SYNTHESIS AND CHARACTERIZATION OF Cu-ZnO THIN FILMS BY SPRAY PYROLYSIS

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Abstract

Copper oxide is a earth abundant , non-toxic p-type semiconductor material .The copper doped ZnO layers are used as absorber layer for thin film solar cell. In this view, copper doped Zinc oxide (Cu-ZnO) thin films are synthesized using spray pyrolysis technique by varying copper content from 1 to 5 mole percentage. The XRD spectra showed the formation of polycrystalline hexagonal wurtzite structure confirming the presence of ZnO. The FT-IR spectral analysis revealed the presence of both Zn-O and Cu-O stretching vibrations. The optical analysis revealed the average transmittance of the coated films are about 70%. The deposited oxide films found to have high absorption in the UV region. The optical band gap were estimated from Tauc's plot analysis. The undoped ZnO films have a band gap of 3.56eV. It was found that the band gap narrowed down to 2.48eV for ZnO film alloyed with 5mole% of copper. The electrical properties of Cu-ZnO films were done by Keithley source meter and the films are found to have a minimum resistivity (ρ) of $13.74x10^{-3}$ Ω cm. The Cu-ZnO synthesized with 5mole% is optimized for the absorber layer in the solar cell.

Keywords: *Thin film, Absorber layer, Polycrystalline, band gap, resistivity.*

Introduction

Nanotechnology is the study of the phenomena that deals with the design, characterization and manipulation of materials at atomic and molecular scales. The nano materials find their application in numerous fields like medicine, food, satellites, computer technology water purification etc. Zinc oxide is an excellent material with different nanostructures to date. It has extensive commercial use during the past 100 years. Zinc oxide is a semiconductor with n-type behavior and posses a wide band gap of 3.32eV. It has large exciton binding energy of 60 meV. In addition it is chemically and thermally stable and environment friendly [1]. ZnO as an important II–VI compound semiconductor has many applications in the fabrication of devices including ultraviolet (UV) light-emitters, varistors, transparent high power electronics, piezoelectric transducers, gas-sensors, smart windows and solar cells [2]. The electrical properties of ZnO can be tailored by thermal treatment with H_2 or by alloying with suitable anionic or cationic substitution [3,4]. Researchers chose metal oxides to dope in order to have better morphological, electrical and optical properties. Since Zn^{2+} and Cu^{2+} have their ionic radii close to each other ,Cu can easily penetrate into ZnO crystal lattice and enhance the oxygen adsorption capacity of the thin film surface [5,6,7].The effect of Cu source on optical properties of ZnO films and blue emission by Cu-ZnO nanocrystals have been reported [8,9,10]. Several methods are available for the synthesis of Cu-doped ZnO films such as spin cating [5], spray pyrolysis [11], Co-Precipitation [12], Sol-gel [13],Dip coating [14], and electrodeposition. Of which spray deposition has many merits such as large area of coating, deposition at atmospheric pressure and low cost. In this paper, we report our investigation about Undoped and Copper doped Zinc oxide thin films. Structural properties of pure and Cu-doped ZnO films, Optical and electrical properties of pure and Cu-doped ZnO films are discussed in detail.

Experimental Details

Materials and Method

Zinc acetate [Zn $(CH_3 COO)_2 . 2H_2O$] (Sigma Aldrich,99% purity) is used as precursor material for preparing pure ZnO and cupric acetate dihydrate as a precursor for Cu-doped thin films.The spray solution was

prepared by dissolving the precursor in Iso-propyl alcohol and de-ionized water in the ratio 3:1. 0.2M of Zinc acetate in 25ml of the solvent is used to deposit pure ZnO. The Cu/Zn ratio in the solvent was varied as 1,2and 5 taken in mole %. Few drops of acetic acid was added to improve the solubility of Zinc acetate and cupric acetate mixture in the solvent. The films are deposited on to a precleaned glass substrate 1mm thick, at an optimized substrate temperature (400˚C), and the substrate to nozzle distance (SND) 25cm. The solution was stirred at 60˚C for 1 h to give a homogenous solution, which is used for coating. The coated films are annealed for 1h after deposition. The doped films are labeled as CZO-1, CZO-2 and CZO-5.

