様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　２ 年　 ４ 月　 ９ 日現在

機関番号：１４６０３
研究種目：基盤研究(C)（一般）
研究期間：2017～2019
課題番号：１７Ｋ０５０３３

研究課題名（和文）Physical understanding of defects in organometal halide perovskite

研究課題名（英文）Physical understanding of defects in organometal halide perovskite

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交付決定額（研究期間全体）：（直接経費）　　3,800,000円

研究成果の概要（和文）：本研究を通じて有無機ハイブリッドペロブスカイト材料の不純物の研究を物理的/体系的に実行し、不純物の原子的/化学的構造とその効果の物理的解釈を完了した。また、分子不純物の場合には、周辺の構造のフォノンモードを別の方法で作成し、これにより、テラヘルツ領域台の吸収が非常に特異に形成されていることを最初に発見した。これをもとに有無機ハイブリッドペロブスカイト材料を用いた新しいテラヘルツベースのアプリケーション、デバイス開発の礎を作った。

研究成果の学術的意義や社会的意義
This study provides important information for conducting atomic/chemical studies of the defect structure of organic-inorganic hybrid perovskite. - Unique study in terms of its surface instability, the change in phonon mode due to defect structure, and the possibility of new terahertz-based devices.

研究成果の概要（英文）：From this KAKENHI, we performed studying defect structure and its effect in organic-inorganic hybrid perovskite materials. We confirmed the defect structure made a new physical property in THz range because of its unique phonon modes and it could make a new THz-based application using organic-inorganic hybrid perovskite thin film.

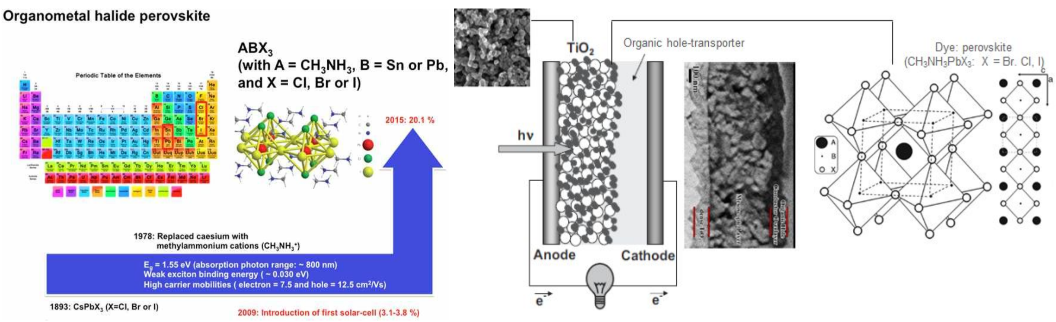
研究分野：Material Science

キーワード：Hybrid perovskite　Defect　Phonon mode　Electronic structure　Surface and interface

１．研究開始当初の背景

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a 3rd generation of cells, based, for example, on nanocrystalline and conducting polymers films. These offer the prospective of very low-cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical cell. Recently, the prototype of this family of devices is the dye-sensitized solar cell (DSSC), also known as Grätzel cell, which realizes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material (Dye: perovskite materials – $CH_3NH_3AX_3$: A = Pb, Sn and X = Br, Cl, I) with a wide band gap semiconductor of nanocrystalline (TiO_2) morphology. (In Fig.1.) And also this is very rapidly developing in the power conversion efficiency from 3.8% to 21% for only 5 years. It is very promising the future solar-cell instead of the silicon-based, compound semiconductor and nano-scale based solar-cell device in 1st and 2nd generation, respectively. Because it has several good merits such as all solution-based fabrication and high efficiency in compatible with industrials.

