Increasing photon absorption and stability of PbS quantum dot solar cells using a ZnO interlayer

Lai-Hung Lai,¹ Mark J. Speirs,¹ Feng-Kuei Chang,² Laura Piveteau,^{3,4} Maksym V. Kovalenko,^{3,4} Jen-Sue Chen,² Jih-Jen Wu,⁵ and Maria A. Loi^{1,a)}

¹Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, Groningen 9747 AG, The Netherlands

²Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan

³Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, Zurich 8049, Switzerland

⁴EMPA-Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, Dübendorf 8600, Switzerland

⁵Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan

(Received 30 September 2015; accepted 20 October 2015; published online 2 November 2015)

We compared PbS quantum dot (QD) solar cells with different cathode interlayer materials, namely, LiF and ZnO nanoparticles, using the same device structure. Solar cells fabricated with the ZnO interlayer gave a power conversion efficiency of 4.8%, which is higher (above the experimental variation) than the 4.1% efficiency obtained with a LiF interlayer. We found that the ZnO interlayer alters the spatial distribution of the optical field, leading to an increase in external quantum efficiency in the visible range. Furthermore, devices with ZnO as interlayer showed more stable performance than the ones using LiF, with practically no power conversion efficiency degradation after 1 month inside a N₂ glovebox. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934946>]

The fast growth of the global population and the limited supply of fossil fuels have made the energy issue one of the most urgent problems of the twenty-first century. Solar to electrical conversion has attracted significant attention because of the abundant energy available from the sun. Recently, quantum dot-based solar cells have been the topic of intense investigation due to their unique optical properties, their tunable bandgap, their high extinction coefficient, and their stability.^{1,2} Room-temperature solution-processed ZnO/PbS quantum dot solar cells with the highest certified power conversion efficiency (PCE) of ~8.5% have been achieved.² In addition, the good air stability of the devices without performance degradation after 5 months indicates a promising future for this new class of solar cells. Furthermore, recently, the low trap density and the long minority carrier diffusion length (~230 nm) in PbS quantum dot (QD) solar cells were realized by passivating the trap states; the device fabricated with this approach shows the record PCE (not certified) of 9.2%.³

A 5.2% PCE in PbS QD solar cells has been demonstrated in the relatively simple Schottky structure where LiF is used as an interlayer between the PbS QDs and the aluminum electrode.⁴ Sargent *et al.* have reported that the LiF interlayer can increase the rectification as well as the device stability.⁵ However, PbS/LiF/Al devices showed 20% efficiency losses after 3 weeks of storage inside a N₂ glovebox, demonstrating that the thin LiF interlayer is not a good protection towards Al inter-diffusion.⁶ Other interlayer materials are therefore desirable to enhance device stability.

Conductive oxides such as ZnO have been demonstrated to enhance the electromagnetic strength in the active layer of organic solar cells when used as an interlayer, resulting in

larger photon capture.⁷ In addition, ZnO was reported to prevent Al diffusion and stabilize the active layer.⁸ However, while the possibility of using ZnO interlayers to enhance the efficiency of organic solar cells have been largely investigated, this approach has been relatively poorly explored in the case of PbS solar cells. Recently, Kim *et al.* reported enhanced performance in the QD solar cells with structure ITO/PEDOT:PSS/PbS/ZnO/Al,⁹ which showed ~70% higher PCE compared to the inverted solar cell ITO/ZnO/PbS/Au. However, the role in the working mechanism and device stability of the inter-layer used at the cathode interface has never been investigated.

In this work, we compared PbS QD solar cells with different cathode interlayer materials, namely, LiF and ZnO, using the same device structure. The solar cells fabricated with the ZnO interlayer gave a PCE of 4.8%, which is higher (above the experimental variation) than the 4.1% efficiency obtained with LiF as the interlayer. In this device structure, we found that ZnO has a beneficial effect on enhancing the light absorption in the visible spectral range. The optical simulation shows that adding ZnO as the interlayer has as much as 8% enhancement on the light absorption for an active layer thickness between 100 and 250 nm. The light intensity dependent measurements show that when the light intensity is above 2 mW/cm², bimolecular recombination is dominant in both devices with ZnO and LiF as interlayers. Finally, we find that ZnO has a significant role in the improvement of the device stability.

