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Growth of pure and doped ZnO thin films for solar cell applications

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ABSTRACT

Thin films form a fair share in the ever growing solar cell research and also in the market. One of the most versatile materials grown as thin films today are from derivatives of pure and doped Zinc Oxide. A combination of dip coating and electrodeposition is a powerful tool in order to achieve good quality thin films. The main advantage is that the basic precursor which is Indium Tin Oxide (ITO) can be safely avoided since its procurement enhances the cost and the availability if selective nowadays. The initial run is made by dip coating process where a supersaturated solution of the material to be coated is taken in a beaker. A glass substrate is dipped into the supersaturated solution and dried for an optimal amount of time. Multi layered thin film coatings are formed and dried consequently before each individual dipping to enhance uniformity. Pure thin films of Zinc Oxide are initially grown with thickness varying so as to reach the optimal solar cell quality. Zinc Oxide is doped with dopants like Chromium, Cadmium, Magnesium and Manganese with dopant levels ranging from 0.01 to 0.10 per wt% in order to investigate an appreciation in the quality of the solar cells. These pure and doped substrates of ZnO thin films are investigated for their structural and optical properties [1-3].

Keywords: ZnO, solar cells, thin films, vacuum coating, PVD, doped solar cells.

INTRODUCTION

Electro-deposition is a versatile and inexpensive technique for the synthesis of materials from solutes. The technique, which is based on controlled current or controlled potential electrochemical deposition on an electrode from a solution containing the appropriate compounds, is therefore frequently used for the deposition of a wide range of compounds including metals, semiconductors, mixed metal oxides and magnetic nanolayered structures [4,5]. The electro-deposition techniques are particularly well-suited for the deposition of single elements but it is also possible to carry out simultaneous depositions of several elements and syntheses of well-defined alternating layers of metals and oxides with thicknesses down to a few nano meters [6]. Since the microstructure of the deposited material can be controlled by adjusting parameters such as the deposition potential or the current density, the composition of the electrolyte, or by employing various pulsed deposition techniques, electrochemical techniques can offer a wide range of possibilities for tailor-made syntheses of materials with different properties. A particularly interesting electro-deposition approach employed by us involves rapid local electrochemical modifications of the composition of the electrolyte (e.g. pH) in the vicinity of the electrode [7]. Electrochemical techniques such as, cyclic voltammetry, chrono-amperometry and chrono-potentiometry are also frequently used to study the electrochemical properties of the obtained materials [8].

MATERIALS AND METHODS

ZnO is a well-known II–VI semiconductor having a direct band gap in the ultraviolet range (3.37 eV) and a large exciton binding energy (60 meV), which makes it very prospective due to its extensive physical properties. With the help of the discovery of carbon nanotubes, nanostructures and nanomaterials have attracted great interest in the recent years [9]. Zinc oxide nanostructures have become attractive building blocks for devices in light-emitting diodes, solar cells, sensors, field emitters, and piezoelectric devices in recent years [10]. It has been shown that band edge, exciton energies, and UV luminescence of ZnO nanostructures are affected by crystallite size and crystal morphology. In order to exploit this broad range of applications, it is desirable to tailor the electronic properties of ZnO [11]. Various techniques have been used to prepare ZnO coatings, such as arc discharge, laser vaporization, pyrolysis, physical vapor deposition, chemical vapor deposition (CVD), and soft chemical method. Generally, ZnO coatings are prepared by high-temperature solidification methods from the vapor-phase elements in vacuum condition [12]. Usually, catalysts such as Au and Co have also been introduced into the synthesis process to orient ZnO growth.

