EMPLOYMENT OF A SIMPLE ELECTRODEPOSITION TECHNIQUE TO FABRICATE ZINC OXIDE FILMS AND ANALYZING THEIR APPLICABILITY FOR CADMIUM SULPHIDE QUANTUM DOT SENSITIZED SOLAR CELLS.

Harini Wijeratne[1*], V.P.S. Perera[1]
[1]The Open University of Sri Lanka, Nawala, Nugegoda.
[*]wijeratneharini@gmail.com

Zinc Oxide (ZnO) is a promising n-type semiconductor material which is very beneficial for solar cell applications due to its desirable properties such as, wide bandgap, low cost, abundance in nature, nontoxicity and its high chemical and mechanical stability. There are many other techniques that could be used to deposit ZnO according to previous work. However, the electrochemical deposition (ECD) technique adopted in this work which contains Zinc nitrate and Zinc acetate in 1:5 ratio in the deposition bath is a simple convenient method which is cost effective that uses inexpensive, abundant chemicals and could be achieved within a short period of time relative to the other techniques.

ZnO is a wide band gap semiconductor which cannot absorb the solar radiation effectively specially in the visible wavelength region of the solar spectrum. Therefore, a narrow band gap semiconducting material such as Cadmium Sulphide (CdS) in the form of quantum dots (QDs) is used for sensitization. In this scenario, these CdS QDs have been prepared by using the reverse Successive Ionic Layer Adsorption and Reaction (SILAR) process by using $Cd(NO_3)_2$ and Na_2S in deionized water to provide Cd^{2+} cations and S^{2-} anions in the precursors.

The ZnO photoanodes thus sensitized with CdS were sandwiched with a Pt-coated Fluorine doped Tin Oxide (FTO) counter electrode and the capillary space between them was filled with polysulfide electrolyte.

The morphological characterization was done using the Scanning Electron Microscopic (SEM) studies in order to study the nature of morphology of the grains produced by ECD technique. J-V characterization of QDSSCs demonstrated a maximum current density of 1.32 $mAcm^{-2}$ with an efficiency of 0.15% for seven Reverse SILAR cycles and the maximum efficiency, η of 0.24% was observed with the voltage of 589.50 mV for 10 Reverse SILAR cycles. The optical properties of ZnO/CdS films were studied with UV-Visible spectroscopy and observed a gradual decrease in the bandgap with the increase in CdS loading in the ZnO films. The impedance spectroscopic analysis showed that the charge transfer resistance at the QD sensitized ZnO and electrolyte interface increased with the number of reverse SILAR cycles.

Keywords: Zinc Oxide, Quantum dots, Sensitization, Cadmium Sulphide, Reverse SILAR method, Electrodeposition

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INTRODUCTION

Quantum dot sensitized solar cell is an emerging field of research among the third-generation solar cells, which has many advantages over the Dye Sensitized Solar Cells such as tunable energy band gap, high absorption coefficient, generation of multiple electron-hole pairs by a single photon (Ali et al., 2015), stability to heat and high theoretical efficiency. There are some widely used quantum dots (QDs) such as CdS (Ali et al., 2015), PbS (Zainudeen & Jaseetharan, 2021), and CdSe (Saad et al., 2018) etc. CdS QDs have many special properties compared to other QDs which make them more suitable as a light harvesting material in the visible region of the solar spectrum (Liyanage et al., 2021). Various methods such as chemical bath deposition (Chen et al., 2009), Successive Ionic Layer Adsorption and Reaction (SILAR) (Liyanage et al., 2021), Reverse SILAR (R.SILAR) (Singh et al., 2016; Becker et al., 2014), etc have been adopted to deposit CdS QDs.

CdS QDs are deposited on high band gap semiconducting materials such as TiO_2 (Ali et al., 2015), ZnO (Liu et al., 2015) and SnO_2 (Liyanage et al., 2021) as the photoanode of Quantum Dot Sensitized Solar Cells (QDSSCs). Among them TiO_2 films deposited on Fluorine doped Tin Oxide (FTO) glasses are widely used (Liyanage et al., 2021). However, the unique properties such as wide band gap, low cost, abundance in nature, nontoxicity and also its high chemical and mechanical stability has attracted ZnO also as a photoanode for QDSSCs.

