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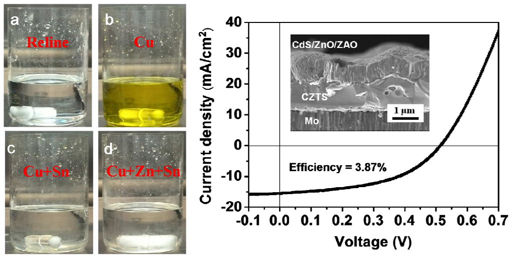

A conversion efficiency of 3.87% was achieved by using Reline as an electrolyte to co-electroplate Cu-Zn-Sn precursor thin films

Electrodeposited CZTS solar cells from the electrolyte of Reline

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Abstract: This work is the first report of using a deep eutectic solvent named Reline as a green electrolyte to electrodeposit CZTS films for photovoltaic applications. The process successfully achieves by co-electrodepositing Cu-Zn-Sn precursor thin films in Reline and sulfurizing the Cu-Zn-Sn precursors in H_2S and N_2 mixture atmosphere at 550 ^{o}C for 1h. The CZTS films are uniform and compact on microscopic scales, which translate to a benign photoresponse of the CZTS solar cell. Photovoltaic devices were prepared from the films and an efficiency of 3.87% has been achieved. The device performance indicates that Reline is a viable green solvent for the electrodeposition of CZTS thin film solar cell in a low cost way.

Keywords: Ionic liquid, Eletrodeposition, CZTS, Choline chloride, Urea

Introduction

The problem of obtaining high quality electroplated coatings while eliminating the harm to the environment caused by electrolytes has received increasing attention in green electrochemical and environmental industries.[1-3] Many efforts have been made to develop green electrolytes for application in electroplating. Some ionic liquids (ILs) have been increasingly used as green electrolytes to electroplate a range of metals, alloys and compound semiconductors over the past decades, due to their wide electrochemical window, high ionic conductivity, high solvation capacity, negligible vapor pressure and excellent thermal, chemical and electrochemical stability.[4-6] However, these ILs are generally too expensive to be used in large-scale commerce applications. Furthermore, many of them are sensitive to moisture and are even made from non-biodegradable components.[5-7]

Research has continued to low-cost and greener alternatives to these ILs that may conquer their limitations. Among such are deep eutectic solvents (DESs), which are a new type of ionic liquids made by mixing a quaternary ammonium salt and a metal salt, a hydrated salt or a simple hydrogen bond donor such as alcohol, amide and carboxylic acid as complexing agent. This mixing reduces the melting points of DESs significantly compared to those of their original precursors. DESs not only possess the common advantages of ionic liquids, but also overcome some disadvantages inherent to conventional ILs. An example is the DES formed from choline chloride and urea (commercially named as Reline).[8] Reline has been shown to have interesting properties that are similar to those of ILs including wide electrochemical window, high conductivities, negligible volatility and other unusual solvent properties. But unlike other ILs Reline is air and water stable and are made from biodegradable components. Choline chloride is a common component to numerous household and industrial products while urea is a familiar fertilizer. More importantly, the low cost materials and the easy synthesis make Reline a good candidate for electroplating in mass production.

Here we report an electrodeposition process based on Reline to fabricate Kesterite Cu_2ZnSnS_4 (CZTS) absorber film, which is regarded as one of the most prospective candidates for the next generation commercial solar cells since it is a non-toxic material with earth-abundant elements. Up to today, the best device efficiency of CZTS thin film solar cell fabricated by electrochemical approach in aqueous solutions showed an efficiency of 8.0%[9]. Compared with aqueous solutions, electrodeposition coatings using DESs have better mechanical properties due to negligible hydrogen embrittlement, which can be explained by wide potential windows. In addition, ionic liquids complexing metals offer the chance to get rid of most of highly toxic complexing agents in aqueous solution which may bring environmental pollution. C. P. Chan et al. report a route to co-deposit Cu-Zn-Sn alloy using the DES containing choline chloride and ethylene glycol (trade name: Ethaline), followed by post sulfurization to form CZTS films.[10] However, long-term electrochemical stability of Ethaline is not good due to the electrolysis, and several toxic decomposition products of Ethaline such as 2-methyl-1,3-dioxolane and a range of chlorinated products like chloromethane, dichloromethane and chloroform could be detected. There is also no further report about photovoltaic performance of the CZTS films electrodeposited in Ethaline. To fabricate higher quality CZTS films in a greener way, we choose Reline as the solvent to electrodeposit CZTS films. To the best of our knowledge, this is the first report on electrodeposition of CZTS using Reline. After some optimizations of plating parameters and annealing processes, a high quality of dense, smooth CZTS polycrystalline films is achieved. Then the glass/Mo/CZTS/CdS/i:ZnO/AZO structure of CZTS solar cell is completed and the device performance is characterized.

