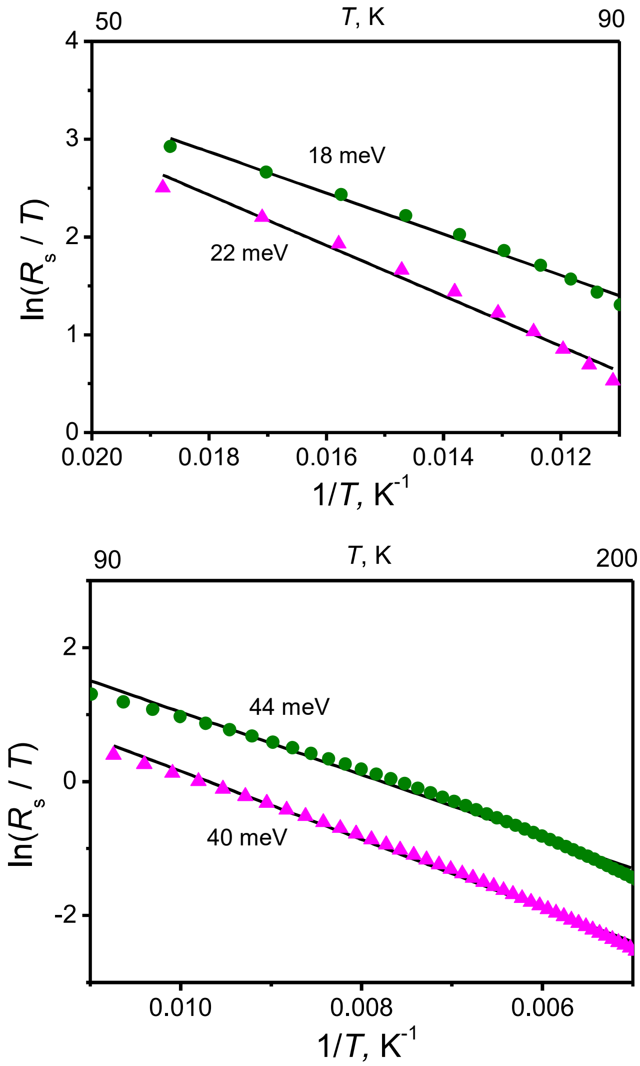
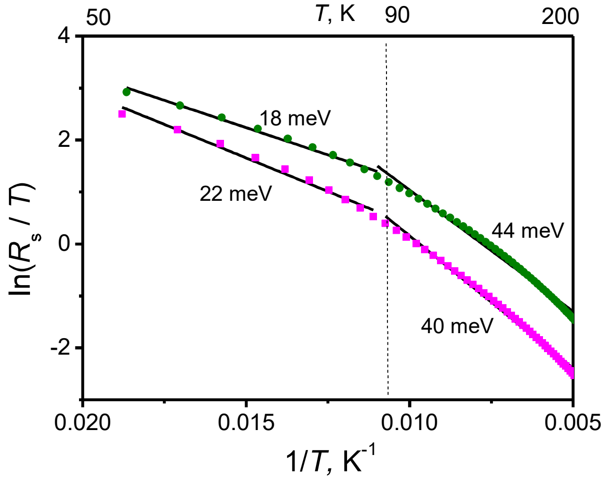


Fig. 4. Arrhenius plots for PEDOT:PSS/MWCNT composite films. Circles denote experimental points for 12 wt% MWCNT loading; triangles denote experimental points for 16 wt% SWCNT loading. Solid lines represent linear fitting.

As can be seen from Fig. 3 and Fig. 4, it is possible to outline two regions with different activation energy. Increasing the amount of SWCNTs and MWCNTs in the composites has little effect on the values of activation energy below and above 90 K. The deviation of 4 meV is connected with error of fitting procedure.

It is known that in disordered materials several conduction mechanisms can be realized that play different roles in different temperature ranges. As in the experiment discussed here, at a lower temperature the mechanism determined by a certain type of electrically active defects with less activation energy prevails, and above 90 K the mechanism controlled by other active defects takes over. The transition temperature is the same for SWCNTS and MWCNTS composites as it is determined by the properties of the host material, that is, the electronic parameters of the PEDOT:PSS polymer itself.

Comparison of Arrhenius plots for PEDOT:PSS/MWCNT and PEDOT:PSS/SWCNT composite films is shown in Fig. 5.



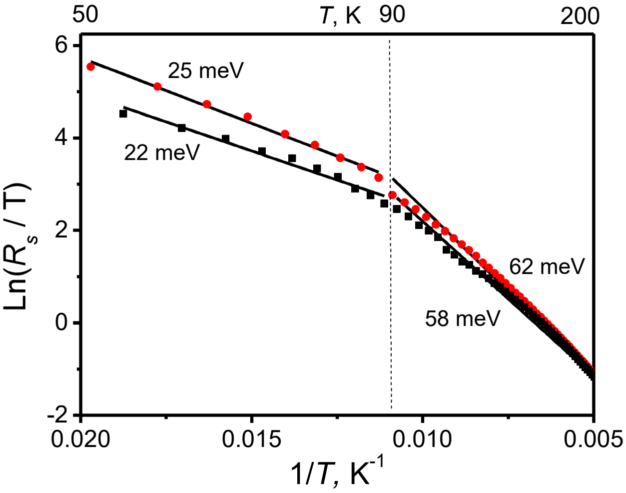


Fig. 5. Comparison of Arrhenius plots for PEDOT:PSS/MWCNT and PEDOT:PSS/SWCNT composite films. Circles denote experimental points for 12 wt% MWCNT loading; triangles denote experimental points for 16 wt% SWCNT loading. Solid lines represent linear fitting.