There are many methods utilized to fabricate ZnO thin film on FTO glass such as sol-gel technique (Yin et al., 2013), Electrochemical deposition (ECD) (Liu et al., 2015), hydrothermal synthesis (Qi et al., 2015), spin coating (Troshyn et al., 2012), etc. The ZnO films prepared by various methods show morphologically different nanostructures unique to its own method of preparation. Among the methods mentioned above, ECD has been used in this study which is convenient and cost-effective method to deposit nano structural ZnO films when compared to other cumbersome techniques. Zinc nitrate or zinc acetate is the main precursor used to electrodeposit ZnO films. However, aforementioned ZnO films showed some drawbacks such as non-uniformity, agglomeration of nanoparticles and tendency of flaking off the film after sintering. Therefore, an efficient and reliable method was employed, which contains nitrate and acetate ions in 1:5 ratio in the deposition bath (Transactions & Society, 2017). This technique led to the formation of consistent and uniform smooth film due to the presence of acetate ions in the electrolyte which prevent the nitrogen gas evolution even when the pH is slightly increased (Transactions & Society, 2017). The thin films of ZnO thus prepared are sensitized with CdS QDs deposited by Reverse SILAR method to fabricate QDSSCs using polysulfide as the electrolyte (Jun et al., 2013).

METHODOLOGY

Electrodeposition of ZnO films

FTO glass substrates with 1cm × 2cm size were ultrasonically cleaned in ethanol, acetone, and deionized water for 30 min and dried well. Subsequently, the electrodeposition was carried out for 20 minutes with the three-electrode system using the pre-cleaned FTO glass as the working electrode, a Zinc plate as the counter electrode and Ag/AgCl as the reference electrode. The electrolytic solution used was 0.05 M of $Zn(NO_3)_2.6H2O$ and 0.01 M of

CH_3COONa. The potential and temperature were maintained constant at -0.9 V vs Ag/AgCl and ~ 70℃ respectively. As prepared films were annealed at 350 ℃ for 45 minutes.

Deposition of CdS quantum dots

CdS QDs were deposited on ZnO electrodes by using R.SILAR method. 0.4 M $Cd(NO_3)_2$ and 0.1 M of Na_2S in deionized water were used as Cd^{2+} cationic and S^{2-} anionic precursors respectively. A single Reverse SILAR cycle consisted of two steps. The initial step was to dip the prepared photoanodes in the cationic precursor solution for 2 minutes and successively dipping in distilled water for 1 minute for rinsing. The next step involved dipping in the anionic precursor solution for 2 minutes following 1 minute of rinsing. This was carried out for ten Reverse SILAR cycles which was the optimized number of cycles.

Solar cell assembling

The ZnO photoanodes thus sensitized with CdS having an active area of 1.0 cm^2 was sandwiched with a Pt-coated FTO counter electrode by using a pair of steel clips. The capillary space between Pt-plate and photoanode was filled with sufficient amount of polysulfide electrolyte prepared by mixing 0.5 M Na_2S, 2 M S, and 0.2 M KCl in methanol/water (7 : 3/v : v).

Characterization techniques

The characterization was done for ZnO sensitized with CdS QDs for different number of Reverse SILAR cycles in order to find out their characteristics, which includes the J-V characterization for photovoltaic measurements, Nyquist plots for Electrochemical Impedance Spectroscopic (EIS) measurements and UV-Visible data for finding the absorbance and calculating the band gap energy by using the Tauc plots.

RESULTS AND DISCUSSION

The overall reaction for electrodeposition of ZnO on FTO glass is given by the following equation where two electrons participate in the deposition of a single ZnO molecule. Figure 1 shows the current vs time graph plotted during the time of electrodeposition of ZnO films on FTO glass.

