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学位論文の要約

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題目　　　Surface Modifications of Mixed Tin–Lead Halide Perovskite Films for Solar Cells
　　　　　（太陽電池のための錫-鉛混合ハライドペロブスカイトフィルムの表面修飾）
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1. General Introduction

Perovskite solar cells, using ABX_3 type metal halide perovskite (A: Cs^+, methylammonium (MA^+), formamidinium (FA^+), etc., B: Pb^{2+}, Sn^{2+}, etc., $X = I^-$, Br^-, etc.) as photoabsorber materials, have attracted intense attention as printable and cost-effective next generation photovoltaics. Thanks to its tunable bandgap, the maximum efficiency could be realized with the perovskite films having the bandgap in the range of 1.1–1.4 eV, based on the principle of detailed balance. Alloying the Sn(II) and Pb(II) cations at the B site of the structure with the ratio of 1:1 makes the perovskite with the bandgap of ~1.25 eV, suggesting the promising capability of this material. The perovskites employed, however, are generally polycrystalline films, which contains abundant surfaces, i.e., grain boundaries and interfaces. Meanwhile, the detrimental imperfections are mostly accumulated at these surfaces, leading to profound non-radiative charge carrier recombination and inefficient charge transport and extraction in the resultant cells. Therefore, improving the surface of the perovskite films should be a pressing pursuit.

On the one hand, the crystallization process strongly determines the final quality of the perovskite films. For mixed Sn–Pb perovskite, tin species have a natural tendency to crystallize faster in an uncontrollable manner, which competes with Pb species and leads to the generation of metal inhomogeneities, morphological flaws and unoriented grains, generating in turn a significant variety of defects. Thus, further research in the understanding on the perovskite colloidal properties and its evolution into thin films to better control the crystallization process needs to be investigated. On the other hand, intrinsic material instability to oxidation, mass loss mechanisms, and ion movement phenomena in materials and devices is another main origin of detrimental imperfections and consequent device performance decline. Particularly, the oxidation and mass loss at the superficial material could lead to the formation of extraction barriers that prohibit charge carrier extraction, leading to the loss of cell efficiency. In the same line, ion movement in the perovskite films and subsequent band flattening in the devices can lead to inefficient charge extraction at the interfaces. Therefore, the development of robust surface modification methods, tuned specifically effective for mixed Sn–Pb perovskite films, is of urgent need. Such treatments will ultimately improve stability, reduce the photochemical reactions, and suppress ion movements, enabling mixed Sn–Pb devices with excellent long-lasting performances.

2. Perovskite Films with >7 μs Charge Carrier Lifetimes

In Chapter 2, Maltol, a naturally occurring flavor enhancer and strong metal binding

agent, is found to effectively suppress Sn(IV) formation and passivate defects in mixed Sn–Pb perovskite films. When used in combination with Sn(IV) scavenging, the maltol surface treatment leads to high-quality perovskite films which show enhanced photoluminescence intensities and elongated charge carrier lifetimes in excess of 7 μs. The scavenging and surface treatments result in highly reproducible solar cell devices, with photo-conversion efficiencies of up to 21.4% under AM1.5G illumination.

3. Optimized Carrier Extraction at Interfaces for Efficient Perovskite Solar Cells

In Chapter 3, the carrier extraction in mixed Sn–Pb perovskite solar cells is improved by modifying the top and bottom perovskite surfaces with ethylenediammonium diiodide and glycine hydrochloride, respectively. Trap densities in the perovskite layers are reduced as a result of surface passivation effects and an increase in film crystallinity. In addition, the orientated aggregation of the ethylenediammonium and glycinium cations at the charge collection interfaces result in the formation of surface dipoles, which facilitate charge extraction. As a result, the treated mixed Sn–Pb perovskite solar cells show improved performance, with a fill factor of 0.82 and a power conversion efficiency up to 23.6%. The unencapsulated device also shows improved stability under AM1.5G, retaining over 80% of the initial efficiency after continuous operation in inert atmosphere for 200 hours. Our strategy is also successfully applied to centimeter-scale devices, with efficiencies up to 21.0%.

4. Synergistic Surface Modification of Perovskite Solar Cells

In Chapter 4, the top surface treatment of mixed Sn–Pb halide perovskite films for p-i-n solar cells is studied. The charge extraction is promoted by treating the perovskite surface with piperazine. This compound reacts with the organic cations at the perovskite surface, modifying the surface structure and tuning the interfacial energy level alignment. In addition, the combined treatment with C_{60} pyrrolidine tris-acid (CPTA) reduces hysteresis and leads to efficiencies up to 22.7%, with open-circuit voltage values reaching 0.90 V, ~92% of the radiative limit for the band gap of this material. The modified cells also show superior stability, with unencapsulated cells retaining 96% of their initial efficiency after >2000 hours of storage in N_2 and encapsulated cells retaining 90% efficiency after >450 hours of storage in air. Intriguingly, CPTA preferentially binds to Sn(II) sites at film surface over Pb(II) due to the energetically favored exposure of the former, according to first-principles calculations.

5. Summary and Outlook

The easy-to-handle and effective approach developed in this thesis should be widely applicable to other perovskite semiconductor devices, such as all-perovskite and perovskite/silicon tandem photovoltaics, perovskite light-emitting diodes, transistors, and X-ray detectors. The understanding on the surface characteristics of the mixed Sn–Pb perovskite films would also be widely applicable to the other perovskite systems, i.e., pure Sn and Pb ones, for achieving superior performance.