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Fabrication of Low Cost Photocell based Nanostructured ZnO Thin Films on ITO Substrates by Chemical Bath Deposition Method

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Abstract

In the present study, we have synthesized ZnO thin films by simple, low cost chemical bath deposition method on an ITO substrate using zinc sulfate and thiourea precursors. The structure, morphological, optical and electrical properties of the deposited thin films were investigated by X-ray diffraction, Field emission scanning electron microscopy, UV-visible spectrometer and I-V measurement system. X-ray diffraction study reveals that, all the films were polycrystalline with the hexagonal Wurtzite structure with orientation (002) plane. Calculated lattice parameters were in good agreement with the standard data (80-0075). The grain size of the film was found to be 41.31 nm. Field emission scanning electron micrographs result showed that, the surface of film was composed of nanorods. The elemental analysis showed that, the material was only composed of zinc (Zn) and oxygen (O). A UV–Visible absorbance spectrum indicates that, direct allowed transition with bandgap of about 2.42 eV was observed. I-V measurement curve showed ohmic nature of the sample in dark condition and responds to the light illumination that indicates photocell properties. Under illumination of 100W light, decrease of resistance was observed from 56.7KΩ to 49.1 KΩ. The change in current and calculated photosensitivity was found to be 2.3 μA and 27.51% respectively.

Keywords: Nanostructured ZnO thin films, chemical bath deposition, photo-cell, etc.

1. Introduction

In recent years, nanostructured ZnO has made remarkable attention because of its low cost, radiation hardness, high optical absorption in UV range, non-toxicity, high-temperature operation capability, environmental compatibility, high transparency and a low resistivity [1,2]. The ZnO has large bandgap energy of 3.37eV and excitation binding energy of 60 meV corresponding to intermediate region in UV and visible light [3]. Zinc oxide is an inexpensive material can be fabricated through number of techniques, producing a diverse range of morphology including nanorods, nanoflowers, nanotubes, nanoneedles, nanoleafs, nanosheets, etc. [4]. Also, the nanorods of ZnO have the significant benefit of a large surface-to-volume ratio. Hence, they are useful for capable of fabricating electronic and optoelectronic devices such as solar cell, ultraviolet photo-detector, gas sensors, photo-electrochemical (PEC) cells, photocatalytic and biological sensors, thin film transistors, LED (light emitting diodes), surface acoustic wave and energy harvesting devices [5-17].

A photocell can be used in photovoltaic or photoconductive modes. Photocells are small in size and inexpensive. Photocell can detect all types of lights in all conditions, viz. moonlight, sunlight lasers, fire, neon, fluorescent and so on.

Growth of ZnO nanorods can be achieved by different deposition techniques, viz. successive ionic layer adsorption and reaction (SILAR) method [18], RF magnetron sputtering [19], reactive sputtering [20], molecular beam epitaxy (MBE) [21], pulsed laser deposition (PLD) [22], etc. Among these methods, chemical bath deposition technique is used to deposit ZnO thin film because of simple, low cost and does not need sophisticated instrumentation. It is applicable for large area deposition and uses a variety of conducting and non-conducting substrates. Also, in this method, growth of the film can be controlled by optimizing various parameters such as, changing the composition of precursor's solution, changing the bath temperature, variation of pH of the solution and deposition time. In the present work, we have deposited nanostructured zinc oxide thin films by a chemical bath deposition method for photocell applications. The film is characterized by structural, morphological, optical and electrical properties.

