Skoltech
Skolkovo Institute of Science and Technology

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

Name of Candidate: Vsevolod Iakovlev

PhD Program: Physics

Title of Thesis: Advanced Synthesis of Single-Walled Carbon Nanotube Films by Aerosol Method for Electro-Optical Applications

Supervisors: Prof. Albert Nasibulin, Skoltech, Russia

Prof. Esko Kauppinen, Aalto, Finland

Chair of PhD defense Jury: Prof. Keith Stevenson, Skoltech *Email:* K.Stevenson@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 dissertation (entitled, *Advanced synthesis of single-walled carbon nanotube films by aerosol CVD method for electro-optical applications*) M.Sc. Vsevolod Iakovlev is reporting on studies of optimized growth of single-walled carbon nanotubes, and their subsequent applications in bolometer, saturable absorber and Bragg grating devices.

The work is a seamless and coherent continuation of the renowned research pursued in the laboratories of Professor Kauppinen (Aalto University) and Professor Nasibulin (Skoltech). The study shows that

despite the nearly three decade history of carbon nanotubes, there is still much to improve of the synthesis of these fascinating materials, and to innovate their practical devices.

The thesis is based on seven papers published in peer-reviewed scientific journals, out of which three the candidate appears as the first author. According to the statement in *Author's contribution*, in the published/submitted papers, he is responsible mainly for reactor design, optimized materials synthesis and sample characterization.

The contribution of the candidate to the contemporary science and technology is substantial with the major novelties associated to optimized aerosol CVD growth of single-walled carbon nanotube films, their improved optical/electrical properties and applications in optoelectronics devices including bolometers, saturable absorbers and fiber Bragg gratings. The presented work is extensive. The experimental data and its interpretation supports well the drawn conclusions. I find only minor flaws in the manuscript (mostly associated with the English of the text), which may be fixed within a round of a minor review (please see the Detailed comments and questions below).

Accordingly, recommend acceptance of the dissertation of M.Sc. Vsevolod Iakovlev, and propose proceeding forward to the public defense of the thesis.

Detailed comments and questions

- In the Chapter *Author's contribution*, please indicate your role in writing the manuscripts, and specify what characterization was performed by you.
- The statement "As the equilibrium ratio between metallic and semiconducting nanotubes is ~0.5 [19], …" is not true in general, and the cited reference is not appropriate to support the claim. When growing CNTs with similar diameters, the statistical probability for having semiconducting CNTs is 2/3, whereas the rest 1/3 is metallic. This 2 to 1 ratio may be shifted under some unique conditions though.
- "… the Young's modulus up to 77 GPa is higher than that for the high strength steel) [21]." The cited reference [21] is only a book review and has no such data. The highest reported Young's modulus of individual CNTs is close to 1 TPa (Nature, 1996, 381, 678–680). Please revise.
- Page 10, eq. 2.1, is the Beer-Lambert law, not "Lambert-Berr". On the other hand, if *h* designates the film thickness, the concentration *c* shall not appear in the equation. The equation in the current form is valid and used when the absorber is dispersed in a non-absorbing medium. For solids, the usual form of the exponent is $a \cdot h$, where *a* is the absorption coefficient and *h* is the layer thickness. Note, that scattering is ignored.
- Page 11, "The formation of carbon nanotubes is affected by certain aspects [28]: … Carbon nanotubes are one of the allotropes of sp^2 carbon among fullerenes, graphene, onion-like carbons, etc." I do not see how the second part of the sentence is connected to the first.
- In Chapter 2.4, some details on the use of CNTs in solar cells, bolometers and saturable absorbers would be useful. Also here, the sentence "… absorbance within the infrared band allowing to "transform" the photons absorbed into a resistive response [38]" is quite sloppy. The phrase "non-linier" à non-linear. Please revise.
- In Fig. 2.7, it is not clear how the different applications are related to each other (e.g. how fuel cells are connected to transparent electrodes or to transistors).
- Pages 22 and 23, "The laser spot diameter on the film surface was about 11.2 μm. In order to avoid the destruction of the SWCNTs during the long exposure, the power density of the incident radiation was set at 0.4 $kWcm^{-2}$ when measuring spectra." The numerical aperture and magnification of the objective should be given. Furthermore, was the diameter assumed for 1/e or $1/e^2$ intensities? For a

Gaussian beam, how can you define the intensity be 0.4 kWcm^{-2}? Is it the maximum intensity or the integrated (averaged) intensity? Please check and revise.

- Page 24. In the sheet resistance measurements, were the CNT films contacted directly by the probes or any contact pads were applied? Please clarify.
- Page 24, eq. 3.3 looks odd. Please check.
- Page 26, "To study the temperature transformation of SWCNTs …" à To study the thermal stability of SWCNTs …
- Inset panels in Figures 4.4, 4.5, 4.8, 4.10, 4.12 and 4.13 are difficult to see. If possible, please add those as separate panels.
- Page 38, "Moreover, the introduction of hydrogen stopped the production of SWCNTs providing more than 1000 ppm of water in the exhaust." Have you considered that the water-gas shift reaction can be responsible for the water product?
- In Chapter 6, TEM images would be useful to see any changes of the crystal structure of the CNTs and microstructure of the junction areas in the films after the laser treatment. Please add if you have some.
- Page 65, "due to the fact that the SWCNTs we have used to have the metallic nature of the resistance dependence on temperature, the sample resistance decreases several times down to liquid nitrogen temperature." Do you have data to show the R(T) function of the films? Despite the metallic nature of well-percolated CNT films (i.e. with linear I-V characteristics) their temperature dependence of resistance is negative due to thermally activated transport processes (see e.g. PRB, 2006, 74, 085403 and PRB, 2008, 77, 125430).
- In the first paragraph of Chapter 7.2, please add a sentence or two on how saturable absorbers work.
- Phrasing and grammar needs to be checked and corrected:
  - Some sentences are difficult to follow/understand
  - Repeated content shall be removed/merged
  - Tenses are not always consistently used
  - The plural/singular forms of nouns are sometimes incorrect
  - In many instances, words are misspelled
  - Definite and indefinite articles are not used correctly

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*