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Chemically derived $Zn_{0.90-x}Mn_{0.05}Fe_{0.05}Al_xO$ thin films: Tuning of crystallite/grain size, optical and dielectric constants and ferromagnetic properties through Al substitutions

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ABSTRACT

In this study, the role of Al substitution levels (x = 0.0–0.05) on the structure, surface morphology, optical constants, dielectric, electrical and magnetic properties of chemically derived $Zn_{0.90-x}Mn_{0.05}Fe_{0.05}Al_xO$ (ZMFO:Al_x) thin films were systematically investigated. The results demonstrated the incorporation of Mn^{2+}, Fe^{2+} and Al^{3+} within ZnO wurtzite structure without any secondary phases. The crystalline quality of thin films was decreased systematically until x = 0.01 and then increased again for x = 0.03 and 0.05 Al substitution levels. Surface morphology analysis indicated homogeneous and smooth surface with spherical grains indicated the same trend with the crystalline quality in size upon ~~on~~ the Mn^{2+} Fe^{2+} and Al^{3+} substitution levels. The confirmation of the Mn^{2+} Fe^{2+} and Al^{3+} ions incorporated in ZnO host structure was successfully observed via XPS analysis. Optical analyses confirmed the blue shift of the band edge depended on the substitution of Mn^{2+} Fe^{2+} and Al^{3+} within the ZnO crystal. Comparatively, the higher refractive index, extinction coefficient and dielectric constants were obtained for the ZMFO: Al_x thin films than those of ZnO, $Zn_{0.95}Mn_{0.05}O$ (ZMO) and $Zn_{0.90}Mn_{0.05}Fe_{0.05}O$ (ZMFO) thin films. Hall measurements showed that all the film samples have n-type conductivity and it varies according to the crystallite size/grain sizes. Magnetic measurements showed higher room temperature ferromagnetic response for the ZMFO: Al_x thin films than those of ZMO and ZMFO thin films due to having different oxygen vacancy concentrations. The highest room temperature was found for the Al substitution level of x = 0.03 thin film.

1. Introduction

During the last decade, transparent oxide materials based on ZnO have attracted attention due to their advantages such as being low cost and abundant materials, nontoxicity, band gap tailoring ability, high chemical stability [1–4]. It is known that ZnO is an important II–VI semiconductor having broad optical energy gap (3.37 eV) and the large exciton binding energy (60 meV) at room temperature. Such superior advantages make ZnO an outstanding candidate for the liquid crystal displays, spintronics, ultraviolet and visible semiconductor lasers, solar cells components, gas sensors and varistors as well as the transparent conductive films [5–8]. Moreover, it has been used as one of the most important materials for the diluted magnetic semiconductors (DMS's).

Recently, a great effort has been made to prepare transition metal doped ZnO based DMS's [9–11]. Mn-doped ZnO has been grown to research its electrical and magnetic properties for the possible applications [12]. It is suggested that Mn-doped ZnO nanoparticles have a ferromagnetic nature [13]. To tune the structural, optical and magnetic properties of the Mn-doped ZnO different elements such as Fe, Co, Cu, Al, etc. have co-doped with Mn in ZnO [14–18]. For example, Ashraf et. al. [17] and Shafig et. al. [14] have reported that Fe and Mn co-doping brings about enhanced room temperature ferromagnetism (RFT) in ZnO thin films as well as variation in structure and microstructure of them. The carriers mediated RTF has suggested for the Ni and Al co-doped ZnO nanocrystallites [19], Tuning of the dielectric and magnetic characterizations of Co and Cu co-doped in ZnO nanoparticles have been reported by Ashokkumar et. al. [20]. Recently, Atiq et. al. [15] have found to increase RTF while decreasing resistivity in Al doped ZnMnO nano-crystallites with increment of the Al doping levels. More recently, Jannesari et. al. [21] has suggested that the improved structural, optical and magnetic properties of Al and Fe co-doped ZnO nanoparticles which are depended on sintering environments.

