

論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Dominant effect of perovskite grain size on solar cell performance and improved stability by all-inorganic light absorber
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11561号, 授与年月日:2020年6月30日, 学位の種別:課程博士, 審査員:伊原 学,山田 明,下山 裕介,脇 慶子,前田 和彦
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11561号, Conferred date:2020/6/30, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

博士課程)
Doctoral Program

THESIS OUTLINE

系・コース: Department of, Graduate major in	Energy science and Engineering	系 コース	申請学位 (専攻分野): Academic Degree Requested	博士 Doctor of (Engineering)
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論文題目 Thesis Title	Dominant effect of perovskite grain size on solar cell performance and improved stability by all-inorganic light absorber
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The first attempt to use a perovskite sensitizer in solar cell application start in 2009 and shift the solar cell technology to the new era. Recently, perovskite solar cells (PSCs) rapidly improve in their photoelectric conversion efficiency (PCE) from 9% to over 24%, which is the best performance for single-junction solar cell. Due to the outstanding developments, PSCs have fascinated scientists and engineers in the field.

In solar cell configuration and fabrication, the development of crystal growth, interface, and fabrication techniques have been studied. It controls final perovskite film quality (e.g., grain size, grain boundary, defect) and crucially influences the PCE of the device. The various approaches have been introduced, for example, polymer and alkaline additives, post annealing, antisolvent extraction, and solvent engineering. Perovskite film quality requires a stable, uniform, and full coverage thin film with dense and large grain sizes. The rapid improvement of PSC now needs consideration to fundamental studies while together with seeking new materials and to improve stability. Much research has been carried out on lead toxicity content is one drawback in these perovskite materials and a reason for the viability of these solar cells. In this thesis, the predominant effect of perovskite grain size on solar cell performance is clarified, and an air-stable all-inorganic material is proposed.

Chapter 1 introduces information on the lead-halide perovskite solar cells (PSCs), which have attracted exciting attention due to their outstanding high power-conversion efficiency. The grain size is the dominant effect on any type of semiconductor solar cells, such as Si and CIGS. In contrast, it is an unclear effect on PSCs. In PSCs with inorganic structure (Transparent conductive oxide (TCO)/ Inorganic electron transport layer (ETL) /Perovskite /Hole transport layer (HTL)/Counter electrode), the grain size has been controlled by changing one or more parameters in the literatures; (1) the additive ratio in perovskite layer, (2) the doping percentage, (3) the perovskite formation temperature, and (4) ratio of raw materials. In these reports, the grain size effect could not be separated from the incidental effects (e.g., grain quality, grain boundary, and perovskite thickness were changed). Therefore, this problem inspired the objectives to clarify the direct effect of perovskite grain size and solar cell performance. The

stability of PSC is also a critical issue that constrains PSCs from a commercial scale. Thus, the new material is proposed to be an all-inorganic air-stable perovskite material to improve PSCs stability.

Chapter 2 describes the optimization of the low-cost and straightforward spray pyrolysis to deposit a flat compact TiO_2 (c- TiO_2) as ETL with controlling the surface roughness (Rms). The effect of different solvents (ethanol, 2-propanol, 1-butanol, and 2-butanol), spray temperature (Ts), and annealing temperature (Ta) induced different Rms of c- TiO_2 . For alcoholic precursor, IPA and 1-butanol show smooth surface without large TiO_2 particles on the surface when compare with EtOH as a solvent. While Ts show at 450oC gives the lowest roughness (Rms =3 nm) with average perovskite grain size around 300 nm at the same Ta. When Ta was varied from 400 to 600oC, the higher Ta, the larger average grain sizes were observed. These results are in contrast with Ts, and average MAPbI₃ grain size distribution was not only affected by the surface roughness of compact TiO_2 layer. For EtOH IPA and 1-butanol, the average PCE at 4%, 6% and 9%, respectively. According to heterogeneous nucleation theory, the surface roughness of c- TiO_2 can be one of the parameters that change the surface energy in the heterogeneous nucleation process. The largest grain size was achieved by using 1-butanol as a solvent. Therefore, the optimization of the spray pyrolysis technique is one route to lower the surface roughness of c- TiO_2 , enlarge the perovskite grain size, and prevent the imperfection of c- TiO_2 surface.

Chapter 3 describes clearly the dominant effect of grain size of methylammonium lead iodide (MAPbI₃) perovskite controlled by Rms of c- TiO_2 on the performance of perovskite solar cells. The direct dominant effect of MAPbI₃ grain size on an inorganic PSC performance was observed by controlling Rms of the c- TiO_2 as an ETL. For PSC with an active area of 0.54cm², perovskite grain sizes changed from 150 nm to 350 nm, the current density increased from 8 to 17 mA/cm², and the photoelectric conversion efficiency increased from 6.1% to 11.4%, respectively. Because the average perovskite grain sizes analyzed from the surface and cross-sectional SEM images were both the same, namely, ranging between 100 and 400nm, isotropic crystal growth was carried out. Dense MAPbI₃ layers with different grain sizes ranging from ≈100 to ≈400 nm was achieved. The dominant effect of a larger grain size (>300nm) yielded higher Jsc and FF (16.4 mA/cm² and 0.64, respectively), indicating an increased diffusion length of carriers due to a decrease in recombination velocity and/or an increase in apparent mobility through the grain boundary. Therefore, to increase perovskite grain size is an effective way for a high-efficiency, large-area, and wafer-size PSCs in commercial modules. This work also found that the average MAPbI₃ grain size can be controlled only by Rms of c- TiO_2 layer without additional factors. The stability of MAPbI₃ based solar cells measured under ambient operation also discussed by using solar cells with different MAPbI₃ grain sizes (100, 250, and 399nm). The results showed slower degradation in a sample with large grain sizes. However, its normalized PCE drastically decreased from 100% to 50% in 24 hours.

Chapter 4 describes research on an all-inorganic light absorber for perovskite solar cells. A tolerance factor was calculated as an indicator to predict the stability

of a perovskite structure from desired inorganic ions. Density function theory (DFT) was adopted to estimate the electronic band structure, bandgap, and density of state (DOS). DFT with the generalized gradient approximation (GGA) showed an indirect bandgap (1.48eV). An air-stable all-inorganic material was synthesized by solid-state reaction. UV-vis and photoluminescence (PL) spectra were measured for the absorption and excitation spectrum, respectively. From the experiment results, this material showed an appropriate bandgap (1.8eV) for solar cell application. X-ray diffraction (XRD) showed phase purity and stability of powder and thin film. However, PL measurement under low temperature and X-ray photoelectron spectroscopy (XPS) revealed the impurity state on the thin-film surface after leaving in ambient for 7 days. These findings are beneficial to the understanding of new material electrical and optical properties. The electronic structure of new material was investigated by the DFT method. The DOS analysis shows that the valence band was ranging from -5 eV to Fermi level. The conduction band was ranging from 1.4 eV to 6.2 eV. These finding is beneficial to understanding of electrical and optical properties and demonstrate an interesting route for optimization of active layer.

Finally, in Chapter 5, the new material was deposited through a solution process for the first time and applied in solar cell applications. The same structure with standard PSC was used to fabricate a solar cell (TCO/c-TiO₂/inorganic absorber/HTL/electrode). However, the initial highest PCE showed only 0.12%. The possible reasons for low efficiency came from a poor thin film morphology, an indirect bandgap, and poor contact between each layer in a solar cell. Although this material has the potential for a solar cell application, it needs further improvement for thin film deposition and device fabrication.