Experimental

The ionic liquids were prepared by mixing Choline chloride (Sigma 99%) and urea (Aldrich 98%) at a molar ratio of 1:2. Anhydrous chloride salts of $CuCl_2$ (Alfar 99.9%), $SnCl_2$ (Alfar 99.9%) and $ZnCl_2$ (Alfar 99.9%) were sequentially dissolved in Reline in the following steps. First, 5 mmol $CuCl_2$ was dissolved in the ionic liquid at room temperature, under constant magnetic stirring, forming a deep yellow liquid. Second, $SnCl_2$ (20 mmol) was dropped into the ionic liquid containing copper chloride, a step which changes the liquid's color immediately from deep yellow to transparent in a few seconds. Then, 20 mmol $ZnCl_2$ was added to the transparent ionic liquid with no color change. Cyclicvoltammetry test and amperometric i-t curve were performed at 65 ^{o}C without stirring using a potentio station (TatriplateCP, MPC, France). The Cu-Zn-Sn precursors were co-electrodeposited at -1.2 V. A three-electrode system was used with a 150 nm copper layer which was evaporated on Mo coated soda lime glass as working electrode, a platinum (Pt) gauze as counter electrode and a Pt wire as reference electrode. N_2 (99.999%) was employed to purge the electrolyte before electrodeposition. The post-annealing treatments were conducted in the atmosphere of N_2+H_2S (5%) in order to form stoichiometric CZTS. The precursor films were heated up to 550 ^{o}C rapidly, held for 1 hour and cooled down to room temperature naturally in a rapid thermal process (RTP) furnace. The CZTS absorber films were then processed into photovoltaic devices by chemical bath deposition of CdS, sputtering of i-ZnO and Al:ZnO, and evaporation of the Ni/Al contact grid.

The morphologies and compositions of prepared CZTS film were analyzed using scanning electron microscope (Hitachi S5200) and X-ray fluorescence (Fischer XDV-XDD). X-ray diffraction (Shimadzu) analysis was performed on a diffractometer using Cu Ka radiation at a scan rate of 8 ^{o}/min under operation condition of 30 kV and 40 mA. Raman spectra were recorded using microscopic confocal Raman spectrometer (Labram HR 800) with an excitation of 514 nm laser light. An active cell area of 0.1 cm^2 was defined by mechanical scribing along the edge of Ni/Al grid. J–V data and power conversion efficiencies were obtained at room temperature under AM 1.5G illuminations (1000 W/m^2) from a solar simulator which was calibrated using a standard silicon solar cell device.

Results and discussion

The chlorocomplex anions of Cu(II), Zn(II) and Sn(II) in Reline are believed to exist as $CuCl_4^{2-}$, $ZnCl_3^-$, $SnCl_3^-$ and $Sn_2Cl_5^-$.[11, 12] The color of the chlorocomplex anion of Cu(II) was observed to be deep yellow in Reline, while other chlorocomplex anions of Sn(II), Zn(II), Cu(I) and Sn(IV) were colorless. When $SnCl_2$ was added to the ionic liquid containing $CuCl_2$, the color of the ionic liquid changed from deep yellow to transparent, as shown in Figure 1b and Figure 1c. This change is due to the fact that Sn^{2+} was oxidized to Sn^{4+} and Cu^{2+} was reduced to Cu^+, corresponding to the following reaction:[13]

$$2Cu^{2+} + Sn^{2+} \longrightarrow 2Cu^{+} + Sn^{4+}$$

The electrochemical properties of the constituent metal elements of Kesterite family in Reline were studied before the co-electrodepositon of Cu-Zn-Sn precursor thin films. Cyclic voltammograms (CV) were performed by a 3-electrode system composed of Pt foil as working electrode, Pt gauze as counter electrode, and Pt wire as reference electrodes at a scan rate of 20 mV/s. The CV measurements were conducted after the open circuit voltage of the electrochemical cell was stabilized. As shown in Figure 1e, the potential window of Reline ranges from -1.25 V to +1.25 V. This result is in accord with previous study by L. M. Peter.[14] Fig 1f shows the reduction potentials peak for Cu(II), Sn(II) and Zn(II) in the certain concentration are -0.37, -0.68 and -1.2 V, respectively, while the anodic peak potentials are 0.02, -0.4 and -1.0 V, respectively. We can also see that the reduction potentials for Cu(II), Sn(II) and Zn(II) are -0.26, -0.58, -1.0 V, respectively. Those are not only in the electrochemically stable region of Reline, but also shift closer in Reline than that in water, which are 0.34 V, -0.14V, and -0.76 V for Cu(II), Sn(II) and Zn(II) ions, respectively, versus standard hydrogen electrode (SHE) in 1 M aqueous solution at 25 ^{o}C. The co-electrodeposition of the three metal elements in Reline tends to get easier without any other additive agents.

