Synthesis and characterization of Al-doped zinc oxide nanorods for TCO application.

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ABSTRACT

Aluminium doped zinc oxide thin films were prepared by chemical bath deposition using zinc nitrate aqueous solution. The effect of Aluminium incorporation on the structural, electrical and optical properties was investigated. The crystal structure and orientation of AZO thin films were studied by XRD patterns which reveal the polycrystalline nature of deposited thin films. The XRD pattern indicates that crystallization of ZnO nanorods and grain size is determined which is about 84nm. Morphological characterizations of the films were performed by SEM analysis, showing almost uniform particle size distribution of the film. The UV-Vis spectra showed absorbance peaks in the 300-1500nm region. Optical transmittance spectra gives excellent transmittance (>80%) and a sharp cut off edge at 385nm. The electrical properties of AZO nanorods were assessed by four point resistivity measurement. The lowest resistivity value of $1.3\times10^{-4}\Omega$cm with 80% transmittance at 300 nm was obtained for film with 15 mM Al doping. This reported work shows that the obtained thin films can be used as transparent conducting oxides (TCOs) and photovoltaic material.

Key words: Chemical Bath Deposition, AZO, XRD, SEM, UV-Vis study, TCO.

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INTRODUCTION

Nanostructured zinc oxide has attracted attention of researchers and scientist as transparent conducting oxides (TCOs). High conductive ZnO films have been achieved by doping with group III elements like aluminium, boron, indium, gallium [1]. It has potential applications in optoelectronic devices due to its direct band gap (3.3eV) [2-4]. It also has some unique and interesting physical and chemical properties such as, large exciton binding energy (60meV) [5-6], chemical [7] and thermal stability [8], radiation hardness [9], piezoelectricity and photoelectricity [10], high conductivity, etc. It has abundant in nature and nontoxic. Due to such intriguing properties zinc oxide became a most attractive semiconducting material for the

applications in photo-detector [11], gas sensor [12], LED's [13], solar cells [14], photonic crystals [15], UV-protectors filters [16], chemical sensors [17] and photodiodes [18].
Zinc oxide thin films have been prepared by a verity of thin film deposition techniques such as Chemical Vapor Deposition (CVD) [19], Magnetron sputtering [20], spray pyrolysis [21-22], Pulsed Laser Deposition (PLD) [23], sol-gel method [24-25], electron beam evaporation [26], Chemical Bath Deposition (CBD) [27]. Among these methods, the CBD method is one of the most important method and widely used for the preparation of metal oxide nanostructures. This is an attractive technique for fabricating uniform thin films due to the homogeneity of precursor, a large-area deposition and low cost fabrication.

In this study, Aluminium doped ZnO thin films were prepared using chemical bath deposition method using glass substrate at 60^0C temperature. Uniformly deposited thin films of AZO were subjected for different characterizations. Structural and morphological characterizations of the samples are performed using X-ray diffraction (XRD) and Scanning electron microscopy (SEM) respectively. Optical characterization is carried out by UV-Visible spectroscopy and electrical properties of the material were studied by four point probe method. Structural, optical and electrical properties of nanostructured AZO is discussed in this paper.

MATERIALS AND METHODS

Zinc nitrate hexahydrate ($Zn(No_3)_2.6H_2O$) (SDFLC,AR), EDTA, Ethylenediamine ($H_2NCH_2CH_2NH_2$) (Merck, AR), Aluminium chloride (Al_2Cl_3) (SDFCL, AR), PEG-600 (FINAR) and double distilled unionized water was used throughout the experiments.
Zinc nitrate hexahydrate (15mM) was dissolved in unionized double distilled water at 60^0C. 0.5M% EDTA was added to trap impurities present in the solution. Ethylenediamine (15mM) was added to start formation of ZnO nanoparticles. Aluminium chloride (15mM) was added to the solution. Aluminium chloride acts as an Aluminium source in the solution. PEG-600 was added as a surfactant. After the slight stirring of solution it was kept at 60^0C for 6 hr using water bath. The solution colour was changed from transparent to white after the addition of ethylenediamine. Ultrasonicated glass plates were used as a substrate and immersed into the solution. After 6 hr of constant heating solution was left to cool for 42 hr in the bath. The pasted AZO thin films were then dried to bind it to the glass substrate. The harvested nanostructures can be attached strongly to substrate by sintering at 300^0C for 10hr. Good quality and highly transparent thin films of nanostructured AZO were obtained and subjected for XRD, SEM, UV-Visible and Resistivity characterizations.

