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Fabrication of planar heterojunction CsPbBr₂I perovskite solar cell using ZnO as electron transport layer & improved solar energy conversion efficiency

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Muhammad Aamir,^{a, b} Tham Adhikari,^a Muhammad Sher,^b Neerish Revaprasadu,^c Waqas Khalid,^d Javeed Akhtar^{*d} and Jean-Michel Nunzi^{*a, e}

Inorganic lead halide perovskite solar cells with mixed halides have achieved reasonable power conversion efficiency with the advantage of an enhanced stability. In this work, we report the fabrication of an all inorganic cesium lead bromoiodide based planar perovskite solar cell with ZnO electron transport layer. The method described herein, includes the use of one step spin coating solution processing using a solvent mixture (DMF + DMSO) to avoid solubility issues of the CsPbBr₂I perovskite in DMF. The substrate temperature during spin coating was found a critical parameter to generate the required crystalline morphology of the perovskite thin films. Post-annealing of the as-deposited perovskite film at 275 °C led to the formation of the cubic phase of CsPbBr₂I with optical band gap of 2.06 eV. Interestingly, the cubic shaped CsPbBr₂I morphology was obtained via single-step spin-coating processing that otherwise required a two-step solution deposition of the hybrid perovskite. The best performing devices reached 4.8% power conversion efficiency with minimal hysteresis and enhanced thermal and photo-stability. Owing to enhanced thermal and photo-stability, inorganic perovskites appear as a viable alternative to the hybrid organic-inorganic perovskites for solar cell applications.

Introduction

Hybrid lead halide perovskite materials have gained tremendous attention in recent years due to rapid upsurge in power conversion efficiency (PCE) from 3.8% to over 20%.¹⁻⁵ Although, high PCE has been achieved, the use of organic cations like methylammonium has rendered these rather thermally unstable under ambient condition, thus limiting their practical applications. On the other hand, inorganic lead halide perovskites which have improved thermal stability^{6, 7} have attracted progressive consideration for their photovoltaic^{8, 9} fluorescent sensing,^{10, 11} photocatalysis¹² and light emitting applications.¹³ The inorganic perovskite, CsPbI₃ have a cubic phase with more desirable band gap of 1.73 eV. Unfortunately, it tends to convert to the yellow insulating non-

perovskite phase at temperatures lower than the cubic orthorhombic phase transition of 315 °C.^{9, 14, 15} However, partial alloying the inorganic perovskite with Br lowers the phase transition temperature,¹⁶ meanwhile increasing the band gap of the resultant perovskite. Recently, CsPbBrI₂ perovskite with a 1.82 eV-band gap has been reported to achieved the highest PCE of 11.5%.¹⁷ Further increase in bromide to iodide ratio leads to the formation of a CsPbBr₂I perovskite which has a low phase transition temperature of 100 °C¹⁸ and a 2.06 eV-band gap,¹⁹ making it a potential candidate to be used as top cell in tandem solar cells.²⁰ Ma et al.²¹ have reported, the first CsPbBr₂I perovskite based planar transport material free solar cell with PCE of 4.7% using dual-source thermal evaporation technique. Lau et al.²² have further improved the PCE to 6.3% by fabricating a mesoporous CsPbBr₂I perovskite solar device via spray assisted solution processed deposition. Li et al. have adopted gas assisted solution process method to fabricate a planar CsPbBr₂I perovskite solar cell with stabilized PCE of 6.07%. However, in these reports, a TiO₂ electron transport layer (ETL) was used, which requires sintering. Therefore, there is potential to use other electron transport materials like ZnO.

Practically, perovskite solar devices have been fabricated by sandwiching perovskite layer between electron transport layer (ETL) and hole transport layer (HTL). These layers (ETL & HTL) facilitate the transportation of carriers generated in the perovskite layer and also prevent carrier recombination at the interfaces^{23, 24}. Organic or n-type inorganic metal oxides ETL were used either as compact film

a. Department of Chemistry, Queen's University, Kingston, ON K7L 3N6, Canada

E-mail: nunzim@queensu.ca

b. Department of Chemistry, Allama Iqbal Open University, Sector H-8, Islamabad-44000, Pakistan.

c. Department of Chemistry, University of Zululand, Private Bag X1001, KwaDlangezwa, 3886, South Africa

d. Department of chemistry, Polymers & Materials synthesis (PMS) Laboratory, Mirpur university of science & Technology (MUST), Allama Iqbal Road, Mirpur Azad Jammu & Kashmir, 10250, Pakistan
E-mail: javeedkt@gmail.com

e. Department of Physics, Engineering Physics and Astronomy, Queen's University Kingston, ON K7L 3N6, Canada

† Footnotes relating to the title and/or authors should appear here.

