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High-speed Electrodeposition of Copper-Tin-Zinc Stacks from Liquid Metal Salts for Cu₂ZnSnSe₄ Solar Cells

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Cu₂ZnSnSe₄-based solar cells with 5.5% power conversion efficiency were fabricated from Cu/Sn/Zn stacks electrodeposited from liquid metal salts. These electrolytes allow metal deposition rates one order of magnitude higher than those of other deposition methods.

In this Communication we report on metal-containing ionic liquids for the high speed additive-free sequential electrodeposition of Cu, Sn and Zn layers for thin film photovoltaics. Subsequent thermal annealing of the electrodeposited Cu/Sn/Zn metal stacks in the presence of selenium, leads to the formation of kesterite, Cu₂ZnSnSe₄ (CZTSe). Solar cells can then be fabricated from this compound, with the configuration depicted in Figure 3(c). Kesterite is a p-type semiconductor absorber layer with a high absorption coefficient that only consists of abundant metals, making it a suitable replacement for the successful Cu(In,Ga)Se₂, which contain the scarce element indium. Kesterite based solar cells have achieved a power conversion efficiency of 12.7 %, approaching commercial viability.¹ Kesterite absorber layers with these high efficiencies are synthesized by annealing a precursor. This precursor is deposited by multiple spin-coating and drying of hydrazine solutions containing Cu, Sn, Zn, and Se. Alternative and more scalable approaches to precursor deposition include vacuum deposition^{2,4}, ink-based methods^{5, 6} and electrodeposition.⁷ Electrodeposition of a precursor is appealing since it is more material and energy-efficient than vacuum based methods and

we show here that it can be faster. Typically for copper thin films chemical vapour deposition rates are 2 nm.s⁻¹, evaporation rates are 3.5 nm.s⁻¹, and sputter rates are 10 nm.s⁻¹, whilst here we observe deposition rates above 100 nm.s⁻¹.⁸⁻¹⁰ A disadvantage of aqueous electrodeposition baths is the limited cathodic potential window where metal ions can be reduced without the competing reduction of protons, which lead to electroplating current efficiency losses.¹¹ In order to tackle the window limitation, Chen *et al.* and Chan *et al.* have both co-electrodeposited Cu-Sn-Zn layers, as precursors for CZTS, from a deep-eutectic solvent, containing millimolar quantities of the metal ions to be deposited.^{12, 13} Other additives such as brighteners and smootheners are often required to ensure uniform adherent deposits, as shown by the Cu/Sn/Zn deposition of Ahmed *et al.*¹⁴ Here we take a new approach to avoid the limited cathodic window, the use of brighteners and smootheners, and the low metal ion concentrations. We use highly concentrated metal-containing ionic liquids, called liquid metal salts (LMS), as the electrolytes to deposit sequentially copper, tin, and zinc at high speed. LMS consist of cations and anions, where the cation is a complexed metal ion. Here, the Cu(I)-, Sn(II)- and Zn(II)-containing cationic complexes are partnered with the bis(trifluoromethylsulfonyl)imide ([Tf₂N]⁻) anion to achieve liquid compounds below 100 °C. The complexes used to electrodeposit the metals are [Cu(MeCN)₄][Tf₂N] (MeCN = acetonitrile), [Sn(G2)(EtOH)][Tf₂N]₂ (G₂ = 1-methoxy-2-(2-methoxyethoxy)ethane or diglyme; EtOH = ethanol), [Zn(EtIm)₆][Tf₂N]₂ (EtIm = 1-ethylimidazole), respectively. The copper and zinc complexes have been prepared according to literature procedures.^{15, 16}

[Sn(G2)(EtOH)][Tf₂N]₂ is the first example of a tin(II) LMS. It was synthesized by reacting [Sn(H₂O)₃][Tf₂N]₂ and G2 in ethanol, followed by removal of the solvent *in vacuo*. The molecular structure, as determined by single-crystal X-ray diffraction, consists of a [Sn(G2)(EtOH)]²⁺ cation and two [Tf₂N]⁻ anions (Figure 1A). The Sn–O bond distances in the cation vary in the range 2.229(3)–2.432(4) Å, with the shortest of those to the oxygen of the ethanol molecule. There are three longer