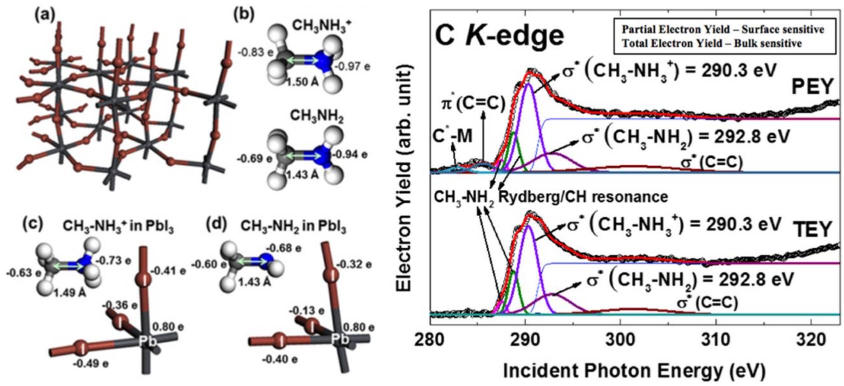
Defects in semiconductor are always caused with many physical effects such as tarp state against carrier and exciton, redistribution of energy level, unexpected performance, doping effect, etc. Basically, these defect effects should be controlled from fabrication process and interface/surface post-treatment to get an expected device performance.



[Fig. 1. Historical background and basic scheme of perovskite-based dye-sensitized solar-cell]

Most researchers are focusing on the main material, organometal halide perovskite and several important results were published such as the useful bandgap (~1.55 eV), weak exciton binding energy (~0.03 eV), and high carrier mobilities (electron = 7.5 and hole = 12.5 cm^2/Vs). However, this material has a critical problem such as material stability because this is a kind of organic-inorganic hybrid material and we did not study this kind of material physically before. Even there are no physical understanding of kind and role of defect structure and state in organic-inorganic hybrid material. We believe now it is time to start quickly studying their defect structure and state to improve this material property for commercial product.

Recently, in our previous research results, one of good hints to understand the defect structure in this organic-inorganic hybrid material was published. (Appl. Phys. Lett. 108, 073901 (2016)) From this publication, we can understand one of chemical defect states, CH_3NH_2 without the structural impurity from the organic part of CH_3NH_3. Even the chemical states at bulk and surface are different in the carbon organic part. It means that we must study and understand the defect of this new organic-inorganic hybrid material. This understanding of the intrinsic surface defect is very important because this surface will become the interface after the deposition of hole transport layer. Also, we should resolve what kinds of defect (structural, chemical and energetically) in this new material. This understanding is very promising to exactly know this material and it will be given with several real information for real device performance.



[Fig. 2. The presence of CH_3NH_2, different configuration between CH_3NH_3 and CH_3NH_2 (defect) | C *K*-edge (measured by NEXAFS): Different carbon states between surface (C^*-Metal and π^*(C=C)) and bulk]

２．研究の目的

In this research, we propose the below studies to understand structural, chemical, and energetically defects at bulk and surface (also interface) in organic-inorganic hybrid material (organohalide perovskite) by using several unique techniques such as THz-TDS (THz-Time Domain Spectroscopy) and synchrotron radiation-based measurements (XRD, GIXD, NEXAFS and XPS).

1. Finding and defining the defect kinds (structural, chemical, and energetically) at bulk and surface in organic and inorganic parts of organometal halide perovskite
2. Role of defect states in organic-inorganic hybrid material such as trap state, effects in valence-conduction bands, energy level, exciton creation, carrier transport, etc.
3. Relationship between material stability and defects
4. Provide a new fabrication or treatment process with and without defects

These finding, understanding, and defining will support to improve the device materials and structures to obtain more easily fabrication, high efficiency performance and be a kind of research database for the industrials. This research will be focused mainly on the structural, chemical and energetically defects in organic-inorganic hybrid material (organohalide perovskite).

