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Growth of ZnO thin films on Mo substrate for PV applications

W. T. R. S. Fernando, K. M. D. C. Jayathilaka, R. P. Wijesundera and W. Siripala
Department of Physics and Electronics, University of Kelaniya
roshanrsff@gmail.com

ABSTRACT

ZnO is an inexpensive and non-toxic n-type semiconductor having band gap value of 3.4 eV. It absorbs UV radiation of the solar spectrum and allows to pass the long wavelength photons to the absorber martial. Therefore, ZnO is a very good window material for solar cell applications. Among the various ZnO deposition techniques, electrodeposition is an attractive technique because of its simplicity, low cost and possibility of making large area thin films. In this preliminary investigation, photoelectronic properties of ZnO have been optimized by changing the growth parameters. Dark and light J-V measurements in a PEC reveal that high quality photoactive n-type ZnO thin films can be electrodeposited at -1.2 V vs. Ag/AgCl in 0.125 M Zinc Nitrate aqueous solution for 5 min at bath temperature of 60 ^{o}C. ZnO thin films electrodeposited using optimum growth conditions have a doping density of 3.17×10^{16} cm^{-3} and consist of 54.92 % Zn and 35.23% O.

1. INTRODUCTION

Zinc Oxide (ZnO) is a promising semiconducting material for PV applications due to the following unique properties. It is direct bandgap material having the bandgap energy of 3.40 eV [1] and good transparency in the visible and high infrared spectrum. Therefore, ZnO is a very good window material in PV devices. ZnO has very large exciton binding energy (~60 meV) which assures efficient exciton emission at room temperature under very low excitation energy [2]. Conductivity type of the ZnO material is an n-type due to its native or intrinsic defects such as oxygen vacancies and interstitial Zinc atoms [3]. Further, ZnO is very stable having a hexagonal wurtzite crystal structure with lattice parameters a = 3.2458 Å and c = 5.2006 Å (c/a = 1.6022) [1]. Among the various ZnO deposition techniques, electrodeposition is a suitable technique because of its simplicity, low cost and possibility of making large area thin films. Especially, the properties of deposits can be easily adjusted by changing the growth parameters. In this preliminary investigation, the possibility of optimising photoactive properties of ZnO by changing the electrodeposition parameters has been explored. ZnO thin films were characterised by using dark and light current-voltage measurements, SEM, EDS and capacitance-voltage measurements. To the best of our knowledge, n-ZnO have not been electrodeposited on Mo substrate in the ZnO literature.

2. EXPERIMENTAL

ZnO layers on Mo substrate were potentiostatically electrodeposited in a three-electrode electrochemical cell containing Zinc Nitrate ($Zn[NO_3]_2.6H_2O$) aqueous solution. Counter and reference electrodes were Pt plate and Ag/AgCl respectively. Prior to the metal film deposition, Mo substrates were polished with sandpaper, cleaned with detergent, diluted HCl and finally rinsed with distilled water. In order to investigate deposition parameters, linear sweep voltammetry curves were obtained using the computer integrated Gamry series G300 potentiostat at different $Zn(NO_3)_2$ concentrations, temperatures and stirring speeds of the bath. Working electrodes which were used for voltammetric curves had a contact area of 1 mm^2 with

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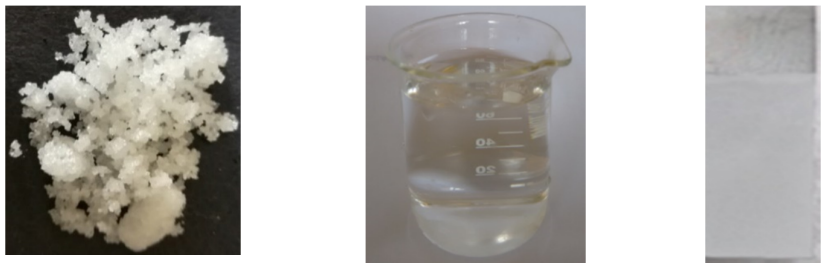
the electrolyte. A set of ZnO thin films on Mo substrates was electrodeposited at -1.2 vs. Ag/AgCl in the electrochemical cell containing aqueous solution of 0.125M $Zn(NO_3)_2.6H_2O$ for different durations (1, 2, 3, 4, 5, 6, 7 min) in different bath temperatures (50, 55, 60, 65, 70, 75 ^oC). All the samples were employed with dark and light I-V measurements in a PEC containing 0.125 M $Zn(NO_3)_2.6H_2O$ in order to study photoactive performance of the samples. Morphology and atomic ratio of the material were studied using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS) respectively. Capacitance–Voltage (C-V) measurements were obtained with Gamry Series G 300 Potentiostat/Galvanostat/ZRA. Capacitance was measured at a frequency of 5 kHz. The physical appearances of $Zn(NO_3)_2.6H_2O$, the deposition bath and the electrodeposited sample are shown in the Figure 1.



