Combined Electrochemical-Chemical Bath Deposited Metal Selenide Nano-film Electrodes with High Photo-electrochemical Characteristics

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***Abstract*— Metal selenide poly-crystalline film electrodes with enhanced photo-electrochemical characteristics can be deposited by electrochemical then by chemical bath depositions onto glass/fluorine doped tinoxide substrates. The resulting film electrode shows the advantages of both electrochemical deposition (film uniformity and adhesion) and chemical bath deposition (suitable thickness). The two systems have been examined, and both showed enhanced conversion efficiency values. The copper selenide electrode showed ~4.5% efficiency while the cadmium selenide showed ~14% efficiency), both of which are much higher than earlier reported values for metal chalcogenide film electrodes. Other photo-electrochemical characteristics such as fill factor, film stability and short-circuit photocurrent density, have also been enhanced by the combined deposition. Moreover, the as-prepared films exhibited enhancement with no need for further treatment.**

Keywords—CuSe; CdSe; combined deposition; photo-electrochemistry; conversion efficiency

I. INTRODUCTION

Semiconductor nano-film electrodes, which involve nano-size polycrystalline particles, are emerging as alternative for mono-lithic photo-voltaics (PVs). There are many reasons for that, most notably the relatively low manufacturing cost and lower environmental impact. Unlike PVs, film electrodes demand no special manufacturing ultra-high vacuums, or sophisticated equipment. Common preparation methods include electro-chemical deposition (ECD), chemical-bath deposition (CBD), dipping and spraying onto fluorine-doped tin oxide (FTO)/transparent glass. Moreover, they use only small amounts of starting materials [1-5]. Despite that, film electrodes show very low conversion efficiencies (1% or lower) compared to PVs (with higher than 25% in recent reports). Another shortcoming in film electrodes is their relatively low stability to photo-corrosion under PEC conditions [3, 6]. In order to make film electrodes compete in future application, their conversion efficiency and stability need to be enhanced. Literature shows different methods to achieve such goals, some of which are costly or environmentally non-friendly. In this work, a simple non-costly technique is described. The assumption is that combining ECD and CBD together should yield electrodes with the virtues of the two methods together. ECD is known to yield very thin uniform films well adherent with the FTO [7]. The CBD method yields thicker films that are more suitable for PEC purposes [8-10]. The ECD-CBD film electrodes are thus anticipated to show high conversion efficiency under PEC conditions. For this purpose, CuSe and CdSe film electrodes, both known to be unstable with low conversion efficiency, are examined here. The results will be presented together with a model that explains the high efficiency and stability of the new prepared film electrodes for renewable energy purposes..

II. EXPERIMENTAL

A. Electrode deposition

First, The ECD-CBD film electrodes were prepared in two stages. In each case a thin film was prepared using the ECD method. The ECD prepared layer was then coated with another CBD layer. Both ECD and CBD preparations followed earlier literature known methods.

The preparation used basic solutions of the metal ion (Cd^{2+} or Cu^{2+}) of known concentrations and Na_2SeSO_3 solutions. The Na_2SeSO_3 was prepared using literature procedures [11].

The ECD preparation was performed by dipping a pre-cleaned glass/FTO substrate (1X3 cm^2) inside a solution of known concentration of Na_2SeSO_3, M^{2+}, NH_4Cl which was stirred under a stream of nitrogen gas. The glass/FTO was used as a working electrode (-0.6 V, Ag-AgCl reference) and platinum counter electrode (CE) for 15 min. Details of ECD preparation for the CdSe and CuSe are reported [12-14].

The ECD-MSe films were then transferred to basic solutions of MSO_4, Na_2SeO_3, HCl, triethanolamine and NH_4OH, keeping the solution basic. Deposition was made at 70°C for 4 h. Details of CBD preparation are reported for CdSe and for CuSe [15-17].

All prepared films were characterized sing electronic absorption spectra, Photoluminescence Emission Spectra (PL), Scanning-Electron Microscope (SEM), X-ray diffraction (XRD) and Atomic-Force Microscope (AFM). Tauc method was used to calculate approximate band gap values. The Scherrer equation was used to measure the nano-scale particle

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sizes. The nano-particles existed inside larger agglomerates, the sizes of which were approximated from the SEM..

B. PEC Characteristics

The Photo current vs. applied potential (I-V) plots were measured under constant illumination intensity of a solar simulator halogen lamp (50 W). The measured intensity at the electrode surface was 0.000 61 W/cm^2 for the CuSe and 0.00196 W/cm^2 for the CdSe electrodes. The measurement was conducted inside a two electrode cell, where the MSe films were used as working electrodes. A platinum sheet was used as CE, which was also connected to the pre-calibrated internal reference cell. All measurements are thus made with reference to NHE. Different redox couples were examined for each film electrode. For the CdSe system, the $[Fe(CN)_6]^{4-}$ (0.050 M)/$Fe(CN)_6]^{3-}$ (0.050 M) showed best results, while for the CuSe systems, the Na_2S (0.100 M)/S (0.100 M)/NaOH (0.100 M) was the best system. Control experiments were made using glass/FTO naked electrodes and showed no PEC activity.

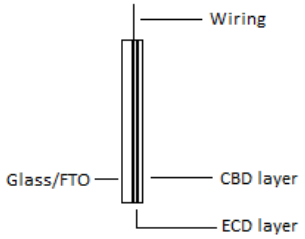
The {I-V} plots, divided by area of working electrode exposed, gave photo-current density vs. potential plots {J-V}. PEC characteristics were then extracted from the J-V plots.

Stability of the electrode to PEC photo-corrosion was assessed by exposing the electrode to constant light intensity lower than PEC J-V experiments to prevent over-heat. The value of short photo-circuit current density {J_{SC}} was measured while keeping the electrode at zero applied bias for up to 180 min.

