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2. 所属機関	物質・材料研究機構 エネルギー・環境材料研究拠点
3. 研究題目	Development of Tin-based halide semiconductor materials for high efficiency photovoltaic device

4. 研究の目的(Purpose of Research)：

The toxicity of Pb in Pb-perovskite solar cells (PSCs) and poor device stability are two issues to be resolved for its practical application. The primary reasons for low device efficiency are the fundamental differences in film growth, optoelectronic quality, and multiple structural dimensionalities. In the case of Sn-HaP, though it was considered as one of the promising alternatives in terms of optoelectronic properties, high-quality film growth is challenging due to severe oxidation and poor film morphology

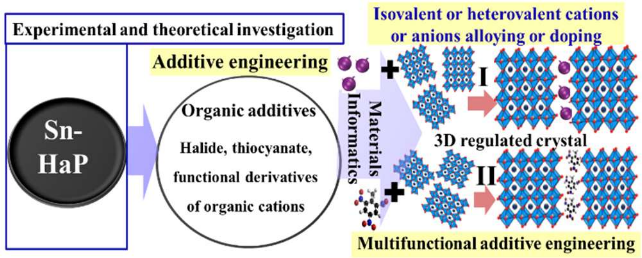

Fig.1 Schematic of additive engineering for the fabrication of high-quality Sn-perovskite films and solar cells.

In this proposal, we proposed to fabricate a highly efficient Pb-free HaP-based device by optimizing the optoelectronic quality of Sn-HaP thin film (morphology and optoelectronic properties) adopting additive engineering and structural regulation adopting approach shown in the schematic diagram. It is believed that the successful completion of the proposed work will pave a way to solve issues on Sn-PSCs.

研究の内容(手法、経過、評価など。書ききれない場合には、同一様式のページを追加してください。).

Method:

For the fabrication of Sn-HaP films, the precursors were prepared by dissolving FAI, SnI_2, and SnF_2 adding different concentration of PEASCN in DMSO solvent. As depicted in schematic of device fabrication (Fig. 2), we prepared inverted Sn-PSCs with PEDOT'PSS (HTL), $PC_{61}BM$ (ETL) by spin coating and BCP (ESL) and Ag deposited by thermal evaporation. Khadka et al. *ACS Appl. Energy Mater. 2021,* 4, 12819.

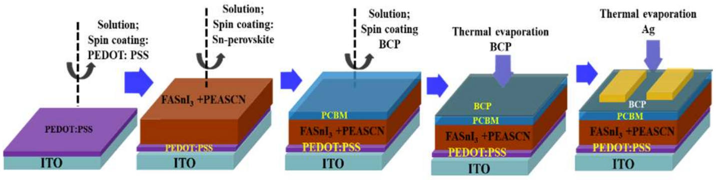

Fig.2 Schematics of fabrication of Sn-perovskite devices.

Progress and evaluation

We observed highly oriented crystallographic planes of (100) and (200) for Sn-HaP films with PEASCN additive whereas the pristine film grows with multiple crystal orientations (Fig. 3a). The absorption spectra of the films (x=0-0.12) (Fig. 3b) demonstrate some effects with a higher content of PEASCN additive. Photoluminescence (PL) spectra of the corresponding films (Fig. 3c) display a slight blueshift with the introduction of PEASCN. The pristine $FASnI_3$ film shows a very poor film coverage with numerous pinholes. The films with PEASCN additive exhibit a significant improvement in film coverage by suppressing the pinhole's densities.

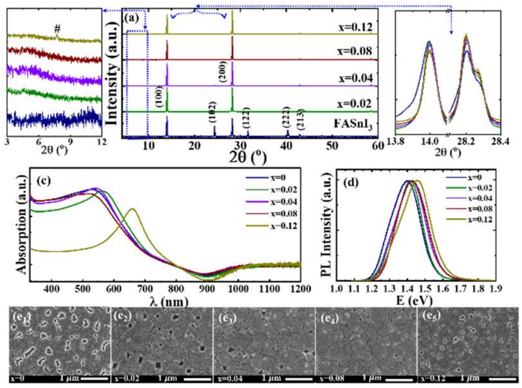

Fig.3 Growth characteristics of the $FASnI_3$ films with different amount of PEASCN additive (x=0-0.12) with respect to FAI. (a) XRD, (b) absorption spectra, (c) PL spectra, and (d1-d5) SEM images of pristine and film with additives.

