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Structural, Optical and Raman Characterization of Nano-Crystalline Cu Doped ZnO Thin Films Deposited by Pulse Laser Deposition Technique

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I. Introduction

Zinc Oxide is one of the most employed nanomaterials by its environmental safety and ease to fabricate by chemical methods. ZnO is commercially available with advantages viz. comparatively low cost, environment-friendly non-toxic material, wet chemical processes [1, 2]. ZnO is a large band gap (3.37 eV) semiconductor with excitonic energy (60 meV) [3]. Usually, ZnO shows intrinsically n-type conductivity due to native defects [4]. ZnO has been investigated extensively for applications in UV photodetectors [5], light-emitting diodes [6], photodiode [7], chemical industry [8, 9] and transparent conductive layer [10]. Optically transparent ferromagnetic DMSs, obtained by doping paramagnetic transition metal ions into semiconductors, has received particular attention for integrated Opto-spintronic applications [11, 12]. ZnO, which has large bandgap and exciton binding energies, excellent mechanical characteristics, and is inexpensive and environmentally safe, has been identified as a promising host material. Stable ferromagnetic configurations arising from carrier-mediated exchange interactions have been predicted for several transition metal-doped ZnO DMSs [13, 14].Among all TMs, Cu doping in ZnO has received a lot of attention owing to less contradictory results about the ferromagnetic property. Herng et al found ferromagnetism in their Cu-doped ZnO thin films, which were prepared at a pressure of 5×10^{-6}Torr [15] and found to have oxygen vacancies. They have shown that the presence ofa coupling between oxygen vacancies and Cu^{1+} isolated impurities is essential for their films to exhibit ferromagnetism. TM doping induced ferromagnetism and Mg/Li doping induced ferroelectricity in ZnO film, efforts have been made to study the effect of co-doping of Mg and Li studies on structural, optical and magnetic properties of Mg- and Li-doped Cu: ZnO films in TM-doped ZnO films [16].

As per the literature available, the ferromagnetic property in doped ZnO still remains controversial. Even though the consensus about absence of ferromagnetic coupling in intrinsic TM-doped ZnO film is grow in rapidly, new reports are claiming ferromagnetic coupling in TM-doped ZnO film. In the present work, Cu doped ZnO thin films were grown on ITO coated glass substrates by PLD method. The substrate temperatures were fixed at 150^{0}C, 250^{0}C, 350^{0}C, 450^0 Crespectively during the growth of samples. The effect of substrate temperature on structural, morphological, optical and magnetic properties of Cu/ZnO have been investigated.

II. Experimental Method

In this Paper ZnO:Cu thin films samples of thickness around 200nm were prepared using pulsed laser deposition technique. The substrate temperatures were fixed at 150^{0}C, 250^{0}C, 350^{0}C, 450^0 Crespectively during the growth of samples. The substrates were clean up sequentially using isopropyl alcohol, detergent solution, methanol followed by deionized water in the ultrasonic bath cleaner. And subsequently ZnO: Cu thin films were deposited by PLD on the highly cleaned Indium Tin Oxide (ITO) coated glass substrates. To obtain free- risking pinhole thin film each parameter of the PLD was optimized (25 m torr, 250 m J) at high vacuum condition using a KrF Laser (248nm, 10 number

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of shots per sec, 30Hz) to ablate a sintered ZnO:Cu target in nitrogen atmosphere. Laser ablation was carried out by scanning the sample inside the vacuum chamber which is kept at 10^{-6}torr, by using a molecular pump together with a mechanical pump. The target was sintered at 900°C in Ar gas atmosphere in vacuum condition for 5 hours. The laser beam was focused onto the target material surface using a leans of focal length 5cm. The target was maintained in continuous horizontal and vertical displacement in order to refresh the ablated zone. The incident laser pulse energy and repetition rate for film deposition on ITO substrates was obtained as 90mJ, and 10 Hz, respectively. The target and the glass substrate holder were rotating at 5rpm and -5rpm, respectively. The distance between the substrate holder and the target inside the vacuum chamber was ~5cm. A resistive type heater was used to heat the substrate temperature to reach the set value. Before deposition, pre-ablation procedure was followed by irradiating the ZnO: Cu target.

