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Nanocrystalline Mn and Fe Doped ZnO Thin Films Prepared Using SILAR Method for Dilute Magnetic Semiconductor Application

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1. Introduction

Zinc oxide (ZnO) is a versatile material of compound semiconductors with excellent properties and extensive applications in electronics, optoelectronics, sensors, and catalyses (Das et al, 2007). ZnO thin films have attracted considerable attention because they can be tailored to possess high electrical conductivity, high infrared reflectance and high visible transmittance by different coating technique (Ryu et al, 2000). Some of the remarkable properties of ZnO are its wide direct-band gap of 3.37 eV, the binding energy of the exciton of ZnO (60 meV) which makes it an excellent material for excitonic devices (Wang et al, 2003). Other favourable aspects of ZnO include its broad chemistry leading to many opportunities for wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility. Together, these properties of ZnO make it an ideal candidate for a variety of devices ranging from sensors through to ultra-violet laser devices and nanotechnology based devices such as displays. As fervent research into ZnO continues, difficulties such as the fabrication of p-type ZnO that have so far stated that the development of devices had overcome (Yang et al, 2008). Mitra et al (1998) has prepared Zinc Oxide thin films using chemical deposition technique. The structural, morphological properties of the prepared films are characterized using X-ray diffraction and scanning electron microscope. They have used Zn salts as precursor and successfully synthesized ZnO films. The growth of highly textured Zinc oxide (ZnO) thin films with a preferred (101) orientation has been prepared by

employing chemical bath deposition using a sodium zincate bath on glass substrates has been reported by (Ramamoorthy et al, 2004).

(Natsume et al, 2000) have studied the d.c electrical conductivity and optical properties of zinc oxide film prepared by a sol-gel spin coating technique. The temperature dependence of the conductivity indicated that electron transport in the conduction band was due to thermal excitation of donor electrons for temperatures from 250 to 300 K. (Chapparro et al, 2003) have proposed the spontaneous growth of ZnO thin films from aqueous solutions. An electroless – chemical process is proposed, consisting in the formation of the super oxide radical (O_2^-) followed by chemical reaction of two O_2^- with $Zn(NH_3)_4^{2+}$ cations. (Wellings et al, 2008) have deposited ZnO thin films from aqueous zinc nitrate solution at 80°C onto fluorine doped tin oxide (FTO) coated glass substrates. Structural analysis, surface morphology, optical studies and electrical conductivity were studied and thickness of the ZnO films was found to be 0.40 μm . (Walter et al, 2007) have studied the characterization of strontium doped ZnO thin films on love wave filter applications. X-ray diffraction, scanning electron microscopy and atomic force microscopy studied the crystalline structure and surface morphology of films. The electrochemical coupling coefficient, dielectric constant, and temperature coefficient of frequency of filters were then determined using a network analyzer. (Vijayan et al, 2008, a, b; Chandramohan et al, 2010) have reported the preparation conditions for undoped ZnO using double dip technique and used them for gas sensor applications. They have also reported the synthesis of Sr doped ZnO using double dip technique and used them for gas sensor applications. Recently (Chandramohan et al, 2010) have synthesized Mg doped ZnO thin films using double dip chemical growth and reported the ferromagnetic properties of the films. Saeed et al. (1995) have deposited thin films of mono phase crystalline hexagonal ZnO from solutions of zinc acetate in the presence of ethylenediamine and sodium hydroxide on to glass microscope slides. Two distinct morphologies of ZnO were observed by scanning electron microscopy. The deposited films were specular and adherent. (Cheng et al 2006) have fabricated thin films transistors (TFTs) with active channel layers of zinc oxide using a low – temperature chemical bath deposition. Current voltage (I-V) properties measured through the gate reveal that the ZnO channel is n-type. (Sadrnezhaad et al 2006) have studied the effect of addition of Tiron as a surfactant on the microstructure of chemically deposited zinc oxide. Addition of tiron changes the surface morphology and causes to form the fine – grained structure. The obtained results indicate that increasing the number of dipping cycles to progress the deposition process. (Piticescu, et al 2007) have studied the influence of the synthesis parameters on the chemical and microstructural characteristics of nanophases synthesized in the two methods. ‘Al’ doping tends to a lower material density and to a smaller grain size. Zhou et al (2007) have studied microstructure electrical and optical properties of aluminium doped zinc oxide films. The ZnO:Al thin films are transparent (~ 90%) in near ultraviolet and visible region A. with the annealing temperature increasing from 300°C to 500°C. The film was oriented more preferentially along the (002) direction, the grain size of the film increased, the transmittance also became higher and the electrical resistivity decreased. Bulk ZnO is quite expensive and unavailable in large wafers. So, for the time being, thin films of ZnO are relatively a good choice. Usually, the doped ZnO films with optimum properties (perfect crystalline structure, good conducting properties, high transparency,