(a) (b) (c)

Figure 1: Physical appearances of the (a) $Zn(NO_3)_2.6H_2O$, (b) deposition bath and (c) electrodeposited sample

3. RESULTS AND DISCUSSION

In order to find out deposition parameters, voltammetic curves were obtained at different $Zn(NO_3)_2$ concentrations, temperatures and stirring speeds of the bath. Figure 2 shows voltammetric curve obtain on the Mo substrate surface in a solution having 0.125 M $Zn(NO_3)_2$ concentration. Temperature and pH of the bath were maintained at 60 ˚C, 5.5 (normal pH of the bath). When deposition potential was increased in the cathodic direction, deposition current is almost zero until - 1.1 V vs. Ag/AgCl and started to have a sharp increase within -1.1 to -1.4 V vs. Ag/AgCl. This result reveals that the electrodepostion of ZnO can be possible at the electrodeposition potential domain of -1.1 to -1.4 V vs. Ag/AgCl. A set of samples was prepared at different deposition potentials within the range of -1.1 to -1.4 V vs. Ag/AgCl. The deposition potential of -1.2 V vs. Ag/AgCl has been chosen for deposition of ZnO thin films due to the high quality of the deposits produced at this deposition condition. ZnO deposition in Zinc Nitrate aqueous solution is taking place by the following mechanisms as shown in equation 1, 2 and 3.

$$Zn(NO_3)_2 \longrightarrow Zn^{2+} + 2NO_3^- \ldots\ldots\ldots\ldots \quad (1)$$

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^- \ldots \quad (2)$$

$$Zn^{2+} + 2OH^- \longrightarrow ZnO + H_2O \ldots\ldots \quad (3)$$

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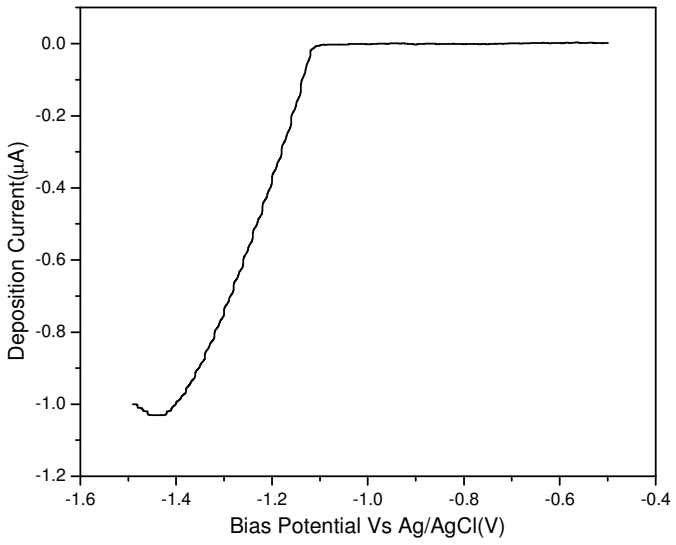

Figure 2: Voltammetric curve obtain on the Mo substrate surface in a solution having 0.125 M $Zn(NO_3)_2$ concentration

