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

Junhao Zhu, Ranjith Kottokkaran, Saba Sharikadze, Laila-Parvin Poly and Vikram Dalal

Iowa State University, Ames, Iowa, 50011, USA

Abstract- ***We report on the properties and stability of inorganic perovskite $CsPbBr_3$ fabricated using vapor deposition. We have obtained the highest voltage ever recorded, exceeding 1.6V, in this material. The material was deposited using vapor deposition process, followed by post-deposition anneal at 450 C. Both layer by layer, and sequential anneal processes were sued for growing the material. After growth and anneals, the material was tested for thermal stability at temperatures of 300 C, and the x-ray data showed that there was no degradation of the material even at this high temperature. n-i-p superstrate devices were fabricated on FTO substrates coated with either TiO_2 or n-CdS. The p layer was P3HT or PTAA. The devices showed an open-circuit voltage of 1.62V, the highest ever reported in this material. The devices were exposed to humid room air for 25 days, and showed no degradation at all in its performance. Detailed material measurements such as subgap quantum efficiency and deep defects were measured. The Urbach energy for valence band tails is found to be 22 meV and mid-gap defect density in the range of few $10^{15}/cm^3$.***

Keywords—Perovskite solar cells, thermal and environmental stability, fundamental properties

I. Introduction

Large bandgap perovskite solar cells are of significant importance for making tandem junction cells with Si acting as the bottom cell [1-3]. A particular concern is the thermal and environmental stability of such high bandgap perovskite solar cells. It is well known that hybrid inorganic-organic perovskite solar cells decompose at relatively low temperatures, ~100°C [4-5]. This fact makes such cells marginally useful in hot, desert environments where the cell temperatures often reach 90-100 °C [6]. To overcome this problem, several authors have used all-inorganic perovskite materials comprising CsPb(I,Br) alloys [7-9]. While such inorganic perovskite materials are thermally stable, they are not stable when exposed to moisture [10], with the cell degrading even during measurements in air. The problem is particularly acute when cells are made using a high I:Br ratio. To overcome this problem, we have investigated materials and cells without any I, an all inorganic cell with Br as the halide. In this paper we describe the deposition technique, the material properties, the device fabrication and properties, and the thermal and environmental stability of devices made in this inorganic Brominated perovskite material.

II. Material and Device Preparation

The material was grown using a vapor deposition process using a well-controlled evaporation from multiple boats fitted inside Luxel Radak furnaces [11]. One boat held the $PbBr_2$ powder and the other boat CsBr powder. Two evaporation methods were used, the first being multiple cycles of layer-by-layer growth, where the individual layers were thin (few nm each) with repeated cycles giving the desired thickness [12]. The second method was sequential deposition where a thick layer of one material was grown followed by the growth of the other material [13]. For sequential growth, we discovered that the best devices resulted when we used a layer of CsBr, followed by a layer of $PbBr_2$, and then followed again with a layer of CsBr. For sequential growth, the best devices were obtained by using thicknesses of 136 nm for each of the CsBr layers, and 367 nm for the $PbBr_2$ layer, resulting in a total thickness of the perovskite after annealing of 650 nm. The substrate was held at 200 °C during deposition. After deposition, the layers were annealed on a hot plate in air in two stages, a 400 °C anneal for 20 minutes followed by an anneal at 350 °C for 40 minutes.

The n-i-p devices were prepared by depositing a spin-coated layer of P3HT or PTAA on top, followed by silver or gold evaporation. Fig. 1 shows the device geometry. It is a superstrate device with light shining from the bottom.

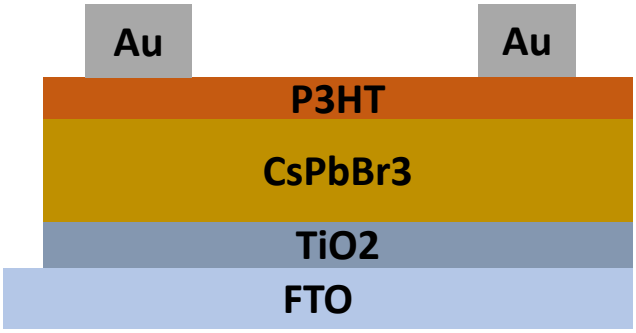

Fig.1. Schematic diagram of the device.