high intensity of luminescence) are obtained when they are grown on heated substrates and annealed after deposition at high temperature in oxygen atmosphere (Peiro et al, 2005; Lokhande et al, 2000; Srinivasan et al, 2006; Chou et al, 2005). However, for an extensive use in the commercial applications pure and doped ZnO films must be prepared at much lower substrate temperatures. Therefore, it is necessary to develop a low-temperature deposition technology for the growth of ZnO films. Many works are seen in the low temperature growth of this interesting ZnO system both undoped and metal doped (Tang et al, 1998; Craciun et al, 1994; Gorla et al, 1999; Kotlyarchuk et al, 2005) thin films and nano thin films.

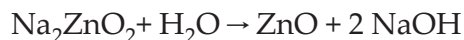
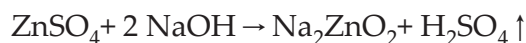
Fe addition is expected to enhance the sensing ability of this system. When sensing of 300 ppm ethanol, the in situ extended X-ray absorption fine structure (EXAFS) spectra indicate that the bond distances of Zn-O and Fe-O are 1.90 and 1.98 Å, respectively and restored to 1.91 and 1.97 Å in the absence of ethanol (Hsu et al., 2007). The single-phase Fe-doped ZnO films ($x \leq 0.04$) exhibit ferromagnetism above room temperature (Wei et al., 2006). The Fe/ZnO composites display photoluminescence properties different from those of the ZnO entities generated similarly but in the absence of Fe powder: (i) a UV emission band is observed over the latter but not over the former, and (ii) the former shows an emission peak around 583 nm (wavelength) with intensity significantly stronger than that of the latter. Because of the encapsulation of the Fe nanoparticles, the Fe/ZnO composites are highly stable in air and high magnetization (Yang et al., 2009). Room temperature ferromagnetic Fe:ZnO film was prepared by chemical deposition of ZnO film and chemical introduction of Fe impurity in aqueous solutions. (Nielsen, et al., 2008) have reported on Magnetization measurements show clear ferromagnetic behavior of the magnetite layers with a saturation magnetization of $3.2\mu_B/\text{f.u.}$ at 300 K. Their results demonstrate that the Fe₃O₄/ZnO system is an intriguing and promising candidate for the realization of multifunctional heterostructures. During recent years different techniques such as chemical vapor deposition (Hu, et al., 1991), magnetron sputtering (Jiang, et al., 2003), spray pyrolysis (Pawar, et al., 2005), sol-gel (Cheong et al., 2002), and molecular beam epitaxy (Kato et al., 2002), have been used for deposition of zinc oxide films on various substrates. The ease with which the deposition can be made and the reproducibility of the method to produce doped oxide films in any laboratory make this method quite attractive (Kato et al., 2002) (Vijayan et al, 2008, a, b) (Chandramohan et al, 2010). While the sol-gel method with double dipping has produced highly oriented thin films of Li, Mg doped ZnO thin films by (Liu et al., 2005), they have introduced a spin in the dipped films using spin coating set up to spread the films over substrate. In the method used in this work no spinning is required as the dehydrogenation of the films is done using a dip in hot water. The magnetic properties of the metal doped ZnO thin films grown by such a method has not been presented in detail to our knowledge. Nanostructured ZnO not only possesses high surface area, nontoxicity, good bio-compatibility and chemical stability, but also shows biomimetic and high electron communication features. A reagentless uric acid biosensor based on ZnO nanorods can be synthesized from SILAR synthesized ZnO thin films. The enzyme is immobilized on ZnO nanocombs and nanorods to construct an amperometric biosensor for glucose biosensing. Besides such systems have prospective applications in Dye-sensitized solar cells (DSSCs), Sensor, optoelectronic devices, UV detector, Spintronics, Dilute Magnetic Semiconductor

