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Deposition of Al-Doped ZnO Thin Films by Spray Pyrolysis for Photoelectrochemical Applications

KEYWORDS: Spray pyrolysis method, Al-doped ZnO, J-V measurements, Power output, Flat-band potential

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ABSTRACT *Al-doped zinc oxide (AZO) thin films have been prepared by spray pyrolysis method. The used spray solution has 0.5 M solution of zinc nitrate hexahydrate and 1 to 10 at.% aluminium chloride. A Photoelectrochemical (PEC) cell with configuration n-AZO ǀ NaOH (1M) ǀ S (1M) + Na2S (1M) ǀ C(graphite) were formed. The PEC cell characterization of the films was carried out by studying current-voltage (I-V) measurements in dark. C-V measurements were taken to determine flat-band potential (Vfb). J-V measurements for a PEC cell in UV light (λ ~ 380 nm) were carried out to determine short circuit current (Isc), open circuit voltage (Voc), fill factor (FF) and power conversion efficiency (η). The junction ideality factor (ηif) and Vfb were found to be 1.2 and 0.1 V, respectively. The measurements of power output characteristic of AZO5 at.% shows Voc, Isc, FF and η were found to be 0.38 V, 38.42 μA, 50.56% and 0.1476 %, respectively*

INTRODUCTION

In the past few decades, nanostructured zinc oxide (ZnO) has attracted extensive attention of researchers and scientists due to the potential applications in optoelectronic devices. It is a most promising material for the future of optoelectronic devices due to its unique and intriguing properties. Among inorganic materials, it plays an important role due to the tailorable, structural, stoichiometrical, chemical and physical properties. It also has wide range of optical, magnetic and electric properties [1]. ZnO is an important II-IV semiconducting material having 3.3 eV direct bandgap energy [2]. It has large exciton binding energy (60 meV) [3]. It exhibits a wide range of nanostructure configurations [4]. Due to such properties, it can be used in verity of applications in fields ranging from optoelectronics [5], optics [6], biotechnology and medicine [7]. In addition to this, it has large photo response, which makes it suitable for UV photo-detector application [8]. ZnO has good thermal stability against the oxidation problem which is major factor affecting the performance of III-V and II-V semiconductors such as GaAs, AlGaAs, InAs, ZnS, etc. [9]. It has abundantly available and non-toxic in nature. Various properties of ZnO can be easily tuneable by adding appropriate dopants. Due to the interesting properties ZnO became a most attractive semiconducting material for the applications in photo-detector [10], gas sensor [11], light emitting diode (LED) [12], solar cell [13], photonic crystal [14], UV-protector filter [15], chemical sensor [16], and photodiode [17]. Recently, change in bandgap of ZnO by introducing various dopants such as Mg^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}, Al^{3+} and In^{3+} has been reported [18]. Tunable bandgap by doping such metal ions make it most suitable material for optical device fabrication. Due to the wide bandgap and high conductivity, it can be used as window layer and transparent conductive oxide for solar cell applications. PEC cell is simple to fabricate and used as an economic chemical rout for trapping solar energy in the form of chemical energy. In the PEC cell, interface between semiconductor electrode and electrolyte is made. The properties of a PEC cell are mainly depends on the interface hence the microstructure of the photoelectrode surface is very important. In this research work, the photoelectrochemical performance of AZO thin films was studied.

EXPERIMENTAL

The spray pyrolysis method is a chemical process in which a mist of fine droplets of desired materials are sprayed onto preheated substrate, where the chemical reaction takes place and the desired solid thin film is formed. The chemical reactants are selected in such a way that only solid film of desired material is formed and other compounds get evaporated at the deposition temperature. The present work demonstrates deposition of Al-doped ZnO thin films by varying concentrations of aluminium onto the ultrasonically cleaned glass substrates. The precursor solution was prepared by dissolving 0.5 M zinc nitrate hexahydrate $[Zn(NO_3)_2.6H_2O)]$ in a mixture (3:1 Vol.) of methanol and de-ionized water. In order to incorporate Al in ZnO thin films, we have used $AlCl_3$ with different concentrations. The substrate temperature was optimized at 400 °C to obtain good quality films. Higher temperature causes loss in transparency of thin film, which limits its optical use [19]. Hence, care has to be taken that temperature does not exceed 400 °C. The oxygen (O_2) gas was used as a carrier gas. The doping concentration of Al into ZnO was varied from 1 to 10 at. %. Before the deposition, glass substrates were washed with hot water. Then dipped in trichloethylene for 5 hr and again washed with double distilled water. The spray rate was maintained at 3 ml/min. After deposition, the films were allowed to cool down at room temperature. Prepared thin films were annealed at 300 °C for 6 hr and then subjected for various characterizations.