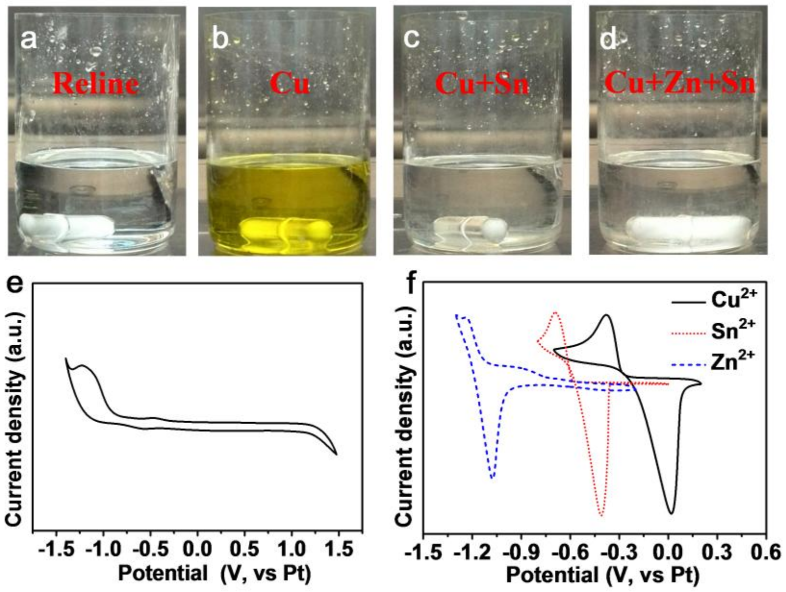

Figure 1. Photographs of (a) the choline chloride-based ionic liquid (IL), (b) $CuCl_2$ + IL, (c) $CuCl_2$ + $SnCl_2$ + IL, (d) $CuCl_2$ + $SnCl_2$ + $ZnCl_2$ + IL. (e) Cyclic voltammograms of the IL. (e) Cyclic voltammograms of the ILs containing $CuCl_2$, $SnCl_2$ and $ZnCl_2$, respectively.

Figure 2a and 2b present surface scanning electron microscopy (SEM) images of the electrodeposited Cu-Zn-Sn precursor film and the sulfurized CZTS film. The electrodeposited Cu-Zn-Sn precursor film exhibits a granular surface morphology. The sulfurized CZTS film shows a flat and compact surface morphology free of pinholes and microcracks. The average grain size of the sulfurized CZTS film could be estimated to be over 500 nm from the morphological studies (Figure 2b). XRD pattern (Figure 2c) confirms that the co-deposited Cu-Zn-Sn precursor film mainly contains elemental Cu, Zn and Sn phases. According to JCPDS card no. 26-0575, the main diffraction peaks for the sulfurized CZTS film, apart from the peaks arising from

Mo-coated substrate, are assigned to the 112, 220 and 312 peaks at 28.51 °, 47.36 ° and 56.17 °, respectively, indicating that the CZTS film has a kesterite crystal structure with a preferred orientation of (112). The (112) peak is sharp and no extra peaks are found, indicating a good crystallinity and a high level of phase purity for the sulfurized CZTS film. Raman spectra of the sulfurized CZTS film (Figure 2d) also shows a single tetragonal CZTS phase with a strong peak at 338 cm^{-1} and three weak peaks at 254, 292 and 371 cm^{-1}.[15]