devices etc. SILAR is a modification of the chemical bath deposition technique. In CBD the solution is in contact with a substrate for a longer period and the reaction is slow and the formation is good (Hodes et. al., 2002). Accelerated by Bath temperature, agitation or bath conditions. The film formation results when ionic product exceeds solubility product. In SILAR originally called as multiple dip method by (Ristov, et al., 1987) and named SILAR (Nicolau, et al., 1988) the reaction Cationic and anionic precursor solutions separated for reaction at chosen conditions like temperature, pH, dipping rate, waiting time, number of dipping cycles. Time is important in ionic layer formations. Since deposition is in air too many microstructural variations are possible. The aim of this work is to investigate the influence of the preparation conditions on structural, optical and electrical properties of ZnO and incorporate magnetic properties by doping Mn/Fe leading to dilute magnetic semi conducting system using CBD method. Advantages are effectiveness and simplicity of the deposition equipment, high deposition rates, wide spectrum of deposition parameters for the control and the optimization of film properties, and film thickness. The sum of all these special features enables the growth of oxide thin films at low temperature substrates with perfect crystallinity. The present work is a preparation and characterization of undoped ZnO, Mn- doped ZnO (MZO) and Fe- doped ZnO (FZO) thin films by chemical deposition technique. In which the influence of solution concentration, solution pH value, film thickness, annealing temperature and concentration of strontium and aluminium atoms of the grown films are investigated. In addition it demonstrates that any dopant can be used in principle along with the precursor to enable them to be included in the system. The technique can be tuned to get the desired morphology and nanocrystallites of desired sizes distributed over any type of substrate for various applications.

2. Synthesis, structure and morphology of the ZnO thin films

2.1. Synthesis

ZnO thin films were grown using a two-step chemical bath deposition technique using a solution comprising 0.1 M Zinc Sulphate (99% emerk), 0.2 M sodium hydroxide with a pH value of 9 ± 0.2 deposited at bath temperature of 90 °C under optimized condition. For Mg doped ZnO (MZO) thin films $\text{Fe}(\text{SO}_4)_3$ was used at a concentration of 0.1mM. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with acetone. The well-cleaned substrates were immersed in the chemical bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. The process of solution dip (step 1) followed by hot water dipping (step 2) is repeated for known number of times. The cleaned substrate was alternatively dipped for a predetermined period in sodium zincate bath and water bath kept at room temperature and near boiling point, respectively. According to the following equation, the complex layer deposited on the substrate during the dipping in sodium zincate bath will be decomposed to ZnO due to dipping in hot water. The proposed reaction mechanism is according to the following equations (Vijayan et al, 2008, a, b) (Chandramohan et al, 2010).



Part of the ZnO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed as a precipitate. The addition of MSO_4 in the ratio of Zn:M as 100:1 in the first dip solution leads to the formation of Mg/Fe doped zinc oxide nano thin films where M stands for Mg/Fe.

2.2. Structural analysis

The crystallographic structure of the films has been studied by X-ray diffraction (XRD). Fig. 1 shows the XRD spectrum of ZnO, MZO and FZO films deposited on the glass substrate under optimized condition. It can be seen from the XRD data, that all samples are polycrystalline and exhibit the single-phase ZnO hexagonal wurtzite structure [JCPDS (36–1451)]. All peaks in recorded range were identified.