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^-$$

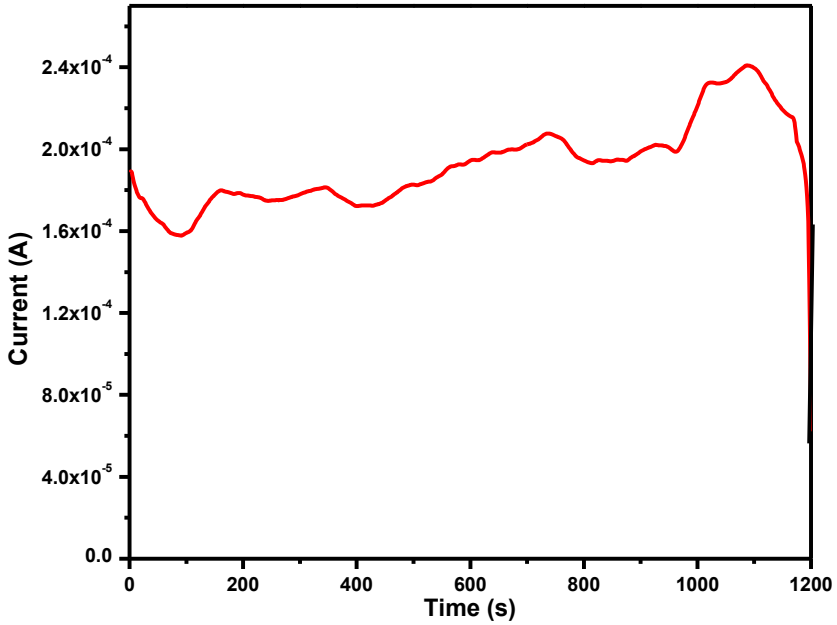

Figure1: Current vs time graph of electrodeposited ZnO film measured under constant potential of -0.9 V vs Ag/AgCl.

The film thickness was calculated by estimating the area under the curve and using the equation (1) given below,

$$T = \frac{It\,(mol\,wt)}{nF\rho A} \quad ----------(1)$$

where $\rho = \frac{mass}{volume}$

$$\rho = \frac{It\,(mol\,wt)}{FAT}$$

$$Volume = AT$$

where, I is the current, t is time, n is the number of electrons, F is the faraday's constant, ρ is the density and A is the area of the film. Accordingly, the film thickness of ZnO film was found to be ~175 nm.

The morphological studies were conducted by analysing the scanning electron microscopic (SEM) images obtained for electrodeposited ZnO. The SEM images clearly indicates that the grains thus produced are nanoparticles.

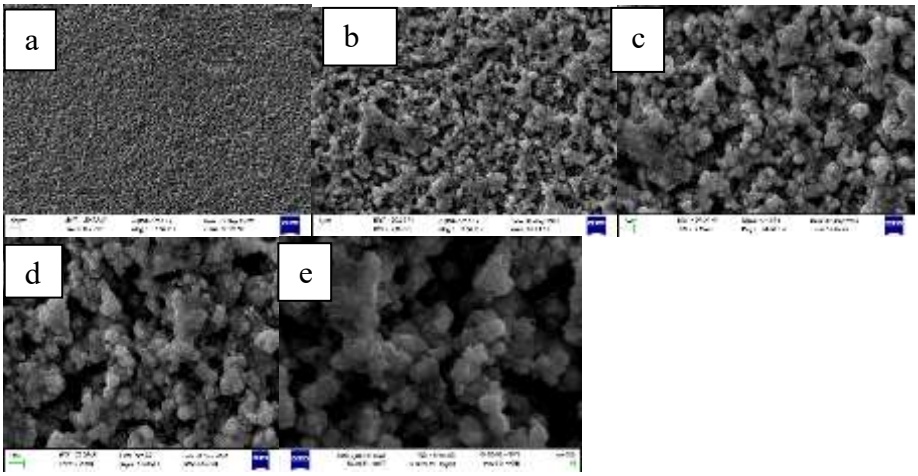

Figure 2: The SEM images obtained for electrodeposited ZnO at different resolutions as (a) 1.00 KX, (b) 5.00 KX, (c) 10.00 KX, (d) 15.00 KX, (e) 25.00 KX.

Figure 3 below shows the J-V Characteristic curves of ZnO films sensitized with CdS for ten consecutive Reverse SILAR cycles.