The solar cells with the ITO/PbS/Al structure have been reported to display poor performance due to the bad rectification properties of the Schottky diode.⁵ The addition of a thin LiF layer sandwiched between the PbS active layer and the Al electrode enhances the rectification and improves the performance of the solar cell. In this work, we replace the LiF

^{a)}E-mail: M.A.Loi@rug.nl. Tel.: +31 50 363 4119. Fax: +31 50363 8751.

by ZnO nanocrystals (NCs) as the cathode interlayer (inset of Figure 1).

The PbS QDs are synthesized according to the previously reported methods,¹⁰ and ZnO NCs are prepared as in Ref. 11. The PbS layers were deposited using a layer by layer (LBL) technique, repeating the spin coating sequence of the QDs and of short bi-functional ligands such as 1,4-benzenedithiol (BDT) to reach ~140 nm thickness.⁴ The functional thiol groups in BDT efficiently replace the original insulating oleate ligands, which are used to prevent the NCs from aggregation in the colloidal solution.⁴ The as-cast film is subsequently annealed at 140 °C for 10 min before ZnO and LiF deposition. To avoid variation or degradation of the PbS properties, we deposited the ZnO NCs by spin coating without further thermal treatment. On the other hand, the 1 nm LiF is deposited on the PbS by vacuum evaporation as a reference. Finally, a 100 nm thick Al electrode is deposited on our two structures by vacuum evaporation with a base pressure lower than 10^{-6} mbar.

The solar cells measurements are performed under 100 mW/cm² AM 1.5G conditions obtained with a solar simulator (SF150 class A, Scientech) and calibrated by a Si reference cell (SRC-1000-RTD-QZ, VLSI Standards, Inc.). J-V curves are measured with a SP-200 Bio-Logic potentiostat with a scan rate of 100 mV/s. The J-V curves of solar cells fabricated with LiF and ZnO interlayers are reported in Figure 1. The PCE for devices with optimized ZnO (20 nm) and LiF (1 nm) interlayers are 4.8% and 4.1%, respectively. The hysteresis of the forward and reverse scans is shown in Figure 1; here, the forward scan shows 10% lower photocurrent compared to the reverse scan, which is ascribed to trapping and de-trapping of the carriers during the scan. To understand the working mechanism of ZnO and LiF interlayers on the diode properties of PbS QD solar cells, the dark J-V curves are used to calculate parameters such as the series resistance (R_s) and shunt resistance (R_{sh}). The simulated device parameters are reported in Table I by performing a fitting with the following equation:

FIG. 1. J-V curves of the best PbS QD devices using LiF (black) and ZnO (red) as interlayers. The hysteresis of forward and reverse scans show 10% difference in the J_{sc} . The inset shows a schematic drawing of the device structure.

TABLE I. Summary of the device parameters. The standard deviation values of reverse scan from 5 devices are reported inside parentheses.

		V_{oc} (V)	J_{sc} (mA/cm ²)	FF	R_s (Ω cm ²)	R_{sh} (Ω cm ²)	PCE (%)
LiF	Forward	0.507	14.2	0.53	4.8	1.1×10^4	3.8
	Reverse	0.506	15.5	0.52			4.1
		(0.01)	(0.1)	(0.01)			(0.1)
ZnO	Forward	0.521	15.1	0.53	7.7	6.8×10^4	4.17
	Reverse	0.532	16.6	0.54			4.8
		(0.03)	(0.3)	(0.02)			(0.19)

$$I = I_0 \left\{ \exp \left(\frac{V + IR_s}{n(kT/q)} \right) - 1 \right\} + \frac{V + IR_s}{R_{sh}},$$