Electro-deposition technique is now emerging as an important method to prepare semiconductor thin films. Preparation of oxide films by electro-deposition from aqueous solution presents several advantages over other techniques conventionally and currently available. This method presents interesting characteristics for large-area, low-cost, and generally low-temperature and soft processing of materials. It has been reported that a wurtzite ZnO film with high optical transparency can be prepared by cathodal deposition from a simple zinc nitrate [Zn(NO3)2] aqueous solution [13].In the present work, the potentiostatic method was chosen to obtain the ZnO nanorod films on several kinds of substrates. The influence of growth conditions such as deposition potential and concentration of constituents of the bath on the morphology of reaction products and composition was investigated. For Glass substrates an additional procedure of dip coating was done prior to electro-deposition as it was found to be non-wetting during electro-deposition. It was observed that dip coating readily formed thin films on glass substrates.

Fig.1: Electrodeposited ZnO on Aluminum foil

All chemicals were from commercial sources, AR grade and they were used without further purification. All solutions in this study were prepared from double distilled water. The working substrates used in the experiment are Zinc, Aluminium and Glass. They were cleaned in detergent, double distilled water or ethanol prior to the film deposition. Then the films were scrubbed with fine quality sand paper for 10 min and then cleaned as described above. In a typical procedure, the electro-deposition was carried out in which the working substrates were used as the working electrode, saturated calomel electrode (SCE) serving as reference electrode, and the Zinc or Aluminium slice working as the count electrode, which was used to maintain a constant Zn ion concentration during the electro-deposition. The ZnO thin films were cathodically electrodeposited from baths containing different molar ratios. The ZnO films were electrodeposited under constant optimal potentiostatic conditions. An electro deposition apparatus was fabricated with glass 12cm x 12cm x 14cm and stainless steel electrodes were fixed at one end. The other end is the deposition substrate on which anodic or cathodic deposition is carried out. A variable DC power supply source (0-12V) is assigned and deposition organized in various substrates like Aluminum foil, Aluminum metal sheet and Zinc metal sheet.