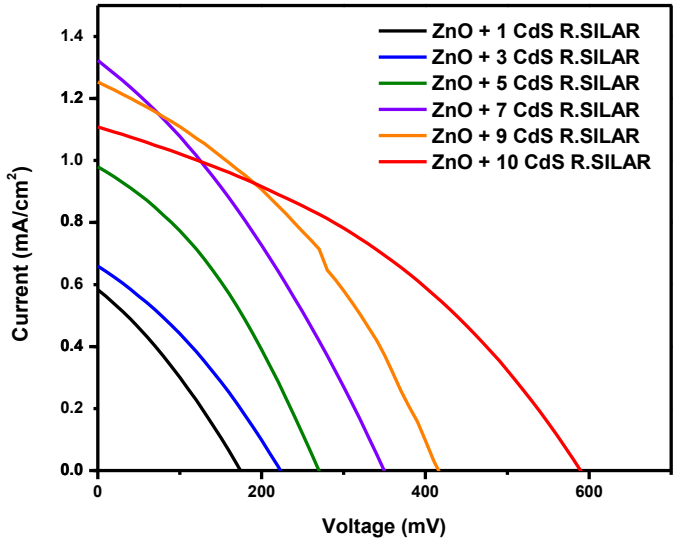

Figure 3: J-V Characteristics curve for ZnO sensitized with CdS QDs for various number of Reverse SILAR cycles.

Table 2 indicates the data obtained from the J-V characteristics curves. The efficiency ,η of QDSSCs was calculated using the equation (2),

$$\eta = (J_{SC}\, V_{OC}\, FF/P_{in}) \times 100\% \quad ----------(2)$$

Here, V_{OC} is the Open Circuit Voltage, J_{SC} is Short-circuit current density, P_{in} is the intensity of incident light and FF is the fill factor, which is calculated by using the following relationship,

$$FF = P_{max}/J_{SC}V_{OC} = I_{max}V_{max}/J_{SC}V_{OC}$$

where, I_{max} and V_{max} are the current and potential at the maximum power point in *J-V* curves of the solar cells respectively.

Table 1: The data obtained for J-V characteristics measurements.

R.SILAR cycles	Voc (mV)	Jsc (mA/cm^{-2})	FF	η (%)
1st	174.30	0.58	0.30	0.03
3rd	222.80	0.66	0.31	0.05
5th	269.80	0.98	0.35	0.09
7th	349.70	1.32	0.32	0.15
9th	416.00	1.25	0.37	0.19
10th	589.50	1.11	0.37	0.24

The above data indicates that there's a gradual increase in V_{OC} with the CdS loading. The J_{SC} follows the same trend up to the seventh Reverse SILAR cycle, while the seventh cycle shows the highest J_{SC} of 1.32 mA/cm^2 and after that there is an anomalous behavior deviating from the general trend. The highest efficiency was shown in the tenth Reverse SILAR cycle which is 0.24 % with the highest FF of 0.37 and V_{OC} of 589.50 mV. The tenth Reverse SILAR cycle gave the highest efficiency but with the further increase in the number of Reverse SILAR cycles the Open Circuit Voltage and short circuit current density tends to decrease gradually. This trend can be described using the UV-Visible spectroscopic data analysis.

Figure 3 shows the UV-Visible spectra for ZnO and ZnO film sensitized with CdS for different Reverse SILAR cycles. According to figure 3 it is evident that absorption of ZnO film is in UV region and absorption of ZnO films loaded with CdS QDs extend to the visible region and further getting red shifted with the increasing number of R.SILAR cycles (Yin et al., 2013).