2. Experimental details

2.1. Method of preparation

Substrate cleaning plays an important role in the deposition of various types of thin films. Extremely clean substrates are required for avoiding the problems of non-uniformity and poor adhesion. Synthesis of zinc oxide thin films on an ITO substrates was carried out by the chemical bath deposition method. In the synthesis of ZnO, first of all 10 ml, 0.15M of zinc sulfate solution was taken in a 50 ml glass beaker. Under continuous stirring, 0.6 M thiourea solution (2.5 ml) was added slowly. Initially, the solution was milky turbid due to the formation of zinc-thiourea complex. After completing the reaction between thiourea and zinc ions, the ammonia solution was added to it slowly under continuous stirring. Addition of excess ammonia solution led to the dissolution of turbidity and made the solution clear and transparent. Then 17 ml of de-ionized water was added to make the final solution of 50 ml volume. The pH of the final bath solution was about 9.5. Pre-cleaned glass and ITO substrates were immersed and kept vertical in the beaker. The beaker was kept in constant temperature water bath and the bath was allowed to stand for 60 minutes at 80^{o}C

temperature. Thereafter, substrates coated with ZnO were removed, rinsed with de-ionized water and allowed air drying. The white color uniform films were obtained. Then, prepared films were annealed at 400°C in a muffle furnace for one hour.

Crystalline properties, the surface morphology, chemical composition, and optical properties of the nanostructured ZnO films were analyzed by X- ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS) and UV-VIS spectrometer. The photosensitivity property of annealed ZnO films deposited on ITO coated glass substrates was studied by using I–V characteristics in the dark and under illumination conditions (visible spectra) using Keithley meter.

3. Results and Discussions

3.1. Structural studies

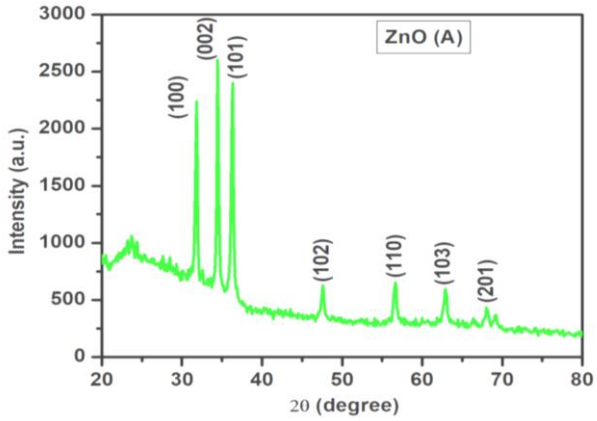

Fig. 1 (b) XRD patterns of ZnO thin film

XRD pattern of ZnO film was observed at 31.81º, 34.40º, 36.23º, 47.47º, 56.79º, 62.84º and 68.12º corresponding to (100), (002), (101), (102), (110), (103) and (201) planes respectively, which belongs to hexagonal crystal structure with lattice parameters of a = 0.3245 nm and c = 0.5209 nm and coincide the peak with JCPDS data (80-0075, a = 0.3253 nm and c = 0.5209 nm).

The lattice parameters of the film “a” and “c” were calculated using the equation,

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}$$

Where, “d” is the inter-planar spacing obtained from Bragg’s law and h, k and l are the Miller indices denoting the planes.

The average crystallite size has been calculated by using Scherer’s formula [23],

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where, k is constant (0.94), λ is the wavelength of X ray radiation (1.54 Å), β is the angular width of the peak at FWHM and θ is Bragg’s angle. The average grain size of ZnO films was found to be 41.31 nm. Table 1 shows the observed and standard 2θ and ‘d’ values, crystalline size and dislocation density for all planes. Table 2 shows calculated lattice parameters a and c were in very good agreement with those of reported values.

The dislocation density for all the samples was determined using equations [24],

$$\delta = \frac{1}{D^2}$$

The average dislocation line density of ZnO thin film was found to be 6.2788 x 10^{14} $(nm)^{-2}$.