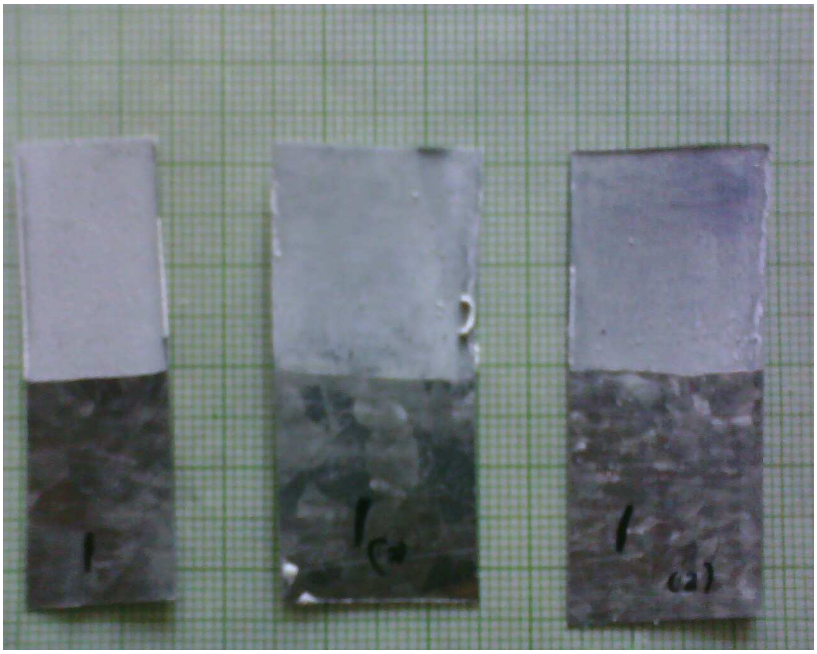

Fig 2: ZnO electro-deposition (1 minute) on Aluminum Substrate

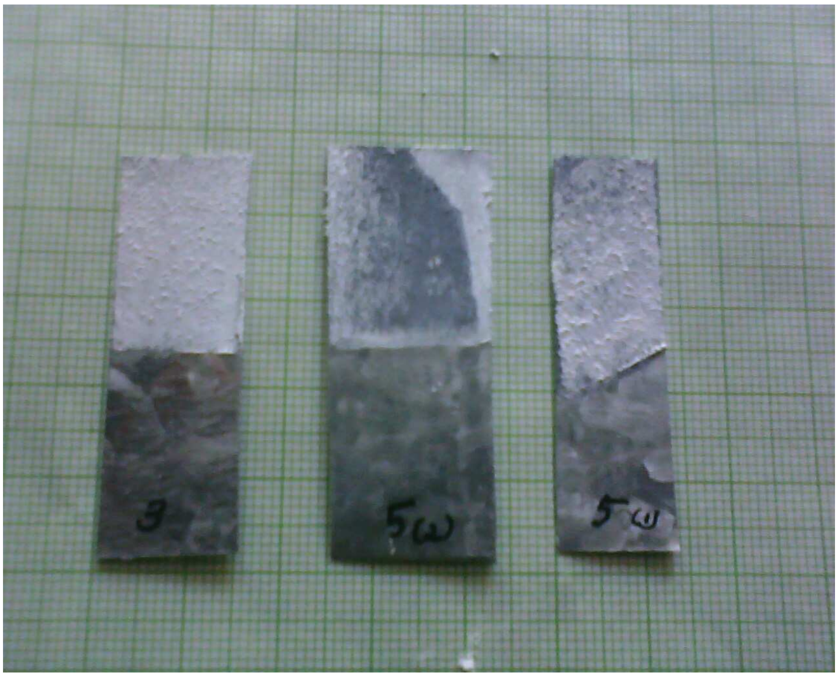

Fig.3: ZnO electro-deposition (5 minutes) on Zinc plates

1. X-Ray Diffraction (XRD Analysis)

Powder XRD provides detailed information on the crystallographic structure and physical properties of materials and thin films. The sample is irradiated with a beam of monochromatic x-rays over a variable incident angle range. Interaction with atoms in the sample results in diffracted x-rays when the Bragg equation is satisfied. Resulting spectra are characteristic of chemical composition and phase. Powder X-Ray diffraction was carried out using a Rich-Siefert diffractogram where the crushed and powdered sample was analysed using X-rays from a CuKα (λ=1.54059 Å) radiation) radiation. The observed peaks were compared with ICDD file no. 35-1482 and hexagonal *ZnO* (wurtzite, *JCPDS* 36-1451. The lattice constants for hexagonal ZnO film are reported in JCPDS standard data a = 3.24982 Å and c = 5.20661 Å. The calculated values of the lattice constants a and c were found to be 3.21907 Å and 5.15760 Å, respectively. XRD diffraction peaks belonging to (100), (002) and (101) planes were observed in all the ZnO films. The XRD patterns of all the samples indicated enhanced intensities for the peaks corresponding to (002) plane, indicating preferential orientation along the c-axis

