Electrical Properties at Low Temperatures of PEDOT-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

It is well-known, that carbon nanotubes are cylindrical objects with sides formed in the results of envelopment 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 in the study have been made into the study of the properties of carbon nanotubes, which in many respects are unique. Composites having good homogeneity are of considerable interest for a wide range of applications, from simple protections 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 from 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. So, information about nanofilter's influence on composite parameters such as loss tangent, dielectric permeability is crucial in the consideration of material science for functional applications as for other functional materials [15-17].

So, the aim of this work is study the electrical properties of single-layer and multilayer carbon nanotubes composites at low temperatures on 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. So, single carbon nanotubes (SWCNTs) with 90 wt.%, average diameter near 1 nm and multilayered carbon nanotubes (MWNTs) with 95 wt%, mean outside diameter of 65 nm and mean inside diameter near 10 nm were obtained.

Such suspension was compounded with PEDOT:PSS polymer solution and ultrasonically processed again 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 a DE-202A closed cycle cryocooler. Temperature control functions were conducted by Cryocon 32 temperature regulator.

III. Results and Discussion

So as to get an idea of the conductivity mechanisms, samples of PEDOT:PSS/CNTs films were exposed to impedance measurements at low temperature. Temperature dependences of the measured resistance of sheets of reinforced SWCNT and MWCNT composite films measured at 100 kHz in the range from 50 to 200 K were 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.

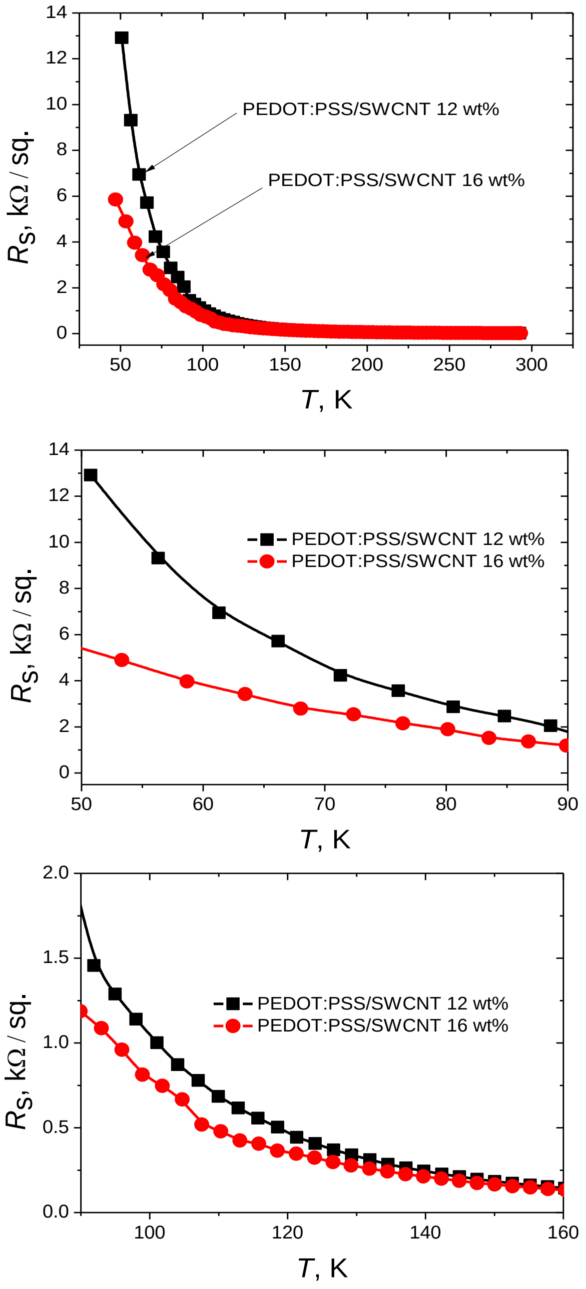


Fig. 1. Dependences of sheet resistances from temperature for PEDOT:PSS/SWCNT composite films measured in cooling regime