where I_0 , n , k , T , and q are the reverse saturation current, the diode ideality factor (1 for an ideal diode), the Boltzmann's constant, the absolute temperature, and the elementary charge. With 20 nm ZnO, the shunt resistance of the PbS diode increases by 6 times (from $1.1 \times 10^4 \Omega$ cm² to $6.8 \times 10^4 \Omega$ cm²), resulting in an increased rectification and Fill Factor (FF). Further increasing the ZnO thickness above 20 nm results in an increased series resistance that degrades both the photocurrent and the FF. The ideality factor provides an indication of the carrier recombination mechanism. For a device with $n=1$, bimolecular recombination is dominant; while in the case $n=2$, Schottky-Read-Hall (trap-assisted) recombination is prevalent. However, often it is difficult to attribute the changes of dark ideality factor to the effect of shunt/series resistance or to the carrier recombination mechanism.¹² To better understand the carrier recombination mechanism in the PbS QD solar cells, the light intensity dependent J-V curves were measured. At an open circuit, the voltage drop on the series resistance is zero, while the shunt (parallel) resistance is still high, which provides a better method to determine the ideality factor than the dark measurements introduced earlier. The V_{oc} of the solar cell under illumination is determined by

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{ph}}{J_0} \right) = \frac{nkT}{q} \ln(I^\gamma) + C,$$

where J_{ph} is the photocurrent, I is the illumination intensity, C is a constant containing all the intensity independent parameters, and γ is an empirical parameter that corrects for non-linear current-intensity behavior and is derived from the slope of J_{ph} against the illumination intensity.^{6,10} Here, γ equals 0.91 and 0.94 for LiF and ZnO devices, respectively. By plotting the semi-logarithmic plot of V_{oc} against the illumination intensity I , the ideality factor n can be extracted from the slope of the line defined by the data points. The ideality factor of solar cells with LiF and ZnO as interlayers are 1.1 and 0.97, respectively (Figure 2), showing that the bimolecular recombination is dominant in both device structures under light intensity between 2 mW/cm² and 100 mW/cm². For lower light intensity (below 2 mW/cm²), the ideality factors become 1.59 and 1.38 for LiF and ZnO devices, respectively, showing that trap-assisted recombination becomes prevalent when charge carrier density is low.^{12,13} Despite the small difference between the ideality factor of the

FIG. 2. Light intensity dependent V_{oc} for 140 nm thick PbS devices. Black, square symbols are measured on devices using the LiF interlayer, and red circles on devices with the ZnO interlayer. The dashed lines are the linear progression fit.

two interlayers at low light intensity, the recombination mechanism is substantially the same, demonstrating that recombination at the interlayer interface does not account for the difference in the power conversion efficiency.

The external quantum efficiency (EQE) spectra of the solar cells are shown in Figure 3(a). The EQE measurements are performed at a short circuit voltage using a 250 W quartz tungsten halogen lamp (6334NS, Newport with lamp housing 67009, Newport). The wavelength selection is obtained with a set of band pass filters (Thorlabs) with full width half max (FWHM) = 10 ± 2 nm. PD300 and PD300IR (Ophir Optics) are used as calibrated photodiodes. The solar cells with a ZnO interlayer show higher EQE in the range between 500 and 800 nm compared to that with LiF as an interlayer. To understand the effect of ZnO as optical spacer, we simulated the optical field ($|E|^2$) distribution in the PbS active layer with variable ZnO thickness using the transfer matrix

formalism developed by Pettersson *et al.*¹⁴ For this, the refractive index (n) and the extinction coefficient (k) for each material layer is required.¹⁵ For PbS and ZnO, these values were determined by ellipsometry (V-VASE, J. A. Woollam Co., Inc.) while literature values were used for the other materials.¹⁶ This model allows us to map the spatial distribution of the generated charge carriers throughout the device. The mapping of the photon absorption rate as a function of distance for devices with 140 nm PbS is shown in Figures 3(c) and 3(d). The peaks and valleys in the generation profile can be clearly seen due to the interference caused by the reflective Al electrode. Regardless of the PbS thickness variation, the optical field concentrates to either the ITO or the ZnO interface. Integrating the photons absorbed by the active layer and assuming an internal quantum efficiency (IQE) of unity, we can simulate the EQE spectra. With a 20 nm ZnO, the EQE is increased in the visible spectral range (550 nm–800 nm), which is in good agreement with the trend observed in the experimental EQE spectra (Figure 3(a)). While the experimental EQE in the wavelength < 600 nm is similar to the simulated values, it is only half in the longer wavelength range. This feature of the experimental data is ascribed to the imbalance of the electron/hole mobility. This causes the electrons/holes to be generated close to the ITO for wavelengths below 600 nm, resulting in a longer drift distance for electrons; as for wavelengths above 600 nm, the electrons/holes are generated closer to the metal, resulting in a longer required drift distance for holes. Due to the two orders of magnitude lower hole mobility compared to the electron mobility ($m_h \sim 5.9 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $m_e \sim 5.5 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),¹⁰ the carriers generated close to the metal electrode have a lower probability to be collected, giving rise to lower than unity IQE and thus a higher deviation from the simulated EQE. Figures 3(e) and 3(f) show the effect of varying the ZnO thickness on the total light