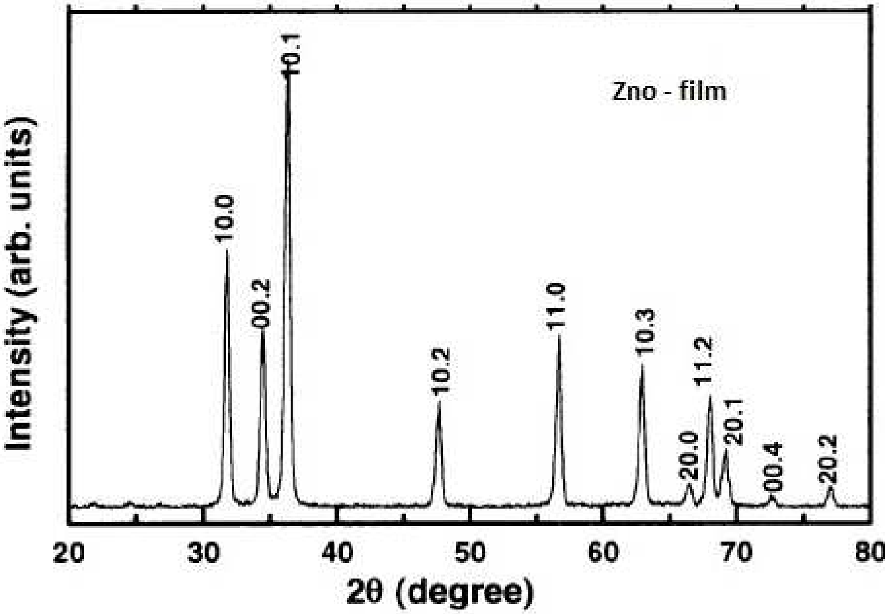

Fig. 4. XRD pattern of ZnO

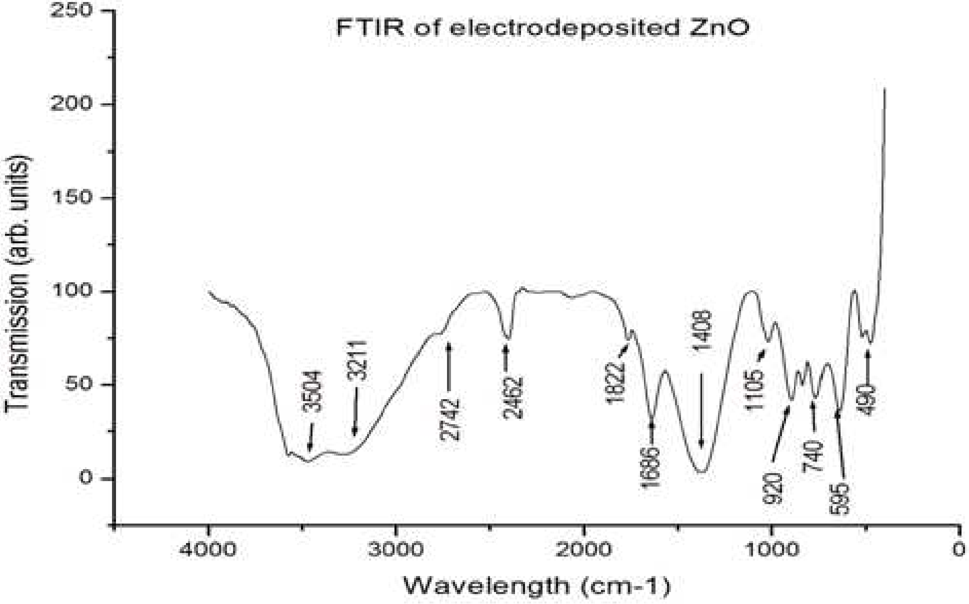

Fig. 5: FTIR investigations on Electrodeposited ZnO

2. Characterization of ZnO by FTIR:

Fig.5, shows the FT-IR spectra of ZnO thin film, taken with a Perkin Elmer Lambda Spectrophotometer between 400-4000 cm^{-1} where the following were observed. The absorption bands near 3504 cm^{-1} represented O-H mode, those at 3211 cm^{-1} are C-H mode, and 1408 cm^{-1} are the C=O stretching mode. As the temperature increases, the organic band at 1686 cm^{-1} is removed, but the bands arising from the absorption of atmospheric CO2 on the metallic cations at 2462 cm^{-1} and bonding between Zn-O (595cm^{-1}, 740 cm^{-1}) are clearly represented [14].

3. UV-Vis spectroscopical investigations:

The UV-Vis spectral analysis (fig.6, fig.7) was done using a Perkin Elmer spectrophotometer on the material of the thin film which showed that there was a good deal of transmission in the absorption spectra. This seems to depict that the layer formed is of crystalline nature and also transparent [15]. The Transmission curve was analysed and found that around 28% absorption against 72% transmission achieved for the electrodeposited sample.