5.　研究の成果と結論、今後の課題（Results and conclusions of research, future issues）:

Results:

We then fabricated a complete device with the inverted structure of ITO/PEDOT:PSS/Sn-HaP/PCBM/BCP/Ag as depicted in the cross-sectional image (Fig. 4a). Figure 4b shows the current density-voltage (*J-V*) curves of devices with $FASnI_3$ with PEASCN additive. The device with pristine $FASnI_3$ achieved a *PCE* of 4.52% and with PEASCN additive demonstrated an improved device performance of 9.65%. The device with PEASCN additive has higher reproducibility (Fig.4c).

The external quantum efficiency (EQE) of the devices (Fig. 4d) shows more efficient harvesting for device with PEASCN additive.

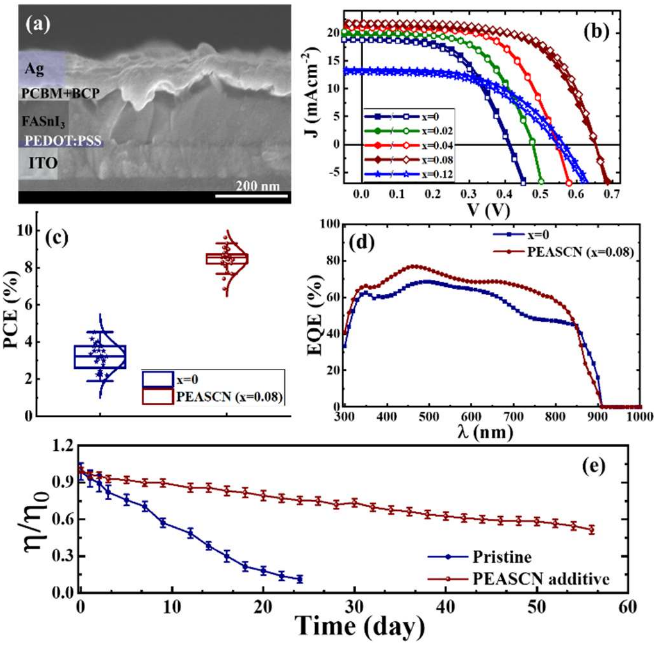

Fig.4 Cross-sectional image of the device (a), J-V curves devices (pristine and PEASCN additive (x~0.12) (■ forward/ □ reverse scan direction) (b), statistics of PCE (η) (c), EQE spectra (d), and stability of encapsulated device (e).

The device performance monitored with time (Fig. 4e) demonstrates that the device with PEASCN additive has superior device stability. The XRD results revealed that the pristine $FASnI_3$ deteriorates stemming from a dominant SnI_2 secondary peak, whereas the film with PEASCN additive is comparatively stable retaining characteristics.

Conclusions

We introduced the phenethylammonium thiocyanate (PEASCN) as a pseudohalide functional additive into $FASnI_3$ perovskite film to improve the optoelectronic properties. This approach is found to be effective for the suppression of Sn-oxidation and formation of compact and larger grain film with a higher degree of crystallinity. The device with PEASCN additive improved the device efficiency from 4.52% (for control Sn-HaP) to 9.65% with superior device stability. This work corroborates that the incorporation of pseudohalide-based functional additive in the $FASnI_3$ is propitious for better film formation, passivation of detrimental surface chemistry, and defects at interface and bulk.

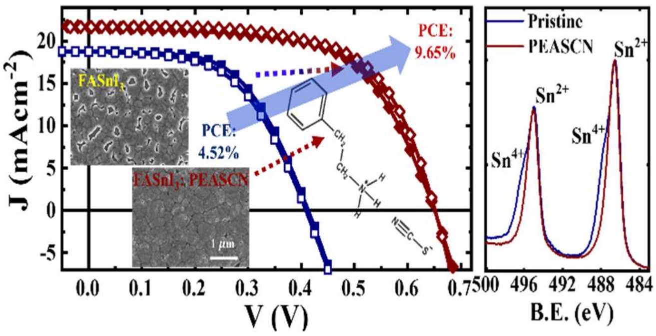

Fig.5 Schematic of additive engineering for the fabrication of high-quality Sn-perovskite films and solar cells.