Characterization

The structural characterization was made by pan analytical XPERT-PRO X-ray diffractometer system with a scan angle from 20˚ to 80 ˚ and the anode material as copper. The optical studies were carried out by UV-Vis spectrophotometer (Shimadzu, model UV-1800, Japan) in the wavelength range 190-1100nm. FTIR Spectra are recorded by Perkin Elmer BX II spectrometer between the wave number region 4000cm^{-1} to 400cm^{-1}. The Keithley source meter model SCS 4600 was used to record the I-V characteristics of the samples.

Results and discussion

Structural properties

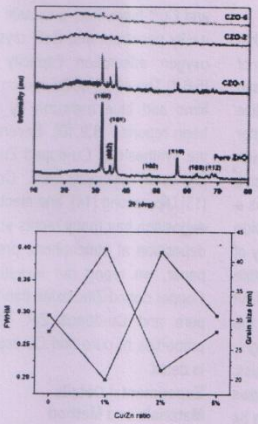

Figure 1(a) XRD pattern of pure and Figure 1(b) Variation of FWHM and grain size Cu doped ZnO thin films with different Cu mole %.

The figure1(a) shows the X-ray diffractograms of pure ZnO and Cu-doped nano thin films .The spectra shows the existence of main diffraction planes for pure ZnO as (100), (002),(101),(102),(110),and (103) corresponding to the hexagonal wurtzite structure (JCPDS card no 36-1451).There are no peaks originating for other compounds apart from pure ZnO. Smaller additional peaks appear along with ZnO phase for1wt % of Cu. A new single peak emerged for (111) plane at 1wt% of Cu which corresponds to CuO phase. Thereafter the intensity of the peaks decreases as the dopant concentration increases. The copper impurity degrades the crystallinity of the CZO thin films which may be due to the lattice distortion caused by the incorporation of Cu^{2+} ions, because of the different ionic radii of Zn^{2+}(0.74A˚) and Cu^{2+} (0.73A˚) [1]. No characteristic peaks arising from impurities are detected.

The size of the crystallites of different samples were determined from XRD data, using Debye- Scherrer formula,

$$D = \frac{0.94\lambda}{\beta \mathrm{Cos}\theta}$$

Where β is the width measured at half maximum intensity (FWHM) of the diffraction peak. λ is the wavelength of the Cu Kα ,X-ray radiation and its value is 1.5406$\dot{A}$ and θ is the Bragg's angle.

Table 1: Variation of FWHM and Grain size with different Cu dopant percentage

Cu-concentration (Mole %)	FWHM for diffraction planes			Grain size (nm)		
	(100)	(002)	(101)	(100)	(002)	(101)
0	0.2952	0.3936	0.4920	27.98	20.68	21.16
1	0.1968	0.1968	0.1968	42.10	43.3	42.5
2	0.3936	0.3197	0.5904	21.46	26.05	14.2
5	0.2952	0.5904	0.5904	28	14.14	14.17

The changes in the size of the crystal with varying copper content is plotted in the figure 1(b). The FWHM value for (100) orientation is narrower indicating larger crystal size than the than the other two orientations. The crystallite size for (100) diffraction plane, first increases for 1 mole % of copper and then decreases sharply with rise in copper content [2]. The same trend is followed for (002) and (101) planes. As long as the copper atoms do not substitute the oxygen atoms there is a increase in the grain size, otherwise if segregation at the grain boundaries or at the film surface occurs that reduces the size of the grain at higher Cu-dopant percentage [3].However the replacement of Cu-atoms preserves the structure as hexagonal wurtzite, only affecting the crystallite size and the texture of the films and there are no phases corresponding to other oxides are found. Kaid et.al observed a similar effect in their study, when ZnO is doped with Al [4].

Fourier Transform Infra red Spectroscopy

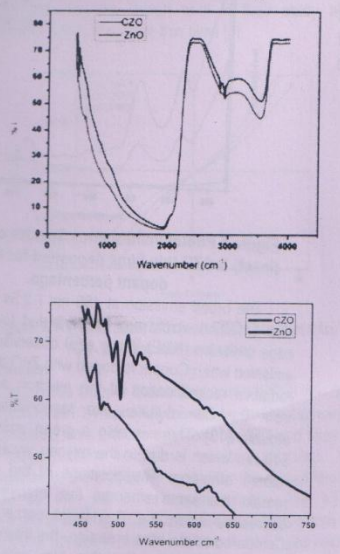

Figure 2 (a) The Fourier Transform Infra Red Transmission (FT-IR) spectra of pure and Copper doped ZnO shown for the wave number region for 400 to 4000cm^{-1} & (b) FT-IR spectra for the same samples shown for the wave number region 400 to 750 cm^{-1}