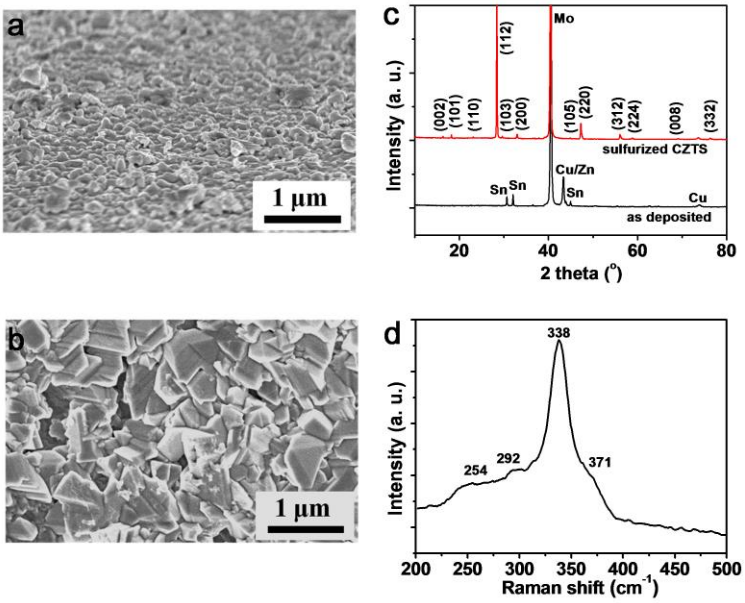

Figure 2. Surface SEM images of the CuZnSn precursor film co-electroplated in ionic liquid (a) and the sulfurized CZTS film using H_2S gas (b). (c) The corresponding XRD patterns of the CuZnSn and CZTS films. (d) Raman spectra of the CZTS film.

The non-stoichiometry for compound semiconductors always correlates with their electrical properties. For high-efficiency CZTS solar cells, there is an empirical rule that the Cu/(Zn + Sn) and Zn/Sn atomic ratios should lie in the range of 0.75-1 and 1-1.25, respectively.[16-19] XRF measurement (Table 1) indicates that Cu/(Zn + Sn) and Zn/Sn ratios are 0.67 and 1.13, respectively, for precursor films, as well as 0.77 and 1.21 for sulfurized CZTS films. The Cu/(Zn + Sn) and Zn/Sn ratios of the CZTS films are slightly higher than that of its precursor film, which is attributed to the loss of Sn element during sulfurization.[20]

Table 1 The elemental compositions in the Cu–Zn–Sn precursor and CZTS thin films

Samples ID	Elemental composition (at%)				Composition ratio	
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn
Cu-Zn-Sn precursors	40.05	31.64	28.11	-	0.67	1.13
CZTS	20.87	14.91	12.38	51.84	0.76	1.21

Figure 3 shows the *J-V* characteristics of the best-performing ionic-liquid electrodeposited CZTS solar cell. From this data, we derive 3.87% conversion efficiency with photocurrent of 15.6 mA cm^{-2}, open circuit voltage of 512 mV and fill factor of 0.48. From cross-sectional scanning electron microscopy (SEM) image shown in Figure 3 inset, the grain size of the CZTS film is comparable with the thickness of the CZTS film, which is considered to be beneficial for carrier transport.[21]

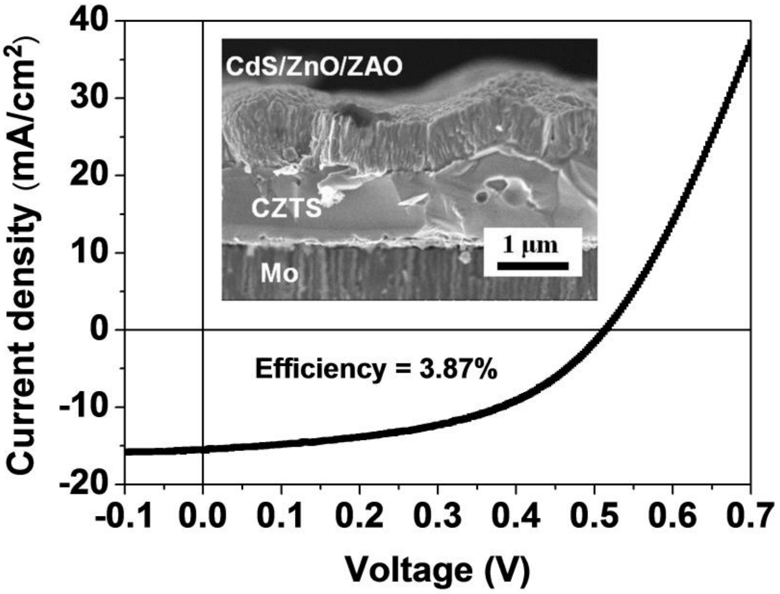

Figure 3. Current-density/voltage curve of the best-performing CZTS solar cell measured under a simulated AM1.5G solar irradiation. The inset is cross-sectional SEM image of completed solar cell constructed from an electroplated CZTS absorber.