The following chemical reactions take place during the synthesis.

$$2Zn(NO_3)_2 6H_2O+O_2\uparrow \rightarrow 2ZnO^*\downarrow+4NO_2\uparrow+2O_2\uparrow+12H_2O$$

$$AlCl_3+ZnO^*+3H_2O \rightarrow Al_2O_3:ZnO\downarrow + 6HCl$$

A PEC solar cell consists of H-shaped glass tube having two arms. One arm of the tube was made from hard glass and another by ordinary test tube. The hard glass arm and ordinary glass arm is having diameter of size 2.7 cm and 1.5 cm, respectively. Both the arms are 7 cm in length and fitted in a copper pot. A window having the dimension of 2 cm × 1.5 cm was made available for illumination (UV).

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The cell can be represented as below,

n-AZO I NaOH (1M) I S (1M) + Na_2S (1M) I $C_{(graphite)}$

Counter electrode was constructed by using a CoS sensitized graphite rod.

The charge transfer mechanism occurring across the electrode electrolyte interface was studied by electrical characterization of the PEC cell. I-V and C-V measurements were carried out to study the built-in potential and power output characterizations under dark and UV illumination. A potentiometer was used to vary the voltage across the junction and current flowing through the junction was measured by current meter. Photoelectrochemical activity of the cell was studied under the illumination of 5 mW/cm^2 (λ=~365 nm). The illumination intensity was measured by Meco Lux meter.

RESULTS AND DISCUSSION

I-V measurements of a PEC cell in dark were carried out at 303 K and shown in **Figure 1.** The PEC cell shows dark voltage and dark current in dark (**Figure 1**). The polarity of the dark voltage was found to be negative, which reveals the n-type conductivity of ZnO. The characteristics are non-symmetrical indicating the formation of rectifying type junction [20]. From the plot of log I vs. V (**Figure 2**) the η_{if} can be determined and it was found to be 1.2. The higher value of ideality factor suggests the dominance of series resistance and it has structural imperfections.

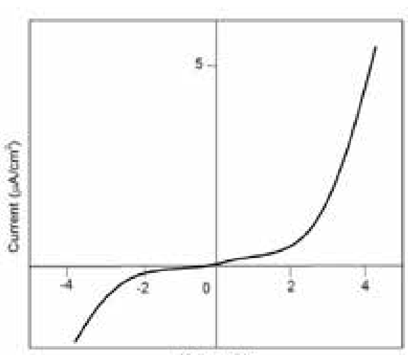
Figure 3 presenting the plot of capacitance (C) vs. applied voltage (V). C-V plot provide the information about the type of conductivity, depletion layer width and V_{fb}. The V_{fb} of a semiconductor gives information of the relative position of the Fermi levels in the photodiode and charge transfer process across the junction. Measured capacitance is the sum of the capacitance due to depletion layer and Helmholtz layer. It is negligible for high ionic concentration.

V_{fb} can be obtained using Mott-Schottky relation,

$$C^{-2} = \left[\frac{2}{q\varepsilon_o N_d}\right]\left[V - V_{fb} - \frac{KT}{q}\right] \qquad (1)$$

where q is the electronic charge, K is the Boltzmann constant, T is the temperature, V_{fb} is flat-band potential. ε_o ε_o is permittivity of vacuum, N_d is the density of free charge carriers.

Intercept of C-V plot on voltage axis determine the V_{fb} value of the junction and it is found to be 0.1 V. It is a potential of electrode at which band bending is zero.



(2)

Figure-1: I-V characteristics of AZO photoelectrode (in dark).