The infra red region of the electromagnetic spectrospic study reveals more details about the nano thin films than their bulk counterpart, since their surface to volume ratio is higher. The presence or absence of characteristic vibrational modes of the elements can be detected through these FTIR studies. The FT-IR spectrum of the pure and copper doped Zinc oxide thin film is shown in figure 2(a). The transmission peak obtained at 461cm^{-1} corresponds to stretching modes of Zn-O bond for pure ZnO which is shifted to 464cm-1 in the CZO film. This may be because of the change in the bond length due to the substitution of Cu in the Zinc lattice . The existence of CuO is affirmed by other peaks at 502,522,542 and 609 cm^{-1} (Figure 2(b)) in the CZO thin film. Since the wave number is a function of bond strength and reduced mass, the copper substitution strengthens the bond as the peak is shifted to higher energy (frequency) [5]. The presence of broad peak at 3526 cm^{-1} shows the -OH group due to the adsorption of H_2O on the film surface [15].

Optical Studies

UV-Absorption Studies

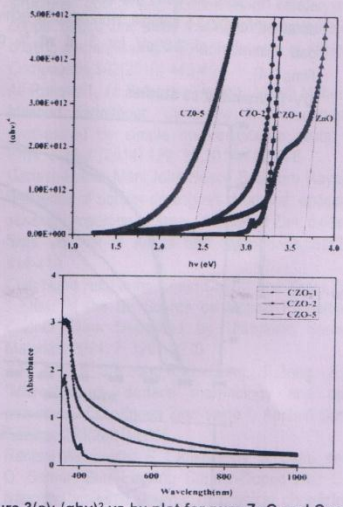

Figure 3(a): $(\alpha h\nu)^2$ vs hv plot for pure ZnO and Copper doped ZnO thin films .

Figure 3(b): Absorption spectra of CZO thin films.

The UV-Visible absorption spectrum is recorded in the wavelength range from 200-1000 nm. From the absorption spectra (figure 3(b)), it is observed that the CZO films show little high absorption in the UV compared to pure ZnO. This characteristic feature of CZO film is useful as absorber layer in the solar cell fabrication. Vanaja et.al demonstrated the same trend in their study when copper is doped with ZnO nano particles [13]. The $(\alpha h\nu)^2$ vs hv plot for CZO and ZnO thin films is shown in figure 3(a). The direct optical band gap of the films was estimated from Tauc's relation.

$$\alpha h\nu = A\,(h\nu - E_g)^{1/2}$$

Where α the absorption co-efficient and hv the photon energy. The extrapolation of the linear portion of the curve gives the band gap value. The pure ZnO found to have a band gap of 3.65eV there after the band gap gradually decreased from3.32 to 2.48eV with increase in the Cu from 1to 5 mole %, indicating a apparent red shift [12]. Muthukumar et.al observed a band gap shortening beyond 0.5 Cu% , which could be due to the formation of impurity band that overlaps with the conduction band edge [4].The narrowing of band gap is also caused by the closely matching energy levels of 3d and 2p bands of copper

impurity and o atoms leading to the hybridization of copper (3d) and o (2p) bands [7]. The alloying of Copper with Zinc atoms reduces the band gap and a minimum of 2.48eV is obtained for CZO-5 sample. Horzum et.al achieved a band gap minimum of 2.09eV for 3 at wt % of Cu-doped films [14].

UV-Transmittance studies

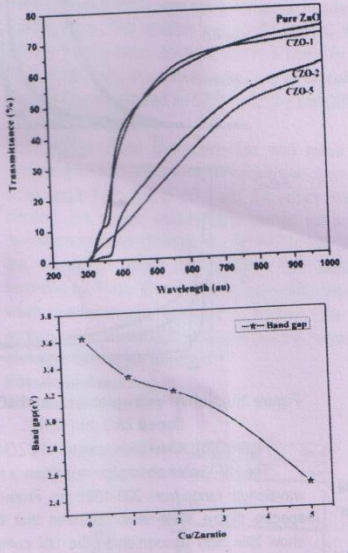

Figure 4(a) The optical transmission spectra of pure ZnO and Cu doped ZnO thin films. Figure 4(b) Variation of band gap (Eg) with copper dopant percentage. Figure 4 (a) shows the transmission spectra of the doped and in doped films .Figure 4(b) shows the variation of band gap (E_g) with copper dopant percentage. The absorption edges of all the doped films lie in the range 358 - 364 nm. The overall transmission of the alloyed films is above 60% in the visible range, except CZO-5 sample. Since there are no interference fringe patterns, this indicates the film surface is somewhat absorptive. With copper the absorption of the ZnO layers are found to increase in the visible from 400-750 nm.