MATERIALS AND METHODS

The XRD analysis was used to identify the phase and structure. XRD data were collected from thin films using an automated X-ray powder diffractometer with scintillation counter using graphite monochromated CuKα radiations. The XRD pattern of AZO sample is as shown in fig.1. XRD pattern is obtained for AZO nanoparticles sintered at 400^0C for 5hr. For aluminium doped ZnO thin films, ZnO diffraction peaks at 31.62^0, 34.3^0, 38.54^0 and 47.22^0 were observed corresponding to (100), (101), (102) and (110) respectively. The XRD pattern of AZO thin film is very similar to the pure film. All the reflections match with the JCPDS file no 36-1451 of ZnO. The XRD pattern of Aluminium doped ZnO nanorods show a shift of (002) reflection at an angle $30\text{-}38^0$. The shift of (002) reflection is clearly indicating the formation of AZO

nanostructures. The peaks due to Al_2O_3 are also observed at an angle 22.84^0 and 38.54^0. The crystallite size can be determined from the line broadening of the peak by Debye-Scherrer equation (1).

$$\delta_m = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where λ is X-ray wavelength (λ=1.5456Å), β is half maximum line width, θ is Bragg angle, and k is constant (k=0.9).

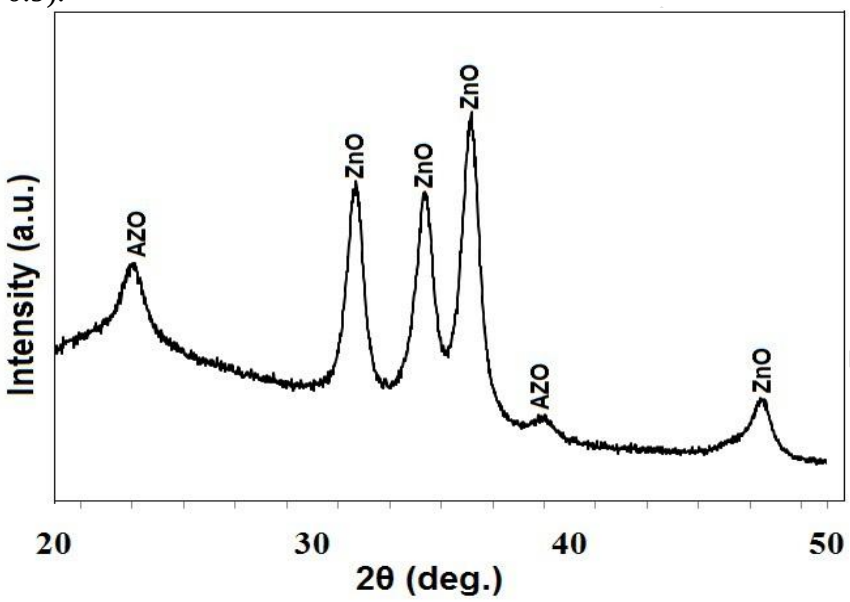

Fig 1: XRD pattern of Al-doped ZnO

Table 1: The d-values, lattice parameters of the synthesized Al-doped ZnO nanomaterial with its crystallographic planes and 2θ values

θ (deg.)	h	k	l	a or b	c	d_{obs}[Å]	JCPDS d_{cal}[Å]
31.64	1	0	0	3.2733	5.6698	2.8352	2.816
34.32	0	0	2	3.0247	5.2393	2.2605	2.602
36.18	1	0	1	2.8737	4.9777	2.1556	2.476
47.3	1	0	2	2.2246	3.8534	1.5916	1.913
56.5	1	1	0	1.8852	3.2655	0.8886	1.626
62.66	1	0	3	1.7163	2.9728	0.5515	1.5478
65.8	2	0	0	1.6429	2.8458	0.5062	---
67.78	1	1	2	1.6176	2.7718	0.4499	1.379
68.96	2	0	1	1.5762	2.7302	0.4301	1.360

We determined the mean crystallite size from the full-width at half maximum is about 8.4nm for AZO nanostructure.