III. Results and Discussion

A. Film Eclectrode Characteristics

Define For each of CuSe and CdSe systems, three different electrodes (ECD, CBD and ECD-CBD) were prepared, characterized and examined in PEC applications. Scheme 1 describes the layer structure for the ECD/CBD film electrodes.



Scheme 1. Layer structure for MSe electrodes prepared by the combined method

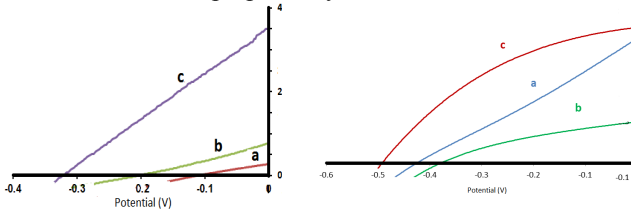
Each prepared film electrode was characterized by a number of methods, as described above. The Tauc method was used to calculate values of approximate band gap values, and the Scherrer equation was used to measure approximate particle sizes. SEM was used to measure agglomerate sizes. Table (1) summarizes all physical properties measured for all electrodes [18, 20].

TABLE I. Physical properties for CuSe and CdSe films prepared by different methods

Film	Preparation	Film thickness	Conduct. $(\Omega.cm)^{-1}$	Agglomerate size (nm)	Nano-particle size (nm)	Band gap (eV)	Crystal type
CdSe	ECD layer	900 nm	$1.5X10^{-4}$	350-400	6.9	2.09	Cubic
	CBD layer	47 µm	$7.5X10^{-4}$	300-350	4.5	2.20	Cubic
	ECD-CBD film	53 µm	$9X10^{-4}$	800-900	7.5	2.07	Cubic
CuSe	ECD	730 nm	$0.4X10^{-4}$	150-200	25 nm	2.30	Cubic
	CBD	43 µm	$1.0X10^{-4}$	200-300	30 nm	2.25	Cubic
	ECD-CBD	50 µm	0.8X10-4	250-300	29 nm	2.20	Cubic

B. PEC Characteristics

In both cases of CdSe and CuSe systems, the ECD electrode exhibited higher PEC characteristics than its ECD and CBD counterparts. Fig.1 shows photo J-V plots for both CdSe and CuSe film electrodes prepared by different methods.



(A) CuSe film electrodes (B) CdSe film electrodes

Fig. 1. Photo J-V plots measured for (A) CuSe and (B) CdSe film electrodes prepared by different methods, (a) ECD, (b) CBD, (c) ECD-CBD

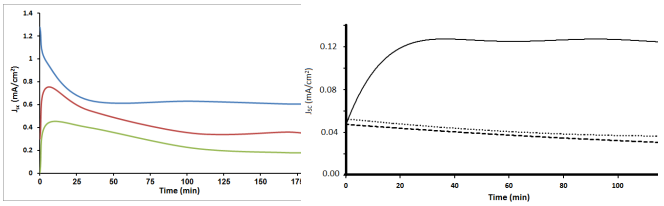
Fig. 1 clearly shows that in each case, the ECD/CBD electrode exhibited higher PEC characteristics than its ECD or CBD counterparts. The results are summarized in Table 2 below.

TABLE 2. PEC characteristics measured for different CuSe and for CdSe different film electrodes

Electrode	Preparation	η%*	Ref.
CuSe	CBD-ECD	15.0	[18]
	CBD	1.8	[18]
	ECD	0.4	[18]
	ECD	Low	[12]
	CuSe	Low	[19]
CdSe	ECD-CBD	4.5	[20]
	CBD	1.2	[20]
	ECD	1.7	[20]
	ECD	Low	[21]
	CBD	Low	[17]

*Efficiency η (%) = [(maximum observed power density)/(reach-in power density)]×100%;

In addition to enhanced PEC conversion efficiency (η), the ECD/CBD film electrodes showed enhanced stability under PEC working conditions. Fig. 2 shows that both CuSe and CdSe films prepared by ECD/CBD showed more steady J_{SC} values, with time, than their counterparts.



(A) CuSe (B) CdSe

Fig. 2. Plots of J_{SC} vs. time for (A) CuSe and (B) CdSe electrodes prepared by different methods (a) ECD), (b) CBD, (c) ECD-CBD.

ECD-CBD film electrode stability to PEC photo-corrosion is justified by the higher values of short circuit current. With enhanced PEC characteristics, the ECD/CND electrodes exhibited higher short circuit photocurrent densities. Photo-current occurs when the semiconductor electrons are excited by incident photons with wavelengths higher or equivalent to the band-gap value. Upon electron excitation, positive holes are produced in the space charge layer (SCL) of the electrode. Such holes may oxidize the electrode surface and cause its photo-corrosion.

Any process that facilitates the hole-transfer across the electrode/redox system would be advantageous. Such a process would prevent hole accumulation in the SCL. The semiconductor electrode is thus stabilized to photo-corrosion. Collectively, the results highlight the future value of preparing metal chalcogenides film electrodes by a combined ECD and CBD method. Work is underway here to assess this method in other unstable and low efficiency MSe electrodes. The goal is to find a simple method to improve different performance of MSe film electrodes.

IV. Conclusion

Copper- & cadmium-selenide nanofilm electrodes can be prepared by electrochemical method (ECD) then by chemical bath deposition (CBD). The resulting electrodes exhibit enhanced PEC performance (becoming more efficient and more stable) compared to ones prepared by separate methods. The ECD-CBD electrodes show benefits of ECD and CBD methods together. The results show the future prospects of using the technique in future renewable energy applications.

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