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Applicability of the polymeric precursor method to the synthesis of nanometric single- and multi-layers of $Zn_{1-x}Mn_xO$ (x=0-0.3).

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Abstract – Single $Zn_{1-x}Mn_xO$ (x = 0-0.3) films and multilayers were prepared by polymeric precursor method onto glass substrates. The soft chemical method consisted in preparing a coating solution from the Pechini process followed by a three-step thermal treatment of the as deposited films up to 550 ℃. XRD analysis revealed würzite structure of b oth single and multilayers being the average grain size ~15 nm. At x=0.3, a secondary Mn-phase could clearly be detected. This was linked to the solubility limit of the Mn ions in ZnO and was discussed within the frame of the ionic radius and valence states.

Spintronics devices exploit both charge and spin to carry information data [1]. As a matter of course, ferromagnetic properties at room temperature should be introduced in semiconducting materials. Among the materials reported so far, Mn-doped GaAs has been found to be ferromagnetic with the highest reported Curie temperature T_C ~ 172 K [2]. Recently, semiconducting ZnO has attracted enormous research attention because its interesting electrical, optical, magnetic, and piezoelectric properties [3]. For example, ZnO has a direct band-gap (E_g = 3.37 eV) and a large exciton binding energy (60 meV). Hence, it is a potential candidate material for technological applications as ultraviolet light emitting devices [4] or UV lasers. Many of such practical applications demand the fabrication of high quality ZnO thin films. Although physical methods as molecular-beam epitaxy (MBE), sputtering or spray pyrolysis have been extensively used in thin film technology, chemical methods as sol-gel processes or polymeric precursor method (Pechini) [5] particularly adapt to produce ZnO colloids and films in a simple, low-cost and highly-controlled way. Theoretical calculations have predicted for the possibility of ferromagnetic phenomenon in transition metal (TM)-doped ZnO even at room temperature [1]. However, this prediction is confirmed only in several groups based on their measurements of magnetic properties for TM-doped ZnO thin film samples. The controversial results seem to come from either the low quality or the poor reproducibility of thin film. Here, it is necessary to investigate the factors of growth parameters that enhance ferromagnetic ordering in Mn–Zn–O systems. In this work, the polymeric precursor method was employed to fabricate $Zn_{1-x}Mn_xO$ (x = 0-0.3) films and multilayers on glass substrates. XRD spectra revealed the typical hexagonal würzite structure of both the single and $Zn_{1-x}Mn_xO$ multilayers. Rietveld refinement yielded an average grain size of 15 nm. The existence of cluster-type structures on the surface was corroborated by Atomic Force Microscopy (AFM). Absorption edge of the doped film was redshifted to 2.9 eV (3.24 eV for undoped ZnO film) and the absorption edge was less sharp due to Mn states extending into the band gap. The decrease in this parameter may be attributed to the *s-d* and *p-d* interactions giving rise to band gap bowing. The temperature dependence of the magnetization measured on the sample with x=0.3 showed typical paramagnetic behavior.

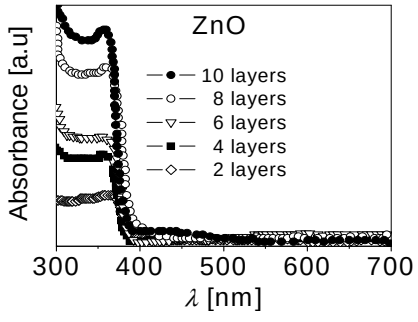

Figure 1: Optical absorbance spectrum of ZnO films obtained by polymeric precursor method.

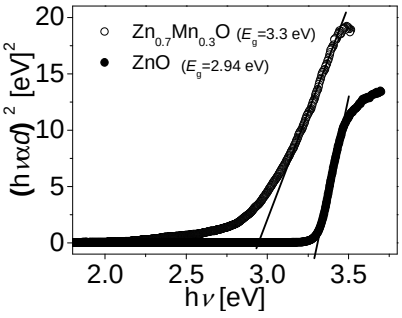

Figure 2: Room-temperature Optical direct band-gap of a $Zn_{0.7}Mn_{0.3}O$ film grown on a glass substrate.

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