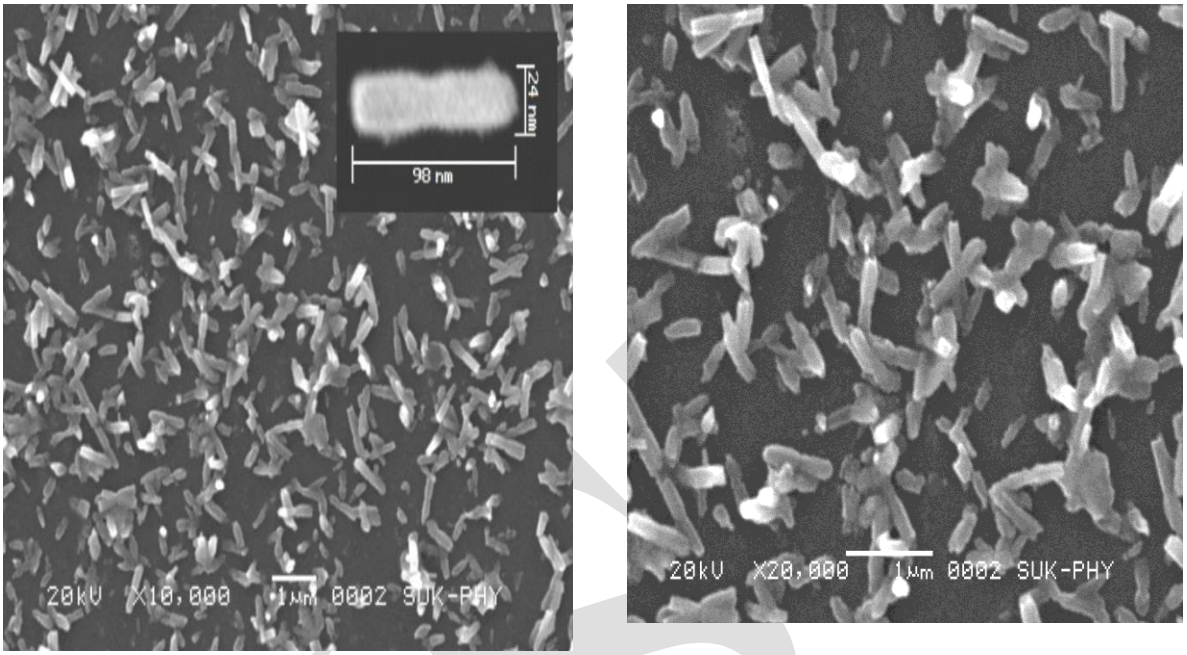

Fig 2: SEM micrograph showing AZO nanorods

Figure 2 shows SEM micrographs of the AZO thin films annealed at 500^0C using zinc nitrate solution (15mM) with Aluminium as a dopant (15mM). SEM of AZO thin film at 10000x and 20000x magnifications clearly indicating that, it has almost homogeneous morphologies. AZO nanorods have a uniform diameter of 24nm with a length of approximately 98nm. The rod like structure was particularly apparent on the chemical bath deposited AZO thin films. It can be noticed that the microstructure of the thin films is influenced by the addition of Al atoms as dopants. The electrical conductivity in semiconducting oxide film is found to be high due to high electron concentration. Aluminium doping in ZnO, Al^{3+} ions substitutes Zn^{2+} ions and act as donars. Undoped ZnO sample had resistivity of ~140 Ω-cm at room temperature while Al-doped ZnO has resistivity of 1.3×10^{-4} Ω-cm. This low value of resistivity of AZO film is due to the formation metal rich film. Al^{3+} ions might have substituted Zn^{2+} site or gone to interstitial position. Due to this increases free charge concentration in the film which increases conductivity and decreases resistivity of the material. The results are obtained as shown in figure 3. From the figure it is clear that the resistance of AZO film decreases as the temperature increases showing the n-type semiconducting behavior of AZO. The activation energy (E_a) of the film is calculated by using Arrhenius equation which is plotted in figure 3. Activation energy of AZO film is found to be 0.3932eV.