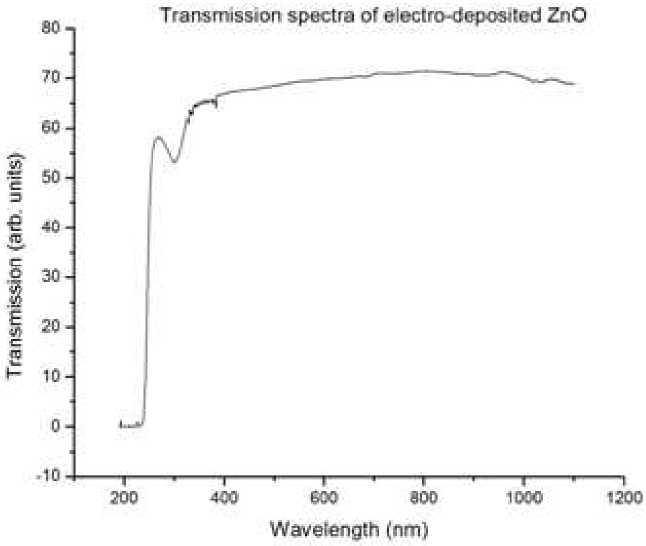

Fig.6: Transmission spectra of ZnO

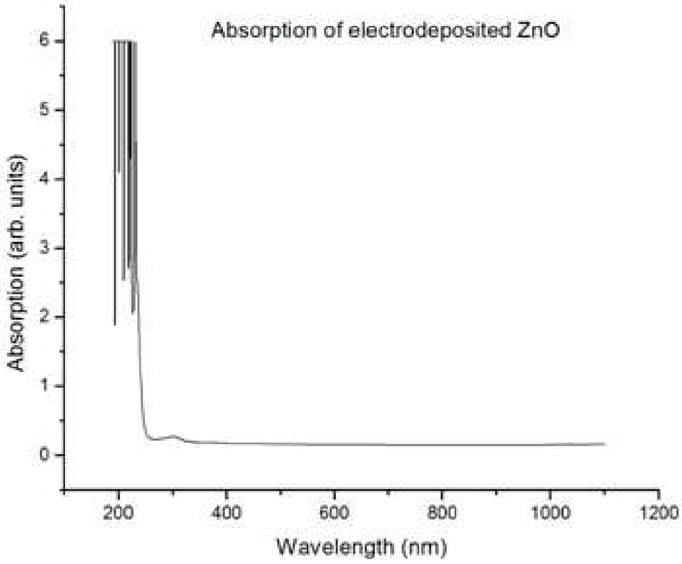

Fig.7: Absorption spectra of ZnO

4. Photoconductivity Tests

Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation such as visible light, ultraviolet light, infrared light, or gamma radiation. When light is absorbed by a material such as a semiconductor, the number of free electrons and electron holes changes and raises its electrical conductivity [16]. To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap, or to excite the impurities within the band gap. When a bias voltage and a load resistor are used in series with the semiconductor, a voltage drop across the load resistors can be measured when the change in electrical conductivity of the material varies the current flowing through the circuit. (Fig.8)

