Inorganic perovskite solar cells with very high voltage and excellent stability against thermal and environmental degradation

Saba Sharikadze, Junhao Zhu, Ranjith Kottokkaran, Arkadi Akopian and Vikram Dalal

Iowa State University, Ames, Iowa, 50011, USA

Abstract

We report on inorganic $CsPbBr_3$ solar cells with very high open circuit voltages and excellent environmental stability. The cells were fabricated using vapor deposition. We show that by using an interfacial n-doped CdS (CdS:In) layer between the cell TiO2, we can obtain voltages of ~1.68 V, the highest ever reported in vapor deposited $CsPbBr_3$ material. A surprising phenomenon was that the crystal structure of the material, and the apparent bandgap, changed when a thicker CdS:In layer was used as the n layer. We also show that there is little environmental degradation in performance for a cell kept for 600 hours in room air, and even for a cell kept at 200 °C for 24 hours in air. The cells were deposited using sequential deposition in vacuum followed by anneals at 450 °C. We study both organic p layers (P3HT) and inorganic p layers (paste coated C).

Keywords—Perovskite solar cells, thermal and environmental stability, fundamental properties, high open circuit voltage

I. Introduction

Large bandgap perovskite solar cells are of significant importance for making tandem junction cells with Si acting as the bottom cell [1]. A major problem with this material has been a low open circuit voltage. In spite of the bandgap of the material being 2.3 eV, the best open-circuit voltage has been limited to ~1.62V [2-4]. This low voltage has been attributed to various causes, such as interfacial band misalignment at the heterojunction between the perovskite and the doped contact layers, excessive grain boundary recombination etc [5]. In this paper, we show that by changing the heterostructure between the normal n-conducting layer (TiO_2) and the perovskite layer, we can significantly change the open-circuit voltage. In particular, the use of doped CdS layers between the perovskite and TiO_2 leads to significant changes (by 60 meV) in open circuit voltage, with the voltage increasing as the thickness of CdS layer increases. We analyze this strange behavior, and show, by detailed device measurements, that the crystal structure of the perovskite itself is function of the interfacial layer, and that the bandgap of the perovskite changes as the thickness of the CdS layer increases.

We also study the thermal and environmental stability of the inorganic perovskite solar cells. It is well known that inorganic perovskite cells containing iodine decompose in moisture. In contrast, we show that Br containing perovskite cells are no affected by moisture, and we show that our cells show no degradation when exposed to air at room temperature for 500+ hours. Even ahigh temperature anneal at 200 °C in air leads to no perceived degradation in performance. We also show that one can make an all-inorganic cell by using C paste as the p layer, eliminating the organic P3HT p-heterojunction layer.

II. Material Fabrication

The cells were fabricated on compact TiO_2 layer deposited on FTO glass substrates. Following the TiO_2 layer, an intermediate n-doped CdS layer was evaporated [6] prior to the deposition of the perovskite layer. The perovskite layer was deposited using sequential deposition [7] from CsBr and $PbBr_2$ sources, with the $PbBr_2$ layer being sandwiched between two CsBr layers. After deposition, the layers were annealed at 450 °C for 20 minutes followed by 40 mins at 350 °C. The p layer was either solution grown P3HT, or a C layer coated from a C paste. A final gold layer completed the cell. Fig. 1 shows the device structure.

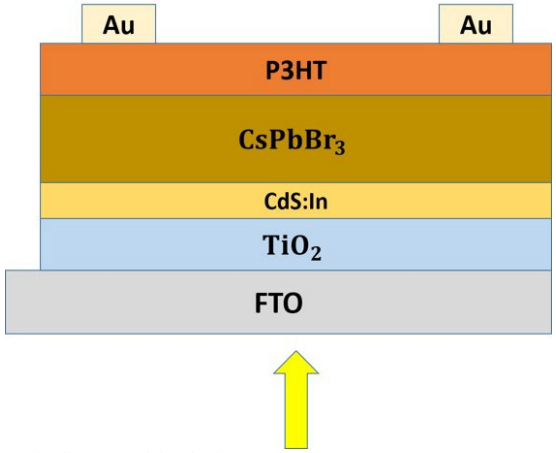

Fig.1. Schematic diagram of the device.