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Electronic Supplementary Information (ESI) available: (1) Synthesis and characterization of Sn LMS including a CIF file for the [Sn(G2)(EtOH)][Tf₂N]₂ (CCDC-1452178). (2) Metallic precursor synthesis and characterization. (3) Absorber synthesis and characterisation (4) Solar cell fabrication and characterization. See DOI: 10.1039/x0xx00000x

Table 1. Properties of the liquid metal salts (LMS) and electrodeposition parameters of the Cu/Sn/Zn stacks. Deposition rates are calculated considering the total deposited mass across the whole sample surface, (circa 4 cm²). DOI: 10.1039/C6CC09225J

LMS	T_m /°C	[Metal]/mol. L ⁻¹	η /mPa.s (80 °C)	j_{dep} /mA.cm ⁻²	t_{dep} /s	Plating efficiency /%	Deposition rate/nm.s ⁻¹
[Cu(MeCN) ₄][Tf ₂ N]	65 (± 1)	3.1	9 (± 1)	-200	3.0 – 3.5	95 (± 5)	140
[Sn(G2)(EtOH)][Tf ₂ N] ₂	72 (± 1)	2.3	29 (± 4)	-200	3.5 – 4.0	69 (± 6)	115
[Zn(EtIm) ₆][Tf ₂ N] ₂	35 (± 1)	1.4	12 (± 2)	-200	3.5 – 4.0	89 (± 6)	85

Sn...O interactions to oxygen atoms of Tf₂N anions at distances 2.690(4), 2.937(4) and 2.992(9) Å. Full synthesis and structure details are given in the ESI. The properties of the LMS are summarized in Table 1. The melting points (T_m) and viscosities (η) of the LMS are relatively high when compared with other organic [Tf₂N]⁻ based ionic liquids (e.g. 1-ethyl-3-methylimidazolium η = 40 mPa.s and T_m = -15 °C)¹⁷, but by working at 90 °C the viscosity is low enough to allow good mass transport. The liquid contains the cation, so the effective metal concentrations are high, ranging from 1.4 to 3.1 M (Table 1), allowing high deposition currents (j_{dep}) and leading to deposition times (t_{dep}) of a few seconds.

Cyclic voltammograms (CV) for each of the LMS have been recorded on a molybdenum electrode to investigate their electrochemical behavior (Figure 1B).

Fig. 1 A: Partial view of the crystal structure of the low-melting ionic tin(II) complex [Sn(G2)(EtOH)][Tf₂N]₂ (Sn: dark grey, C: light grey, S: yellow, O: red, F: green, N: blue; disorder omitted for clarity). B: Offset cyclic voltammograms of i) [Cu(MeCN)₄][Tf₂N], ii) [Sn(G2)(EtOH)][Tf₂N]₂ and iii) [Zn(EtIm)₆][Tf₂N]₂ on a Mo working electrode at T = 90 °C. Open circuit potentials are denoted by the dotted cross.

All the reduction onsets appear close to E = 0.0 V (the potential was measured versus the deposited metal). The cathodic currents continuously increase as the potential is swept negatively and a diffusion-limited regime is not observed due to the high metal concentration.¹⁵ The difference between the

LMS presented here and concentrated electrolytes containing reducible species, which also do not enter a diffusion-limited regime, lies in the fact that there is no competing solvent reduction. Since the LMS only contains one reducible species, an increase in the cathodic over-potential always leads to an increase in the deposition rate. A further consequence of the potential-controlled deposition rate is that the thickness uniformity of a thin film deposit depends on the electrical resistance of the substrate and the growing deposit. Closer inspection of the CVs shows that the reduction potentials deviate negatively from E = 0.0 V (Figure 1B), and they feature nucleation loops indicating that nucleation is difficult, which is commonly observed for electrodeposition of metals on molybdenum.^{18, 19} On the reverse scan, broad and asymmetric stripping peaks are observed, and the position of the peak depends on the sweep rate amongst others. The broad asymmetry suggests slow stripping of the deposit and is particularly evident on CVs ii) and iii) in Figure 1B, where the oxidation current reaches zero at a potential as high as E = +1.0 V.

Cu, Sn and Zn are galvanostatically deposited at j = -200 mA.cm⁻² in a total electrodeposition time of 12 s. Deposition rates of 140 nm.s⁻¹, 115 nm.s⁻¹ and 85 nm.s⁻¹ were achieved for Cu, Sn and Zn, respectively (Table 1). These rates are higher than those of most chemical and physical deposition methods. The plating efficiencies for the metal depositions are 95% for Cu, 69% for Sn and 89% for Zn (Table 1). Although the values for Cu and Zn are similar to those reported for aqueous electrolytes, the value for Sn is lower. A reason for this lower value could be a side reaction such as decomposition of the G2 or EtOH, although no evidence of this could be observed. By knowing the plating efficiency of the metals, the composition of the Cu/Sn/Zn semiconductor precursor layers is controlled.