Effects of temperature of the deposition bath and deposition duration on the photoactivity of the ZnO thin films in PEC was further explored in order to optimize the photoactive quality of ZnO thin films. In this respect, a set of samples were prepared by electrodeposition at -1.2 V vs. Ag/AgCl in 0.125 M Zinc Nitrate aqueous solution for different durations (1, 2, 3, 4, 5, 6, 7 min) in different bath temperatures (50, 55, 60, 65, 70, 75 ^oC). pH of the bath was kept at 5.5. Samples were employed with J-V characterizations in PEC containing 0.125 M Zinc Nitrate. Figure 3 shows the dark and light J-V characteristics for the samples prepared at different deposition bath temperatures (50, 55, 60, 65, 70 ^oC) with 5 min deposition duration. Open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) values of the samples are shown in the Table 1. Results revealed that both V_{oc} and J_{sc} values show a behaviour of an increment followed by a decrement with increasing bath temperature from 50 to 70 ^oC. Optimum photoactive performance can be obtained when films were grown at 60 ^oC of bath temperature. Then a set of samples was prepared by electrodeposition at -1.2 V vs. Ag/AgCl in 0.125 M Zinc Nitrate aqueous solution for different durations (1, 2, 3, 4, 5, 6, 7 min) at bath temperature of 60 ^oC. Figure 4 shows the dark and light J-V characteristics for the samples prepared at different deposition durations (1, 2, 3, 4, 5, 6, 7 min) at 60 ^oC. V_{oc} and J_{sc} values of the samples are shown in the Table 2. Again, it can be seen that both V_{oc} and J_{sc} values show a behaviour of an increment followed by a decrement with increasing the deposition duration. Results revealed that best photoactivity exhibited when films were deposited for 5 min. Since ZnO film thickness determines the film deposition duration, thickness of the ZnO films increases with deposition duration. Low photoactivity for the films deposited below 5 min is due to the insufficient film thickness to produce optimum photoactivity while the films deposited above

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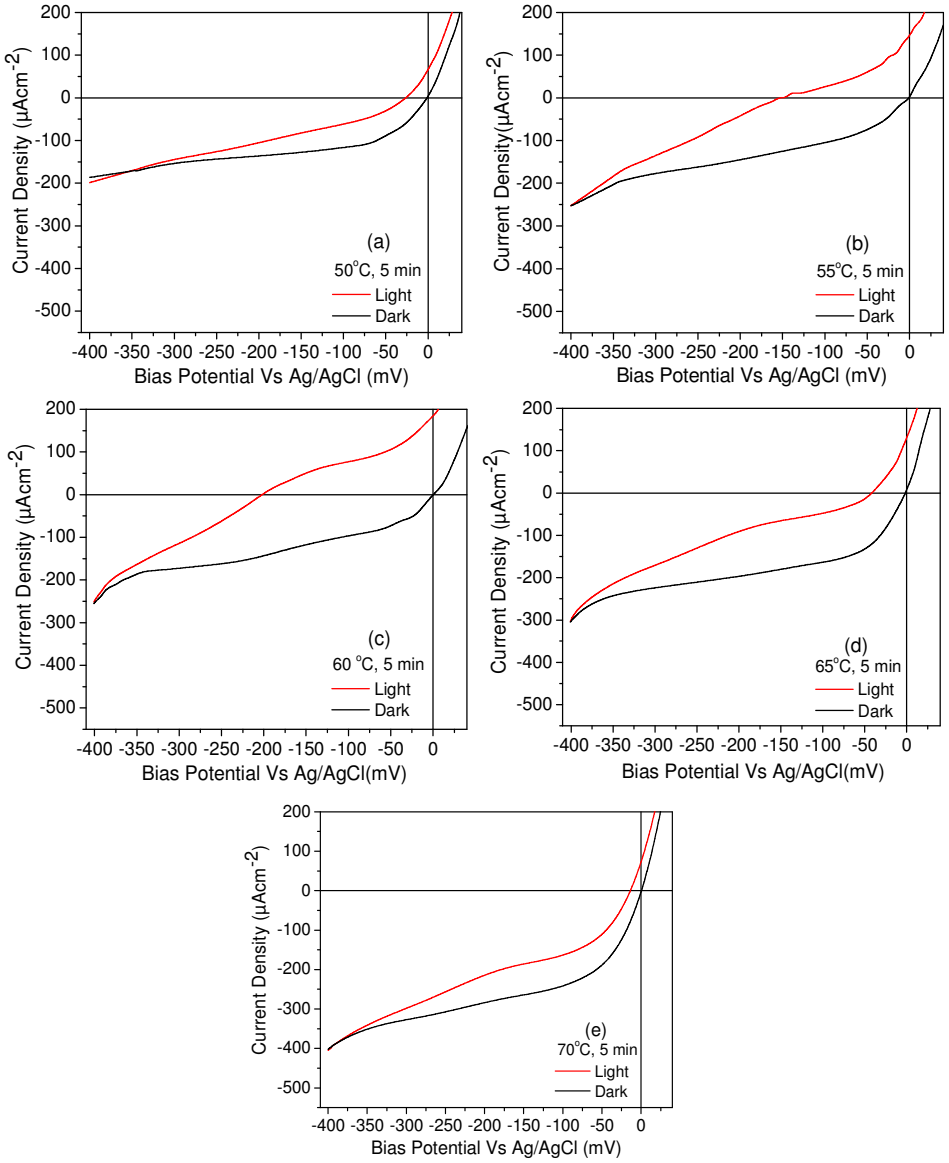