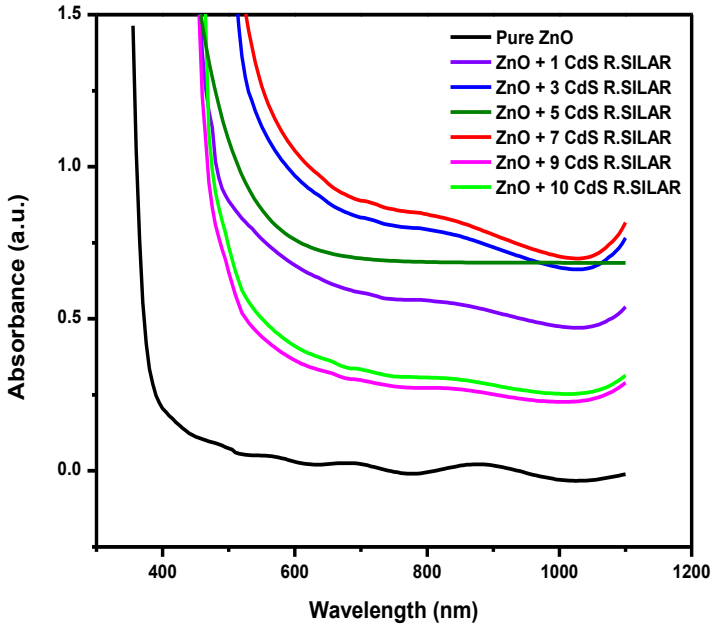

Figure 4: UV-Visible absorption spectra for ZnO sensitized with CdS for various number of Reverse SILAR cycles.

The figure 4 depicts the Tauc plot which is the plot of $(\alpha h\nu)^2$ vs $h\nu$ obtained from the UV-Visible data given in the figure 3. The single slope in the Tauc plot indicates that the films have direct and allowed transitions between conduction and valence band.

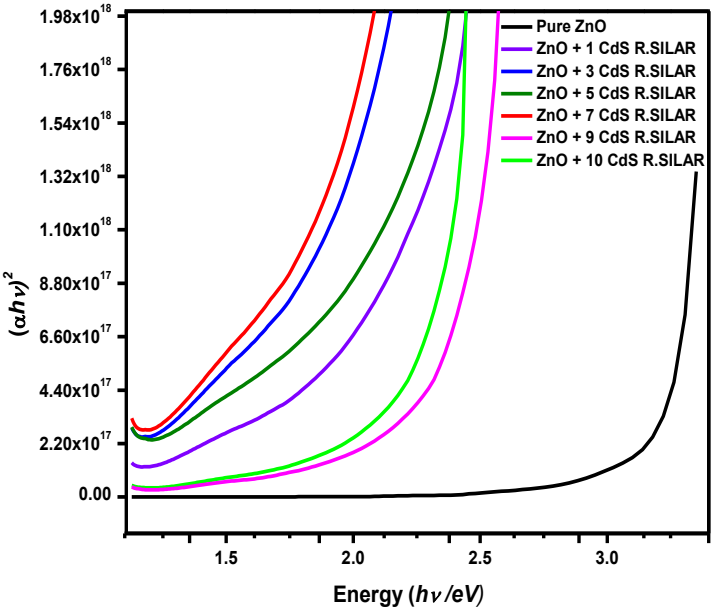

Figure 5: Tauc plots obtained from UV-Visible data with E_g representing bandgap. (a) pure ZnO, E_g =3.19 eV (b) ZnO/CdS 1 cycle, E_g = 2.56 eV (c) ZnO/CdS 3 cycles, E_g = 2.38 eV (d) ZnO/CdS 5 cycles, E_g = 2.58 eV (e) ZnO/CdS 7 cycles, E_g = 2.23 eV (f) ZnO/CdS 9 cycles, E_g =2.59 eV (g) ZnO/CdS 10 cycles, E_g = 2.52 eV.

The relationship between the absorption coefficients α and the photon energy hν for direct allowed transition derived from theory of optical absorption is denoted by the following equation.

$$(\alpha h\nu)^2 = A(h\nu - E_g),$$

where A is a function of the index of refraction and hole/electron effective masses. The direct band gap can be determined by extrapolating the linear portion of the Tauc plots in figure 4 to intersect the energy axis at α = 0 (Viezbicke et al., 2015). It can be seen that a degreasing effect in the bandgap with the number of Reverse SILAR cycles attributed to the increase in the particle size of the CdS. (Yin et al., 2013).

Figure 5 shows the Nyquist plots for pure ZnO films, ZnO films sensitized with seven SILAR cycle of CdS which showed the highest J_{SC} and tenth SILAR cycle which showed the highest efficiency and highest V_{OC}. Table 2 below gives the EIS simulated data corresponding to the above Nyquist plots.