III. Results and Discussion

a) *Structural properties*

The structural properties of the ZnO thin films were studied from the X-ray diffraction (XRD) patterns in the 2θ scan range of 10˚ to 80˚. Fig. 1 shows the XRD patterns of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 250°C. The observed XRD peaks verify the polycrystalline nature with the hexagonal wurtzite structure of ZnO. XRD spectra indicated the presence of substrate peak and denoted (*) in the XRD pattern. The obtained XRD spectra were well matched with JCPDS (Card No. 36-1451) of the wurtzite ZnO structure [17, 18]. All the diffraction peaks are indicated to ZnO (except for the diffraction peaks of ITO substrate indicated by star) and no other peaks were detected for any impurities on the XRD pattern. The diffraction peaks correspond to (100) and (002) planes, which indicate that the film have preferential c-axis orientations.

The crystal size for the films was calculated by using Debye Scherer's formula [19].

$$D = \frac{0.94\lambda}{\beta\cos\theta} \quad (1)$$

where, θ is the Bragg's diffraction angle, β is the full width at half maximum of (002) peak of XRD pattern and λ is the X-ray wavelength (1.54 Å). The crystallite size observed forZnO:Cu thin film on ITO substrate is 38 nm.

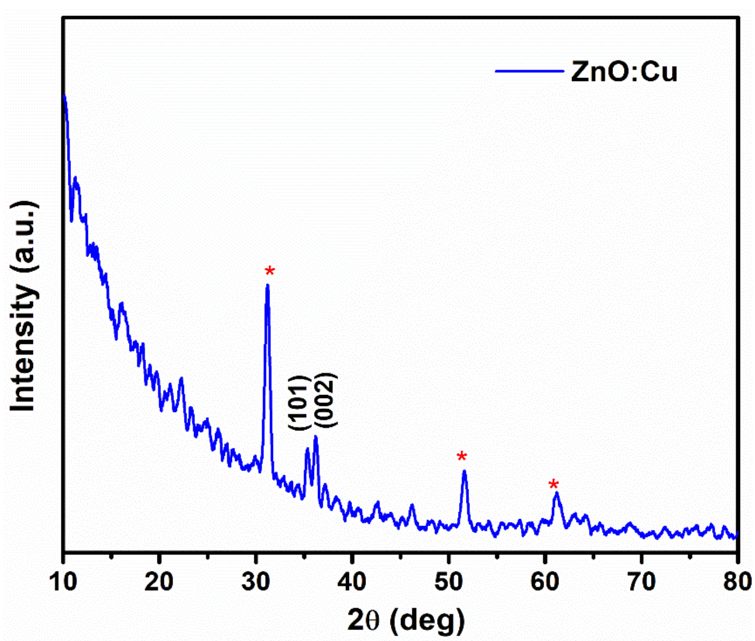

Fig. 1: XRD patterns of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 250°C

b) *Surface Morphology*

AFM measurements were performed to study the differences on the surface microstructure and roughness of the ZnO:Cu thin films. The AFM images (Fig. 2) were taken in a 5×5 μm²areaand show that all the films consisted of nanoparticles while the particle size continuously decreased with increasing substrate temperature. The surface root-mean-square roughness values of different films were found to be 32, 28, 25 and 22 nm for substrate temperature 150°C, 250°C, 350°C, 450° Crespectively. It has been observed that the samples had agglomerated particles. The average grain sizes were found to be almost in the same range of 100nm for all of the samples. Similar results were obtained by Trilok et al. [1] in CdZnO thin films on glass substrates by sol-gel method with different Cd concentration. It was observed that the surface characteristics of all samples were the same, only the grain size and roughness changed with relative oxide proportion.

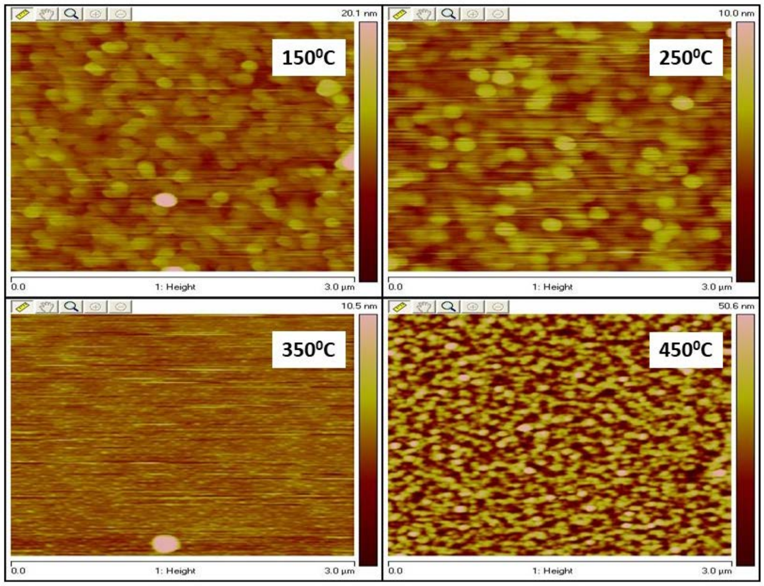

Fig. 2: AFM images of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 150^{0}C, 250^{0}C, 350^{0}C and 450^{0}C