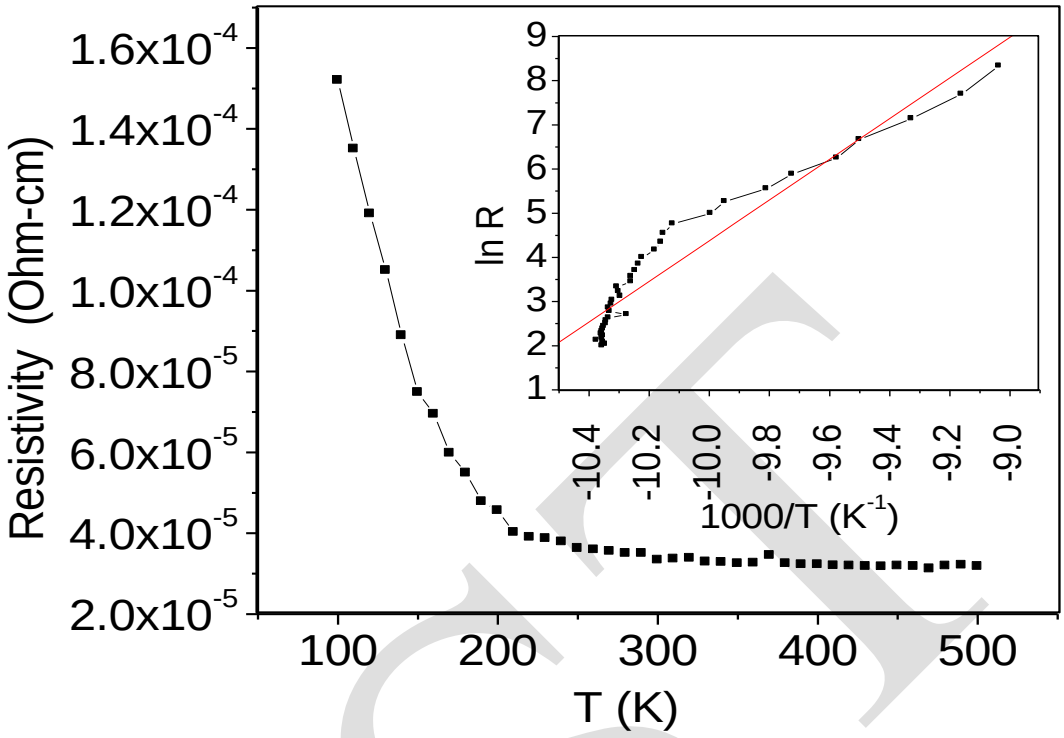

Fig 3: Temperature dependant resistivity of AZO film.

The optical absorption spectrum of AZO thin film was recorded in the region ranging from 300 to 1500 nm using UV-Vis spectrometer (Fig.4). For the optical device fabrication, the thin film should be highly transparent and conductive. The UV cut-off wavelength for the AZO film was found to be 350 nm which make it a potential candidate for optical device fabrication. The optical absorption coefficient is depend on the energy of incident photon and determined by equation,The band gap energy (E_g) of the ZnO can be determined by Tau plot of $(\alpha h\gamma)^2$ versus photon energy hν (eV), by using equation,

$$(\alpha h\gamma) = A(h\gamma - E_g)^n \quad (2)$$

Where n is 0.5, 1.5, 2 and 3 for direct, indirect forbidden, direct forbidden and indirect transitions respectively. A is absorption coefficient, A is band edge sharpens constant, h is planks constant and hν is the photon energy.