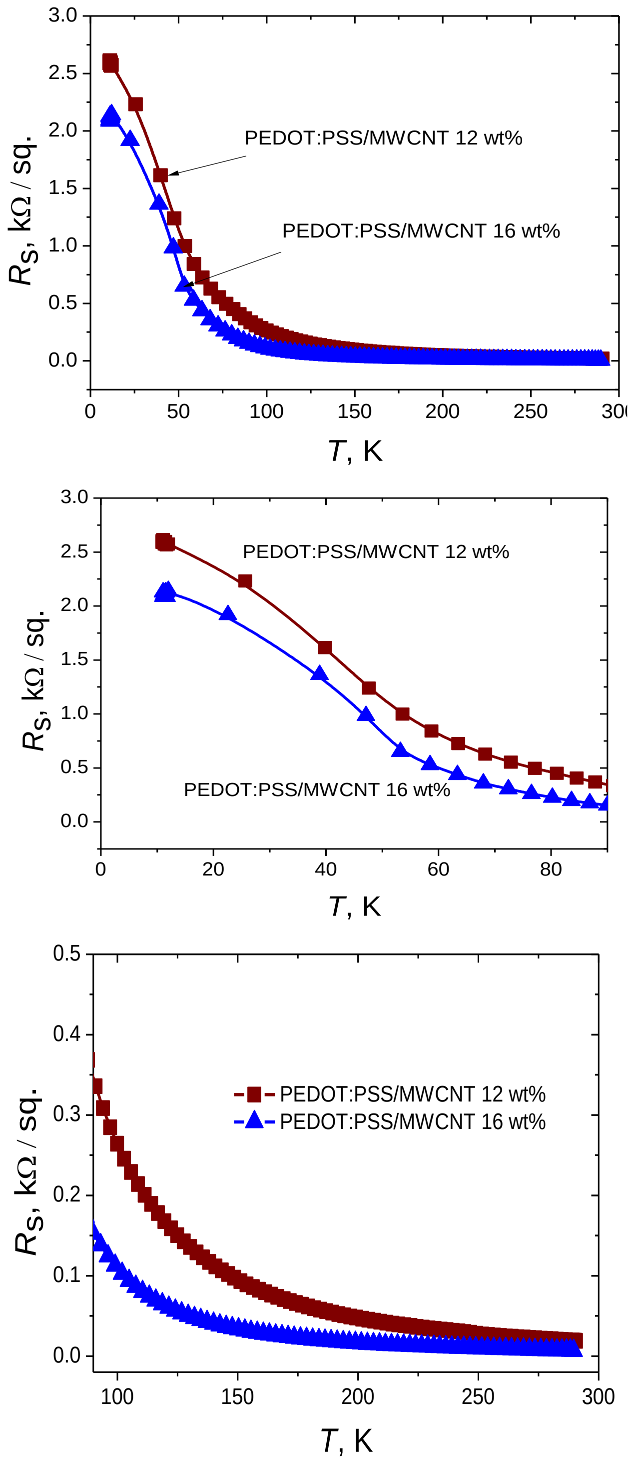


Fig. 2. Dependences of sheet resistances from temperature for PEDOT:PSS/MWCNT composite films measured in cooling regime

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 (measurement ranges for the RLC meter) [13,18].

In general, lateral resistance of PEDOT:PSS/CNTs composite films extend 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 relation of the type of activation, the reinforced stability can be expressed as

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

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

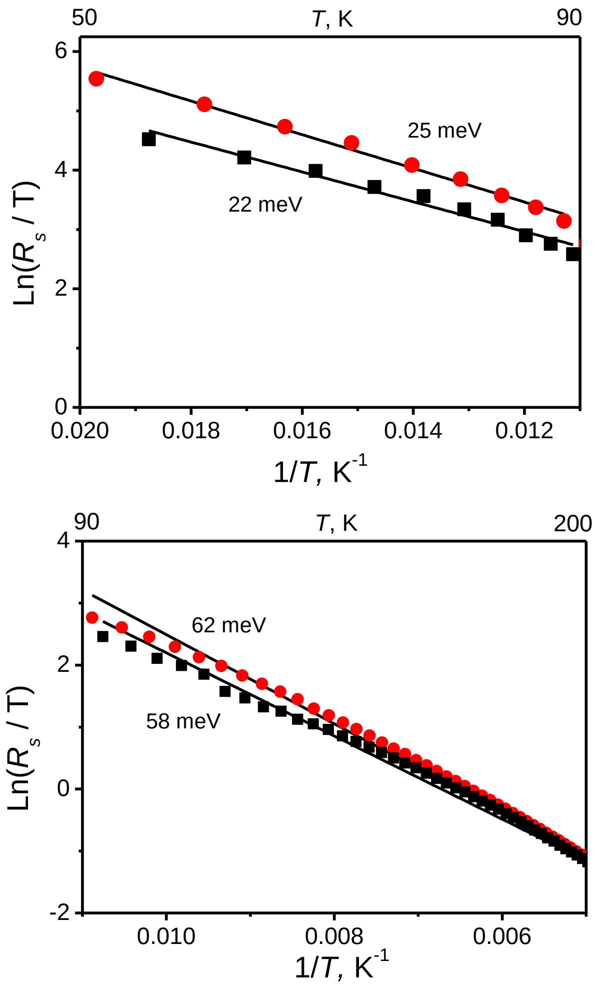


Fig. 3. Arrhenius plots for PEDOT:PSS/SWCNT composite films. Circles denote experimental points for 12 wt% SWCNT load; squares denote experimental points for 16 wt% SWCNT load. Solid lines represent linear fitting