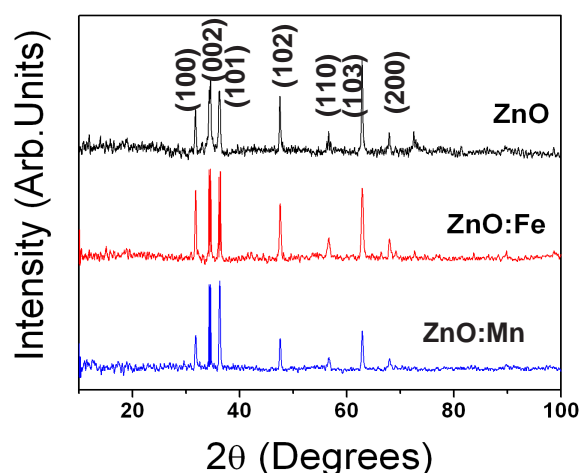


Figure 1. Typical XRD patterns of doped and undoped ZnO thin films

The XRD pattern clearly showed the polycrystalline nature of the ZnO, MZO and FZO films, whose *c*-axis was preferentially oriented normal to the glass substrate. In other words, those grains of undoped and doped films are mainly grown with *c*-axis vertical to the glass substrate. Hence, the multiple-coating or the piling up of each film was considered not to disturb the overall growth of the films with *c*-axis orientation. Therefore, the *c*-axis orientation may be a common phenomenon in the ZnO film deposition by the chemical process using organo-zinc compounds. Such preferred basal orientation is typically observed also in metal doped ZnO films (Vijayan et al, 2008, a, b) (Chandramohan et al, 2010). Moreover, from the recorded spectrums the minor diffraction peaks of (102) and (103) are approved of randomly oriented of the ZnO film (Roy, et al., 2004). The crystallite size was estimated to be 80 nm for undoped film, 26 nm for MZO and 20 nm for FZO films from the Debye Scherrer formula.

2.3. Morphological studies

Figures 2(a, b, c) shows the scanning electron micrograph (SEM) of ZnO, MZO and FZO films deposited at room temperature. The SEM micrograph of MZO thin film show the uniform polycrystalline surface of the film with a hexagonal morphology consistent with XRD result of P63mc crystal-structure with an average grain size of 300 nm. They are found to be single-crystalline in nature. It can be seen that, films grown at room temperature by varying Mn and Fe concentration consist of slightly agglomerated particles with less voids in the surface of the film with average grains 200 nm for undoped and 300 nm for doped ZnO films (Fig. 2(b)). This result confirmed that Mn and Fe doped into ZnO lattice and in good agreement line with XRD result.