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or compact/mesoporous layers. However, planar device architectures are of interest due to their ease of processing.²⁵ During device fabrication, Some metal oxide ETL require high sintering temperature like the widely used TiO_2 which requires about 500 °C,^{2, 4, 26} making it incompatible with plastic substrates. On the other hand, ZnO which has the same energy levels as TiO_2 , has the advantage of low temperature fabrication, tunable morphology and high electron mobility.²⁷⁻²⁹

In this work, we report the fabrication of CsPbBr_2I inorganic perovskite by a single step spin-coating onto a low temperature processed ZnO layer on ITO glass substrate. A series of experiments investigating the effect of substrate temperature (Ts) on the perovskite film and photovoltaic efficiency was performed. Aiming at a simple architecture and low temperature solution processed devices, we fabricated the planar ITO/ZnO/ CsPbBr_2I /Spiro-OMeTAD/Ag solar cell, first of its kind with best efficiency of 4.8%, a short-circuit current (Jsc) of 8.7 mA/cm², open circuit voltage (Voc) of 1.04 V and fill factor (FF) of 52.5% at substrate temperature (Ts) of 150 °C.

Experimental

Materials

Cesium iodide, lead bromide, zinc acetate, 2,2',7,7'-Tetrakis-(*N*, *N*-di-p-methoxy phenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD), Lithium bis(trifluoromethylsulphonyl) imide (Li-TFSI) and 4-tert-butylpyridine (TBP), chlorobenzene, Dimethyl sulfoxide (DMSO) and *N*, *N*-dimethylformamide (DMF) were purchased from Sigma Aldrich. All chemicals and reagents were used without further purification.

Characterization

Indium tin oxide (ITO) coated glass used as substrate was purchased from Luminescence Technology Corporation. ITO film thickness was 135 ± 15 nm with 15 W/sq sheet resistance. UV-visible absorption spectra were acquired using a Hewlett-Packard 8453 spectrometer or an Olid HP8452 Diode Array Spectrometer. Current density-voltage (J-V) was characterized using a Keithley 4200-SCS in the dark and under illumination. All the photovoltaic parameters of the cells were measured under ambient conditions using Xenon light with an intensity of 100 mW/cm² calibrated with an AM 1.5 solar simulator. XRD was obtained using an Xpert Pro Philips powder X-ray diffractometer. Field emission scanning electron microscopy (FEI Quanta 650 FEG) supplemented with EDAX (Bruker XFlash detector 1.9) was used for morphology, size and composition of the nanocrystals. Surface morphology was characterized using an

Ambios multimode Atomic Force Microscope (AFM) in the tapping mode at 300 KHz frequency. Photoluminescence (PL) was acquired using Flau Time 300 (FT-300) steady-state and life-time spectrometer, PicoQuant GmbH, Germany, with pulsed LED laser excitation source. XPS spectra were measured on a Kratos Nova AXIS spectrometer equipped with a 150 W Al-K α source at 1486.69 eV. Samples were mounted onto a coated aluminum plate using double-sided adhesive Cu tape and kept under 10⁻⁹ Torr vacuum overnight inside the preparation chamber before being transferred into the 10⁻¹⁰ Torr analysis chamber of the spectrometer. Binding energies are referred to the C 1s peak at 285 eV. Survey spectra were recorded from -5 to 1200 eV at a pass energy of 160 eV using 1 eV-energy step and 100 ms-dwell time. High resolution spectra for Cs 3d, O 1s, C 1s, Pb 4f and Br 3d were recorded in the appropriate regions at a pass energy of 20 eV using 0.1 eV-energy step and 60 s-sweep time of. XPS maps for the elements Cs, I, Pb and Br were acquired in the same 300 × 700 μm^2 -area as above using the same radiation source.

