REPORT

of the official opponent, doctor of physic-mathematical sciences, professor, professor of the Department of Material science and nanotechnologies, Belgorod national research university, Ivanov on Ph.D. thesis "THERMOELECTRIC EFFECTS IN POLYMER-BASED COMPOSITES" by Yusupov Khabib Umaralievich submitted to the application of the scientific degree of a Candidate of Physical and Mathematical Sciences in a specialty 01.04.10 – Physics of semiconductors

It is well known that certain advantages of thermoelectric generators, among which are reliability, environmental friendliness, noiseless operation, scalability, are largely canceled out with the main disadvantage, which is the low coefficient of efficiency (not exceeding 10%). In its turn, the efficiency coefficient is determined by the figure of merit of utilized material. For the efficient thermoelectric performance, the utilized material is supposed to exhibit high values of electrical conductivity and Seebeck coefficient alongside with low values of thermal conductivity. There is the restricted number of materials in which the described combination of properties is being respected for the appropriate utilization as thermoelectric materials. In general, such materials are inorganic based. Among which the majority, in spite of exhibiting reasonable thermoelectric properties, are of the high prize, often toxic and demand complex manufacturing process. Because of that, the development of organic-based thermoelectric materials is the highly perspective direction of the modern trend in thermoelectricity. The polymer-based thermoelectric materials are non-toxic and easily operable in contrast to inorganic materials. Among other advantages of polymer-based materials, one can highlight small weight and flexibility. Due to the latter feature, thermoelectric polymers can be used in such cases when the polymer is in contact with the surfaces of different shapes including bodies with the random form. The major asset for thermoelectric polymers is low thermal conductivity if one speaks about the possibility of reaching high values of thermoelectric efficiency. Though at a time the values of electrical conductivity and Seebeck coefficient of organic materials cannot compete with inorganic-based materials, the case can be changed considering all scientific and technical approaches that are under development and are being adjusted to improve thermoelectric properties. In case of such improvement, one can expect that shortly polymer-based thermoelectric materials become competitive with inorganic thermoelectric materials, at least for the applications in the region of low temperatures.

That is why the dissertation work represented by Yusupov K.U., which is focused on the determining the influence of single- and multi-walled carbon nanotubes on electrical conductivity and Seebeck coefficient of polymer matrix poly (3,4 ethylenedioxythiophene) polystyrene sulfonate is of the interest at the time.

The methodology of the dissertation is based on scientific approaches to the development of thermoelectric polymer materials with improved thermoelectric efficiency. Such is due to the utilization of the polymer composite, which consists of the polymer matrix (poly (3,4 ethylenedioxythiophene) polystyrene sulfonate) with low values of thermal conductivity, and the filler, which improves electrical conductivity and Seebeck coefficient. As the fillers, the author used single- and multi-walled carbon nanotubes, including the tubes which were doped with aurum chloride. Composites, which are obtained with certain technological patterns and with further chemical post-treatment, can form the systems with the controlled orientation of carbon nanotubes. In the case of the orientation, it is shown that such can be reached with the utilization of the vertically oriented "forest" of nanotubes, which allows obtaining layers of "forest." The number and the order of sequence of such layers give the additional possibility to control the tuning of thermoelectric properties for multi-layered structures.

While conducting the research, the author used modern methods of polymer composites manufacturing: growth of carbon nanotubes by chemical vapor deposition, creation of multi-layered composites with variation of the sequence of layers of filler and polymer matrix, the structure and properties modification with chemical post-treatment by different media, and creation of hybrid materials to adjust the band structure. To investigate the structure, composition, and properties the experimental methods of study were performed including scanning electron microscopy, transmittance electron microscopy, atomic force microscopy, Raman microscopy, and measurement of electrical conductivity and Seebeck coefficient. To further strengthen the results and deeply understand the mechanisms of doping, the band structure modeling was performed for carbon nanotubes and its hybrids using density functional theory in the framework of the Vienna ab-intion simulation package.

The main scientific result of the dissertation represented by Yusupov K.U. is in the experimental confirmation of the possibility of significant improvement of power factor for polymer-based composites of type: matrix is poly (3,4 ethylenedioxythiophene) polystyrene sulfonate, fillers are "forest" of multi-walled carbon nanotubes, single-walled carbon nanotubes, and hybrids of the latter. For example, polymer-based composite with single-walled carbon nanotubes as filler after treatment with aurum chloride exhibits values of power factor ~ 200 $\mu W/mK^2$ at room temperature, which is significantly higher of known values for the similar thermoelectric systems.

Other most important scientific results, which are represented in the dissertation and were obtained during the research of thermoelectric properties of investigated polymer-based composites, are:

1. Consistent patterns of the influences of concentrations, types of filler (multi- and single-walled carbon nanotubes, hybrids of the latter), and structures of composite (dispersed nanotubes or multi-layered composites) on thermoelectric properties of polymer-based composites with the matrix of poly (3,4 ethylenedioxythiophene) polystyrene sulfonate.