Cu₂ZnSnSe₄ was prepared by electrodepositing a ≈ 900 nm Cu/Sn/Zn stack on to 4 cm² Mo substrates followed by gas phase selenization. The precursor stacking order was chosen from the most noble to the least noble metal, to avoid the dissolution of the already deposited layers. Figure S4 of the ESI shows the different surface morphologies of the deposited layers. Figure 2 shows the surface SEM micrograph of the Cu/Sn/Zn precursors and the corresponding energy dispersive X-ray spectroscopy (EDX) elemental maps. The surface of the precursors consists of a relatively flat lower layer with crystal-like deposits scattered on the surface. The EDX maps revealed that Cu and Sn are distributed uniformly whilst Zn only

crystallized as large surface crystals. The scattered Zn crystals indicate a low nucleation density on the Sn surface despite the large over-potential applied, and that it does not alloy with Sn, as expected by the phase diagram.²⁰ EDX survey spectra were conducted to check for impurities coming from the electrodeposition bath. Oxygen was present in the films, but other impurities such as fluorine could not be detected. Secondary ion-mass spectrometry (SIMS) showed that the oxygen was mostly at the surface consistent with oxidation due to exposure to air rather than coming from a side reaction of the Sn deposition process. Grazing incidence X-ray diffraction (GIXRD) analysis of the precursor showed the presence of elemental Cu, Sn and Zn, as well as Cu_6Sn_5 (see ESI figure S5). To convert the Cu/Sn/Zn precursor to kesterite, it was alloyed at 300 °C under nitrogen for 30 minutes. Later experiments showed that annealing for one minute would have been sufficient to alloy the precursor. Subsequently the alloyed sample was heated by infra-red radiation at 20 °C.s⁻¹ up to 550 °C in the presence of Se and SnSe for a total time of 4 min. The sample then cools in 10 min to room temperature.

Fig. 2 SEM surface micrograph of a Cu/Sn/Zn metal precursor is presented in A. The Cu, Sn and Zn EDX mappings are shown in B, C and D, respectively.

The composition of the absorber was $[\text{Cu}]/([\text{Zn}]+[\text{Sn}]) = 0.88 \pm 0.10$, $[\text{Zn}]/[\text{Sn}] = 1.24 \pm 0.13$, and $[\text{Se}]/[\text{metals}] = 0.96 \pm 0.11$ as measured by EDX (see ESI for individual atomic percentages) indicating a Cu-poor and Zn-rich layer. The measured composition is close to the edge of the single phase kesterite region.²¹ However, the presence of ZnSe could be

expected given the uncertainty of the EDX measurement. Deviation from stoichiometry towards Cu-poor and Zn-rich film compositions is normally found to be beneficial to solar cell efficiency.²² GIXRD of the absorber revealed the presence of CZTSe and MoSe_2 which comes from the selenization of the substrate during the annealing process. No ZnSe could be detected (ESI Figure S6).

The cross section SEM micrograph of the absorber is shown in Figure 3A, displaying a compact morphology, a thickness of 2.5 μm, and an apparent grain size above 1 μm (the surface view is given in Figure S7 of the ESI). The bright crystals present on the surface are ZnSe. This is supported by Raman spectroscopy (Figure 3B spot 2) showing a peak at 250 cm⁻¹, which is the main Raman mode of ZnSe.²³ CZTSe peaks are observed at 190, 232 and 167 cm⁻¹ (spot 1).²³ By mapping a 60×60 μm² area and plotting the main ZnSe mode at 250 cm⁻¹ (Figure 3B inset) ZnSe is observed to be randomly distributed on the surface of the absorber. SIMS measurements showed that Cu, Sn, and Zn were equally distributed through the depth of the film, except for the surface which was Zn rich in accordance with the surface ZnSe phase found by Raman spectroscopy (see ESI Figure S8). Se was found in the Mo layer consistent with the formation of MoSe_2 in accordance with the instability of kesterite on Mo.²⁴ To show that the metal precursor electrodeposited from the LMS gives a semiconductor with suitable opto-electronic properties for photovoltaic application, solar cells were fabricated. To this end, a CdS layer (50 nm) was deposited by chemical bath deposition on top of the absorber, followed by the deposition of an intrinsic ZnO layer (80 nm) and of a Al-doped ZnO layer (380 nm) by sputtering. Ni-Al electric contacts were deposited by electron beam evaporation (Figure S9 of the ESI shows a cross section of the device). The best performing solar cell had a total area efficiency of 5.5 %, open circuit voltage of 320 mV, a fill factor of 52.7 %, and a short circuit current (J_{sc}) of - 32.3 mA.cm⁻², as obtained from the current-voltage curve depicted in Figure 3C. The J_{sc} is 1 mA.cm⁻² higher than the state-of-the-art selenide kesterite solar cell made by electrodeposition but 8 mA.cm⁻² lower than the record selenide cell prepared by evaporation.^{2, 7} The V_{oc} of our device is 105 mV lower than both the current best electrodeposited and evaporated devices.^{2, 7}