Device fabrication

ITO-glass substrates were cleaned by sonicating successively in a solution of detergent, NaOH, ethanol, acetone and isopropanol for 15 min. After drying on a hot plate, the substrate was treated with oxygen plasma for 20 min. The ZnO sol-gel was prepared as reported previously.³⁰ The ZnO compact layer was fabricated by spin coating the as-prepared sol-gel at 2000 rpm for 30 sec and annealing for 30 min, at three different temperatures. The perovskite film was deposited by single step spin coating. The solution of 367 mg of PbBr_2 and 259mg of CsI in DMF: DMSO (1:1.2) was spin coated at 2000 rpm for 30 sec, followed by annealing at 275 °C for 30 minutes. The perovskite layer thickness was measured with a profilometer and found to be around 150 nm. After perovskite formation and cooling down to room temperature, a solution of 72.3 mg of Spiro-OMeTAD, 9.1 mg of Li-TFSI and 28.8 μL of TBP was spin coated at 4000 rpm for 30 sec, as reported previously.³¹ Finally, a set of four 100 nm-Ag electrodes was deposited behind a shadow mask using thermal evaporation under 1 × 10⁻⁶ mBar-vacuum. Device structure is shown in Figure 4 (a). Active area of each individual element is 6 mm².

Results and discussion

The ZnO electron transport layer was deposited on cleaned substrates using sol-gel method via spin coating followed by annealing at three different temperature of 100 °C, 150 °C and 200 °C. It was found that the increase in temperature increases the roughness of the ZnO film.

Figure S1 (a-d) (supporting information) shows the AFM images of ZnO thin films. The mean roughness of ZnO annealed at 100 °C and 150 °C was 12.6 nm and 13.2 nm, respectively. Roughness increases to 14.0 nm at 200 °C which reflects the well-known

fact that annealing temperature increases crystallinity. SEM images of as-deposited ZnO layer shows a flack like morphology at all annealing temperatures as presented in Figure S2 (supporting information). Similar topography was been reported in the literature.³²

To obtain the perovskite layer, we adopted the single step solution processing method. CsPbBr₂I is insoluble in pure DMF. To bypass the solubility issue, we used a solution of CsPbBr₂I in a solvent mixture of (DMF: DMSO). In order to get better coverage and crystallinity, the ITO/ZnO substrate temperatures were set at room temperature (25 °C), 150 °C and 200 °C during the fabrication of the CsPbBr₂I film. Samples were then post-annealed at 275 °C for 30 min. Elevated temperature post-annealing yields the cubic phase CsPbBr₂I perovskite. Figure S3 (supporting information) shows the p-XRD pattern of as-deposited CsPbBr₂I perovskite. The diffraction peaks at 17.38°, 24.60° and 35.19° correspond to the (100), (111)

<600 nm cubic-shaped crystals with well separate boundaries (Figure 1(e-f)). According to the literature, the formation of cubic shaped morphologies is associated with a two-step deposition process.^{35, 36} However, in our work, similar cubic shaped crystals appeared under a single-step spin coating.

Energy dispersive X-ray spectroscopy (EDX) was performed to determine the stoichiometry of as-deposited samples. The composition of as-deposited CsPbBr₂I perovskite films at all substrate temperatures shows the atomic ratio of 1:1:2:1 which matches the expected CsPbBr₂I stoichiometry. In addition, the distribution of Cs, Pb, Br and I in the perovskite film was determined by EDX elemental mapping. Figure S4 (supporting information) reveals the uniform distribution of Cs, Pb, Br and I in the probed area of the perovskite film. The crystallinity of CsPbBr₂I perovskite film was also determined by AFM. Figure 2 shows the AFM images of as-deposited CsPbBr₂I perovskite films at different

Figure 2. AFM wave mode and phase mode images of as-deposited CsPbBr₂I at different substrate temperatures (Ts).