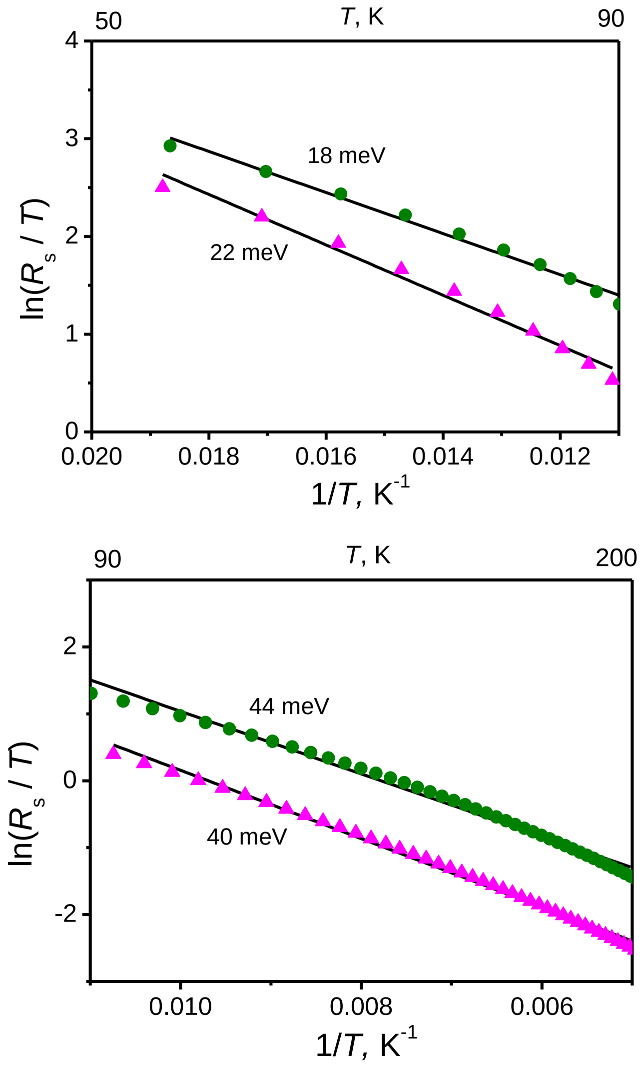
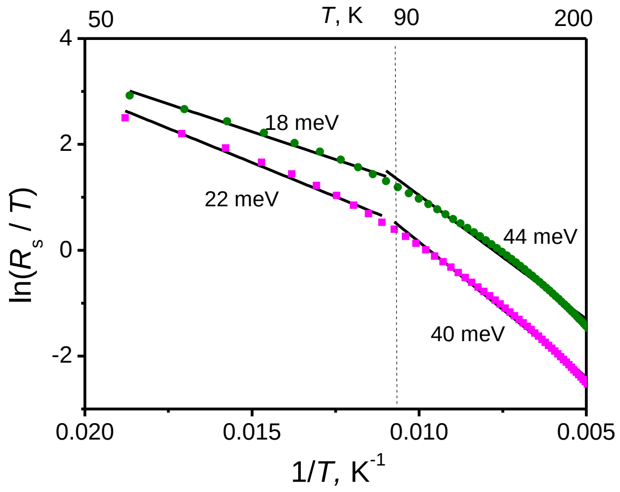


Fig. 4. Arrhenius plots for PEDOT:PSS/MWCNT composite films. Circles denote experimental points for 12 wt% MWCNT load; triangles denote experimental points for 16 wt% SWCNT load. Solid lines represent linear fitting.

As can be seen from the Fig. 3 and Fig. 4, it is possible to divide two regions with different activation energy. Rise the amount of SWCNTs and MWCNTs composites have little effect on values of activation energy below and above 90 K. The deviation of 4 meV is connected with error of approach 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 is a mechanism controlled by other active defects. 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 plots for PEDOT:PSS/MWCNT and PEDOT:PSS/SWCNT composite films is shown in Fig. 5.



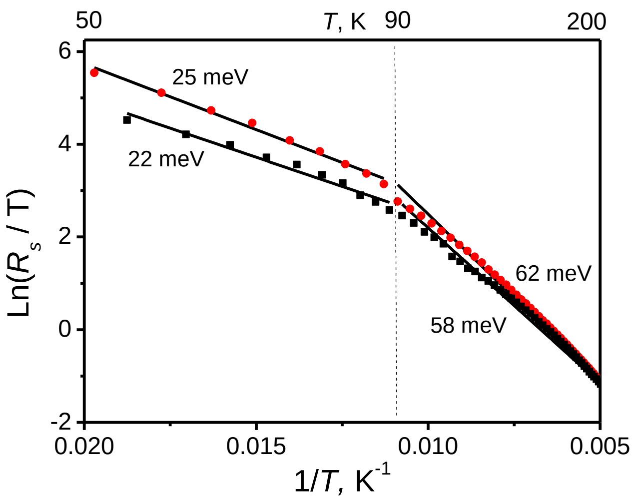


Fig. 5. Comparison of plots for PEDOT:PSS/MWCNT and PEDOT:PSS/SWCNT composite films. Circles denote experimental points for 12 wt% MWCNT load; triangles denote experimental points for 16 wt% SWCNT load. Solid lines represent linear fitting.

IV. Conclusion

Electrical resistance for PEDOT: PSS composite films with some amount 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.

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