Skoltech

Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis

Name of Candidate: Pramod Mulbagal Rajanna

PhD Program: Physics

Title of Thesis: Hybrid heterojunction solar cells using single-walled carbon nanotubes and amorphous silicon thin films

Supervisors: Prof. Albert G. Nasibulin (Skoltech);

Prof. Peter D. Lund (Aalto University);

Chair of PhD defense Jury: Prof. Nikolay Gippius

Date of the Thesis Defense: 07 May 2020

Name of Reviewer: Prof. Pavel Troshin

I confirm the absence of any conflict of interest	**Signature:**  **Date: 06-04-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at the latest on April 23. 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

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications
- The summary of issues to be addressed before/during the thesis defense

The presented Doctoral Thesis by Pramod Mulbagal Rajanna entitled “Hybrid heterostructure solar cells based on single-walled carbon nanotubes and amorphous silicon thin films” is focused on the application of nanotube-based electrodes in photovoltaics. The overall quality of the presented work is good and the thesis structure is quite well organized. Author provides a detailed discussion of the used experimental techniques and additionally refers to his publications. The results obtained look very promising and correspond to the state-of-the-art in the field of a-Si solar cells with carbon nanotube electrodes. The developed approaches for fabrication of semitransparent electrodes using SWCNTs can be potentially applied in other types of solar cells.
The candidate published 4 journal articles mostly in high-impact scientific journals. The presented work in great and I strongly support the candidate and recommend him to proceed with the Thesis Defense.

Nevertheless, there are still some issues, mostly of purely technical nature, to be considered, as I summarize below.

General comments:

1) Section 1/section 2.3: I recommend author to describe more clearly the nature of SWCNTs. State the nature and the typical ratio between metallic and semiconducting tubes, explain p-type doping mechanism of semiconducting tubes. Otherwise, terminology such as “p-type conductor or semi-metal” looks very confusing. Showing band structure of the pristine and doped SWNTs might be worthy.
2) PEDOT:PSS was extensively used in this study. There are many different commercial formulations of this material with completely different properties (tens of products existing). However, I was not able to find information on the type(s) of the used PEDOT:PSS in the methodology part of the thesis. Providing this information is crucially important.
3) Figure 4-6 shows very strange effect: the shape of EQE spectra changed dramatically due to top electrode material variation, though the absorber material stays the same. Shift of the maximum by 50 nm is especially spectacular. What is the origin of this effect? Similar effect is also seen in figure 4-13, showing a great spectral change after applying a reflecting mirror on the device back side. Since simulated spectra are given, explanation of the effect (as well as a detailed description of the techniques used for simulation) needs to be provided.

Some technical issues:

Page 11 “solar photovoltaics” better replace with “photovoltaics”

Page 12 The claim “They are categorized as fourth generation PV devices and are termed ‘hybrid solar cells (HSCs)’.” needs to be supported with the reference. There are three commonly accepted generations of PV technologies, which are differentiated by the cost of the produced energy. Generation 3 is currently emerging. Flexible solar cells based on a-Si fall in generation 1 according to the common criteria.
Page 12 The claim “An energy efficient, environmentally friendly and low cost process technology is developed for fabrication of hybrid thin film solar cells combining a-Si:H and SWCNT films” is very demanding. Analysis of product embodied energy, life cycle and cost structure are needed to support such strong statements.
Page 15 “to overcome their limitation” needs clarification: what is “their?”

Page 15 terminology “has a higher absorption edge and a larger optical absorption constant than c-Si.” Looks not precise. Revise using e.g. has lower band gap, higher extinction coefficient, becomes direct band gap material…
Page 15. Wording “The mobility gap of a-Si:H is larger than the bandgap of single crystal silicon and has a typical value between 1.7 eV and 1.8 eV [11]. Therefore, just 1 μm in thickness of a-Si:H is sufficient to absorb virtually all of the light above the absorption edge [11].” is very misleading. Extinction coefficient and direct band gap structure should be mentioned. Above absorption edge usually means at longer wavelengths, while the intended meaning is just opposite.
Page 20 “through the doping of polar solvents, strong acids, ionic liquids”. To keep terminology correct, this is not doping, it is modification.
Page 22. Statement “In addition to that, the film thickness can be easily estimated when the absorbance is known” is not fully correct since absorption coefficient is needed. Moreover, light interference effects can affect the accuracy of the measurements.
Page 28 typing “would leads to”
Page 32. The statement “The experimentally measured adhesion force shown in Figure 4-2d can explain the following observations: SWCNT thin films are easily dry-transferred onto a-Si:H, Si, SiO_2, and PDMS in air, while under the same conditions their transfer onto ITO and Pt is complicated and completely failed on ZrO_2.” Is not really clear. Figure 4-2 shows virtually identical AF values for SiO_2 and Pt in air. Why then SWNT transfer on SiO_2 is easy, while on Pt it is complicated?
Page 33. I would not use term “fluorination” for HF treatment. The statement “Moreover, after the fluorination process SWCNT films can be easily dry-transferred even onto problematic materials, such as ITO, Pt, and ZrO_2.” is not clear. AF for HF-treated ZrO_2 is still below the value for Pt (not HF-treated) in air, which was called problematic on the previous page. Is there any AF values range to characterize “easy”, “problematic” and “completely failed”? I aslo recommend to explain “HF-treatment” in the caption of Figure 4-2
Page 35 Statement “The decrease in the sheet resistance of the SWCNT-PEDOT:PSS (composite) film and the increase in its work function compared to the pristine SWCNT film can account for the fact that the PEDOT:PSS filled micropores in the film and, consequently, doped the SWCNTs.” is not fully clear. How can PEDOT:PSS dope SWCNTs? What is the chemistry of doping? Alternatively, can it be just contribution of PEDOT:PSS higher WF to the overall increase in the WF of the composite?
Figure 4-5 What is “Morphological SEM image”?
Table 4.3 Giving efficiency values with the extreme accuracy such as “2.704” might be misleading. I suggest to give it as 2.7% only. Usually, some statistics is given (average +/-) in such tables and number of cells in the batch contributing to the average is indicated in the footnote to the table.

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*