By plotting $(\alpha h\gamma)^2$ the optical bandgap energy was determined by extrapolating the linear portion of the plot to hν=0. It is found that for the film straight line is obtained for n=1/2 which is expected for direct allowded transition.

Where, A is constant, E_g is the band gap and υ is the frequency of incident light.

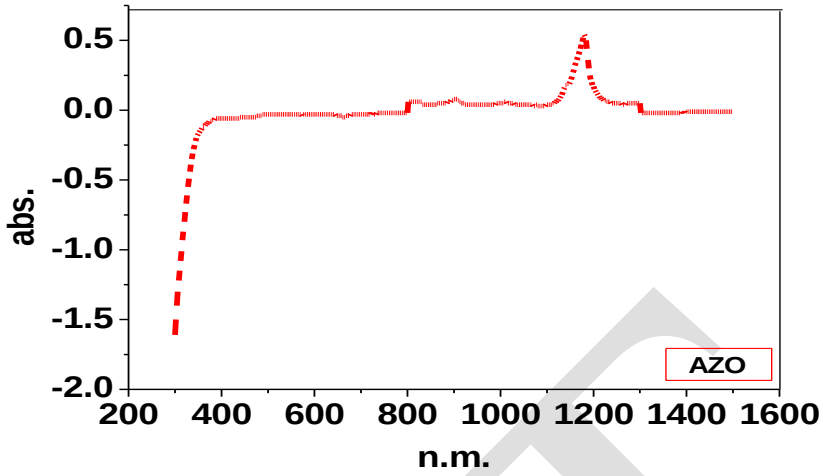

Fig.4: UV-Vis absorption spectra of the AZO film.

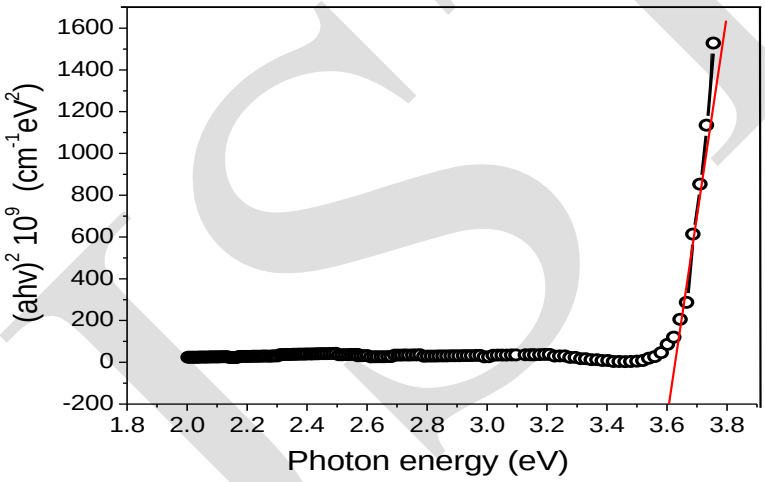

Fig.5: Variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) of AZO

The result indicate that film has more than 80% transmittance which shows that film has less absorption and better transparency. The optical energy band gap was estimated at 3.6 eV (Fig.5). It is also found that the energy gap of AZO (3.6eV) is larger than the ZnO (3.3eV) (Kim *et al* 2000) due to Burstein-Moss effect.

CONCLUSION

In this present study, AZO nanorods have been successfully synthesized by chemical bath deposition method. Change in morphology of ZnO hexagonal wurtzite nanostructures to rods is observed on doping with aluminium. The effect of aluminium doping on the structural, electrical and optical properties of the AZO films were studied. The SEM images of the films showed that the surface morphology is strongly affected by the aluminium content. A minimum resistance was measured to be about $1.3\times10^{-4}\Omega$cm associated to a high transmittance (>80%). The optical band gap of AZO material is found to be 3.6eV. We obtained a good transmittance in the visible

region. So, especially 15mM AZO film is suitable for TCO material and also for the solar cell applications.

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