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研究課題名（和文）Imaging ultrafast photocarrier trapping in perovskite photovoltaic materials

研究課題名（英文）Imaging ultrafast photocarrier trapping in perovskite photovoltaic materials

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研究成果の概要（和文）：太陽発電有力材料ペロブスカイトの欠陥はデバイス性能を制限している。欠陥がどう性能に影響するかの解明にはナノメートルかつフェムト秒規模の解像度技術が必要で双方満たすのは難しいが、それを満たす私達が開発してきた時間分解電子顕微鏡で欠陥状態を映像化、光キャリアトラップ構造の解明をし[Nature580,360(2020)]、様々な欠陥状態を発見[Energy&Environ.Science 14,6320(2021)]、この材料の化学的不均一性の役割を研究[NaturNanotech17,190(2022)]、欠陥のシード劣化への影響も示した[Nature(2022)]。

研究成果の学術的意義や社会的意義
Our work visualizes and identifies nanoscale defects, and their impact on degradation. These results contribute towards the large-scale commercialization of perovskite photovoltaic technology, which is a critical component of the global strategy to address climate change and energy sustainability.

研究成果の概要（英文）：Over the past decade, perovskite photovoltaic materials have become the leading contenders for solar devices. Yet, the presence of defects has limited device performance. Understanding the nature of the defect states and their impact on performance required the use of a technique with nanometer- and femtosecond-scale resolution, which are challenging to obtain simultaneously. Using our novel technique of time-resolved photoemission electron microscopy (TR-PEEM), which offers such resolutions, we succeeded in imaging the defects states and understanding the mechanism of photocarrier trapping [Nature 580, 360 (2020)]. We then identified the different types of defect states [Energy & Environ. Science 14, 6320 (2021)], and studied the role of chemical heterogeneity in these films [Nature Nanotech 17, 190 (2022)]. Recently, we showed that these defects also played a critical role in seeding degradation [Nature DOI 10.1038/s41586-022-04872-1 (2022)].

研究分野：Perovskite photovoltaics

キーワード：Time-resolved　photoemission　microscopy　perovskite　photovoltaics　ultrafast　dynamics

１．研究開始当初の背景

Hybrid Organic Inorganic Perovskite (HOIP) materials had become one of the most promising photovoltaic technologies, since the demonstration of a 3.9% efficient solar cell in 2009. However, they were still far from the theoretical maximum conversion efficiency predicted for a single junction direct-bandgap semiconductor, indicating that much can still be done to improve the materials and device architecture.

All-optical studies of HOIP materials suggested that non-radiative recombination centers, or defect sites, prevented efficient carrier collection and reduced overall device efficiency [Science 348, 683 (2015)]. Further, there were also reports of nanoscale variations in device parameters, such as photovoltage and photocurrent [Nature Energy 1, 1 (2016)]. To understand these variations, it was important to study the distribution and nature of defect states on the nanoscale and the pathways they offer for non-radiative carrier recombination losses. These non-radiative loss pathways are typically on ultrafast timescale, thus required sophisticated techniques that offer both high spatial and high temporal resolution simultaneously.

２．研究の目的

In this Kakenhi project, I proposed to use our novel technique of time-resolved photoemission electron microscopy (TR-PEEM) to directly image defect sites with nanoscale resolution and to study the ultrafast trapping of photocarriers at these sites with femtosecond-scale resolution. At the time, I had applied TR-PEEM techniques to semiconductors to visualize charge carrier dynamics and transport in semiconductor structures caused by band structure variations [Nature Nanotech 12, 36 (2017)]. Further, using TR-PEEM, I had also showed the ability to manipulate the photocarrier transport in a semiconductor using tailored optical pulses [Science Advances 4, eaat9722 (2018)]. With these demonstrated capabilities, I planned to study the ultrafast trapping dynamics at nanoscale defect sites in the technologically important HOIP materials.

３．研究の方法

In this study, with the help of collaborators from the Stranks Group in Cambridge, we prepared various HOIP perovskite films, such as mixed-cation lead iodide $(Cs_{0.05}FA_{0.78}MA_{0.17})PbI_3$, and mixed-cation lead trihalide $(Cs_{0.05}FA_{0.78}MA_{0.17})Pb(I_{1-x}Br_x)_3$ (FA=formamidinium, MA=methylammonium, x=0-0.2) films through solution processing. These films represented materials used in high efficiency solar cell devices.