Photoluminescence studies

The photoluminescence (PL) measurement at room temperature was carried out to investigate more on the optical properties. Undoped Zno thin films show a near band emission peak at 380 nm. The CZO -PL spectra shows a prominent blue and green emission when excited close to the absorption edge.

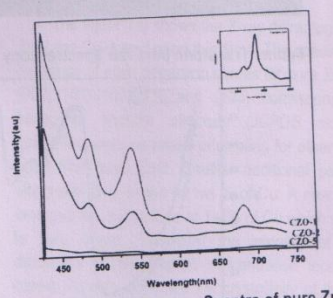

Figure 5 Photoluminescence Spectra of pure ZnO (inset) & CZO thin films deposited for different Cu dopant percentage.

The broad emission at 486 nm (2.54 eV) shows the blue emission which may be attributed to the near band edge emission (NBE) Wang et.al observed a similar blue emission when Copper is doped with ZnO thin films [9].The radiative recombination of the electron and hole arising from the Cu+ d-states are responsible for the blue emission[10]. There is also a green emission exactly at 540 nm which is due to the oxygen vacancies or surface related emission. The positions of the emission peaks remain the same whereas the intensity of the peaks decreases when the Cu-dopant percentage increases. Compared to the blue emission, the intensity of the green emission more for the thin film with 1 mole % of Copper.(CZO-1). A small peak at 683 nm in the red region and a hump at 601 nm are characteristics of CZO-1 sample. There are reports that the near-IR emission originates from defects similar to those responsible for the red emission in ZnO, that is, oxygen vacancy [8]. The inetnsity of all the peaks drastically reduced for CZO-5 sample, According to Ibrahim et.al the quenching involve some nonradiative recombination that would have taken place in the thin films [5].

Elecrical properties

The electrical resistivity of the pure and Cu-doped ZnO nano thin films are studied by Keithley source me er model SCS-4600.The volt-ampere characteristics of the alloyed CZO films are shown in figure 6.It exhibits a better conductivity behaviour for the low dopant concentration (CZO-1) than the CZO-2 and CZO-5 thin films.

The resistivity (ρ) is minimum for the CZO-1 film and it is 13.74×10^{-3} Ω cm, which is much lower than the undoped ZnO. The decrease in the resistivity (ρ) is due to the replacement of Zn atoms by Cu atoms which can be easily ionized than Zinc atoms. Hence the introduction of the charge carriers are more thereby lowering the resistivity of the films [2].However with further increase in the dopant concentration at 2 wt % and 5wt % of Cu further disorder in

the crystal lattice is produced . This leads to increase in the phonon scattering mechanism and scattreing of the ionized impurity which affects the conduction mechanism as demonstrated by Tewari et.al in their study about aluminum doped Zinc oxide thin films [8].

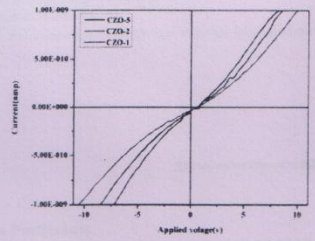

Figure 6 I-V Characteristics of CZO thin films for Cu- dopant concentration

Conclusion

Large area Copper doped Zinc oxide (CZO) thin films are synthesized by spray pyrolysis deposition technique. The prepared films are characterized by XRD and found to have polycrystalline hexagonal wurtzite structure. The degradation in the crystalline quality for the doped films is marked by the grain size measurements. The FT-IR spectra of the pure and Cu-doped ZnO thin films affirm the presence of copper in the Zinc lattice. A band gap narrow down was observed and a minimum band gap (Eg) of 2.48 eV is achieved for 5 wt % of copper. The overall transmission of the alloyed films are above 60% in the visible range, except CZO-5 sample. The absorption of the Cu-doped layers in the UV-region is found to be greater than the pure ZnO. The PL emission shows prominent peaks at the blue and green region of the visible spectrum. The electrical resistivity (ρ) is less for CZO-1 sample. As the prepared CZO samples found to have greater absorption in the UV region and a band gap suitable for solar cell application, these films can be used as absorber layer for thin film solar cell.

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