III. Thermal Stability

The thermal stability of the material was measured using x-ray diffraction analysis. It is well known that an unstable perovskite decomposes into a Pb phase (eg PbI_2 or $PbBr_2$) upon heating and this peak can be easily picked up in the x-ray spectrum. In

Fig.2, we show the x-ray data for our perovskite material before heating at 300 °C for 24 hours, and after such a heating. The heating was done inside a glove box. It is clear from this figure that there is no decomposition of the all inorganic material after heating even at 300 °C in air. This is a remarkable result which makes such materials potentially useful for large bandgap, stable, solar cell partner with Si in a tandem cell arrangement.

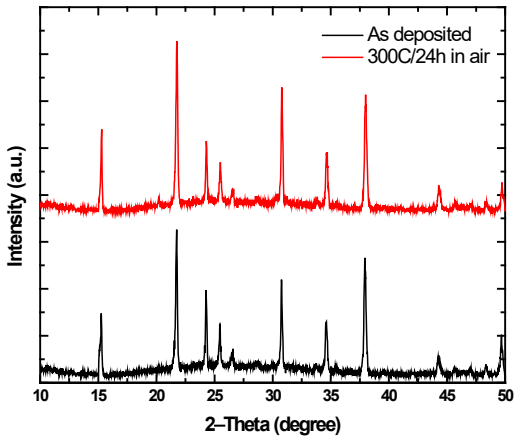

Fig.2. XRD spectra of CsPbBr3 perovskite before and after annealing 300 °C/24 hours.

IV. DEVICE 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. 3 shows the I-V curve for one of our cells coated with P3HT as the p-layer. Note the remarkably high voltage, 1.62 V, the highest ever achieved in this material. A remarkable observation was that the performance of the cell improved if we left the perovskite material exposed to air for 96 hours before depositing P3HT and gold. This is a reproducible observation, confirmed by using identical materials, one exposed to outside and the other kept inside the glove box, and it clearly indicates that moisture maybe playing a role in improving the material. We are trying to understand and optimize this phenomenon by controlling the exposure to various moisture levels post-deposition at different temperatures.

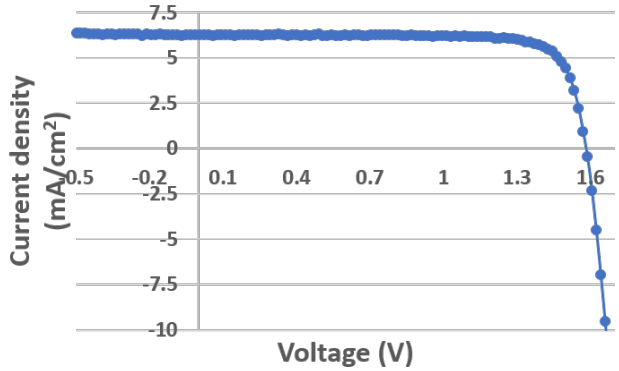

Fig.3. Light IV curve of the fabricated device with Voc 1.60 V, Jsc=6.30 mA/cm^2 and PCE of 8.1%.

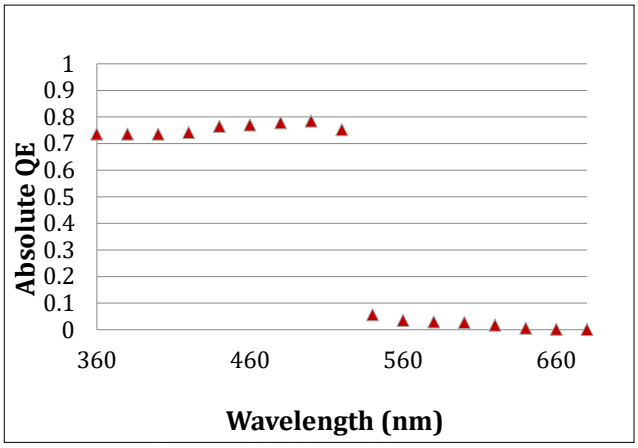

Fig.4. Quantum efficiency of the fabricated device.

