Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis / Pre-examination statement for Aalto University

Name of Candidate: Alexey Tsapenko

PhD Program: Physics

Title of Thesis: Enhancing Optoelectronic Performance of Randomly Oriented Single-Walled Carbon Nanotube Films

Supervisors: Prof. Albert Nasibulin, Skoltech, Russia

Prof. Esko Kauppinen, Aalto, Finland

Chair of PhD defense Jury: Prof. Nikolay Gippius, Skoltech *Email:N.Gippius@skoltech.ru*

Date of Thesis Defense: October 4, 2019

Name of the Reviewer:

I confirm the absence of any conflict of interest	Signature:  Date: 02-08-2019

The purpose of this report is to obtain an independent review from the members of PhD defense Jury / Pre-examiner before the thesis defense. The members of PhD defense Jury / pre-examiner are asked to submit signed copy of the report at the latest on August 13th. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

In his thesis, the candidate, M.Sc. Alexey P. Tsapenko is studying and proposing enhanced optoelectronic properties of tangled single-walled carbon nanotube films using a combination of dry-deposition, compounding, chemical reduction and aerosol doping methods. The effects of various preparation routes on the optical and electrical properties are assessed using a number of state-of-the-art characterization techniques allowing for a proper optimization of the optoelectronic properties resulting in various films with optical transparency and sheet resistance (e.g. 3.2 Ω/sq at T=50% or 36 Ω/sq at T=85%) that compete with those of indium-doped tin oxide, the gold standard in the field.

The thesis starts with a general introductory section (Chapter 2) on carbon nanotubes (synthesis, doping and physical properties) while placing those in the context of transparent conductive materials and films. In Chapter 3, various methods important for the analyses (including optical, electrical, spectroscopy, electron microscopy, particle size distribution) are carefully and discussed highlighting the basic concepts and peculiar features that are to be considered when assessing carbon nanotubes. Here, I would like to note, that this section is extremely well written, and can even serve as a text book for education purposes.

The results in Chapter 4 are divided into two major parts. In the first, discussion charge carrier dynamics based on THz spectroscopy data and associated models of conduction in solids. In the other, compounding SWCNTs with reduced graphene oxide and absorption doping using $AuCl_3$ are elaborated with the goal to improve the electrical transport in the composite films without sacrificing the optical transparency.

At last, the major findings of the thesis are summarized in the section Conclusion including:

- Superiority of H_2 assisted reduction of graphene oxide compared to thermal reduction in terms of sheet resistance of the composite films
- Influence of solvent boiling point (evaporation rate) and its relation to the dispersive component of Hansen solubility on the doping process
- Control of the work function and sheet resistance of the films by doping with chloroauric acid
- The conduction mechanism with contributions from the (i) free (delocalized) carriers according to the Drude model in solids, and (ii) resonant plasmons as well as (iii) tunneling barriers in the intersections/contacts of the nanoparticles in the films, and
- An apparent negative photoconductivity in both pristine and doped films

The thesis is based on five scientific papers published in reputed journals with high visibility and impact. Although the candidate appears as the first author only in two of these five papers, his claimed contribution to the experiments, evaluation and discussion of the results, and writing/publishing is substantial. Furthermore, it is important to point out that he co-authored several other papers that are associated with carbon nanotube films, and applied in important and fascinating devices such as solar cells, bolometers and stretchable and transparent interconnects.

Apart from some minor inconsistencies (see Detailed comments below), the manuscript is well written, and organized in a logical manner. The topic of the thesis is timely, and not only the scientific novelty but also the practical implications of the work are important achievements for which M.Sc. Alexey P. Tsapenko deserves to earn his PhD degree. Accordingly, I suggest acceptance of the manuscript with minor revisions, and recommend proceeding forward to the public examination.

Detailed comments

- Grammar and phrasing shall be corrected.
- 2.1 Limited indium resources and increasing price of associated commodities should be mentioned.
- 2.3.1 CO_2 as “catalyst stimulant”??? What do you mean by that? Etching the amorphous carbon from the surface of the Fe catalyst? Have you considered that inserting additional CO_2 to the reaction gas of the disproportionation reaction will change (slow down) the reaction rate by reversing the process?
- Conclusions: “The lowest value of 40 Ω/sq at a wavelength of 550 nm is measured for SWCNT films doped with HAuCl4 dissolved in ethanol.” The sentence is a kind of fragment as it is not important what the optical wavelength is when mentioning the sheet resistance. (Probably the optical transmittance was also to be mentioned in the sentence.) Please note that there are also some similar confusing sentences at other places in the manuscript.

Provisional Recommendation
☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*
☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*
☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*