2022 IEEE 49th Photovoltaics Specialists Conference (PVSC) | 978-1-7281-6117-4/22/$31.00 ©2022 IEEE | DOI: 10.1109/PVSC48317.2022.9938899

III. Solar Cell Properties

The cells were measured for their electrical performance using an ABET full-spectrum AM1.5 solar simulator. The cells were measured both inside and outside the glove box. Fig. 2 shows the I-V curves for our cells with varying thicknesses of the CdS:In layer. Note how increasing the thickness of the CdS:In layer increases the open circuit voltage - a very surprising development. We also study the quantum efficiency of the device, in particular the fall-off in QE at around 540 nm. The data is shown in Fig. 3, where we show that as the thickness of the CdS:In layer is increased, the fall-off becomes more pronounced, and shifts to 520 nm for larger thickness. This is a very remarkable and surprising result, which suggests that the effective bandgap of the material is changing, with the bandgap becoming slightly larger as the thickness of the CdS:In layer increases.

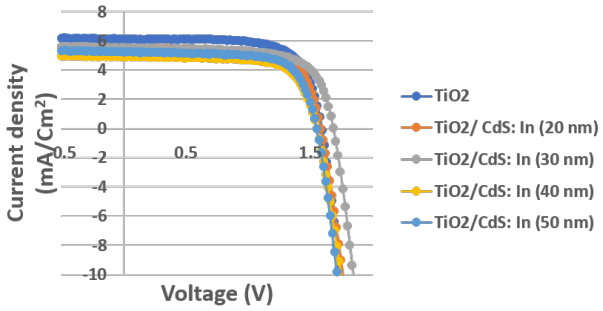

Fig.2. Light IV curves of the devices with various thickness of CdS:In

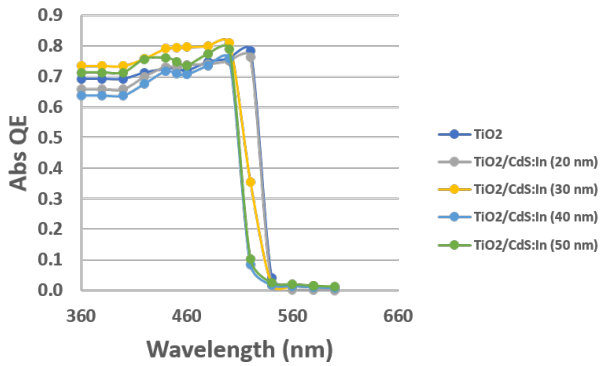

Fig.3. QE of the devices with various thickness of CdS:In

To understand this behavior, we study the crystal structure of the perovskite material, using x-ray diffraction. The data is shown in Fig.4. Note how additional planes appear in the spectrum as the thickness of the CdS:In layer is increased.

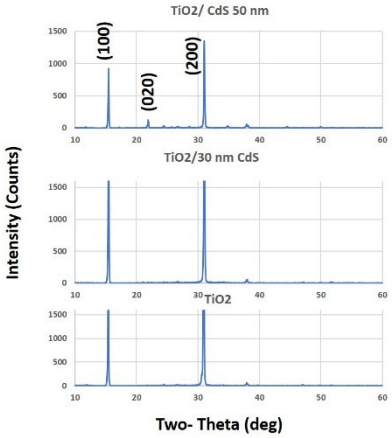

Fig.4. XRD spectrum of the perovskites

IV. Stability of the Device Against Moisture

The device was exposed to air for 1000 hours, and measured periodically for tis properties. In Fig. 5 we show the I-V curves for initial and 500 hours of exposure. From the figure, it is clear that there is virtually no degradation of the device when exposed to room air. We also studied the influence of higher temperatures on stability against moisture by subjecting a cell to room air at a cell temperature of 200 °C for 24 hours. The data is shown in Fig. 6. From Fig. 6, we can see that there is no degradation in cell performance even at 200 °C, thus confirming that both the material and the cell are stable at high temperatures, even when exposed to room air.

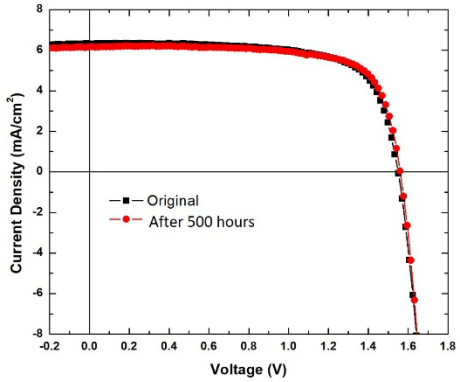

Fig.5. Light IV curves before and after 500 hours of air exposure.