c) *Optical analysis*

The optical properties of Cu doped ZnO thin films deposited on ITO coated glass substrate at different substrate temperature were studied. Fig.3 shows the optical transmittance spectra in the wavelength range 300-800 nm. The thin films show average 25 % optical transmittance in the visible region 400 - 800 nm and a sharp absorption edge in the ultraviolet region was observed. The transparency of thin films minimum for Cu:ZnOthin film deposited at 450^{0}C substrate temperature.

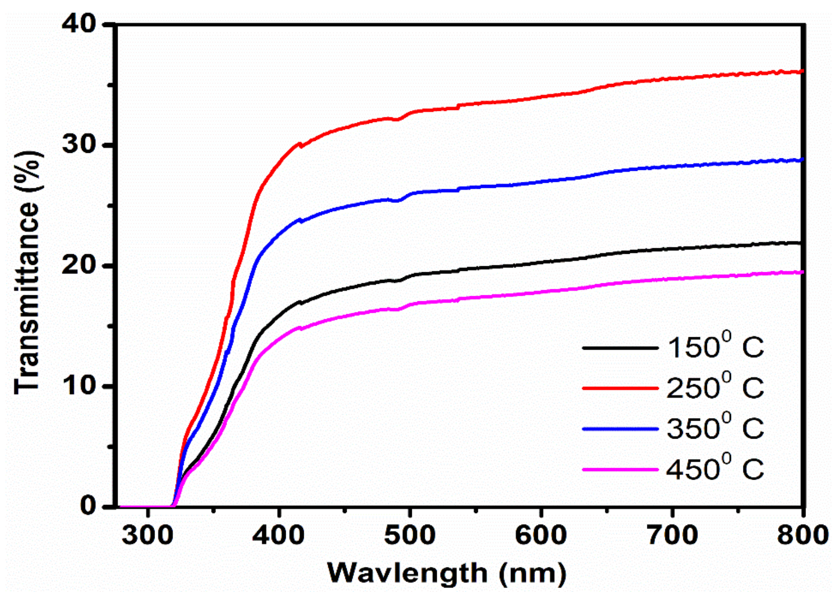

Fig. 3: Transmittance spectra of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 150^{0}C, 250^{0}C, 350^{0}C and 450^{0}C

The optical band gap of Cu doped ZnO thin film of different substrate temperature was calculated from Tauc's plot method as shown in Fig. 4.

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \qquad (2)$$

Where, α is the absorption coefficient, $h\upsilon$ is the photon energy, A is an energy independent constant and E_g is the optical band gap. The optical bandgap E_g values were obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$vs hν [20]. The resulting optical band gap of 250°C film was highest 3.28eV due to highest transmittance in violet region and it continuously decreases as substrate temperature increases and the smallest band gap 3.14 eV was obtained for highest substrate temperature film 450°C. The increase in the crystalline size and the reduction of defects might be the reason for the decrease in band gap energy with increase in deposition substrate temperature [21].