３．研究の方法

Target OHPs: 3D AMX_3

- Samples: Hybrid perovskite thin films ($MAPbI_3$, $MAPbBr_3$, $FAPbBr_xI_{3-x}$) and P3 polymer (poly[4- (5-(4,8-bis(5-(6-((2-hexyldecyl)oxy)naphthalen-2-yl)thiophen-2-yl) benzo[1,2-b:4,5-b ′]dithiophen-2-yl)-4-octylthiophen-2-yl)-5,6-dif- luoro-7-(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole])

Fabrication method: Sequential Vacuum Evaporation (SVE) method (Fig. 3)

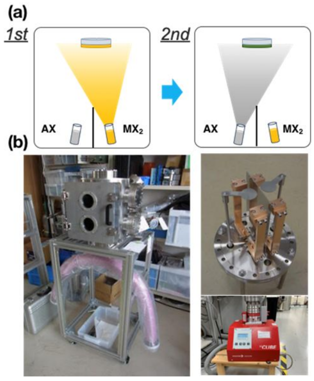


Figure 3. (a) The SVE method and (b) our original system with the dual evaporator and pumping system.

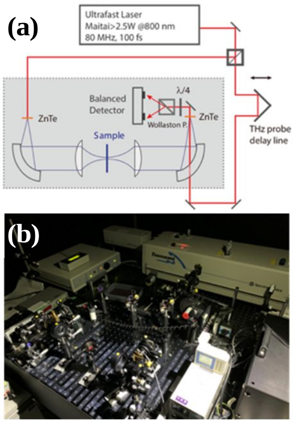


Figure 4. (a) A standard THz-TDS and (b) our original system.

Basic characterizations: XRD, UV-Vis., AFM, SEM, and XPS – We used all of tools of the common facility section in NAIST.

THz-wave absorption property: The original system – THz-Time Domain Spectroscopy (THz-TDS) (Fig. 4)

Synchrotron radiation-based measurements: High-resolution angle-resolved photoelectron spectroscopy (National Synchrotron Radiation Laboratory, USTC, China)

International collaboration work: In this research, we had the tight and deep collaborators from South Korea, China, and Australia.

４．研究成果

FY2017 (1st year)

In this year, the most important research targets were 1) Construction of vacuum chamber and 2) Confirmation of organohalide perovksite thin film fabrication. We completed the plan smoothly. The first manuscript using the constructed chamber is published at The Journal of Physical Chemistry Letters (IF=9.353)

The detailed progress:

- We have performed the constructuion of vacuum chamber for the fabricaiton of organohalide perovksite thin film. And in the pre-testing experiment, we confirmed the sequntial vacuum evaporation method was useful.
- To understand the instability of Sn-based perovskite, $CH_3NH_3SnI_3$, photoelectron spectroscopy with synchrotron radiation and theoretical calculations, such as density functional theory and ab-initio molecular dynamics, were performed. Findings from this experimental and theoretical study highlight the crucial changes of surface-chemical states, the broken chemical bondings in Sn-I, and the depletion of a CH_3-NH_3^+ cation on the surface region. The material instability origin of Sn-based perovskite can be explained by the chemical state instability in the surface.
- Now, the manuscript is published at The Journal of Physical Chemistry Letters (IF=9.353). (https://pubs.acs.org/doi/10.1021/acs.jpclett.8b00494) (The reviewer mentioned our manuscript would be in TOP 10% reading in Journal of Physical Chemistry Letters.)

FY2018 (2^{nd} year)

- We established the sequential vacuum evaporation (SVE) method to control defects in organohalide hybrid perovskite (OHP) thin film. (M.-C. Jung, *et al*., Applied Physics Express 12, 015501 (2019))
- We published the review paper for the defect understanding in organic-inorganic hybrid perovskite materials. (Focus Review: Y.M. Lee, *et al*., Frontiers in Energy Research – Solar Energy, 6, 128 (2018))
- In the case of $MAPbI_3$ thin film fabricated by the SVE method, we found the THz-wave absorption at 1.58 THz with 50% of transmission and 11000 cm^{-1} of absorption coefficient which is originated from CH_3NH_2 molecular defect-incorporated perovskite structure. (The new finding of physical property, I. Maeng, *et al*., Scientific Reports, 9, 5811 (2019)
- In the case of $FAPbI_3$, we found the THz-wave absorption at 1.62 THz with 60% of transmission which is originated from - and -phase mixed perovskite structure. (New finding of physical property, Y.M. Lee, *et al*., Applied Physics Express, 12, 05103(2019))
- From these results, we confirmed that the understanding of Pb-I (metal cation-halogen anion) vibration mode with defect structure is the main key to control the THz-wave absorption property.