Fig. 3 A: Cross-section SEM micrograph of a CZTSe absorber. B: Raman spectrum measured on two spots of the surface of the absorber. The inset color map represents the intensity of the Raman signal at 250 cm⁻¹ as a function of sample position. The J-V curve and external quantum efficiency of the resulting solar cell are depicted in C and D, respectively. The inset in C shows the solar cell structure.

Our device exhibited a series resistance of $0.63 \Omega \cdot \text{cm}^2$ and a shunt conductance of $7.0 \text{ mS} \cdot \text{cm}^{-2}$, similar to an evaporated device of near equal efficiency.²⁵ However, the record evaporated device has half the series resistance and four times lower shunt conductance.² The external quantum efficiency (EQE) is the ratio between the photogenerated electrons and the incoming photons, as a function of the wavelength, and was measured on the best device. Figure 3D shows the external quantum efficiency, with a maximum near 550 nm and gradually decreasing for $\lambda > 700 \text{ nm}$. This decrease suggests that collection of charge carriers generated far from the CZTSe/CdS interface is difficult and may be related to a narrow space charge region and/or a low carrier diffusion length.²⁶ From the EQE measurement, a bandgap of 0.89 eV was obtained, which is in the range of values that can be found in the literature for the bandgap of CZTSe. This variability in bandgap is attributed to the ordering of Cu and Zn atoms in the crystal lattice caused by different cooling rates after the annealing. The bandgap value found here is in good agreement with thin films where the disordered structure is predominant, which is expected for kesterite films cooled rapidly, as was done here.^{27, 28}

To conclude we introduced a high-speed method to electrodeposit metal layers and a reasonably rapid annealing routine for kesterite based solar cells. By using the metal-containing ionic liquids to deposit these layers, the number of process variables is reduced since no additives or solutes are added and neither pH control nor mass transport control are required. Moreover, during our work - using the same LMS baths for over 100 runs - no significant degradation of the electrolytes has been observed. Efficient devices were obtained via a fast metal stack precursor deposition route, which is compatible with industrial high-speed roll-to-roll processes and shows large potential for improvement. The liquids are suitable for any electrodeposition application where coherent layers deposited at high speed are required.