978-1-7281-6117-4/22/$31.00 ©2022 IEEE

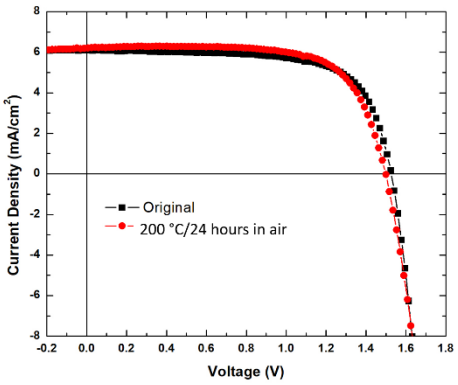

Fig.6. Light Iv curves before and after 200 °C for 24 hrs in air.

V. Devices With C paste As P-layer

We studied the use of C paste as the p-heterojunction layer. the C paste was diluted with 1-Ethoxy-2- propanol and then coted using a MTI Carbon paste coater. After coating, the C was annealed in air at 130 °C for 30 minutes. In Fig. 7, we show the results on one of our first C paste device, showing a good voltage and a good low resistance contact. The results of further optimization and stability of such, all inorganic, devices are under progress and will be reported at the conference.

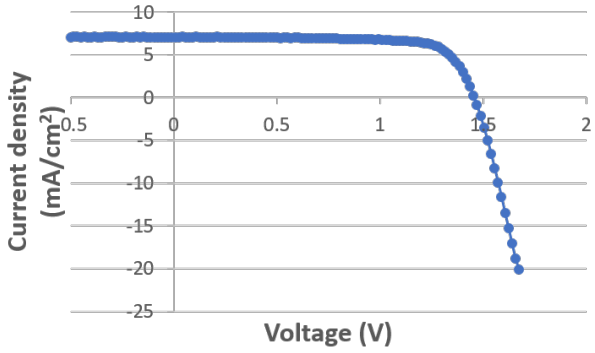

Fig.7. Light Iv curve of the device with carbon as P layer

VI. Conclusions

In summary, we report on an inorganic perovskite material and a device with record high open-circuit voltages, and excellent environmental stability, even at high temperatures. We show that interfacial layers change the crystal structure, the apparent bandgap, and the open circuit voltage of the device. we also show an all-inorganic device, with inorganic heterojunctions, with good device properties. The material was deposited using vacuum deposition techniques.

VII. Acknowledgments

We acknowledge funding from NSF for this project. we also thank Max Noack for his technical help.

VIII. References

[1] Saad Ullah et al. “All-inorganic CsPbBr3 perovskite: a promising choice for photovoltaics” *Mater. Adv.*, 2, 646-683, 2021.

[2] X. Li et al., “All-Inorganic CsPbBr 3 Perovskite Solar Cells with 10.45% Efficiency by Evaporation-Assisted Deposition and Setting Intermediate Energy Levels” *ACS Appl. Mater. Interfaces,* 11 , 29746 —29752, 2019.

[3] J. Zhu, R. Kottokkaran, S. Sharikadze, L. -P. Poly and V. Dalal, "Inorganic perovskite solar cells with high voltage and excellent stability against thermal and environmental degradation," *2021 IEEE 48th Photovoltaic Specialists Conference (PVSC)*, 2021, pp. 0425-0428

[4] Y. Zhao et al., “Using SnO2 QDs and CsMBr3 (M = Sn, Bi, Cu) QDs as Charge-Transporting Materials for 10.6%-Efficiency All-Inorganic CsPbBr3 Perovskite Solar Cells with an Ultrahigh Open-Circuit Voltage of 1.610 V” *Sol. RRL*, 3 , 507 1800284, 2019.

[5] H. Gaonkar, J. Zhu, R. Kottokkaran, M. Noack and V. Dalal, "Thermally Stable Inorganic Perovskite Solar Cells," *2020 47th IEEE Photovoltaic Specialists Conference (PVSC), 2020*, pp. 0167-0169.

[6] H. Gaonkar, J. Zhu, R. Kottokkaran, B. Bhageri, M. Noack and V. Dalal, “Thermally Stable, Efficient, Vapor Deposited Inorganic Perovskite Solar Cells” *ACS Applied Energy Materials* 3 (4), 3497-3503, 2020

[7] R. Kottokkaran, H. Gaonkar, B. Bagheri, and Vikram L. Dalal, “Efficient p-i-n inorganic $CsPbI_3$ perovskite solar cell deposited using layer-by-layer vacuum deposition” *Journal of Vacuum Science & Technology A* 36, 041201, 2018