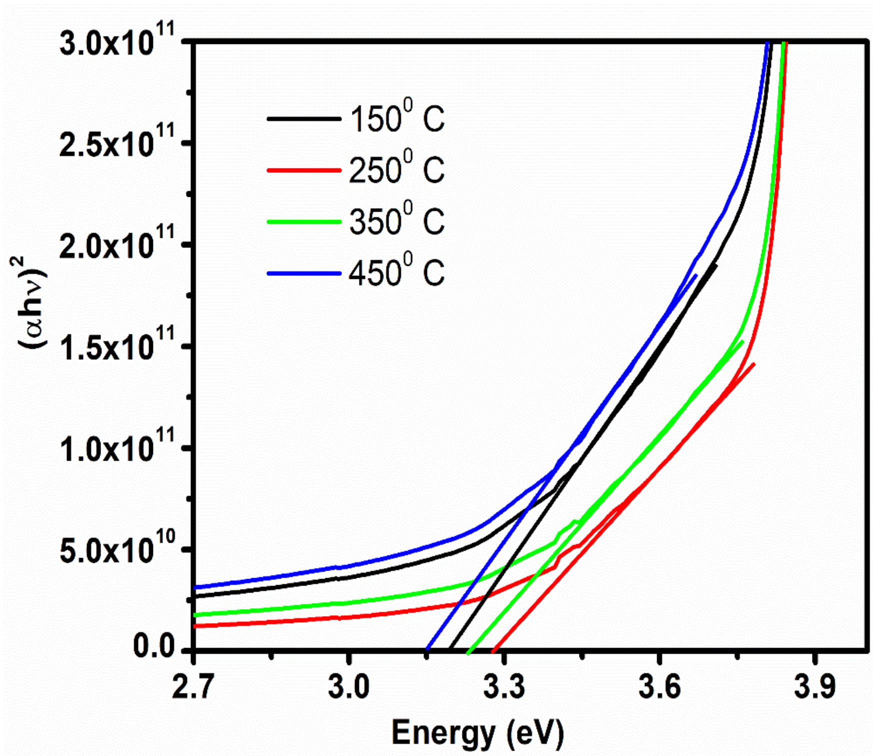

Fig. 4: Bandgap spectra of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 150°C, 250°C, 350°C and 450°C

IV. Raman Analysis

Fig.5 shows low temperature Raman spectra for Cu-doped ZnO films deposited on ITO coated glass substrate, substrate temperature 250°C, keeping the incident light near normal to the surface. The temperature varied from -153°C to room temperature 27°C to observed Raman spectroscopy. Only two modes should be observed for Cu doped ZnO film, i.e. E2and A1(LO), if the incident light is near normal to the surface, because other modes are forbidden according to the Raman selection rules in this situation [22]. In Cu:ZnO films, a broad band ranging from 500 to 620cm^{-1} is observed. No E2(high) mode is observed in these films, possibly due to the breaking of translational symmetry caused by the intrinsic defects or by the dopant. It has been reported that the breakdown of the translational symmetry due to structural disorder results in an enhancement and broadening of the A1(LO) mode (at 564 cm^{-1}). No Raman peaks from CuO are present in the Raman spectra for any of the films, which further supports structural results from the XRD patterns that there is no CuO phase present in the ZnO: Cu thin films.

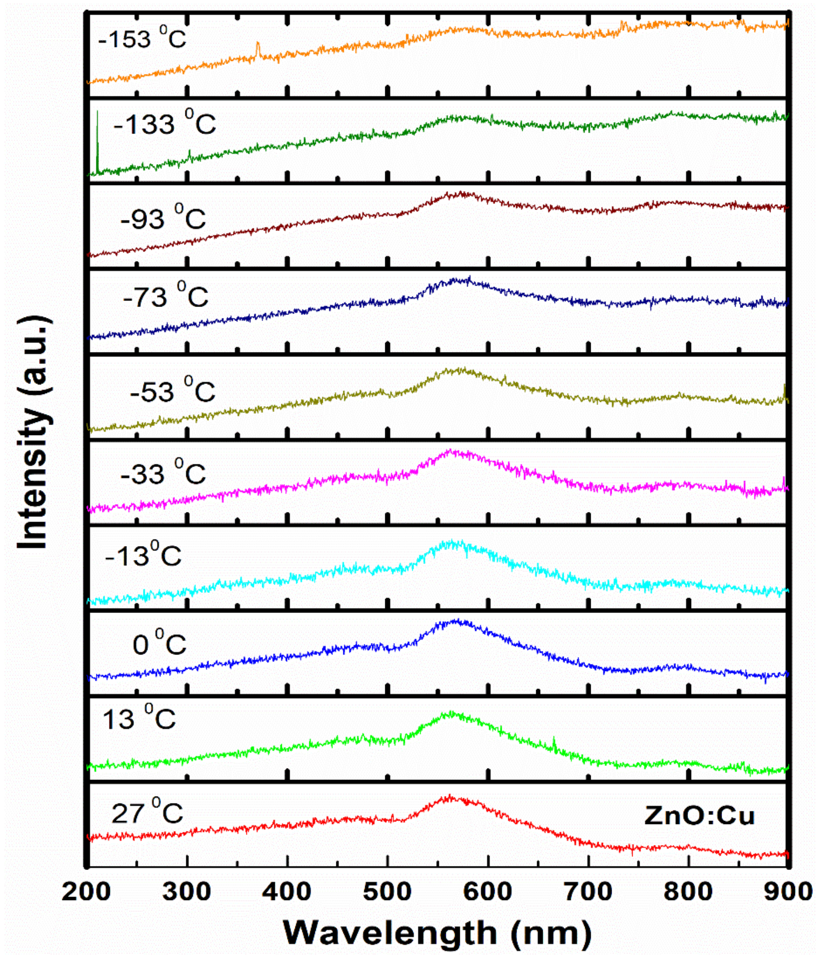

Fig. 5: Low temperature Raman analysis of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 250°C