Table 1: Structural parameters of ZnO thin film

2θ		d values (Å)		Crystallite Size (nm)	Dislocation density x 10^{15}
observed	Standard	observed	Standard		
31.81	31.72	2.8107	2.8179	43.8534	5.1999
34.40	34.40	2.6048	2.6049	49.4415	4.0909
36.23	36.21	2.4773	2.4786	44.9686	4.9452
47.47	47.94	1.9136	1.9128	33.5303	8.8946
56.79	56.51	1.6197	1.6269	34.7872	8.2634

Table 2: Lattice parameters of the ZnO thin film

a (nm)		c (nm)	
Calculated	Standared	Calculated	Standared
0.3245	0.3253	0.5209	0.5209

3.2. Morphological investigation

The morphological investigation of the film was carried out by field emission scanning electron microscopy. Fig. 2 (a) and (b) shows the field emission scanning electron microscope images of ZnO film with different magnifications. FE-SEM result showed that, different size of nanorods was observed. The film was continuous, dense, crack less, uniform grain distribution homogeneous which covers an entire area.

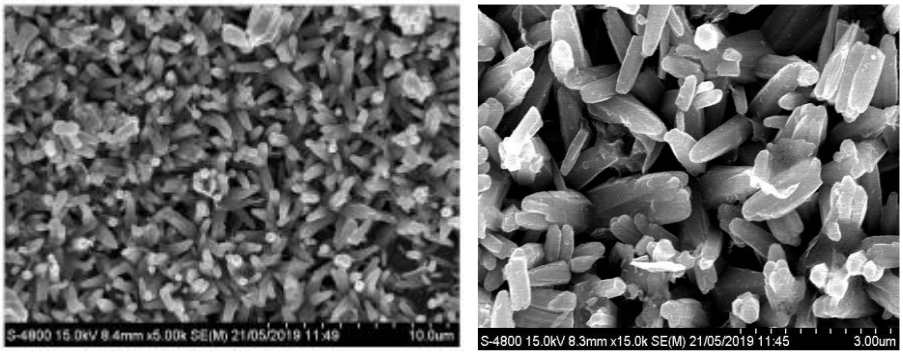

Fig. 2 (a)-(b) FE-SEM images of ZnO thin film

3.3 Compositional studies

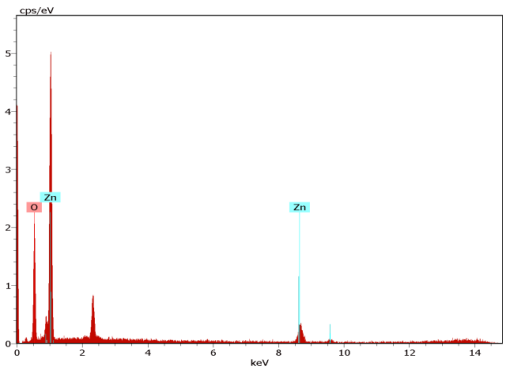

Fig. 3: EDAX Pattern of ZnO film

An elementary compositional study was carried to obtain the elementary composition in ZnO thin film using energy dispersive X-ray spectrum (EDS). An elemental analysis shows that, the material was only composed of zinc (Zn) and oxygen (O). The atomic percentage of Zn and O atoms was found to be 33.05 and 66.95 respectively. Fig. 3 shows the elementary analysis result. The film was oxygen rich as compared to zinc.

3.4 Optical studies

To study the optical properties of ZnO thin film, absorbance spectroscopy in the UV-visible wavelengths is widely used. Figure 4 show the variation in absorption spectra of ZnO thin films within the wavelength range 200-800 nm. The optical absorption spectra studies revealed that, characteristics ZnO band edge absorption at 345 to 351 nm in normalized UV-VIS absorbance.

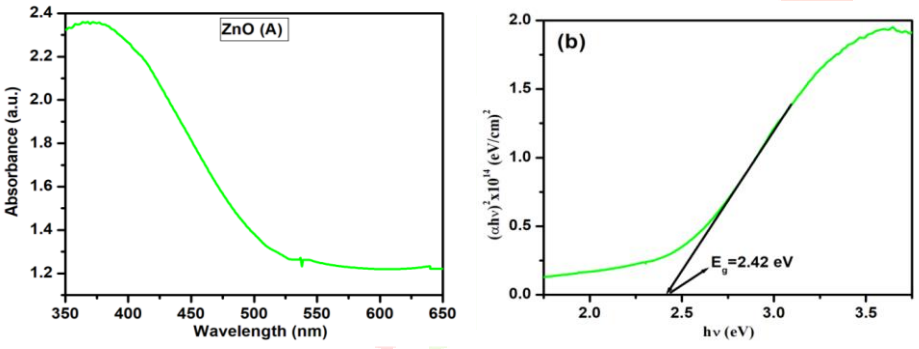

Fig. 4(a) : absorbance spectra and **(b)** Plot of $(\alpha h\nu)^2$ Vs hν of ZnO film