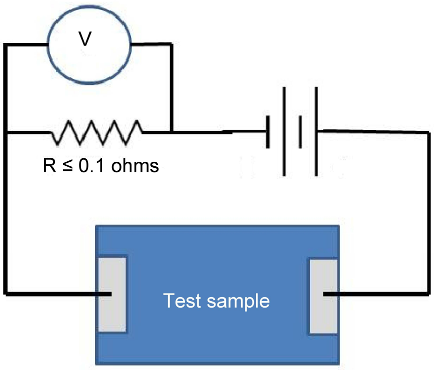

Fig.8: Photoconductivity circuit

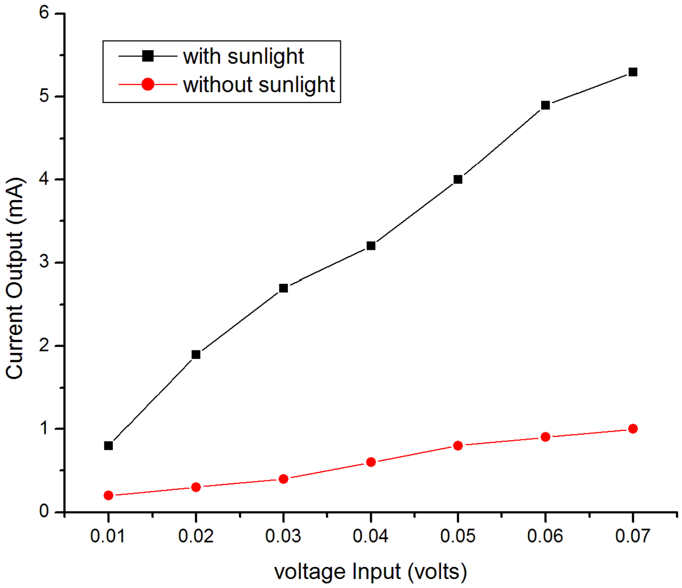

Fig.9: Photoconductivity on ZnO sample (coated for 5 minutes)

Photo-conductivity [17] of thickly coated ZnO sample with coating time 5 min was taken using a simple photoconductive circuit. The variation in the output for the dark current and the photo-current was very large order (Fig.9). For an initial input value of 0.01 V the variation was smaller than 0.5 mA whereas for 0.07V the variation was approximately 4mA

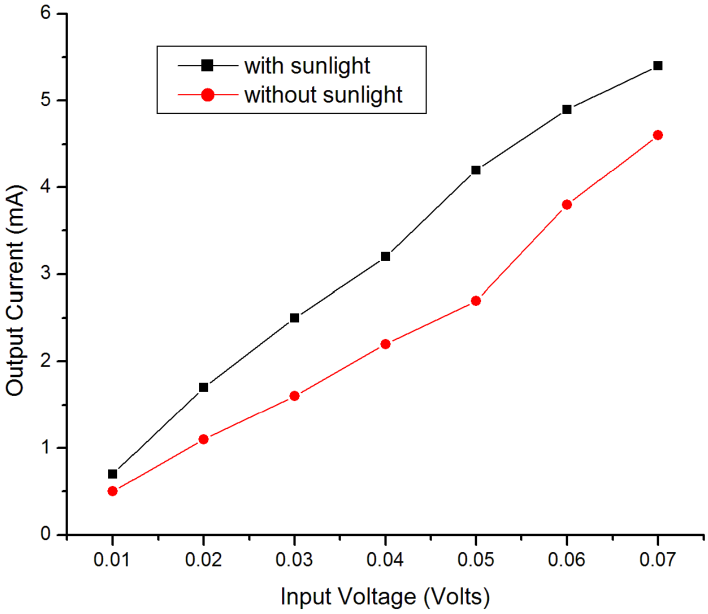

Fig.10: Photoconductivity of ZnO thin film (coated for 1 minute)

Similarly the photocurrent and dark current values for ZnO samples electrodeposited were experimented. It was found that for an initial input of 0.01V the photo current output increase was around 0.2mA whereas for a final input of 0.07V the photo current output increase with respect to dark current was around 1mA (Fig.10). This infers that the coatings with larger thicknesses (coating time 5 minutes) were able to generate more photo current than the thinner coatings (coating time 1 minute).

RESULTS AND DISCUSSION

In electrodeposition of thin films, there are mainly two parts: solution chemistry process and electrochemistry process, respectively. First, precursor dissolved in the water formed electrolyte, which contains mass of zinc cation and other anion [17]. Secondly, the basic reaction of oxygen reduction on the surface of substrates leads to hydroxide ions formation, then the zinc hydroxide, generated by OH ion absorbed on or near the substrate surfaces and Zn ion in the electrolytes, which is transformed into Zinc oxide at room temperature [18].

CONCLUSION

Zinc Oxide thin films [19-22] are formed by electrodeposition of Zinc Nitrate. Their structural and optical characteristics [23] were confirmed using UV-VIS absorption and emission [24]. The FTIR of ZnO was also investigated [25]. Their photoconductive performance was verified which makes them promising candidates for Solar Cells.

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