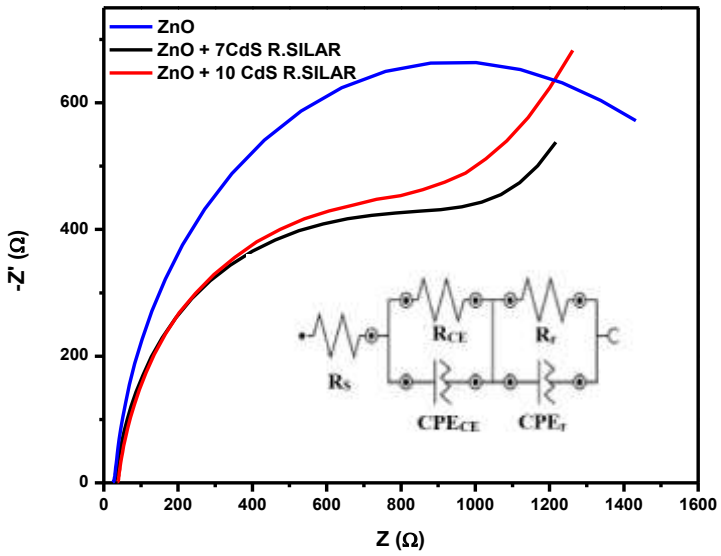

Figure 6: Nyquist plots obtained for pure ZnO film, ZnO films sensitized with seven SILAR cycles and ten SILAR cycles (inset: simulated circuit diagram obtained from the experimental EIS measurements)

Table 2: EIS simulated data obtained from the Nyquist plots given in the figure 5.

No. of Reverse SILAR cycles	***R_S (Ω)***	***R_{CE} (kΩ)***	***R_r (kΩ)***
ZnO	25.80	1.62	0.31
ZnO + 7R.SILAR	29.80	0.72	1.51
ZnO + 10R.SILAR	37.00	0.54	2.55

The basic equivalent circuit (inset in figure 5) for the corresponding Nyquist plot of QDSSCs consists of a series resistance in combination with two pairs of parallelly arranged resistance and a Constant Phase Element (CPE). The R_s value in the circuit denotes the series resistance for the charge transport within the FTO glass and the electrodeposited ZnO photoanode. R_{CE} denotes the charge transfer resistance between the counter electrode (CE) and the electrolyte and R_r represents the charge transfer resistance at the QD sensitized ZnO and electrolyte interface. The Constant Phase Elements (CPE) values, CPE_{CE} and CPEr show the corresponding capacitance related to the R_{CE} and R_r respectively. The *J-V* characteristic results denote that J_{SC} for seven Reverse cycles is correspondingly greater than the tenth Reverse cycles as a consequence of the reduction in R_s value in table 2. It is evident from the above results that the reduction in R_{CE} value of tenth Reverse SILAR cycle which denotes the resistance between the counter electrode and electrolyte is responsible for the increase in V_{OC} of the tenth Reverse SILAR cycle which is consistent with the results of *J-V* characteristics. The increase in the recombination resistance R_r, which implies that there is minimal recombination in tenth Reverse cycle which has a positive effect on cell performance has resulted in increasing the efficiency of the overall cell performance. It is also evident from the R_r values that there is a reduction in recombination with the CdS sensitization when compared to the ZnO.

CONCLUSIONS/RECOMMENDATIONS

This work is based on employing a fast, simple, facile, and economical thin film deposition technique as an alternative to the previous cumbersome techniques of ZnO thin film deposition and analyzing its applicability to the CdS QDSSCs. However, the efficiency of the present work still remains low, therefore it is crucial to optimize several factors so as to increase its overall efficiency. Therefore, it is necessary to focus on the deposition of a seed layer of ZnO prior to the deposition of the required ZnO layer. The ZnO photoanode which has a higher resistivity can be doped to reduce its resistivity thereby increasing its conductivity. Some of the elements that can be used for doping of ZnO film are Al, Mg, Ga etc. ZnS can be deposited as a buffer layer on top of CdS QDs which can prevent the degradation of CdS by reacting with atmospheric air.

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