The optical bandgap energy of ZnO thin film was found out by a graph plotted between photon energy and $(\alpha h\upsilon)^2$ shown in Fig 4(b) and has been calculated using the Tauc's relation [25].

$$\alpha h\upsilon = A(h\upsilon - E_g)^n$$

Where α is the absorption coefficient, $h\upsilon$ is the photon energy, Eg the bandgap energy. 'n' is equal to 2 for indirect and ½ for direct band semiconductor respectively [26, 27].

The optical bandgap energy of the ZnO film was found to be 2.42 eV. Due to the thermal stress effect produced in films, optical bandgap of ZnO thin film is less than the reported value [28].

3.5. Photosensitivity

The photo-sensing performance of ZnO nanostructured thin film was studied by I-V system interfaced with the computer in dark and illumination of light (100W). I-V measurements were performed by changing the bias voltage from -0.6V to +0.6V. In dark condition, ZnO indicates ohmic nature as the graph

passes through the origin which confirms the semiconducting nature of the film. As the illumination of light, there is improvement in current of film which is due to the incident photons. Incident photons increases charge carrier concentration in the material which contributes to increase in current. The I-V curve is shown in figure 5. Change in current was calculated from the I-V curve which was found to be 2.3 μA. Resistance of the film from dark to light condition was calculated and found to be 57.7 KΩ to 49.1 KΩ respectively. Photosensitivity of deposited ZnO material can be calculated by [29],

$$S = \frac{R_d - R_l}{R_d}$$

Where, R_d is a dark resistance and R_l is the light resistance of the film. The calculated sensitivity was found to be 27.51%.

From the I-V plot, it is observed that the recorded current in the existence of light was relatively higher than the current measured in dark condition due to the generation of free electron-hole pairs in the conduction and valance band because of incident photons.

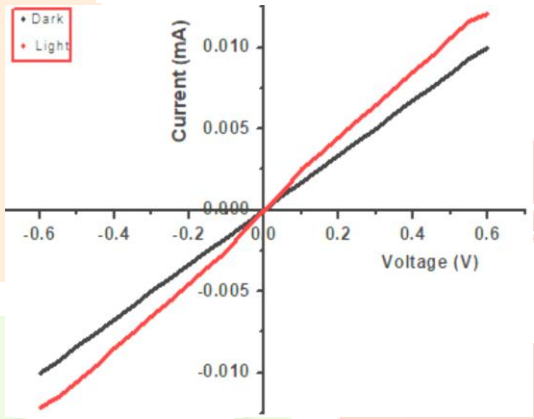

Fig. 5: I-V Plots of ZnO thin film for photo sensing

4. CONCLUSIONS

1. Low cost, simple and efficient chemical bath deposition method was used to prepare ZnO thin films for the photocell application in visible light.
2. Structural, morphological, optical and electrical characterizations of ZnO thin film were performed.
3. XRD measurement studies indicated that, ZnO film shows polycrystalline structure in the hexagonal phase.
4. Lattice parameters are a = 0.3245 nm and c = 0.5209 nm and coincides with JCPDS reported data.
5. FESEM studies indicated that, nanorods of ZnO thin films were uniformly distributed over the surface.
6. Optical studies indicated that, the bandgap of ZnO film was found to be 2.42 eV.
7. Photo-sensing studies indicated that, sensitivity of the ZnO thin film was found to be 27.51%.

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