and (211) planes of the cubic phase perovskite.^{33, 34}

Morphology of the perovskite film was studied by SEM as shown in Figure 1 (a-f). It was found that increasing temperature increases the crystallinity and promotes a well-defined cubic morphology of the film. The CsPbBr₂I perovskite deposited at substrate temperature (Ts) 25 °C appears rather flat with pinholes (Figure 1 (a-b)). However, larger (<300 nm) cubic shaped fused crystals appear at substrate temperature (Ts) 150 °C as shown in Figure 1 (c-d). Further increase in substrate temperature (Ts) (200 °C) produces

substrate temperatures. The film deposited at Ts = 25 °C shows small crystallinity and the mean roughness of the CsPbBr₂I film is 130.8 nm. However, crystallinity increases at Ts= 150 °C and mean roughness decreases to 90.9 nm. The decrease in roughness reveals a smoother film and may lead to the formation of a better composite with the ZnO layer at elevated temperature. Whereas, the mean roughness increases to 202.3 nm at 200 °C substrate temperature (Ts) which may be due to well-formed cubic crystals as shown in Figure 1.

X-ray photoelectron spectroscopy (XPS) was employed to analyse the chemical composition and valence states of the surface, as shown in Figure S5 (a-d) (supporting information). The Cs $3d_{3/2}$ and Cs $3d_{5/2}$ binding energy curves were observed at 738.4 eV and 724.5 eV. The peaks of Pb $4f_{5/2}$ and $4f_{7/2}$ were found at 138.3 eV and 143.1 eV respectively. However, relatively weak intensity signals of I $3d_{3/2}$ and I $3d_{5/2}$ were positioned at 630.6 and 619 eV. Similarly, the weak intensity peaks of Br $3d_{3/2}$ and Br $3d_{5/2}$ are positioned at 69.3 and 68.2 eV, respectively. This tells that the elements Cs, Pb, Br and I belongs to 1+, 2+, 1- and 1- formal valence states, respectively.³⁷ The elemental distribution of as-deposited CsPbBr₂I perovskite thin film at substrate temperature 150 °C was also determined by XPS elemental mapping which shows the uniform distribution of Cs, Pb, Br and I in the interrogated area of the inorganic perovskite thin film, as shown in Figure S6 (a-d) (supporting information). Figure 3 shows the UV-Vis spectra of CsPbBr₂I perovskite films. The as-deposited perovskite material shows broad absorption peak with an onset around 600 nm. The band gap of perovskite material was calculated by Tauc-plot as shown in the inset of Figure 3. The estimated band gap was found at 2.06 eV, which matches to the band gap reported in literature.^{21, 22} Figure S7 (supporting information) shows the PL life-time of CsPbBr₂I perovskite films deposited at three different substrate temperatures (T_s = 25 °C, 150 °C and 200 °C). Photoluminescence radiative recombination lifetimes are generally quality indicators for perovskite thin-film application to solar cells and other optoelectronic devices.³⁸⁻⁴⁰ Perovskite thin film growth conditions and treatments after the deposition^{40, 41} can be pivotal in attaining the desired film morphology, lifetime of carriers and device performance.^{38, 42} The time resolved photoluminescence (TRPL) of CsPbBr₂I was carried out by exciting the specimen at 600 nm. The TRPL indicates that longest recombination life time of 6.1 ns is achieved for the perovskite film formed on T_s = 150°C treated ZnO/ITO substrate. The spectra indicate single to stretched exponential decay functions.

AFM images in Figure. 2 indicate increased crystallinity for T_s =150°C, with minimal film roughness of 90.9 nm for this set of depositions. As the substrate temperature is increased to 200°C, the roughness of the film increases to 202.3 nm. This large roughness might increase the density of quenching sites, thus favouring non-radiative recombination of the charge carriers.

Similar sort of behaviour was described for CH₃NH₃PbI₃ perovskite thin films by Yu Li et al.⁴³ where fluorescent decay was associated to film thickness and disappears for thicker films. As SEM (Figure 1.e-f) suggests well-formed cubic structures might be responsible for the increased roughness and thickness of the films.

Figure 3. UV-Vis absorption spectra of as-deposited CsPbBr₂I perovskite.