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Notes and references

1. J. Kim, H. Hiroi, T. K. Todorov, O. Gunawan, M. Kuwahara, T. Gokmen, D. Nair, M. Hopstaken, B. Shin, Y. S. Lee, W. Wang, H. Sugimoto and D. B. Mitzi, *Adv. Mater.*, 2014, **26**, 7427-7431.
2. Y. S. Lee, T. Gershon, O. Gunawan, T. K. Todorov, T. Gokmen, Y. Virgus and S. Guha, *Adv. Energy Mater.*, 2015, **5**, 1401372.
3. G. Brammertz, M. Buffiere, S. Oueslati, H. ElAnzeery, K. Ben Messaoud, S. Sahayaraj, C. Koeble, M. Meuris and J. Poortmans, *Appl. Phys. Lett.*, 2013, **103**, 16390.
4. A. Fairbrother, E. García-Hemme, V. Izquierdo-Roca, X. Fontané, F. A. Pulgarín-Agudelo, O. Vigil-Galán, A. Pérez-Rodríguez and E. Saucedo, *J. Am. Chem. Soc.*, 2012, **134**, 8018-8021.
5. Q. Guo, G. M. Ford, W.-C. Yang, B. C. Walker, E. A. Stach, H. W. Hillhouse and R. Agrawal, *J. Am. Chem. Soc.*, 2010, **132**, 17384-17386.
6. J. van Embden, A. S. R. Chesman, E. Della Gaspera, N. W. Duffy, S. E. Watkins and J. J. Jasieniak, *J. Am. Chem. Soc.*, 2014, **136**, 5237-5240.
7. L. Vauche, L. Risch, Y. Sánchez, M. Dimitrievska, M. Pasquinelli, T. Goisard de Monsabert, P.-P. Grand, S. Jaime-Ferrer and E. Saucedo, *Prog. Photovolt: Res. Appl.*, 2016, **24**, 38-51.
8. K. M. McPeak, S. V. Jayanti, S. J. P. Kress, S. Meyer, S. Iotti, A. Rossinelli and D. J. Norris, *ACS Photonics*, 2015, **2**, 326-333.
9. B. H. W. Toh, D. W. McNeill and H. S. Gamble, *J. Mater. Sci.: Mater. Electron.*, 2005, **16**, 437-443.
10. J. H. Boo, M. J. Jung, H. K. Park, K. H. Nam and J. G. Han, *Surf. Coat. Technol.*, 2004, **188**, 721-727.
11. A. P. Abbott and K. J. McKenzie, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4265-4279.
12. C. P. Chan, H. Lam and C. Surya, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 207-211.
13. H. Chen, Q. Ye, X. He, J. Ding, Y. Zhang, J. Han, J. Liu, C. Liao, J. Mei and W. Lau, *Green Chemistry*, 2014, **16**, 3841-3845.
14. S. Ahmed, K. B. Reuter, O. Gunawan, L. Guo, L. T. Romankiw and H. Deligianni, *Adv. Energy Mater.*, 2012, **2**, 253-259.
15. N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt, K. Binnemans and J. Fransaer, *Chem. Eur. J.*, 2011, **17**, 5054-5059.
16. M. Steichen, N. R. Brooks, L. Van Meervelt, J. Fransaer and K. Binnemans, *Dalton Trans.*, 2014, **43**, 12329-12341.
17. F. Endres, A. Abbott and D. MacFarlane, eds., *Electrodeposition from Ionic Liquids*, Wiley-VCH, Weinheim, 2008.
18. J. C. Malaquias, D. Regesch, P. J. Dale and M. Steichen, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2561-2567.
19. D. D. Shivagan, P. J. Dale, A. P. Samantilleke and L. M. Peter, *Thin Solid Films*, 2007, **515**, 5899-5903.
20. Z. Moser, J. Dutkiewicz, W. Gasior and J. Salawa, *Bull. Alloy Phase Diagrams*, 1985, **6**, 330-334.
21. L. Choubrac, A. Lafond, M. Paris, C. Guillot-Deudon and S. Jobic, *Phys. Chem. Chem. Phys.*, 2015, **17**, 15088-15092.
22. X. Liu, Y. Feng, H. Cui, F. Liu, X. Hao, G. Conibeer, D. B. Mitzi and M. Green, *Prog. Photovolt: Res. Appl.*, 2016, **24**, 879-898.
23. R. Djemour, M. Mousel, A. Redinger, L. Guetay, A. Crossay, D. Colombara, P. J. Dale and S. Siebentritt, *Appl. Phys. Lett.*, 2013, **102**, 222108.
24. J. J. Scragg, P. J. Dale, D. Colombara and L. M. Peter, *ChemPhysChem*, 2012, **13**, 3035-3046.
25. A. Redinger, M. Mousel, R. Djemour, L. Guetay, N. Valle and S. Siebentritt, *Prog. Photovolt: Res. Appl.*, 2014, **22**, 51-57.
26. R. Scheer and H.-W. Schock, *Chalcogenide Photovoltaics*, WILEY-VCH Verlag GmbH & Co., Weinheim, Germany, 2011.
27. M. Mousel, T. Schwarz, R. Djemour, T. P. Weiss, J. Sendler, J. C. Malaquias, A. Redinger, O. Cojocaru-Miredin, P.-P. Choi and S. Siebentritt, *Adv. Energy Mater.*, 2014, **4**, 130043 - 130048.
28. G. Rey, A. Redinger, J. S. Ler, T. P. Weiss, M. Thevenin, M. Guennou, B. El Adib and S. Siebentritt, *Appl. Phys. Lett.*, 2014, **105**, 112106.