Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Aleksandra Boldyreva

PhD Program: Materials Science and Engineering

Title of Thesis: Unraveling Bulk and Interfacial Degradation Mechanisms in Perovskite Solar Cells

Supervisor: Prof. Pavel Troshin

Chair of PhD defense Jury: Prof. Alexei Buchachenko *Email: a.buchachenko@skoltech.ru*

The thesis document includes the following changes in answer to the external review process.

In respond to A. Buchachenko review:

- The references to Consensus statements by Resse et al. (ref.107) and Khenkin et al. (ref 108) are added in the list of references and additional comments are added in thesis on Page 30, Chapter 2.2:
  "It was developed following the recommendations of ISOS L-2 stability testing protocol initially proposed for organic photovoltaics (OPVs)[107] and later adjusted for PSCs[108] ISOS L-2 protocol suggests performing light soaking aging experiment in inert atmosphere at 65-85 ˚C, with light power within 80-100 mW/cm^2 for at least 1000 h. Device measurement is recommended to perform in MPP or OC mode. In our experiment light power was 50 mW/cm^2 (with reduction to 40 mW/cm^2 in the exp. described in Chapter 3) and temperature 45 ˚C, which is less than recommended, but sufficient to reveal important T-UV degradation mechanisms."
- Additional comment about PSCs application in space is added on Page 86, Chapter 4.1:
  "High solar irradiation (up to 100 Sun), proton and electron irradiation was already found to be harmless for perovskite solar cells at ambient temperatures.[99, 128, 129] The impact of gamma rays is still unknown."
- All technical mistakes are corrected.

In respond to A. Nasibulin review:

- The lists of Figures, tables and schemes are deleted.
- Sections "Author's contribution" is deleted from chapters and transferred to a separate Chapter after list of publication combining all deleted sections in one place (Page 6). However, sections "Materials and Methods" remained divided by chapters, as each Chapter describes different experiment with different materials and methods used.

- Formatting of formulas and equations was updated
- Publication list (Page 5) was updated
- Meaning of colours on a map in Fig.60 is added
- Precision of numbers in Tables 2 and 3 are corrected
- Missing info in references is added

In respond to E. Gudilin review:

- Though TEM / HREM investigation could provide a valuable information about local defect generation, unfortunately, due to COVID-19 restrictions, we have no access to the lab facilities and cannot accomplish such analysis within given time period.
- Interrelation between thermal photochemical and thermodynamic processes was not studied. The focus of this thesis was on photochemical processes, while thermal degradation was minimized by applying 45 ˚C temperature. It is known that $MAPbI_3$ decomposes at 55-60 ˚C and other perovskite systems at higher temperatures. Thus, we set a threshold T of 45 ˚C and performed all degradation experiments at this temperature. To exclude any contribution of thermal decomposition, for all samples we performed a dark test at 45 ˚C and did not observe any degradation processes.

In respond to A. Di Carlo review:

- Figure 7 (Page 19) is updated with new PSCs record efficiency value and new graph (c) showing c-Si panel cost. Additional reference (22) is added in the Reference list. The following text is added on Page 19 in response to Prof. Di Carlo comment:
  "In 2018 the production of PSCs was estimated twice cheaper than of CSSCs (Figure 7b), however, the massive production of c-Si wafers, as well as updated power conversion efficiency, pushes the price down below 0.3 \$/W[22] (Figure 7c) and makes Si technology highly competitive. Nevertheless, the cost of PSCs potentially also can go down with massive production."
- The statement about PTA advantages over PTAA is corrected (Page 25) :
  "The main advantages of PTA over PTAA is deeper-lying HOMO and Fermi energy levels which helps to minimize interface recombination."
- Device fabrication procedure is added in Chapter 2.2 on Page 32:
  "Device fabrication
  The n–i–p ITO/SnO_2/$MAPbI_3$/spiro-OMeTAD and p–i–n ITO/PEDOT:PSS/$MAPbI_3$/ETL (ETL: $PC_{61}BM$ or $PC_{71}BM$) samples were prepared following standard procedures.[50] The SnO_2 nanoparticle ink was purchased from Alfa Aesar, while spiro-OMeTAD was doped with LiTFSI and tBuPy following standard procedures.[56] The aforementioned multilayered stacks without top

electrodes were exposed to light soaking under the same conditions as specified above. After completion of the aging period, the samples were processed to complete solar cell architectures by depositing Mg/Ag (20/80 nm) electrodes for p–i–n structures and Au/Ag (20/80 nm) electrodes for n–i–p structures. Electrodes were evaporated in high vacuum (10^{-5}-10^{-6} mbar) through a shadow mask defining the active area of each device as 0.16 cm^2."

- The statement about the impact of film crystallinity on degradation rate is supported by reference #112 on Page 36.
- Additional comment about light power source is added in Page 37:
  "All samples were subjected to the light soaking of 50 mW/cm^2 in the inert atmosphere."
- Aging conditions *(50±2 mW/cm^2, 45±1 °C)* are added in the captions for Fig. 10, 13 and 17.
- XPS results in Chapter 2: the text about XPS data on P.41 is rewritten, starting from pristine $MAPbI_3$. Tables 1, 2 and 3 were combined in 1. Figure 16 was updated with 2 additional graphs (e, f) suggested by prof. Di Carlo showing surface composition dynamics of glass/CTL/$MAPbI_3$ samples under light soaking.
- Scheme 2 is updated (word "heat" was removed from the image) and supported with the following comments on P.44:
  "Note, that the experiment was performed under light soaking conditions at 45 ˚C. The same test in the dark did not reveal any decomposition of $MAPbI_3$, thus we can conclude that $MAPbI_3$ degradation followed by adduct formation has a photochemical nature."
- Additional text about PCBM passivating properties is added on Page 48:
  "Moreover, fullerene derivatives are known to passivate perovskite grain boundaries eliminating in this way non-radiative recombination.[122] PCBM molecules can penetrate in the bulk of perovskite material and passivate Pb–I antisite defects or under-coordinated Pb_2^+ vacancies at grain boundaries.[122]"
- Additional reference (122) is added to the Reference list.
- In Chapter 3 the device measurement was performed after PCBM refresh. We did not study device characteristics without PCBM refresh (As was in Chapter 2), as we expected dramatic decay in solar cell characteristics of MA-based systems due to MAI diffusion into ETL layer. As we were interested in HTL contribution in solar cell performance, we eliminated the impact of PCBM layer, by refreshing it before IV measurement.
- On Page 100 the additional comments about degradation mechanism are added. The reason why V_{OC} remains stable and J_{SC} goes down is clarified by:
  "However, the light-induced phase segregation usually leads to the formation of recombination centers and causes a reduction in V_{OC}.[125] In our case, we do not see any V_{OC} changes, so the

mechanism of gamma ray-induced Hoke effect is still requiring additional studies to be completely understood. We also cannot exclude some contribution of the radiation-induced substrate darkening in decrease of the device J_{SC}, which we found later and discuss below."

In respond to F. Brunetti review:

- In Chapter 1.1.3 words "careful film preparation" are clarified by adding the text:
  "…*annealing temperature should be optimized to exclude the formation of the beta phase and PbI_2.***"**
- Spectra mismatch of used metal halide lamp with the AM1.5G spectra is 22% (based on integrated J_{SC} values). Additional text was added on Page 32.
  "For perovskite material, the mismatch of J_{SC} gained from AM1.5 G and metal halide lamp spectra is 22%."
- All technical mistakes are corrected

In respond to E. Katz review:

- No comments for consideration

In respond to M. Lira review:

- No comments for consideration