The origin of the RTM in transition metals (TM; Mn, Fe, Co, Ni, etc.) doped/co-doped ZnO is highly variable upon the used dopants and

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preparation methods as well as sintering conditions. Possible origin of the RTF can be followed as: the secondary phases due to the doping of the TM (1); intrinsic ferromagnetism (2); the TM clusters (3); defects in the ZnO system interacting with TM (4); electron or hole interaction with TM for the TM doping levels up to 10%; and super-exchange or double-exchange interaction (5) [3,11].

The main optical properties of materials are depended highly upon on the optical constants such as absorption coefficient (α), refractive index (*n*), extinction coefficient (*k*), and dielectric constant (ε), which are certain parameters for device fabrication. They can be determined via optical spectra of transmittance, absorbance, and reflectance [9,22,23]. ZnO is a relatively good reflector and dielectric filter owing to its high refractive index (2.4) and high transparency in visible range [9]. Several researchers have reported that its optical and dielectric properties of ZnO thin films and nanoparticles can be tuned by various metals as well as their doping concentrations. For instance, Wang et. al. [24] have recently reported that the *n* of Na doped ZnO is gradually improved and He et. al. [25] have suggested that the optical constants such as α, *n*, *k* and ε have considerably increased through La doping in ZnO thin films. More recently, Goktas et al. [9] have found that enhanced *n* and k values for the Mn and Co doped ZnO thin films.

Taking into account the above theoretical and experimental studies, it is clearly seen that the structural, micro structural, optical, dielectric and magnetic properties of co-doped TM or different metals in ZnO are highly sensitive on the dopants kind, concentrations and preparation conditions. With this aim Al substituted for $Zn_{0.90}Mn_{0.05}Fe_{0.05}O$ (ZMFO) thin films have been synthesized by chemical route (known as sol-gel) and dip coating technique to investigate the role of Al doping concentrations on the structural, micro structural, optical, dielectric and magnetic properties of the ZMFO thin films systematically. In more detail, the aim of this study is to explain the origin of the enhanced room temperature ferromagnetism by changing doping level of Al in Fe and Mn co-doped ZnO. To explore it the detailed structural and optical characteristics were investigated. Currently, this technique is widely used as one of the most efficient ones besides other conventional techniques due to its advantages such as simplicity, low cost, easy control, mixing of reactant at molecular level, and being environmentally friendly. Moreover, it helps to prepare different kind of oxide/sulphide materials and others with high crystallization and required phases of nanostructures in a very convenient time [26–29].

2. Experimental

Undoped ZnO, $Zn_{0.95}Mn_{0.05}O$ (ZMO), $Zn_{0.90}Fe_{0.05}Mn_{0.05}O$ (ZFMO) and $Zn_{0.90-x}Fe_{0.05}Mn_{0.05}Al_xO$ (x = 0.0–0.05) thin films were synthesized by wet chemical process and dip coating technique. These thin films were prepared from highly pure zinc acetate dihydrate (99.99%), aluminum nitrate nonahydrate (99%), iron nitrate monohydrate (99.95%), and manganese nitrate tetrahydrate (99.98) as precursor chemicals as well as 2-metoxyethanol and ethanolamine as solvent and stabilizer, respectively.

The precursor chemicals were dissolved in 2-metoxyethanol at room temperature to get the desired solution and it was constantly stirred for 1 h without any premise distillation/purification. The molar ratio of any powder precursor and 2-metoxyethanol was fixed to 0.1 and 1 M in the solutions. The molar ratios of the Zn/Mn and Zn/Mn/Fe were kept at 95/5 and 90/5/5 for the Mn doped ZnO and Mn and Fe co-doped ZnO. However, in case of the Fe, Mn and Al co-substitution for ZnO, where the Fe and Mn substitutions had a fixed molar ratio of 5%, whereas it was changed from 0% to 5% and 89–85% for the Al and Zn, respectively. The pH of the obtained homogeneous and transparent solutions was adjusted by adding 0.05 M ethanolamine drop wise and it fixed to 4.6. The final solutions were aged for 24 h to get more stable and obtain the desired gelation. These last solutions were coated on the glass substrates by dip coater at 773 K. To get the crystallization of the coated films they were sintered at 823 K and under air environment for 1 h in furnace.