Figure 4 (a) shows the architecture of planar devices used to explore the photovoltaic properties of inorganic CsPbBr₂I perovskite-based devices in dark and light. The current density voltage (J-V) characteristic in dark and light of planar ZnO/CsPbBr₂I/spiro-OMeTAD/Ag device is shown in Figure 4 (b-c). The best PCE was 4.8% with J_{sc} = 8.7 mA.cm⁻², V_{oc} = 1.04 V and FF = 52.5%. Ma et al.²¹ reported hole transport layer free planar c-TiO₂ electron transport layer based CsPbBr₂I perovskite solar cell with forward scan efficiency of 3.7% and reverse scan of 4.7%. Our present work clearly shows improved efficiency over their devices, with comparable J_{sc} and FF. Similarly, J_{sc} obtained in our work is also larger than with the Glass-FTO/c-TiO₂/m-TiO₂/CsPbBr₂I/ Spiro-OMeTAD/Au devices fabricated by Lau et al.²² In addition, both Ma and Lau et al.^{21, 22} devices were fabricated at high temperature owing to the use of a TiO₂ electron transport layer, unlike ours.

Figure 4. (a) Device architecture with current density voltage (J-V) curve of (b) best device, (c) comparative J-V curves of three devices fabricated at different substrate temperature and (d) hysteresis of devices fabricated at Ts = 25 and 150 °C.

The variation in substrate temperature (Ts) preparation affects device performance. It was found that devices fabricated at Ts = 25 °C (room temperature) show lower current density ($J_{sc} = 5.64 \text{ mA/cm}^2$), open circuit voltage ($V_{oc} = 0.92 \text{ V}$), fill factor ($FF = 49.9\%$) and PCE (2.59%) than devices fabricated at Ts = 150 °C ($J_{sc} = 8.78 \text{ mA/cm}^2$, $V_{oc} = 1.04 \text{ V}$, $FF = 52.5\%$, $PCE = 4.8\%$). The decrease in PCE and other parameters can be attributed to poor crystallinity of CsPbBr₂I under room temperature processing; Whereas the obtained cubic crystals at Ts = 150 °C have fused boundaries which may possibly lead to increase charge mobility and reduced charge recombination. Seo et al.³⁵ also reported that the cubic shaped CH₃NH₃PbI₃ perovskites support larger carrier densities and fewer defect states than non-cubic perovskites.

We also notice that devices fabricated at Ts = 150 °C show lower series resistance ($R_s = 574 \Omega$) and larger shunt resistance ($R_{sh} = 24174 \Omega$) than devices fabricated at Ts = 25 °C ($R_s = 715 \Omega$, $R_{sh} = 23743 \Omega$) which suggests improved film-forming quality during device processing at Ts = 150 °C.

The devices processed at Ts = 200 °C show a PCE of 4.16%, J_{sc} of 8.6 mA/cm^2 , V_{oc} of 0.96 V and FF of 50%. Again, PCE and other parameters in these devices are improved with respect to devices processed at Ts = 25 °C owing to better interface and crystalline quality, meanwhile the optimum is achieved at Ts = 150 °C. This decrease in efficiency at higher Ts may be attributed to the formation of larger crystals with well separated boundaries (Fig.

1e), which may reduce mobility and increase charge recombination, although these devices show lower series resistance and increased shunt resistance compared to both lower Ts processed devices. Figure 4 (d) shows the hysteresis curve of the ZnO/CsPbBr₂I/spiro-OMeTAD/Ag devices processed at Ts = 25 °C and Ts = 150 °C. It is observed that as-fabricated inorganic perovskite solar cells have limited hysteresis. Figure S8 (supporting information) shows the incident photon-to-current efficiency (IPCE) of best devices processed at Ts = 150 °C, which matches the absorption spectrum in Fig. 3.

Photostability of the devices was assessed by measuring photocurrent density across a 2000 Ω external load under repeated illumination - darkness cycles. The duration of each cycle was 250

Figure 5. Cyclic photocurrent and dark current with 250 sec. repetition.

seconds. Figure 5 show that no decrease in current density was observed upon light - dark cycles which suggest that inorganic CsPbBr₂I perovskite-based devices are photo-stable. Current density was also monitored under continuous illumination for 3600 seconds and a 2.5% drop in current density was observed, as shown in Figure S9 (supporting information), which also suggests that ZnO based inorganic perovskite solar devices are photo-stable.