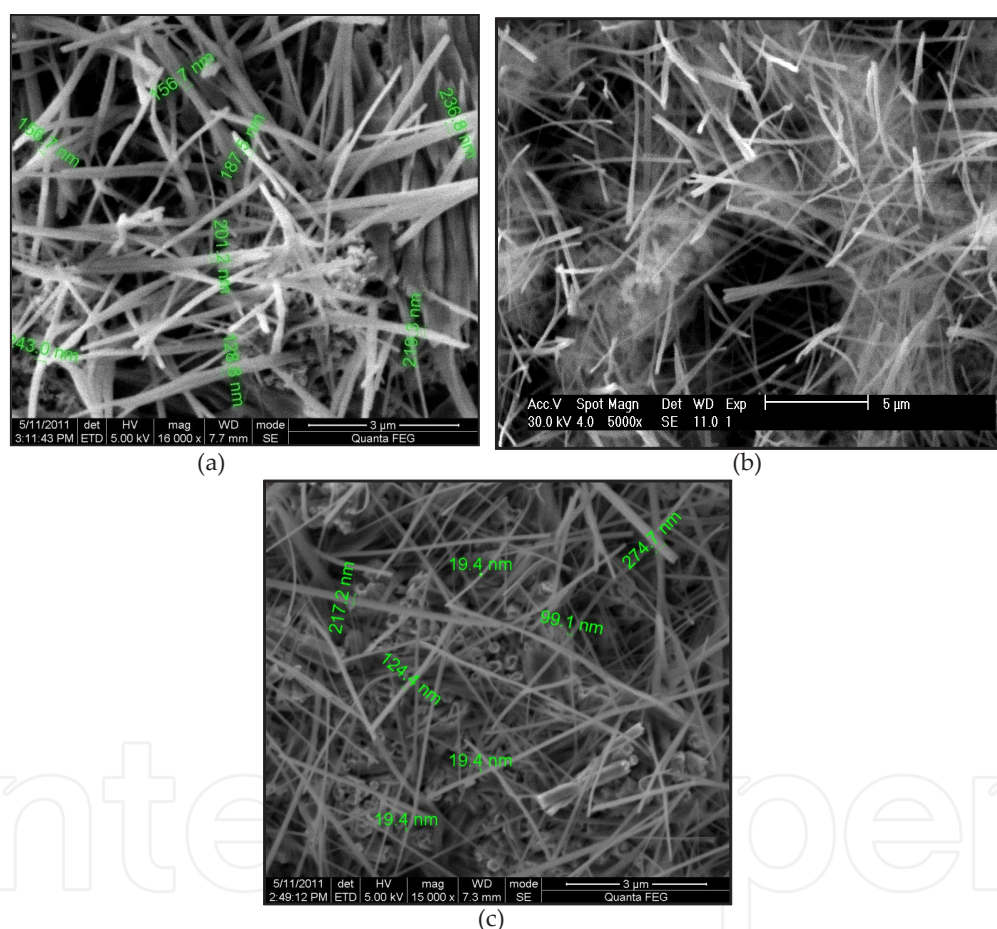


Figure 2. (a,b,c,) Typical SEM micrographs obtained for (a) undoped ZnO thin films and (b) Mn (2%), (c) Fe (2%) doped thin films prepared by SILAR

3. Optical properties of undoped and Fe doped ZnO thin films

Figure 3 shows the transmittance spectrum of the MZO, FZO thin films grown on glass substrate. ZnO is a non-stoichiometric oxide and is known to contain zinc-ion excess de-

fects based on the presence of either zinc interstitial or oxygen vacancies. The films have excellent transmittance and very low absorption and reflectance. The optical band gap of the FZO and MZO thin films has decreased on Fe and Mn doping, respectively. Assuming doping levels are well below Mott's critical density, the change in optical band gap can be explained in terms of Burstein–Moss band gap widening and band gap narrowing due to the electron–electron and electron–impurity scattering. At high doping concentrations, fermi level lifts into the conduction band. Due to filling of the conduction band, absorption transitions occurs between valance band and fermi level in the conduction band instead of valance band and bottom of the conduction band. This change in the absorption energy levels shifts the absorption edge to higher energies (blue shift) and leads to the energy band broadening. While on Mn and Fe doping into the ZnO matrix can explain the increase in shift in the band gap value indicating that either it may due to any charged defects or the charged defects formed had been neutralized by other defects. Hence, the blue shift in the band gap value by Mn and Fe doping suggest an increase in the n-type carrier concentration, most of the Fe ions must be incorporated as interstitial donors into the structure rather than substitution of acceptors.

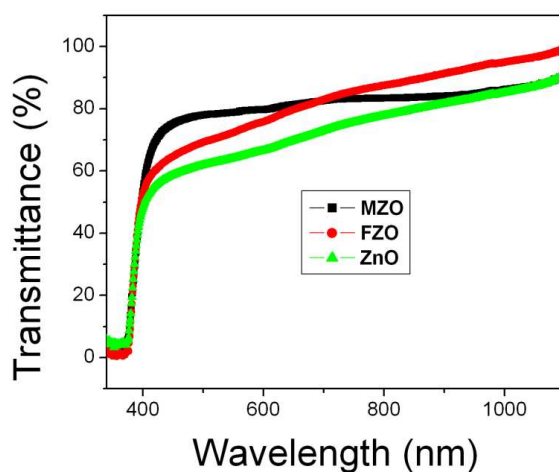


Figure 3. Optical transmittance of typical doped and undoped ZnO thin films

4. Magnetic properties of undoped and Mn, doped ZnO thin films

The ZnO thin films when studied using VSM show a Coercivity (H_{ci}) 238.70G Under Field at $M_s/20$ G, its H_{ci} , Negative -230.81 G and H_{ci} , Positive 246.60 G, respectively. The undoped sample had Magnetization (M_s) $3.0830E-3$ mu/cm² and Retentivity (M_r) $368.68E-6$ emu/cm² respectively. The field at $m_s/20$ G specifies the absence of any soft or hard magnetic property. The magnetization M-H curve (Figure 4) also shows a behaviour analogous to a non magnetic material for undoped ZnO thin films. However the FZO and MZO sample showed the characteristics of a ferromagnetic behaviour magnetic field, and the saturated

magnetization (M_s) is $697.32 \times 10^{-6} \text{ emu/cm}^2$. It's a well known fact that the magnetic properties of dilute magnetic systems can be explained by bound magnetic polaron (BMP) model (Hu, et al., 1992; Jiang, et al., 2003). According to this model an impurity site (donor or acceptor) plays the role of a trap and captures the carrier (electrons or holes) to form a bound polaron. These polarons are usually surrounded by the magnetic Mg ions. The polaron interaction with magnetic Mg ions causes the alignment fully or partially to generate the magnetic property of the system. Considering the morphology of the Metal doped ZnO films which had Zn defects and $\text{Fe}^{2+}/\text{Mn}^{2+}$ in the ZnO:Mn film. The ferromagnetism observed in the film can be explained by using the BMPs model. The magnetic exchange interaction between ZnO and $\text{Fe}^{2+}/\text{Mn}^{2+}$ occupying the same space is aligned with $\text{Fe}^{1+}/\text{Mn}^{1+}$ spins, forming BMPs. Thus, the sample can exhibit ferromagnetism. Similar behavior of room temperature ferromagnetism is exhibited by Mn doped ZnO thin films grown by SILAR.