The corresponding quantum efficiency is shown in Fig.4, and it shows a relatively uniform QE from 360 nm to 520 nm, with a fall-off at around 540 nm. By plotting (QE x photon Energy)^2 vs. photon energy, one can estimate the bandgap which is ~2.28 eV (See Fig. 5). We recognize that this is too large a bandgap, and we need to bring it down to 1.8-1.9 eV, which can be done in the future by using mixtures of Pb and Sn and mixtures of Cs and Rb., while keeping Bromine as the halide.

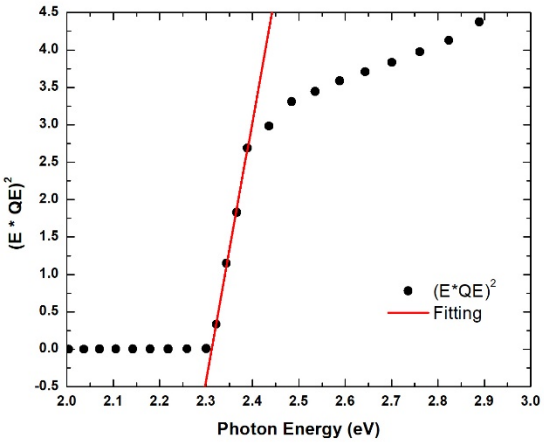

Fig.5. (QE x photon Energy)^2 vs. photon energy plot.

V. STABILITYOF THE DEVICE AGAINST MOISTURE

The device was exposed to air for 1000 hours, and measured periodically for its properties. In Fig. 6 we show the I-V curves for initial and 25 day exposure. From the figure, it is clear that there is virtually no degradation of the device when exposed to room air.

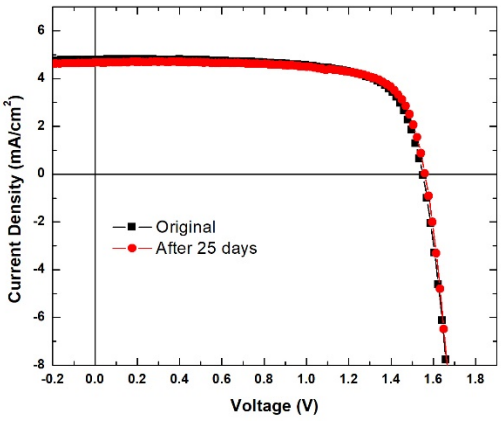

Fig.6. Light IV curve of the fabricated device (initial and after air exposure for 25 days).

VI. Meausremnts of Fundamental Material Properties

We measured subgap quantum efficiency vs. photon energy to determine the value of Urbach energy of the valence band tails. Urbach energy is an important parameter because it impact open circuit voltage, a high value indicating that tail state defects are extending far into the gap, and will limit the movement of quasi-Fermi levels upon illumination, and therefore, limit the open-circuit voltage. The data is shown in Fig. 7, and it shows a value of 22 meV, in the usual range observed in all device-quality perovskite materials.

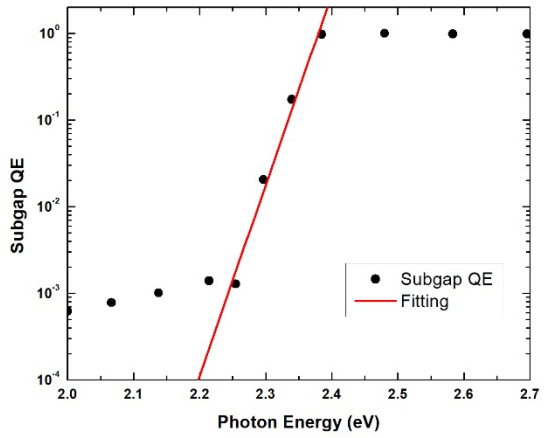

Fig.7. Subgap QE vs Photon Energy plot.

We also measured C-V curves to determine the shallow defect and doping densities. The data for $1/C^2$ vs. V curve is shown in Fig. 8. It shows a shallow state density of 2.4 x 10^{15}/cm^3.

