論文 / 著書情報
Article / Book Information

題目(和文)	太陽電池応用に向けた錫ペロブスカイト薄膜のキャリヤ挙動解析
Title(English)	Modeling and analysis of carrier behaviors in Sn perovskite thin films for solar cell application
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	電気電子 系 電気電子 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（ 工学 ）
学生氏名： Student's Name	野間 大史	指導教員（主）： Academic Supervisor(main)	間中 孝彰 教授	
		指導教員（副）： Academic Supervisor(sub)		

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Organo lead halide perovskites such as $CH_3NH_3PbI_3$ have attracted much attention as next-generation solar cell materials. However, the toxicity of Pb is a critical issue for commercialization. At present, Sn perovskites such as $CH_3NH_3SnI_3$ ($MASnI_3$, MA = CH_3NH_3), $CH(NH_2)_2SnI_3$ ($FASnI_3$, FA = $CH(NH_2)_2$), etc. are the most promising lead-free solar cell materials. In the present study, I built up a model and analyzed the carrier behaviors in Sn perovskite thin films for solar cell application. In this doctoral dissertation, I have described the following contents.

In Chapter 1, I introduced the research background of perovskite solar cells (PSCs). PSCs have become promising photovoltaic technologies in just ten years. However, despite the tremendous efforts of many researchers, there are many ambiguities in the carrier behaviors. This is because the conventional electrical measurements such as displacement current measurement (DCM) and impedance spectroscopy (IS) are indirect methods for probing carrier behaviors. In particular, the carrier behaviors in Sn perovskites have not been sufficiently investigated. This ambiguity is the motivation of the present study, and I employed optical measurements for the direct evaluation of carrier behaviors in Sn perovskite thin films.

In Chapter 2, the principles and experimental methods of the measurements used in the present study were described. The proposed optical measurements are charge modulation spectroscopy (CMS) and electric-field-induced optical second-harmonic generation (EFISHG). In CMS measurement, we can analyze carrier behaviors from an energetic point of view, by measuring the change in the transmission spectra of the devices. In EFISHG measurement, we can directly probe the internal electric field in materials. Further, I have shown that the conventional DCM is not suitable for the direct evaluation of carrier behaviors, by describing the examples of organic double-layer devices.

In Chapter 3, I modeled the carrier behaviors in Sn perovskite single layer devices. It was found by electrical measurements that the fabricated Sn perovskites behave like an insulator. Importantly, CMS measurements have revealed that the trap filling occurring at defects such as Sn vacancies significantly affects the I-V hysteresis of $MASnI_3$ thin films. The hysteresis behaviors of the $MASnI_3$ thin films were fully explained in terms of both electrical properties and carrier energetics, and we came to the conclusion that we need to reduce the defects in

films in order to suppress the I-V hysteresis of Sn PSCs. We also discussed the ionic motion in $FASnI_3$ thin films on the basis of the EFISHG results.

In Chapter 4, I discussed the carrier behaviors in Sn PSCs, on the basis of the knowledge acquired in Chapter 3. I have clarified that the electron injection into the $MASnI_3$ layer affects the I-V hysteresis by applying CMS measurements to $MASnI_3$ solar cells. This electron injection may involve the trap filling in $MASnI_3$. Noteworthy, the simultaneous analysis of $MASnI_3$ and electron transport C_{60} layers has been realized by analyzing the CMS signals at different wavelengths. On the other hand, EFISHG measurements provided more direct evidence for the presence of the trapped carriers. The EFISHG signals from C_{60} have revealed that the electrons trapped in the bulk of $MASnI_3$ or at the $MASnI_3/C_{60}$ interface generate the space charge fields and these have a significant impact on the I-V hysteresis.

In Chapter 5, I aimed at broadening the application range of the measurement techniques to Pb-based perovskites. From the electrical properties of Pb perovskites under illumination, I proposed a large difference of the photocarrier density between Pb and Sn perovskites. It is of importance to have confirmed that Pb perovskites also generate EFISHG. Further, I successfully evaluated the stability of high efficiency Pb PSCs using the EFISHG techniques. The Pb PSCs degraded under light soaking, but this was slight degradation compared to the serious decomposition of perovskite induced by heat soaking. EFISHG can measure $\chi^{(3)}$ and electric field E, which cannot be obtained from other conventional measurements. Therefore, this point will become a powerful tool for the evaluation of the slight degradation of perovskites.

In conclusion, I obtained a general perspective on the physical properties of Sn perovskites: Sn perovskite is an ionic conductor where trap filling occurs in a film. In frequency domain (e.g. C-f characteristics), we observed a diffusive behavior of ions, whereas under the application of DC voltages (e.g. C-V characteristics), we confirmed trap filling. It seems that these properties of Sn perovskites are unfordable for solar cell application, but the optimization of the fabrication processes would improve them. The new point of the present study is that the direct evaluation methods of carrier behaviors such as CMS and EFISHG were applied to perovskite materials for the first time, and that the relationship between the I-V hysteresis and trap filling has been clarified. I believe that modeling and analysis of carrier behaviors by CMS and EFISHG measurements will pave the way for further development of lead-free Sn perovskite solar cells.