REPORT

of the official opponent, doctor of physic-mathematical sciences, head of the laboratory of thin film nanostructured materials of Institute of nanostructures and biosystems of the Saratov state university 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

The Ph.D. thesis of Yusupov Khabib Umaralievich is focused on the investigation of the thermoelectric properties of polymer-based thermoelectrical materials. The best heat-to-power conversion efficiency of the conventional thermoelectric (TE) materials is far from being at least 10%. The efficiency of the TE materials is expressed in the dimensionless figure of merit $ZT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the average temperature of the TE device. The most important goal of the research work within the topic of TE study is the search of materials with $ZT > 3$. In bulk materials of the inorganic nature S, ρ, and κ are interrelated and depend on the electronic structure and the microstructure of the material. However, going down in size, i.e., nano fragmentation, leads to the possibility to adjust transport properties through the quantum size effects, and the grain boundary scattering of phonons (phonon-blocking/electron-transmitting effect).

For example, the TE system SiGe after being modified through the nano structurization process exhibits a significant improvement in TE performance. In the example, such was achieved via going down in the size of the grains, which led to the electron-phonon scattering process on the boundaries of the grains. Such was the cause of the improvement of electrical conductivity which became more sufficient for the application in the TE field. The similar pattern can be observed for many other research works.

However, inorganic semiconductors, though showing the highest efficiency, exhibit some disadvantages, such as high thermal conductivity, abundance, long manufacturing process, and especially high cost. For this reason, other materials are considered an alternative, among which ceramic-based, hybrid-based and polymer-based. Among the latter conductive polymers are considered as alternative materials for TE applications at temperatures close to room due to their low thermal conductivity, non-toxicity, low operating temperature, and abundance. Apart from the described advantages and features polymer are easily adjustable to the random shapes. The latter makes polymers the ideal candidates for TE generators in flexible applications such as wearable devices (watches, bracelets, etc.) and clothing. All above mentioned made polymers the main interest as a study material among various research groups concerning what numerous publications have appeared in past years.

Among conductive polymers, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has been the most used for the investigation of the TE properties, due to its good electrical conductivity (achieved sheet resistance is about 300 Ohm/square with the addition of conductivity-enhancement agents). However, the low values of Seebeck coefficient for pure polymer encouraged significant efforts to increase its efficiency. Significant improvements were observed through the incorporation of nanosystems (fillers) and treatment with chemical agents. The most successful fillers were carbon nanotubes. Ph.D. thesis of Yusupov K. U. is devoted just to all these aspects. According to the mentioned it could be stated that the topic of the thesis is of the current interest.

The thesis has an introduction and three chapters.

In **Introduction** the actuality of the research was discussed. A list of conceptual issues for the defense of the thesis is shown. List of publications consists of 3 papers in journals which are included in the Web of Science and Scopus databases.

Chapter 1 is a review part. In Chapter 1 the author describes traditional, i.e., inorganic thermoelectric materials, basic transport properties of conductive polymers and polymer-based TE materials. Among conductive polymers, the author highlights polyacetylene, polyaniline (PANI), poly (3-hexylthiophene) (P3HT), poly(3,4-ethylene dioxythiophene) polystyrene sulfonate as a basis for thermoelectric materials due to the high publication activity related to them. The chapter follows the pattern of describing separately the influence of fillers (both organic and inorganic-based) and chemicals on TE properties of polymers. Among organic or carbon-based fillers author highlighted carbon nanotubes due to the impact on the transport properties of the polymers. In the last paragraph of chapter 1, the author made conclusions based on the analysis of literature.

Using the experimental data from various groups, the strategy for creating new composite materials with high TE performance was determined. Since the stable, and the highest values of TE performance were achieved for PEDOT:PSS-based composite with the incorporated of carbon materials, the author decided to use CNTs as fillers. It is known for the carbon-based materials create agglomerates, which can further negatively affect transport properties. Thus, the applicant used the vertically aligned carbon nanotubes forest (VA-CNTF) and aerosol synthesized single walled carbon nanotubes (AE-SWCNTs) as filler for composite materials because optimized by the author manufacturing process allows preventing agglomeration of fillers within the polymer matrix. Pulled VA-CNTF allowed him to fabricate different sandwich-type structures. During utilization of AE-SWCNTs and author changed the composition of the tubes by treatment with an alcohol solution of $AuCl_3$ with further incorporation into the polymer matrix. The last step of research was the investigation of the behavior of samples with chemical post-treatment. Dimethyl sulfoxide (DMSO) and ethylene glycol (EG) were chosen for the post-treatment process as they were mentioned in the literature as a convenient way of tuning TE performance.