FIG. 3. (a) EQE spectra of devices fabricated with different interlayers. The integrated current values are indicated in the figure. (b) Simulated EQE spectra of 140 nm PbS with LiF and with the ZnO interlayer. (c) and (d) Maps of the photon absorption rate (G) distribution as a function of wavelength and distance within the 140 nm thick PbS active layers with LiF (c) and with (d) 20 nm ZnO interlayer. (e) The map of the variation in charge generation depending on the ZnO and PbS thicknesses. (f) The map of the shift of the average position of the photon absorption in the active layer depending on the ZnO and PbS thickness.

FIG. 4. Stability over time of the main device parameters (normalized with respect to the fresh sample) of solar cells with different interlayers stored in a N_2 glovebox.

absorption in the PbS active layer. Adding a layer of ZnO in between the active layer and the aluminum cathode enhances the total light absorption for PbS thicknesses between 100 and 250 nm by as much as 8%. Below 100 nm or above 250 nm, the effect can either be positive, non-existent, or negative, depending on the ZnO thickness. We calculate also the shift of the average absorption location $\Delta d_{avg} = d_{avg,ZnO} - d_{avg,ref}$ (Figure 3(f)), the ZnO spacer shifts the average location of the absorption towards the cathode, but this effect is quite small (3–9 nm) and not likely to play a big role in the solar cell performance.

Importantly, the stability over time (35 days test) of the main device parameters is reported in Figure 4. The devices with ZnO interlayer have a more stable V_{oc} , J_{sc} , and PCE than that with the LiF interlayer. The PCE of devices using LiF degrades linearly $\sim 20\%$ in 1 month, while for the devices with ZnO, the PCE shows no obvious degradation, demonstrating that 20 nm of ZnO play an important role in protecting PbS QDs. Interestingly, the devices containing ZnO show an increase of the V_{oc} after ageing.

In conclusion, we compared PbS QD solar cells with different cathode interlayer materials, namely, LiF and ZnO, using the same device structure. The solar cells fabricated with the ZnO interlayer gave a PCE of 4.8%, which is higher (above the experimental variation) than the 4.1% efficiency obtained with the LiF interlayer. We found that the ZnO interlayer alters the spatial distribution of the optical field, leading to an increase in EQE in the visible range. The optical simulations give further evidence of the impact of the optical spacer effect on the charge generation with an 8% enhancement on the light absorption for an active layer thickness between 100 and 250 nm. The light intensity

dependent measurements show that when the light intensity is above 2 mW/cm^2 , bimolecular recombination is dominant in both devices with ZnO and LiF as interlayers. Finally, devices with ZnO as the interlayer showed more stable performance than the ones using LiF, with practically no power conversion efficiency degradation after 1 month inside a N_2 glovebox.

The financial support from the Foundation for Fundamental Research on Matter (FOM) for the Project “Towards bio-solar cells” (FOM15) and the Zernike Institute for Advanced Materials is acknowledged. The authors thank A. Kamp, R. Gooijaarts, and J. Baas for their technical support.