IV. Conclusion

Electrical resistance of PEDOT: PSS composite films with different loadings of single- and multi-layered nanotubes were investigated by conductivity measurements. Multi-layer nanotube composites show lower resistance at the same temperatures than single-walled nanotube composites.

Acknowledgment

The research of I. Karbovnyk has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 778156. H. Klym thanks to the Ministry of Education and Science of Ukraine for support under Project No 0118U000261.

References

[1] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, "Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load," Science, vol. 287(5453), pp. 637-640, 2000.

[2] E. T. Thostenson, Z. Ren, and T.W. Chou, "Advances in the science and technology of carbon nanotubes and their composites: a review," Composites science and technology, vol. 61(13), pp. 1899-1912, 2001.

[3] V. Bajpai, L. Dai, and T. Ohashi, "Large-scale synthesis of perpendicularly aligned helical carbon nanotubes," Journal of the American Chemical Society, vol. 126(16), pp. 5070-5071, 2004.

[4] M.H. Al-Saleh, and U. Sundararaj, "Electromagnetic interference shielding mechanisms of CNT/polymer composites," Carbon, vol. 47, pp. 1738-1746, 2009.

[5] N. Li, Y. Huang, E. Du, X. He, X. Lin,H. Gao, and P.C. Eklund, "Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites," Nano Lett., vol. 6(6), pp. 1141-1145, 2006.

[6] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M.E. Tompson, and C. Zhou, "Transparent, conductive, and flexible carbon nanotube films and their application in organic light-emitting diodes," Nano Lett., vol. 6, pp. 1880-1886, 2006.

[7] X. Luo, C.L. Weaver, D.D. Zhou, R. Greenberg, and X. T. Cui, "Highly stable carbon nanotube doped poly (3, 4-ethylenedioxythiophene) for chronic neural stimulation," Biomaterials, vol. 32, pp. 5551-5557, 2011.

[8] Y. H. Kim, C. Sachse, M.L. Machala, C. May, L. Müller-Meskamp, and K. Leo, "Highly conductive PEDOT: PSS electrode with optimized solvent and thermal post-treatment for ITO-free organic solar cells," Adv. Funct. Mater., vol. 21(6), pp. 1076-1081, 2011.

[9] I. Olenych, O. Aksimentyeva, L. Monastyrskii, and O. Dzendzelyiuk, "Effect of radiation on the electrical and luminescent properties of conjugated polymer – porous silicon composite," Molecular Crystals and Liquid Crystals, vol. 640, pp. 165-172, 2006.

[10] J. Park, A. Lee, Y. Yim, and E. Han, "Electrical and thermal properties of PEDOT: PSS films doped with carbon nanotubes," Synthetic Metals, vol. 161, No 5, pp. 523-527, 2011.

[11] A. M. Nardes, M. Kemerink, M. M. De Kok, E. Vinken, K. Maturova, and R.A.J. Janssen, "Conductivity, work function, and environmental stability of PEDOT: PSS thin films treated with sorbitol," Organic Electron., vol. 9(5), pp. 727-734, 2008.

[12] I. Olenych, O. Aksimentyeva, L. Monastyrskii, Yu. Horbenko, and L. Yarytska, "Sensory properties of hybrid composites based on poly (3, 4-ethylenedioxythiophene)-porous silicon-carbon," Nanoscale Res. Lett., vol. 10, pp. 187, 2015.

[13] I. Karbovnyk, I. Olenych, O. Aksimentyeva, H. Klym, O. Dzendzelyuk, Y.Olenych, and O. Hrushetska, "Effect of radiation on the electrical properties of PEDOT-based nanocomposites," Nanoscale Res. Lett., vol. 11, pp. 84, 2016.

[14] D. Zhao, Q. Zhang, W. Chen, X. Yi, S. Liu, Q. Wang, Y. Liu, J. Li, X. Li, and H. Yu, "Highly flexible and conductive cellulose-mediated PEDOT: PSS/MWCNT composite films for supercapacitor electrodes," ACS Appl. Mater. Interfaces, vol. 9, pp. 13213-13222, 2017.

[15] I. Karbovnyk, J. Collins, I. Bolesta, A. Stelmashchuk, A. Kolkevych, S. Velupillai, H. Klym, O. Fedyshyn, S. Tymoshuk, and I. Kolych, "Random nanostructured metallic films for environmental monitoring and optical sensing: experimental and computational studies," Nanoscale Res. Lett., vol. 10(1), pp. 151, 2015.

[16] H. Klym, A. Ingram, O. Shpotyuk, L. Calvez, E. Petracovschi, B. Kulyk, R. Serkiz, and R. Szatanik, "'Cold' crystallization in nanostructurized $80GeSe_2$-$20Ga_2Se_3$ glass," Nanoscale Res. Lett., vol. 10(1), pp. 1-8, 2015.

[17] I. Hadzaman, H. Klym, and O. Shpotyuk, "Nanostructured oxyspinel multilayers for novel high-efficient conversion and control," Int. J. Nanotechnol., vol. 11, pp. 843-853, 2014.

[18] A. Benchirouf, S. Palaniyappan, R. Ramalingame, P. Raghunandan, T. Jagemann, C. Müller, M. Hietschold, and O. Kanoun, "Electrical properties of multi-walled carbon nanotubes/PEDOT: PSS nanocomposites thin films under temperature and humidity effects," Sens. Actuat. B: Chem., vol. 224, pp. 344-350, 2016.