Rigaku Ultima III (CuKα, 40 kV, 40 mA, 1.54 Å) x-ray diffractometer (XRD) was employed to characterize the films structurally. The chemical bond state of the Zn, Fe, Mn, Al, and O atoms was analyzed through x-ray photoelectron spectroscopy (XPS) (PHI-5000 Versaprobe). The morphology and the composition of the all film samples were scrutinized via FESEM with attached energy dispersive X-ray (EDX) spectrometer (QUANTA 400 F) at an operating voltage of 20 kV. Optical properties were investigated by Ultraviolet–visible (Uv) spectrophotometer (Perkin Elmer 45 UV–VIS) in the wavelength range of 300–900 nm. The conductivity of the film samples were analyzed through Hall measurements system with using a four terminal van der Pauw configuration. Magnetization studies were performed on vibrating sample magnetometer, VSM (Cryogenic Limited PPMS, XL-5T) in the temperature range 2–300 K.

3. Results and discussion

3.1. Structural properties

The XRD patterns of the ZnO, ZMO, ZFMO and $Zn_{0.90-x}Mn_{0.05}Fe_{0.05}Al_xO$ (ZMFO: Al_x) thin films for various substitution levels (x = 0.0–0.05) were presented in Fig. 1a. It is represented that the thin films have intense peak diffraction along (002) plane, indicating typical hexagonal wurtzite ZnO structure (JCPDS card no. 01-071-5959) with no existence of the secondary phases such as metallic Mn, Fe, Al, and their oxides, confirmed there is no change in single phased hexagonal wurtzite ZnO structure. As seen in Fig. 1b, the presence of other weak diffraction planes, (100) and (101), is much more apparent than those in Fig. 1a, showing the polycrystalline nature of the films. There is a

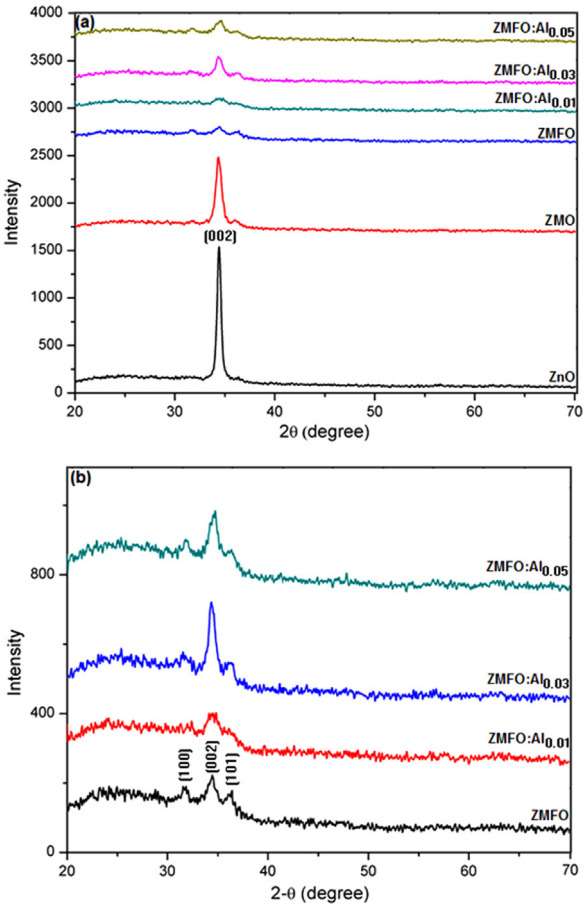

Fig. 1. (a) XRD patterns for the ZnO, ZMO, ZMFO and ZMFO:Al_x (x = 0.0–0.05) and (b) ZMFO: Al_x (x = 0.0–0.05) thin films.