In Chapter 2 with a title "Methodology," the author described manufacturing processes for each type of samples. Vertically aligned carbon nanotubes forest (VA-CNTF)-based composites were obtained via the following procedure. Firstly CNTs of the CNTF were pulled from the Si-substrate to create a carpet-like surface which was then covered on top of the glass substrate. Then the created layer was covered with the polymer matrix via the spin-coating process. After the annealing process created, samples were chemically post-treated. Dimethyl sulfoxide and ethylene glycol were used as chemical agents. Both chemicals tend to affect negatively charged ions of the matrix (PSS), which is also an insulator. Thus, the treatment was used to improve electrical conductivity. Apart from the described samples, two more series of samples with CNTF as filler was obtained. In the additional series, the amount and sequence of layers varied. The same type of obtaining process was performed to create samples with the AE-SWCNT and their hybrids.

After that, there is a part regarding analysis methods utilized during the investigation of the materials. The author used standard equipment such as scanning electron microscopy (SEM), Raman spectrometer, transmission electron microscopy (TEM).

In Chapter 2 the author also included theoretical considerations and some calculations. He described the essence of Density Functional Theory (DFT), Kohn-Sham equations; the concept of Pseudopotential and supersell is introduced.

Chapter 3 describing results and discussions. This chapter can be divided into two main parts. First is describing the results related utilization of CNTF as a filler with further chemical post-treatment. The highest PF (92 $\mu W/mK^2$) at 414 K was achieved for the samples with a single layer of VA-CNTF. The second part is related to the results of the utilization of AE-SWCNTs and its hybrids. In this chapter apart from the experimental part author described results obtained via theoretical calculation using VASP package. The author used VASP package to calculate two possible mechanisms of doping: 1) doping with Au and 2) doping with $AuCl_4$. Graphical representation of doping mechanisms and DOS of each mechanism are demonstrated. The changes in Fermi level is represented in the table. The Au-doping leads to the shift of the Fermi level towards the conduction band alongside with the formation of additional quantum states near the Fermi level. The decrease of the band gap is observed as well. The AuCl4-doping the p-type doping is observed with the shift if the Fermi level towards to valence band and an increase of the band gap. The author compared two mechanisms and based on the experimental results concluded that the p-type doping took place within the composite. Such perfectly explains the behavior of the Seebeck coefficient and the electrical conductivity.

Finally, thin flexible polymer-carbon nanotubes films were fabricated and were found rather high power factor in this films, which is 200 $\mu W/mK^2$.

There are some remarks in the thesis, they are:

1. One could expect the data of the experimentally performed studies: parameters of the SEM and TEM analysis. It would be more valuable to include the regimes of conducted research in the Chapter 2 with its expansion.
2. The author does not perform experiments related to the manufacturing of the n-type polymer composites, which is an essential part to further creation of TE generators.
3. There is no data regarding the thermal conductivity of the studied composites. It is known that the performed changes within polymer matrix affect the thermal properties to a lesser degree; however, it is advised to perform such research for a better determination thermoelectric efficiency.
4. Author theoretically studied the influence of two various dopants on DOS, Band structure and the tendency of the Fermi level shift. However, there are no additional theoretical studies of the transport properties or changes of represented data concerning the temperature change.

However, though there are the remarks, they are relevant only concerning the shown results and not for main concepts. In the whole, the thesis has a high level rather. In the respect that the obtained data are new and of high interest, they should be considered as important for the field of thermoelectricity.

The reliability and reproducibility of the data are both highlighted by the author and confirmed by the use of certificated equipment.

The results are important not only for both fundamental understanding of the TE processes within the polymer and for the practical usage. They show the way to fabricate cheap, flexible films with rather high thermoelectric performance. The represented data were published in international journals and approbated at international conferences.

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. Aftoreferat corresponds to the submitted thesis.

Thus, the applicant, Yusupov Khabib Umaralievich deserve the scientific degree of a Candidate of Physical and Mathematical Sciences in a special 01.04.10 – Physics of semiconductors

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