Figure 3: Dark and light current density - voltage characteristics of samples electrodeposited at different temperature a) 50 °C b) 55 °C c) 60 °C d) 65 °C e) 70 °C

5 min is due to the existence of dead layer in the thicker films. Film thickness of ZnO prepared under the optimum conditions was calculated and it was around 4 μm. Further, all the dark and light J-V characteristics produce anodic photocurrents and this anodic photocurrent decreases with increasing cathodic potential vs. Ag/AgCl indicating the formation of the anodic potential barrier between ZnO and electrolyte. These results revealed that the conductivity type of grown ZnO thin films is n-type.

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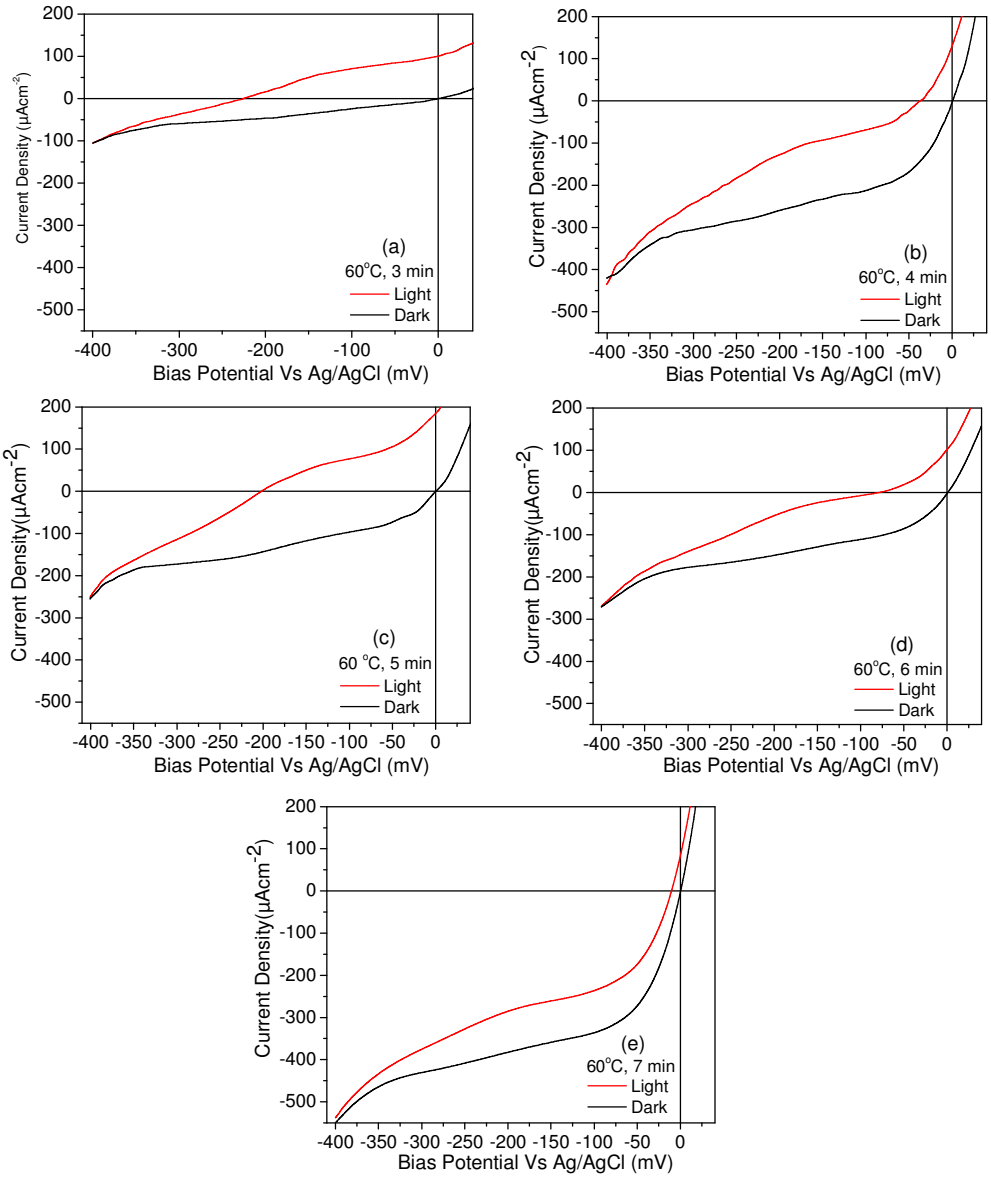