Figure 4 shows the external quantum efficiency (EQE) curve for ZnO/CdS/CZTS heterojunction solar cell. The EQE starts slowly at 800 nm, which is related to optical absorption of the CZTS absorber, reaches a maximum value of 68% at 535 nm, and then drops rapidly at about 400 nm due to the cut-off of AZO window layer. The optical absorption coefficient α of CZTS film has a close relation with the EQE value of CZTS according to the equation,[22, 23] EQE = 1-exp(αW), where W is the width of the space charge region. The incident photon energy ($h\nu$) and the optical bandgap energy (Eg) are related to the optical absorption coefficient α by applying the Tauc model, $\alpha h\nu = D(h\nu - E\mathrm{g})^n$, where D is the constant and n is 1/2 for direct transition[23, 24]. Some experimental results and calculation of the electronic band structure of CZTS have revealed a direct bandgap.[25, 26] Thus, by plotting $(h\nu\ln(1-EQE))^2$ against $h\nu$ (shown in Figure 4 inset) and by extrapolating the linear portion of the absorption edge to find the intercept with energy axis, the band gap of 1.46 eV of the CZTS film is obtained, a result which is well consistent with the data reported elsewhere.[27]

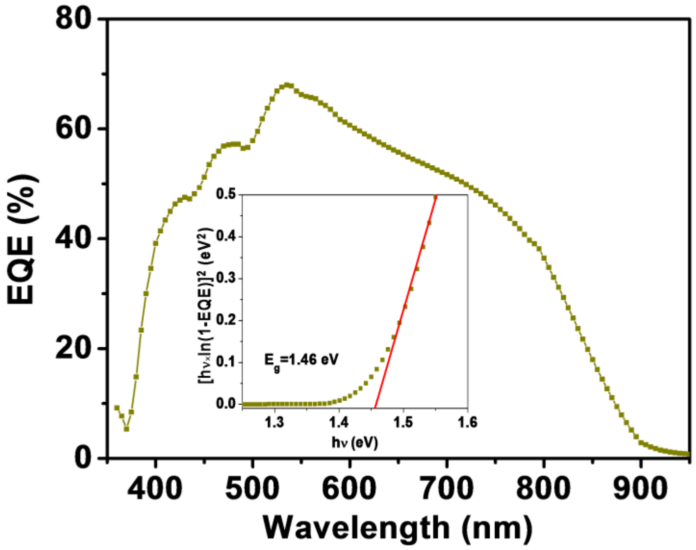

Figure 4. External quantum efficiency (EQE) curve of ZnO/CdS/CZTS heterojunction solar cell. The inset is plot of $[h\nu \times \ln(1\text{-}EQE)]^2$ against $h\nu$ to determine band gap of the absorber.

The diode parameters as the shunt conductance *G*, the series resistance *R*, the ideality factor *A*, and the saturation current density J_o can be further extracted from the illuminated J-V curve. *A* shunt conductance *G* of 4.87 mS/cm^2 is calculated from the derivative d*V*/d*J* against *V* near J_{sc} after the *J-V* curve was smoothed to reduce some noise. The series resistance $R = 1.92$ Ω.cm2, the ideality factor $A = 3.2$, and the saturation current density $J_o = 6.8 \times 10^{-2}$ mA/cm^2 were further determined by using a set of plots (Figure S2) according to the diode equations.[28] The high series resistance *R* may mainly come from CZTS/Mo interface resistance and electrode resistance. In comparison to previously published results of high-efficiency CZTS devices,[21, 29] our ideality factors are also slightly higher. For the IBM record device, the diode ideality factor is as low as 1.3.[21] Moreover, the saturation current densities of our device are two orders of magnitude higher than those of the IBM devices.[29] The ideality factor *A* for our CZTS cell greatly affects the open circuit voltage and fill factor, and thus the efficiency. The ideality factor *A* can be associated with recombination mechanisms of CZTS devices. For $A > 2$, it would imply stronger SCR recombination or that the tunneling enhanced interface recombination would be the dominant limiting factor.[30] The high J_o value in our case also correlates with the high *A* value or the high recombination losses. Therefore, further works should be done to decrease recombination losses and series resistance, thus resulting in higher efficiency.

Conclusions

This work shows that Reline is a green and low cost electrolyte to electrodeposit Cu-Zn-Sn precursor thin films. The C-V measurements indicate the electrodeposition in Reline is much easier and is free of other complexing agents compared to the conventional electrodeposition in aqueous solution, and is offer the promise of a low-cost, mass-production solar technology. Pure phase CZTS films with controlled composition and large grain have been successfully obtained by sulfurizing the electrodeposited Cu-Zn-Sn precursor films. With this approach we have achieved a power conversion efficiency of 3.87%. The EQE curve indicates that the CZTS absorber has an optical band gap of 1.46 eV. Further improvements in conversion efficiency are expected by extending the absorption range by substituting S with Se, and decreasing recombination losses and series resistance of solar cells.

Acknowledgement

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