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

平成 29 年　 6 月 22 日現在

機関番号：38005
研究種目：若手研究(B)
研究期間：2015～2016
課題番号：15K17925

研究課題名（和文）High stability perovskite solar cells

研究課題名（英文）High stability perovskite solar cells

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交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：有機無機ハイブリッドペロブスカイト太陽電池による太陽光発電技術を商業化に向けて進めるために、スケールアップの開発が必要である。また、高い太陽エネルギー変換効率、長期安定性、毒性の最小化も同時に重要である。私たちの研究の主な結果は次のとおりである。1.ペロブスカイト太陽電池の基本的な分解特性の理解。2.ペロブスカイト型太陽電池でよく使用されるSpiro-MeOTAD正孔輸送材料の最上層に起こる基本分解プロセス。3.高品質ペロブスカイト膜をもたらすメチルアミンガス誘起結晶化処理と呼ばれる新規プロセスの開発。4.真空共蒸着法と逐次法によるCH3NH3SnBr3系鉛フリーペロブスカイト太陽電池の制作。

研究成果の概要（英文）：In organic-inorganic hybrid perovskite solar cells, development of up-scaling processes with high solar energy power conversion efficiency, long-term stability, and minimum toxicity is important for moving forward this photovoltaic technology towards commercialization. The main findings from our research includes (1) fundamental understanding of CH3NH3PbI3-based perovskite solar cell degradation processes; (2) fundamental degradation processes taking place in the top-most layer of spiro-MeOTAD hole transport material often used in perovskite solar cells; (3) development of a novel process denoted as methylamine gas induced crystallization treatment that leads to high quality perovskite films; (4) initial trials of CH3NH3SnBr3-based lead-free perovskite solar cells by the vacuum co-evaporation and sequential methods.

研究分野：有機無機ハイブリッドペロブスカイト太陽電池

キーワード：有機無機ハイブリッドペロブスカイト　太陽エネルギー　毒性最小化　太陽光発電　長期安定性　正孔輸送材料　鉛フリーペロブスカイト　真空共蒸着法

１．研究開始当初の背景

(1) Organic-inorganic hybrid perovskites are advantageous for photovoltaic applications because of their readiness to form long-range ordering in the crystal structure, abundance and low price as raw materials, and the easy processability under 150 ℃ temperature (solution and vacuum evaporation). To move this technology forward towards commercialization, major considerations include development of fabrication techniques compatible with up-scaling, toxicity of Pb, and long-term lifetime of perovskite solar cells.

(2) Currently, methyl ammonium lead iodide ($CH_3NH_3PbI_3$ resulted from the reaction between CH_3NH_3I and PbI_2 or $PbCl_2$) is the major perovskite material under study. $CH_3NH_3PbI_3$ shows a high absorption coefficient (direct bandgap ~1.7 eV) and high mobilities for electrons (7.5 $cm^2{\cdot}V^{-1}{\cdot}s^{-1}$) and holes (12.5 – 66 $cm^2{\cdot}V^{-1}{\cdot}s^{-1}$) resulting in long carrier diffusion lengths (100 nm – 3 μm). These properties are essential for high performing solar cells. Despite many advantages associated with high efficiencies of $CH_3NH_3PbI_3$ based solar cells, several problems remain to be solved. The most critical issue is the rapid degradation of $CH_3NH_3PbI_3$ solar cells under ambient operation conditions (environmental conditions such as humidity, temperature, and light induced degradation, etc.). Therefore, perovskite solar cell lifetime is an important issue that needs to be investigated and optimized to make such a technology practical and applicable to industrial-scale.

２．研究の目的

(1) Fundamental level understanding of solar cell degradation processes ③.

(2) Development of high-quality perovskite films and large-area perovskite solar cell fabrication processes aiming at high PCE, high-throughput, and minimum batch-to-batch variation ⑨.

(3) Development of Pb-free perovskite solar cells.

３．研究の方法

(1) **Synthesis of new perovskite materials**: Perovskite materials have the general ABX_3 structure where organic compounds such as methylammonium (MA = $CH_3NH_3^+$), formamidinium [FA = $HC(NH_2)_2^+$] occupy site ‘A’. Metals (Sn and Pb) and halogen elements such as Cl^- and I^- occupy sites ‘B’ and ‘X’, respectively. If the tolerance factor for the perovskite formation does not deviate substantially from 1, it is possible to synthesize alternative perovskite materials to be tested as candidates for solar cell applications. In addition to the optimization of solar cell devices, guidance and feedback/verification from surface science analytical tools are also essential for efficiently achieving our goals.