Figure 4: Dark and light current density -voltage characteristics for samples prepared at 60 ^{0}C for different deposition duration a) 3 min, b) 4 min, c) 5 min, d) 6 min, e) 7 min

This investigation revealed that ZnO thin films electrodeposted at -1.2 vs. Ag/AgCl in 0.125 M Zinc Nitrate aqueous solution for 5 min at bath temperature of 60 ^{o}C produced the best photoactive performance for PV applications. pH of the bath should be maintained at 5.5. Figure 5 shows SEM of the ZnO sample grown using optimum growth conditions. SEM shows that ZnO thin films are polycrystalline, uniform and fully covered on the Mo substrate.

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Table 1: V_{OC} and J_{sc} for the samples prepared at different deposition bath temperatures

Deposition temperature(^oC)	V_{OC} (mV)	J_{SC} ($\mu A\ cm^{-2}$)
50	25.2	66.64
55	145.45	145.6
60	200.5	127.97
65	41.95	72.16
70	13.82	63.92

Table 2: V_{oc} and J_{sc} for the samples prepared at 60 ^oC for different durations

Depostion duration(min)	V_{OC} (mV)	J_{SC}($\mu A\ cm^{-2}$)
3	10.64	83.76
4	83.84	100.7
5	200.5	127.97
6	9.8	73.24
7	10	17.99

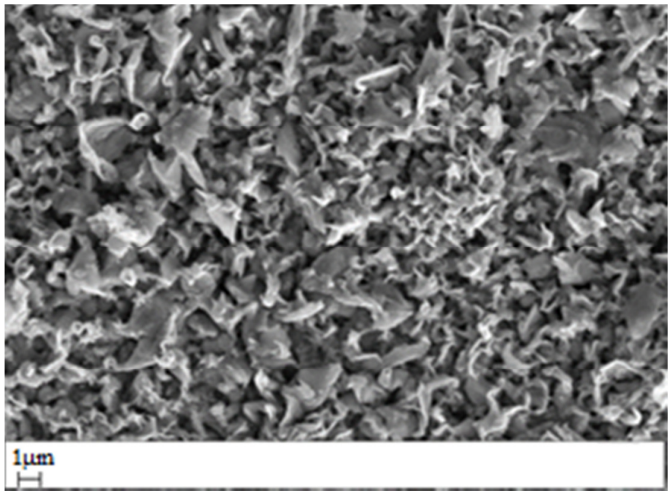

Figure 5: SEM of ZnO thin film electrodeposited using optimum growth conditions

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The elemental composition of electrodeposited ZnO thin films was studied using EDS. Figure 6 shows the EDS spectrum of ZnO thin films. EDX results revealed that the film mainly consists of zinc and oxygen elements. The elemental analysis of the ZnO evidence that ZnO thin film consists of 54.92 % Zn and 35.23% O. However, there is an indication of existence of small amount of carbon but origin of carbon can't be explained at this stage.