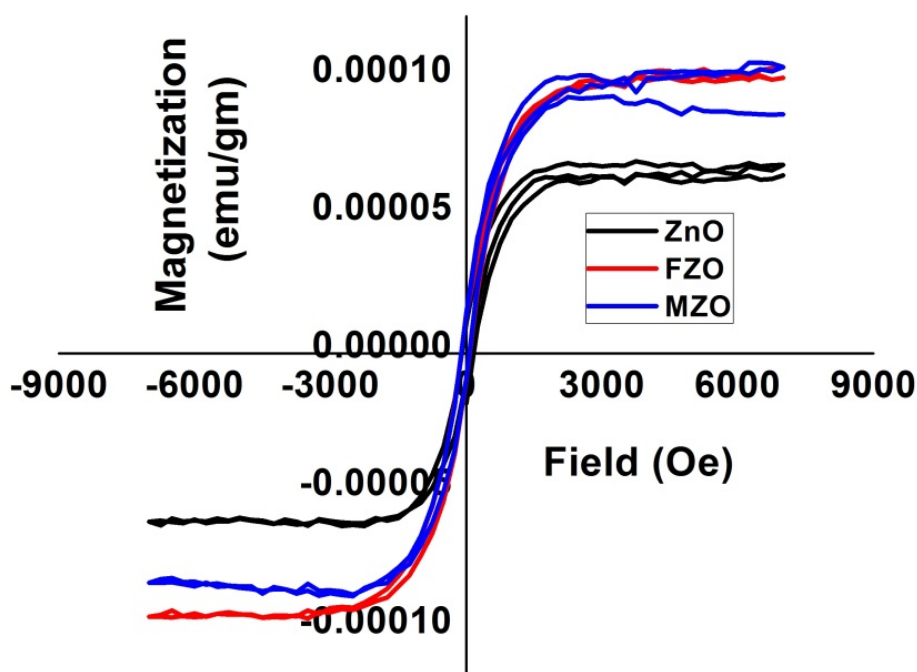


Figure 4. (a) The VSM spectra of undoped and Fe and Mn doped ZnO thin films grown by SILAR.

In summary, Polycrystalline, hexagonal ZnO, MZO and FZO thin films with (002) preferential orientation have been deposited from aqueous solutions using a modified two-step chemical bath deposition technique onto a glass substrate. The microstructure of the films are studied and reported. The studies revealed the potential of this SILAR method in creating and designing varieties of morphologies suitable for various applications. Optical absorption indicated the shift in band gap to 3.21 and 3.22 eV respectively for FZO and MZO films with respect to band gap of ZnO matrix and refractive index to be around 2.34 for FZO films and the bandgap decreased to 3.22 eV for MZO films with a refractive index around 2.3. The transmittance became higher for both MZO and FZO films with increase in doping concentration. In the doped ZnO films, the films were oriented more preferentially along the

(002) direction, the grain size of the films decreased, the transmittance also became higher and the electrical resistivities decreased. It is shown that doped ZnO thin films deposited with a CBD technique can have high temperature ferromagnetic property and this transition may be explained by the BMP model. Extensive characterizations on the structure, micro-structure optical and electrical properties have been made and the exotic choice available in this simple method has paved way for the synthesis of many similar systems by our group like Fe, Mg and Mn doped ZnO thin films and other TCO systems like CdO, etc. Also the properties of these thin film nanocrystallites can be tailored to suit variety of applications like, phosphors, display panels, thermal conduction and opto electronic devices. The technique is easy for automation and anticorrosive coatings can be coated employing doped ZnO systems on to various mechanical spares. The potential of this technique is yet to be exploited in full by the industrial community. The crystallite shape and size control is also feasible in this excellent method.

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