V. Magnetic Properties

The magnetic measurements for ZnO: Cu thin film is carried out using the VSM at 300 K. The results for ZnO: Cu thin film (deposited at 250°C) is shown in Fig. 6. The film with the substrate shows diamagnetic behavior. No evidence of ferromagnetic behaviour is observed for the film. Herng et al [15] have studied Cu-doped ZnO films and found that oxygen vacancies play an important role in favouring ferromagnetism in films deposited by PLD. The films in the present study are prepared under a base pressure of 10^{-5}Torr butthey are not found to be ferromagnetic, although we have also observed a broad peak at 564 cm^{-1} in the Ramanspectra, which confirms the presence of oxygen vacancies in the films. It was found that an oxygen vacancy in the first nearest shell can suppress ferromagnetism quite a lot, and if it is in the second nearest shell the suppression is less. So, in either case the oxygen vacancies should decrease any ferromagnetism as compared to film without oxygen vacancies, as per our theoretical calculations. Furthermore, the position of an oxygen vacancy is also important in determining its effect on magnetism, in addition to its concentration. So, the difference in magnetic propertyin our Cu:ZnO films and in films reported in [15] may be due to the different position of oxygen vacancies present in the wurtzite structure.

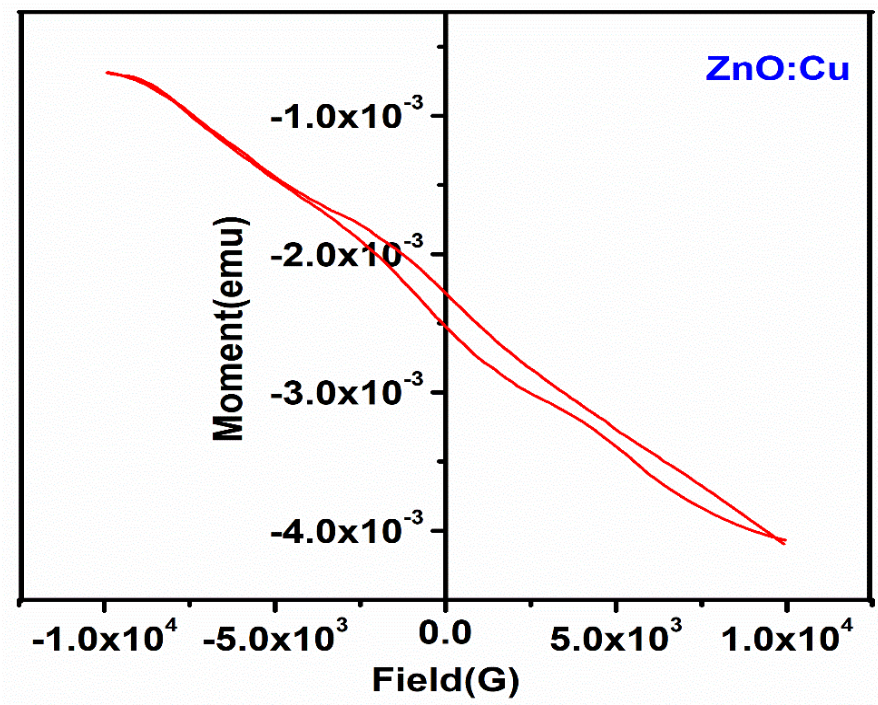

Fig. 6: Magnetic properties of Cu doped ZnO thin films deposited on the ITO coated glass substrate at substrate temperature 250°C

VI. Conclusion

Cu doped ZnO films, prepared by PLD, show a single phase as determined by X-ray diffraction pattern. X-ray diffraction pattern shows the wurtzite structure with a preferential c-axis (002) orientation. Atomic force microscopy is used to measure particle size of thin films. The average transmittance of the thin film was 25% and highest band gap observed 3.28 eV. A further structural analysis by Raman spectroscopy does not show any evidence of an impurity phase in the films. The VSM result shows the diamagnetic behaviour of Cu doped ZnO thin films. It is concluded that the concentration of oxygen vacancies is not the only important parameter for the occurrence of ferromagnetism in Cu: ZnO but that the position of oxygen vacancies also plays an important role.

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