Future Issues

The progress of Sn-PSCs is obstructed by their poor stability arising from tin oxidation. Our report substantiates that the pseudohalide functional is expedient for the improvement of film morphology and optoelectronic quality of $FASnI_3$ film that hikes the performance as well as stability of Sn-HaPSCs. There is still much room for the improvement for the growth of highly crystalline Sn-perovskite film growth, control of oxidation and interface engineering to fabricated Sn-PSCs as a competitive alternative to Pb-PSCs. The functional additive engineering method could be an effective route for the progress of Sn-perovskite based device.

6.　成果の価値(Value of results)

7.1_学術的価値(Academic Value):

The results of this proposal paved a way for tailoring pseudohalide-based functional additive in Sn-halide perovskite. We found that the pseudohalide halide additives is propitious for better film formation, passivation of detrimental surface chemistry, and defects at the interface and in the bulk. Our report substantiates that the pseudohalide functional additive hikes the performance and stability of Sn-HaPSCs. This research will also open up multiple applications of Pb free halide perovskite materials; indoor applications, IoT devices and so on.

7.2_社会的価値（Social Value):

The sun provides more than enough energy to meet the whole world's energy needs. Unlike fossil fuels, no greenhouse gas emissions are released into the atmosphere when you use solar panels to create electricity. This proposed work will contribute to the reduction of greenhouse gases. This proposal will develop cost-effective and environment-friendly solar harvesting Pb free- HaPSCs. This work will add some values on zero carbon emission mission for GREEN Earth.

7.3_研究成果(Research Results):

"Research Papers (Original)"

[1] Dhruba B. Khadka, * Y. Shirai, M. Yanagida, K. Miyano, Pseudohalide Functional additive in Tin Halide Perovskite for Efficient and Stable Pb-free Perovskite Solar Cells, *ACS Applied Energy Materials*. 4, 12819-12826, **2021.** "0"

[2] Dhruba B. Khadka, * Y. Shirai, M. Yanagida, K. Miyano, Insights into Accelerated Degradation of Perovskite Solar Cells under Continuous Illumination Driven by Thermal Stress and Interfacial Junction, ACS Applied Energy Materials, 4, 11121-11132, **2021.**

[3] Dhruba B. Khadka, * Y. Shirai, M. Yanagida, T. Tadano, K. Miyano, Interfacial Embedding for High-Efficiency and Stable Methylammonium-Free Perovskite Solar Cells with Fluoroarene Hydrazine, 2022, (manuscript under review)

[4] Dhruba B. Khadka, * Y. Shirai, M. Yanagida, K. Miyano, Analysis of Degradation Kinetics of Halide Perovskite Solar Cells Induced by Light and Heat Stress, Sol. Energy Mater. Sol. Cells, 2022, (under revision).

"International Conference Presentations"

[1] D. B. Khadka, Y. Shirai, M. Yanagida, K. Miyano, Phenethylammonium Thiocyanate Additive in Tin Perovskite for Efficient and Stable Pb-free Perovskite Solar Cells, 2022 69th JSAP Spring Meeting, Sagamihara Campus, Aoyama Gakuin University, March 22nd - 26th, **2022**, **Oral Presentation.**

[2] D. B. Khadka, Y. Shirai, M. Yanagida, K. Miyano, Unraveling Accelerated Degradation of Perovskite Solar Cells under Continuous Illumination Driven by Thermal Stress, nanoGe Fall Meeting 2021, Online conference, 18th -22nd October, **2021**, **Oral Presentation.**

[3] D. B. Khadka, Y. Shirai, M. Yanagida, K. Miyano, Insights into Accelerated Degradation of Perovskite Solar Cells Driven by Light and Heat Stress, Association of Nepali Physicists in America (ANPA), ANPA Conference, USA, 16th July -18th July, **2021**. **Invited Talk.**

"Patent": NA ;

"Awards": NA