Thermal stability of as-deposited CsPbBr₂I on ZnO thin films was assessed at 100 °C for 8 hours with oxygen and moisture levels of 6 ppm and 45 ppm in a LC-glove box. Figure S10 (supporting information) shows no detectable phase change or appearance of impurity peak or change in colour of CsPbBr₂I suggesting that limited thermal degradation of CsPbBr₂I perovskite takes place. On the other hand, hybrid perovskites deposited on a ZnO electron transport layer were found unstable. They undergo degradation upon heating due to the very nature of ZnO which absorbs protons from methyl ammonium and convert it into methylamine.⁴⁴ We attribute the improved stability of our CsPbBr₂I perovskite on ZnO substrate to its non-protonic inorganic nature.

Conclusions

In summary, we have fabricated inorganic CsPbBr₂I perovskite solar cell via single step spin coating process at three different substrate temperatures. A mixture of DMF and DMSO solvents was used to dissolve the CsPbBr₂I perovskite material for spin coating. Single step spin coating process at different substrate temperatures followed by annealing at 275 °C allow successful formation of the CsPbBr₂I cubic phase perovskite with 2.06 eV optical band gap. Devices processed at 150 °C-substrate temperature shows the best efficiency of 4.8%. Substrate temperature happens to be the critical parameter to achieve the best crystalline morphology of the film meanwhile it does not affect the stoichiometry of the perovskite material. The as processed perovskite devices show limited hysteresis and improved stability, making the CsPbBr₂I perovskite material a promising alternative to the hybrid perovskite solar cells.

Conflicts of interest

There are no conflicts to declare.

Supporting Information

Supporting information contains AFM, SEM, p-XRD, XPS, EDX mapping, XPS Q-mapping, photoluminescence life-time, photo- and thermal stability data.

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The table of contents entry.

All-Inorganic cesium lead bromoiodide based planar perovskite solar cells with ZnO electron transport layer are deposited from one step spin coating. The required cubic crystalline morphology is obtained using appropriate substrate temperature during the process and post-annealing treatment. Best devices reach 4.8% power conversion efficiency with minimal hysteresis and enhanced thermal and photo-stability.

Keywords Perovskite Solar Cell, Inorganic Perovskite, Single step deposition, Hysteresis, Stability.

Muhammad Aamir, Tham Adhikari, Muhammad Sher, Neerish Revaprasadu, Waqas Khalid, Javeed Akhtar^{*} and Jean-Michel Nunzi^{*}

Title

Fabrication of planar heterojunction CsPbBr₂I perovskite solar cell using ZnO as electron transport layer & improved solar energy conversion efficiency

ToC figure

Supplementary Information

Fabrication of planar heterojunction CsPbBr₂I perovskite solar cell using ZnO as electron transport layer & improved solar energy conversion efficiency

Muhammad Aamir, Tham Adhikari, Muhammad Sher, Neerish Revaprasadu, Waqas Khalid, Javeed Akhtar* and Jean-Michel Nunzi*

Figure S1 (a-d). AFM images of as-deposited ZnO layer on ITO glasses annealed at 100 °C, 150 °C and 200 °C for 30 minutes.

Figure S2. SEM image of ZnO deposited on ITO glass and annealed at 100 °C, 150 °C and 200 °C.

Figure S3. P-XRD spectra of as-deposited CsPbBr₂I perovskite at substrate temperature (Ts) at 25 °C, 150 °C and 200 °C.

Figure S4. EDX mapping of CsPbBr₂I showing the well distribution of (a) Cs, (b) Pb, (c) Br and (d) I in the interrogated area of film.

Figure S5 (a-d). High resolution XPS analyses of CsPbBr₂I corresponding to Cs, Pb, Br and I.

Figure S6. XPS Q-mapping of CsPbBr₂I perovskite thin film deposited at substrate temperature of 150 °C.

Figure S7. Life time photoluminescence of CsPbBr₂I perovskite layers deposited at Ts = 25 °C, 150 °C and 200 °C.

Figure S8. IPCE (QE) of the best device deposited at Ts = 150 °C.

Figure S9. J-V curve of CsPbBr₂I device before and after exposure to continuous illumination of 3600 second to assess photostability.

Figure S10. P-XRD spectra and pictures of thermally treated films of ZnO/CsPbBr₂I at 100 °C, to assess the thermal stability of CsPbBr₂I perovskite.