(2) **New perovskite material characterization**: Solar cell performance and stability using those new materials are correlated with their film properties such as uniformity and smoothness using optical microscope and atomic force microscopy (AFM), film crystallinity by X-ray diffraction (XRD), stoichiometry by X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), and electronic energy levels determined by a combination of ultraviolet photoelectron spectroscopy (UPS) and UV-vis measurements.

４．研究成果

(1) **Solar cell degradation issue**: As described in references ①, one important aspect of the degradation mechanism in $CH_3NH_3PbI_3$ has been achieved. $CH_3NH_3PbI_3$ is currently the perovskite material widely studied and applied for solar cell applications. Our work showed that exposure of $CH_3NH_3PbI_3$ to iodine vapor leads to rapid decomposition. This infers that I_2 generation from the normal solar cell operation conditions leads to a self-degradation, which represents an inherent degradation mechanism limiting the long-term stability of iodine-containing perovskite based solar cells. Strategies to improve stability are being studied currently in my group.

(2) Reaction pathway of $CH_3NH_3PbI_3$ decomposition: It is suitable to use combined thermal gravimetric and differential thermal analysis (TG-DTA) and mass spectrometry (MS) to simultaneously determine the mass loss and chemical nature of the products during thermal degradation of $CH_3NH_3PbI_3$ perovskite ④. In contrast to the common wisdom that $CH_3NH_3PbI_3$ is thermally decomposed into CH_3NH_2 and HI, the major gas products were found to be methyl iodide (CH_3I) and ammonia (NH_3) ④ under the several conditions that were investigated

in our study.
(3) **Solar cell degradation issue related to hole transport layer:** The top-most layer in perovskite solar cells, spin-coated spiro-MeOTAD films using chlorobenzene as the solvent showed a high density of pinholes (small sized pinholes ~4 pinholes/μm^2 with an average diameter of ~135 nm and large sized pinholes ~289 pinholes/mm^2 with diameters in the range of 1-20 μm). Additional cross-sectional view scanning electron microscopy (SEM) measurements revealed that these pinholes form channels wiggling across the film thickness (~240 nm). These pinholes were observed to facilitate the inward diffusion of gas molecules present in ambient air (e.g. H_2O and O_2) leading to detrimental effects of the underneath perovskite layer. In addition, these pinholes can also facilitate the outward diffusion of chemical elements/compounds with high vapor pressure such as iodine-containing volatile species (MAI and/or HI) as a result of the degradation and/or decomposition of the $CH_3NH_3PbI_3$ perovskite film. Moreover, the pinholes in spiro-MeOTAD HTL were demonstrated to be one of the causes for the reduced device performance as a function of operation time of solar cells ③⑦.
(3) **Synthesis of high-quality perovskite films:** The processes based on the more basic chemical components of methylamine (CH_3NH_2) (as opposed to CH_3NH_3I) was developed aiming minimum sample-to-sample variations ②⑩. This process denoted as methylamine gas induced crystallization can heal defects by the melting and re-growth of perovskites grains leading to high quality perovskite films. The quality of perovskite films is one of the most important influencing factors for perovskite solar cells. Our proposed method is shown to significantly improve the grain boundary-related issues ⑤. Such a gas-induced reaction also enabled the successful preparation of high quality perovskite films with a size of 100 cm^2.
(4) **Pb-free perovskites:** Co-evaporation and sequential evaporation of $SnBr_2$ and MABr for fabricating Pb-free perovskites have been developed ⑪. $MASnBr_3$ showed photovoltaic properties generating 1.12% efficiency. We have demonstrated that the fast formation of Sn oxide by air exposure can be avoided employing vacuum vapor-deposition methods, which is unavoidable in solution processing techniques

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

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〔図書〕(計０件)

〔産業財産権〕
○出願状況（計０件）

○取得状況（計０件）

〔その他〕
ホームページ等

① Webpage Title: Stability challenge in perovskite solar cell technology
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