- ¹O. E. Semonin, J. M. Luther, S. Choi, H. Y. Chen, J. Gao, A. J. Nozik, and M. C. Beard, *Science* **334**, 1530 (2011); R. J. Ellingson, M. C. Beard, J. C. Johnson, P. R. Yu, O. I. Micic, A. J. Nozik, A. Shabaev, and A. L. Efros, *Nano Lett.* **5**, 865 (2005); G. Nair, L. Y. Chang, S. M. Geyer, and M. G. Bawendi, *ibid.* **11**, 2145 (2011); A. J. Nozik, M. C. Beard, J. M. Luther, M. Law, R. J. Ellingson, and J. C. Johnson, *Chem. Rev.* **110**, 6873 (2010); L. H. Lai, W. Gomulya, L. Protesescu, M. V. Kovalenko, and M. A. Loi, *PCCP* **16**, 7531 (2014); L. H. Lai, L. Protesescu, M. V. Kovalenko, and M. A. Loi, *ibid.* **16**, 736 (2014); M. Yuan, O. Voznyy, D. Zhitomirsky, P. Kanjanaboos, and E. H. Sargent, *Adv. Mater.* **27**, 917 (2015); H. Wang, T. Kubo, J. Nakazaki, T. Kinoshita, and H. Segawa, *J. Phys. Chem. Lett.* **4**, 2455 (2013).
- ²C. H. Chuang, P. R. Brown, V. Bulovic, and M. G. Bawendi, *Nat. Mater.* **13**, 796 (2014).
- ³G. H. Carey, L. Levina, R. Comin, O. Voznyy, and E. H. Sargent, *Adv. Mater.* **27**, 3325 (2015).
- ⁴C. Piliego, L. Protesescu, S. Z. Bisri, M. V. Kovalenko, and M. A. Loi, *Energy Environ. Sci.* **6**, 3054 (2013).
- ⁵J. Tang, X. Wang, L. Brzozowski, D. A. Barkhouse, R. Debnath, L. Levina, and E. H. Sargent, *Adv. Mater.* **22**, 1398 (2010).
- ⁶K. Szendrei, W. Gomulya, M. Yarema, W. Heiss, and M. A. Loi, *Appl. Phys. Lett.* **97**, 203501 (2010).
- ⁷A. K. Kyaw, D. H. Wang, D. Wynands, J. Zhang, T. Q. Nguyen, G. C. Bazan, and A. J. Heeger, *Nano Lett.* **13**, 3796 (2013).
- ⁸L. Qian, J. Yang, R. Zhou, A. Tang, Y. Zheng, T.-K. Tseng, D. Bera, J. Xue, and P. H. Holloway, *J. Mater. Chem.* **21**, 3814 (2011).
- ⁹G. H. Kim, B. Walker, H. B. Kim, J. Y. Kim, E. H. Sargent, and J. Park, *Adv. Mater.* **26**, 3321 (2014).
- ¹⁰M. J. Speirs, D. M. Balazs, H. H. Fang, L. H. Lai, L. Protesescu, M. V. Kovalenko, and M. A. Loi, *J. Mater. Chem. A* **3**, 1450 (2015).
- ¹¹H. L. Yip, S. K. Hau, N. S. Baek, H. Ma, and A. K. Y. Jen, *Adv. Mater.* **20**, 2376 (2008); S. K. Hau, H.-L. Yip, N. S. Baek, J. Zou, K. O'Malley, and A. K. Y. Jen, *Appl. Phys. Lett.* **92**, 253301 (2008).
- ¹²T. Kirchartz, F. Deledalle, P. S. Tuladhar, J. R. Durrant, and J. Nelson, *J. Phys. Chem. Lett.* **4**, 2371 (2013).
- ¹³E. L. Ratcliff, A. Garcia, S. A. Paniagua, S. R. Cowan, A. J. Giordano, D. S. Ginley, S. R. Marder, J. J. Berry, and D. C. Olson, *Adv. Energy Mater.* **3**, 647 (2013).
- ¹⁴L. A. A. Pettersson, L. S. Roman, and O. Inganäs, *J. Appl. Phys.* **86**, 487 (1999).
- ¹⁵M. Law, M. C. Beard, S. Choi, J. M. Luther, M. C. Hanna, and A. J. Nozik, *Nano Lett.* **8**, 3904 (2008).
- ¹⁶A. Kondilis, E. Aperathitis, and M. Modreanu, *Thin Solid Films* **516**, 8073 (2008); J. D. Kotlarski, P. W. M. Blom, L. J. A. Koster, M. Lenes, and L. H. Slooff, *J. Appl. Phys.* **103**, 084502 (2008).