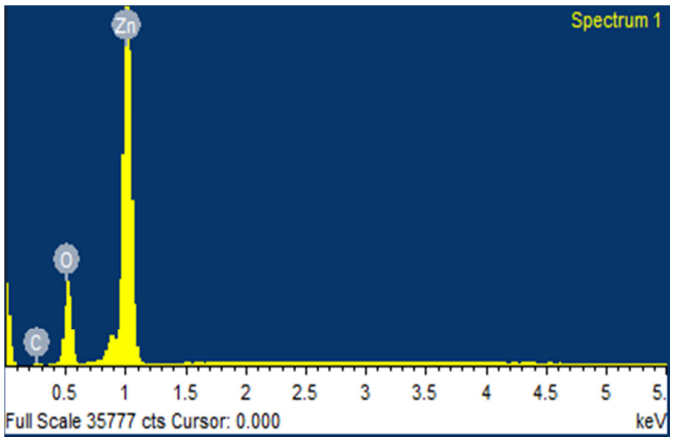

Figure 6 EDS spectrum of ZnO thin films deposited using optimum growth conditions

Mott-Schottky analysis is a standard technique, commonly used to determine both doping density and flat band potential at semiconductor/electrolyte interface. The Mott–Schottky relation is given by equation 4.

$$\frac{1}{C^2} = \frac{2}{q\epsilon\epsilon_0 A^2 N_D}\left(V - V_{FB} - \frac{KT}{q}\right) \qquad (4)$$

In the equation, C is the space charge layer capacitance of the semiconductor, V is the applied potential, V_{fb} is the flat band potential measured with respect to a standard electrode potential, ε is the dielectric constant of the semiconductor, ε_0 is the permittivity of free space, N_D is the donor density, A is the electrode area in contact, *k* is the Boltzmann constant, *q* is the electronic charge, and *T* is the absolute temperature. The intercept of the Mott–Schottky plot gives the extrapolated flat band potential and the gradient of the plot gives the doping density. Figure 7 shows Mott–Schottky plot obtained in a PEC containing 0.125 M Zinc Nitrate aqueous solution for ZnO thin film electrode electrodeposited using optimum growth conditions. Mott–Schottky measurement revels that conductivity type, doping density and flat band potential of the ZnO film are n-type, 3.17×10^{16} cm^{-3} and -0.34 V vs. Ag/AgCl respectively.

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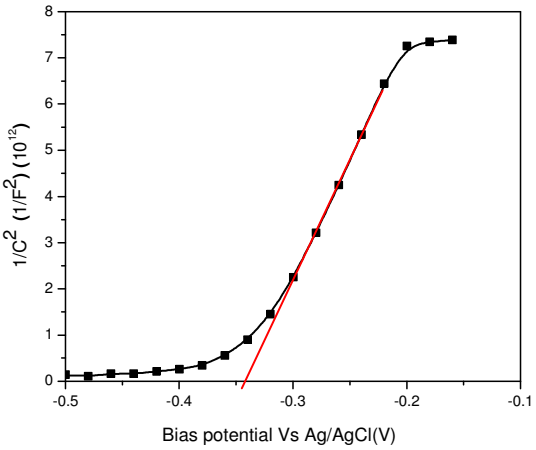

Figure 7: Mott–Schottky plot of ZnO thin film in 0.125 M Zinc Nitrate aqueous solution

4. CONCLUSION

In this study, n–ZnO were electrodeposited on Mo substrate successfully. Possibility of growth of photoactive ZnO thin films has been explored. Results revealed that photoactive n-type ZnO thin films can be electrodeposited at -1.2 V vs. Ag/AgCl in 0.125 M Zinc Nitrate aqueous solution for 5 min at bath temperature of 60 ^{o}C for PV applications. pH of the bath should be maintained at 5.5. SEM shows that ZnO thin films are polycrystalline, uniform and fully covered on the Mo substrate. EDX indicates that the film consists of Zinc and Oxygen elements. The elemental analysis of the ZnO thin film shows existence of 54.92 % Zn and 35.23% O. The flat band potential of ZnO in 0.125 M Zinc Nitrate solution was found to be -0.34 V vs Ag/AgCl and the estimated doping densities was found to be 3.17×10^{16} cm^{-3}.

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