(1) Imaging Defect Sites

For this, I used the static imaging (PEEM mode). A 4.6 eV probe pulse was used to photoemit electrons from very close to the Fermi level of the sample surface. These photoemitted electrons were collected by the objective lens of the microscope and imaged in real space. The PEEM images were compared with spatially-resolved confocal PL maps, AFM images, SEM images and also nano-XRD maps. The comparison of these various images allowed us to visualize defects and understand their properties, such as location, distribution and structural properties.

(2) Measuring the photocarrier trapping dynamics at the defect sites

I also photoexcited the sample with a 100 fs, 1.5 eV or 3.0 eV pump pulse. Then, I used a time-delayed 4.6 or 6.2 eV probe pulse to photoemit electrons. I imaged the photoemitted electrons at different pump-probe time delays and assembled the images sequentially to construct a movie of the trapping of carriers at the defect sites. By analyzing the movie quantitatively and separately for the different defect types, I obtained rich information about the trapping kinetics with nanoscale spatial and femtosecond-scale temporal resolution.

(3) Measuring the alteration of defect states on exposure to light

To understand how defect states impacted degradation, we imaged and studied the defect states as described in (A) with PEEM, AFM, SEM and nXRD. We then exposed the perovskite film to varying degrees of light with and without the presence of oxygen. We then reimaged the changes in the film with the above technique. This allowed us to study changes in the defect sites on exposure to light, which initiated the process of degradation.

４．研究成果

The studies associated with this Kakenhi resulted in four major results, as described below:

(1) Imaging performance limiting Defects in Halide Perovksites

[*Nature* 580, 360 (2020)]

In this work, we showed for the first time the nanoscale presence and distribution of trap clusters in a mixed-cation mixed-halide HOIP films. We observed that there are local nanoscale regions which display a high density of mid-gap trap states compared to other regions or the spatially averaged response. We found that these locations contained nanoscale clusters of traps, which occur primarily at junctions between particular material grains, where one grain is distorted structurally and compositionally, as revealed through correlated scanning electron diffraction (SED) microscopy and scanning transmission electron microscopy (STEM-EDX) measurements. We then studied the effect of these trap clusters on carrier recombination in the film. From regions of low photoluminescence (PL) yield, we measure the subsequent trapping dynamics at these trap clusters using time-resolved PEEM measurements. We find that there is hole carrier trapping which happens only at the nanoscale trap clusters and not at other locations. By analyzing the trapping kinetics from many trap clusters simultaneously, we find that the trapping dynamics are consistent with a diffusion-limited trapping process.

(2) Unravelling the Varied Nature and Roles of Defects in Hybrid Halide Perovskites

[*Energy & Environ. Science* **14**, 6320 (2021)]

In this work, by combining PEEM with synchrotron based x-ray microscopies, we have uncovered the presence of multiple types of defects. By employing time-resolved photoemission electron microscopy (TR-PEEM), we found that depending on their nature, these defects played surprisingly varied roles in charge carrier trapping – from highly detrimental to relatively benign. They also showed a varied response to passivation strategies. The presence of multiple types of defects, with varied roles in device performance and varied responses to passivation strategies, highlights the need to develop targeted approaches that address each type of defect and their detrimental impact.

(3) Nanoscale chemical heterogeneity dominates optoelectronic response

[*Nature Nanotech* **17**, 190 (2022)]

Here, we provided a global visualization of the nanoscale chemical, structural and optoelectronic landscape in halide perovskite devices, made possible through the development of a new suite of correlative, multimodal microscopy measurements combining quantitative optical spectroscopic techniques and synchrotron nanoprobe measurements. We showed that compositional disorder dominated the optoelectronic response over a weaker influence of nanoscale strain variations even of large magnitude. Nanoscale compositional gradients drive carrier funnelling onto local regions associated with low electronic disorder, drawing carrier recombination away from trap clusters associated with electronic disorder and leading to high local photoluminescence quantum efficiency.