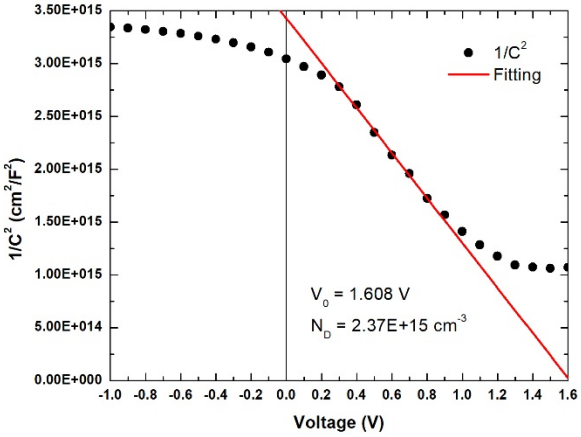

Fig.8. $1/C^2$ vs Voltage plot of the fabricated device.

VII. Conclusions

In summary, we report on an inorganic perovskite material and a device which are both very stable against anneals at high temperatures and against high moisture environments. We have obtained the highest open-circuit voltage ever achieved in this material system. Fundamental properties such as shallow defects and Urbach energy of valence band tail states have been measured and are shown to be comparable to other perovskite materials. The material was deposited using vacuum deposition techniques.

VIII. Acknowledgments

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

IX. References

[1] Bo Chen et al., “Grain Engineering for Perovskite/Silicon Monolithic Tandem Solar Cells with Efficiency of 25.4%” *Joule* 3, pp. 177–190, January 2019.

[2] Hou et al., “Efficient tandem solar cells with solution-processed perovskite on textured crystalline silicon” *Science* 367, pp. 1135–1140, March 2020.

[3] P. Tockhorn et al., Three-Terminal Perovskite/Silicon Tandem Solar Cells with Top and Interdigitated Rear Contacts” *ACS Appl. Energy Mater.* 3, pp. 1381−1392, January 2020.

[4] R. Kottokkaran et al., "Highly reproducible vapor deposition technique, device physics and structural instability of perovskite solar cells," *2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC)*, 2015, pp. 1-4

[5] B. Conings et al., “Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite” *Adv. Energy Mater.*, 5, pp 1500477, June 2015.

[6] H. Gaonkar et al., “Thermally Stable, Efficient, Vapor Deposited Inorganic Perovskite Solar Cells”, *ACS Appl. Energy Mater.* 3, 4, pp. 3497–3503, March 2020.

[7] T. Wang et al., “Vacuum-Controlled Growth of CsPbI2Br for Highly Efficient and Stable All-Inorganic Perovskite Solar Cells”, *ACS Appl. Mater. Interfaces*, 12, 19, pp. 21539–21547, April 2020

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

[9] Z. Q. Lin et al., “Water assisted formation of highly oriented CsPbI2Br perovskite films with the solar cell efficiency exceeding 16%” : *J. Mater. Chem. A*, 8, pp. 17670-17674, 2020.

[10] Q. Zeng et al., “Inorganic CsPbI2Br Perovskite Solar Cells: The Progress and Perspective”, *Solar RRL*, 3, 1, pp. 18200239, January 2019

[11] R. Kottokkaran, H. A. Gaonkar, H. A. Abbas, M. Noack, V. Dalal, “Performance and stability of co-evaporated vapor deposited perovskite solar cells” *J Mater Sci: Mater Electron* 30, pp 5487–5494, February 2019.

[12] R Kottokkaran, H A. Gaonkar, B. Bagheri, and V. L. Dalal, “Efficient p-i-n inorganic CsPbI3 perovskite solar cell deposited using layer-by-layer vacuum deposition” *Journal of Vacuum Science & Technology A* 36, pp. 041201, May 2018.

[13] H. A Abbas et. al., “High efficiency sequentially vapor grown n-i-p CH3NH3PbI3 perovskite solar cells with undoped P3HT as p-type heterojunction layer*”, APL Materials* 3, pp. 016105 January 2015