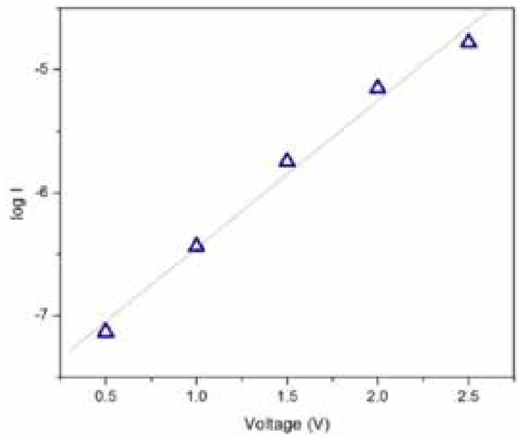


Figure-2: Plot of log I vs. V for AZO photoelectrode.

Figure 4 shows the J-V measurements for a PEC cell under the UV illumination. FF and η was calculated by using equations (2) and (3), respectively.

$$F\ \% = \left[\frac{I_m V_m}{I_g V_g}\right] \times 100 \qquad (2)$$

where symbols have their usual meaning.

(3)

$$\eta_{max} = \left(V_{redox} - V_{fb}\right)\left(\frac{e}{E_g}\right) \qquad (3)$$

where V_{fb} is flat-band potential, V_{redox} is the redox potential and E_g is the energy bandgap.

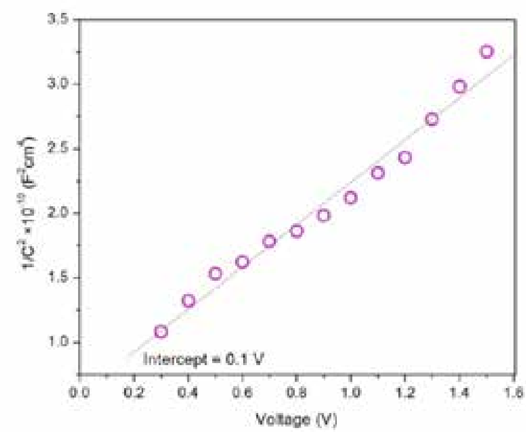


Figure-3: C-V characteristics of AZO photoelectrode.

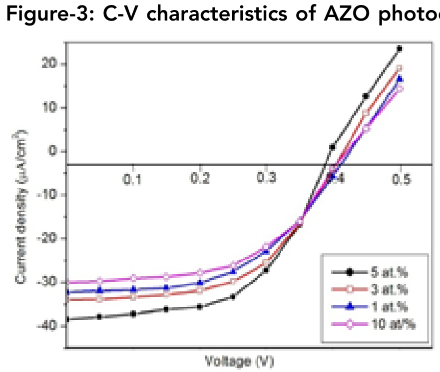


Figure-4: Power output curve for AZO photoelectrode (in UV light).

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Table 1: PEC output parameters obtained from J-V under UV illumination.

Sr. No.	Thin films	J_{sc} (μA/cm²)	V_{oc} (V)	FF %	η %
1	AZO_1	31.75	0.41	49.82	0.1297
2	AZO_3	34.14	0.40	50.29	0.1374
3	AZO_5	38.42	0.38	50.56	0.1476
4	AZO_{10}	30.05	0.40	68.53	0.1647

AZO photoelectrodes can be used to fabricate high sensitive and low cost UV sensors [21]. The PEC output parameters are presented in **Table 1**. The observed PEC parameters J_{sc}, V_{oc}, and FF for AZO_5 thin films are 38.42 μA/cm^2, 0.38 V and 50.56%, respectively. Similarly, the observed PEC parameters for ZnO thin films with different doping content are presented in **Table 1**. The low efficiency is due to the high series resistance. The efficiency is also reduced due to the photogenerated electrons in n-type materials recombine with holes or leak out into the electrolyte. Better performance is observed for $AZO_{5at.\%}$. The $AZO_{10at.\%}$ photoelectrode shows highest efficiency of about 0.1647%. I_{sc} linearly increases up to 5 at.% Al content. It could be due to the doping content decreases the nanoparticle size, hence surface area of the electrode increases.

CONCLUSIONS

AZO photoelectrodes are successfully deposited using spray pyrolysis method. Various photovoltaic parameters of the fabricated PEC cell were obtained. The fill factors, Ideality factor and power conversion efficiency of the $AZO_{5\,at.\%}$ PEC cell were, 50.56%, 1.2 and 0.1476%, respectively. AZO thin film photoelectrodes can be used to fabricate semiconductor-liquid junction solar cells due to its better PEC response. The improved values of FF and V_{oc} can enhance the efficiency of semiconductor-liquid solar cells.

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