(4) Local Phase Impurites act as degradation sites

[*Nature* DOI 10.1038/s41586-022-04872-1 (2022)]

Here, we revealed that in leading formamidinium-rich perovskite absorbers, nanoscale phase impurities including hexagonal polytype and lead iodide inclusions are not only traps for photo-excited carriers, but are also sites at which photochemical degradation of the absorber layer is seeded. We visualized illumination-induced structural changes at phase impurities associated with trap clusters, revealing that even trace amounts of these phases, otherwise undetected with bulk measurements, compromise device longevity. The type and distribution of these unwanted phase inclusions depends on film composition and processing, with the presence of polytypes being most detrimental for film photo-stability. Importantly, we revealed that performance losses and intrinsic degradation processes can both be mitigated by modulating these defective phase impurities, and demonstrate that this requires careful tuning of local structural and chemical properties.

５．主な発表論文等

〔雑誌論文〕　計4件（うち査読付論文　4件／うち国際共著　4件／うちオープンアクセス　1件）

１．著者名 Kosar Sofiia、Winchester Andrew J.、Doherty Tiarnan A. S.、Macpherson Stuart、Petoukhoff Christopher E.、Frohna Kyle、Anaya Miguel、Chan Nicholas S.、Madeo Julien、Man Michael K. L.、Stranks Samuel D.、Dani Keshav M.	４．巻 14
２．論文標題 Unraveling the varied nature and roles of defects in hybrid halide perovskites with time-resolved photoemission electron microscopy	５．発行年 2021年
３．雑誌名 Energy and Environmental Science	６．最初と最後の頁 6320～6328
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D1EE02055B	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 Macpherson Stuart、Doherty Tiarnan A. S.、Winchester Andrew J.、Kosar Sofiia、Johnstone Duncan N.、Chiang Yu-Hsien、Galkowski Krzystof、Anaya Miguel、Frohna Kyle、Iqbal Affan N.、Nagane Satyawan、Roose Bart、Andaji-Garmaroudi Zahra、Orr Kieran W. P.、Parker Julia E.、Midgley Paul A.、Dani Keshav M.、Stranks Samuel D.	４．巻 -
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３．雑誌名 Nature	６．最初と最後の頁 -
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41586-022-04872-1	査読の有無 有
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１．著者名 T.A.S.Doherty, A.J.Winchester, S.Macpherson, D.N.Johnstone, V.Pareek, E.M.Tennyson, S.Kosar, F.U.Kosasih, M.Anaya, M.Abdi-Jalebi, Z.Andaji-Garmaroudi, E.L.Wong, J.Madeo, Y.-H.Chiang, J.-S.Park, Y.-K.Jung, C.E.Petoukhoff, G.Divitini, M.K.L.Man, C.Ducati, A.Walsh, P.A.Midgley, K.M.Dani, S.D.Stranks	４．巻 580
２．論文標題 Performance-limiting nanoscale trap clusters at grain junctions in halide perovskites	５．発行年 2020年
３．雑誌名 Nature	６．最初と最後の頁 360-366
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1．著者名 Frohna Kyle、Anaya Miguel、Macpherson Stuart、Sung Jooyoung、Doherty Tiarnan A. S.、Chiang Yu-Hsien、Winchester Andrew J.、Orr Kieran W. P.、Parker Julia E.、Quinn Paul D.、Dani Keshav M.、Rao Akshay、Stranks Samuel D.	4．巻 17
2．論文標題 Nanoscale chemical heterogeneity dominates the optoelectronic response of alloyed perovskite solar cells	5．発行年 2021年
3．雑誌名 Nature Nanotechnology	6．最初と最後の頁 190～196
掲載論文のDOI（デジタルオブジェクト識別子） 10.1038/s41565-021-01019-7	査読の有無 有
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〔学会発表〕　計6件（うち招待講演　3件／うち国際学会　6件）

1．発表者名 Keshav M. Dani
2．発表標題 Understanding the role of nanoscale defect clusters in hybrid perovskite photovoltaics with time-resolved photoemission electron microscopy,
3．学会等名 NanoGe Spring Meeting 2022（招待講演）（国際学会）
4．発表年 2022年

1．発表者名 Sofiia Kosar
2．発表標題 Exploring defects in triple cation mixed halide perovskite thin films using time-resolved photoemission electron microscopy
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1．発表者名 Sofiia Kosar
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Andrew Winchester

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Keshav M. Dani

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2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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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

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
英国	The university of Cambridge			