2. Improvement of the Seebeck coefficient and electrical conductivity of developed thermoelectric composites based on polymer matrix due to the utilization of vertically aligned carbon nanotubes "forest" as the filler in the composite.

3. Improvement of the electrical conductivity of the developed polymer-based composites with chemical post-treatment by the ethylene glycol and dimethyl sulfoxide, which leads to partial withdrawal of anions from the matrix.

4. Technological method of obtaining polymer-based composites which exhibit a high degree of both the homogeneity and distribution of the filler and absence of agglomerates. The method is based on the spin-coating method of polymer matrix above the filler - vertically aligned carbon nanotubes "forest."

5. Representing features of the band structure changes of the single-walled carbon nanotubes with aurum and aurum chloride doping. The changes were obtained via modeling of the band structures through the density functional theory.

The practical significance of the dissertation represented by Yusupov K.U. is in the determined patterns of changes for electrical conductivity and Seebeck coefficient that can be used during development of the scientific and technological ways to approach of obtaining of new or modified thermoelectric polymers with high values of thermoelectric efficiency. Note that such should be done with consideration of the type of filler, its concentration, and structure of the composite. Developed, during the research work, materials are highly perspective thermoelectric polymers for application as thermoelectric generators at low temperatures.

Conclusions, which are based on the dissertation represented by Yusupov K.U., creates necessary scientific basis for the development of physical interpretations about specifics of thermoelectric effects as well as about mechanisms and influences of changes of thermoelectric properties of polymer-based composites. The changes are dictated by both the polymer matrix and the fillers of the composite, and the alterations of the properties, which are due to the interactions between matrix and filler.

Obtained by Yusupov K. U. research results and conclusions on their basis are grounded and reliable, which is due to the list of reasons: utilization of highly technological methods of manufacturing with reproducible properties of materials, application of approved and complementary methods of structure and properties investigations, and consistency of obtained results with respect to the known physical paradigms and theories.

The dissertation represented by Yusupov K.U. is not without disadvantages, which can be expressed in the following way:

1. Though usually the filler is known to affect the thermal conductivity of the polymer-based composites in a lesser degree in comparison with electrical conductivity and the Seebeck coefficient, however, it is recommended to determine the influence of the filler on thermal conductivity of the investigated polymer-based composites, especially because of the increase of power factor, for the full evaluation of the

thermoelectric figure of merit.

2. As a filler for the polymer-based composites, the author used carbon nanotubes. However, there is no information in the dissertation regarding the technology of nanotubes manufacturing process, which is an important part of the work considering that it is an important step in the technology of composite manufacturing.

3. The chapter two of the dissertation contains information about both the ways of composites obtaining, methods which were used to study them and about the theory behind the band structure modeling of carbon nanotubes. It seems logical to divide this chapter into two parts: one could describe the obtaining process with the methods of study, the second could be about modeling process. The information in these parts are weakly bonded to each other, even more so, the first part (obtaining and study) is more methodology and informative, whereas the "modeling" part contains results which form the basis for one of the conceptual issues ported-out for the defense.

4. Chapter two exhibits figures (12-15) of research equipment used for the dissertation fulfillment. The presence of such figures does not help the reader to figure out the features of the conducted experiments, i.e., there is no necessity in them. At the same time, there is no such valuable data in the dissertation as the resolution of the microscopes, the temperature change rate during the investigation of thermoelectric properties, and temperature gradient. However, such data is important particularly in confirming the reliability of the obtained results.

5. The dissertation contains two parts: the technological and the physical. The technological part of the work is better described than the physical if one considers the development of a physical aspect of material science. To strengthen the physical part, it is suggested to provide the reader with a deeper analysis of determined influences on thermoelectric properties of the materials in question, including determining the mechanisms of scatterings for charge carriers, change of the concentration and mobility of the charge carriers, etc.

Mentioned remarks, however, do not reduce the overall favorable impression from the dissertation work made by Yusupov K.U.

The dissertation work, represented by Yusupov K.U., exhibits a strong correlation of research goals and aims as well as goals and obtained results. The results of the work are fully published in 8 research publications including 3 papers indexed by the databases Web of Science and Scopus, and 5 reports on the international research conferences. Autoreferat corresponds to the submitted thesis.

The content of the thesis corresponds to the passport of specialty 01.04.10 — Physics of Semiconductors (physics and mathematical science), and criterium in paragraphs 2.1–2.5 statute of conferment scientific degree in M.V. Lomonosov Moscow State University according to applications № 5, 6 statutes of dissertation council.

Thus, the applicant, Yusupov Khabib Umaralievich deserves the scientific degree of a Candidate of Physical and Mathematical Sciences in a specialty 01.04.10 – Physics of Semiconductors.

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