FY2019 3^{rd} year

We performed a below;

- The phonon mode study to find a new physical property in the hybrid perovskite thin film.
- We were trying to exactly know a structure/state of the molecular defect (CH_3NH_2) and its effect. We found a significant THz-wave absorption property firstly which is due to the molecular defect-incorporated hybrid perovskite. Also, we understood that the partial defect structure could make a different phonon mode. (I. Maeng, *et al*., Nanomaterials, Accepted.)
- The interface study between the polymer protection layer and hybrid perovskite thin film. (M.-C. Jung, *et al*., Scientific Reports, 9, 10853 (2019))
- We were trying to find a good protection layer in polymer materials with ultra-thin (< 10 nm) and minimized interface region (no intermixed state). We found the P3 polymer can be a good protection layer with a 7 nm-thick, no intermixed state, and no penetrating.

Finally, we confirmed the new physical property (THz-wave absorption in the range of 0.5~2.5 THz) with the defect incorporated structure and found the enough protection polymer layer. We believe these results will be a seed for the next step to realize a THz-based application using organic-inorganic hybrid perovskite materials

５．主な発表論文等

〔雑誌論文〕　計6件（うち査読付論文　6件／うち国際共著　6件／うちオープンアクセス　3件）

１．著者名 Lee Young Mi、Maeng Inhee、Park Jinwoo、Song Myungkwan、Yun Jung-Ho、Jung Min-Cherl、Nakamura Masakazu	４．巻 6
２．論文標題 Comprehensive Understanding and Controlling the Defect Structures: An Effective Approach for Organic-Inorganic Hybrid Perovskite-Based Solar-Cell Application	５．発行年 2018年
３．雑誌名 Frontiers in Energy Research	６．最初と最後の頁 128
掲載論文のDOI（デジタルオブジェクト識別子） 10.3389/fenrg.2018.00128	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Jung Min-Cherl、Kobori Sora、Matsuyama Asuka、Maeng Inhee、Lee Young Mi、Kojima Hirotaka、Benten Hiroaki、Nakamura Masakazu	４．巻 12
２．論文標題 Formation of CH3NH2-incorporated intermediate state in CH3NH3PbI3 hybrid perovskite thin film formed by sequential vacuum evaporation	５．発行年 2018年
３．雑誌名 Applied Physics Express	６．最初と最後の頁 015501～015501
掲載論文のDOI（デジタルオブジェクト識別子） 10.7567/1882-0786/aaf0ac	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Lee Young Mi、Yun Jung-Ho、Matsuyama Asuka、Kobori Sora、Maeng Inhee、Lyu Miaoqiang、Wang Shenghao、Wang Lianzhou、Jung Min-Cherl、Nakamura Masakazu	４．巻 12
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掲載論文のDOI（デジタルオブジェクト識別子） 10.7567/1882-0786/ab0eec	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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２．論文標題 Significant THz absorption in CH3NH2 molecular defect-incorporated organic-inorganic hybrid perovskite thin film	５．発行年 2019年
３．雑誌名 Scientific Reports	６．最初と最後の頁 5811
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41598-019-42359-8	査読の有無 有
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1．著者名 YoungMi Lee, Jinwoo Park, Byung Deok Yu, Suklyun Hong, Min-Cherl Jung, and Masakazu Nakamura	4．巻 9
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpclett.8b00494	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

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オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

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4．発表年
2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

Research page of laboratory
http://mswebs.naist.jp/LABs/greendevice/research/index_e.html

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考