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Effects of codoping in ZnO-based semimagnetic semiconductor thin films

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Abstract. Single doped $Zn_{1-x}Mn_xO$, $Zn_{1-x}Fe_xO$ and codoped $Zn_{1-x-y}Mn_xFe_yO$, $Zn_{1-x-y}Mn_xSn_yO$, $Zn_{1-x-y}Mn_xLi_yO$, $Zn_{1-x-y}Fe_xAl_yO$ thin films were grown on sapphire and glass substrate by pulsed laser deposition and RF sputtering techniques. No secondary phases was detected from XRD analysis. Among the studied oxide films single doped with Fe and codoped with (Mn,Fe) and (Fe, Al) exhibit n-type conductivity and room temperature ferromagnetic behaviour. For the films codoped with (Mn, Sn) formation of clusters including nanowire-like structures was shown from AFM analysis. Optical and magnetooptical studies suggest of Mn, Fe, Sn and Li substitution for Zn^{2+} ions in ZnO lattice.

1. Introduction

In recent years semimagnetic semiconductor (SMS) or diluted magnetic semiconductor oxides are subjects of considerable attention because of their potential applications in optoelectronic and spintronic devices [1-3]. In particular, a key point to realize spintronic devices is to fabricate material with ferromagnetic ordering at room temperature. Among different SMS materials, ZnO-based systems doped with transition metals (TM) belong to the most attractive, since there is possibility to control independently the concentration of the charge and spin of the carriers. However, the experimental confirmation of ferromagnetism in ZnO-based SMS is controversial, and the mechanisms of such an ordering are unclear [4-8]. One of the possible explanations of the ferromagnetism in these materials is to reveal defects which increase concentration of free carriers. Such delocalized carriers can hybridize with the localized spins of magnetic impurity atoms and provide exchange coupling between d-spins localized on magnetic atoms [4]. Another possible pathway for inducing ferromagnetism was pointed out by consideration of codoping, i.e. the simultaneous presence of two kinds of defects [7]. It was considered the role of the Cu ions in codoped Zn(Co,Cu)O which act as superexchange mediators.There is suggestion that the role of Cu ions is analogous to that played by the free electron in the development of RKKY interaction. The interesting

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point should be mentioned which consists in a concept that the presence of TM is not necessary for providing of the ferromagnetic properties of ZnO-based oxides [8]. Even pure ZnO can be ferromagnetic, critical is the low grain size, and not the doping with magnetic atoms as it was originally supposed.

In our previous works [9, 10], we carried out studies of the Mn single doped ZnO bulk crystals and thin films. In this work, in order to study effects of codoping we focus main attention on growth and characterization of single doped $Zn_{1-x}Mn_xO$, $Zn_{1-x}Fe_xO$ and codoped $Zn_{1-x-y}Mn_xFe_yO$, $Zn_{1-x-y}Mn_xSn_yO$, $Zn_{1-x-y}Mn_xLi_yO$, $Zn_{1-x-y}Fe_xAl_yO$ thin films.

2. Experimental

Two different techniques were used for growth of ZnO-based oxide thin films. The single doped $Zn_{1-x}Mn_xO$ and $Zn_{1-x}Fe_xO$ thin films with composition in range of $0 \leq x \leq 0.1$ were deposited by pulsed laser deposition (PLD) technique. In PLD set-up an ultrahigh vacuum chamber with a base pressure of 10^{-7} Pa and XeCl excimer laser (λ=308 nm, τ=30 ns) were applied. Laser was operated at a repetition rate of 10 Hz, and laser fluence was about 5.5 J/cm^2.

Codoped $Zn_{1-x-y}Mn_xFe_yO$, $Zn_{1-x-y}Mn_xSn_yO$, $Zn_{1-x-y}Mn_xLi_yO$, $Zn_{1-x-y}Fe_xAl_yO$ were grown by RF-diode sputtering technique with planar cathode and 1.76 MHz power source in argon-oxygen mixture.

Targets for both techniques were prepared by pressing with using of ZnO, Mn_3O_4, Fe_3O_4, SnO_2, Li_2O pure powders as initial components. Mainly glass and sapphire were used as substrates. The substrate temperature was varied between 20 and 350^{o}C.

X-ray diffraction (XRD) technique with Cu K+ radiation was used to characterize the crystal structure of the films. Atomic force microscopy (AFM) [Nanotec Cervantes AFM] was used to evaluate the surface morphology of the films. Optical transmission and absorption spectra were measured in range of (0.2-25) µm at temperatures of (4.2-300) K. Magneto-optical Faraday effect was measured in range of (400-700) nmm in magnetic field up to 5 T.

3. Results and discussion

Figure 1 shows XRD patterns of the as-prepared $Zn_{1-x-y}Mn_xFe_yO$ and $Zn_{1-x-y}Mn_xSn_yO$ thin films on sapphire substrates. It can be seen that the samples possess hexagonal wurtzite structure. The only difference was observed in the relative intensity of [002] peak to [004] peak and in width of diffraction lines for two different codoped films. No secondary phases can be detected from XRD analysis of the studied oxide films.

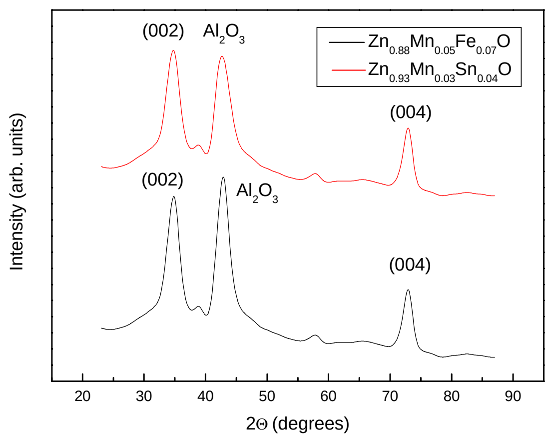
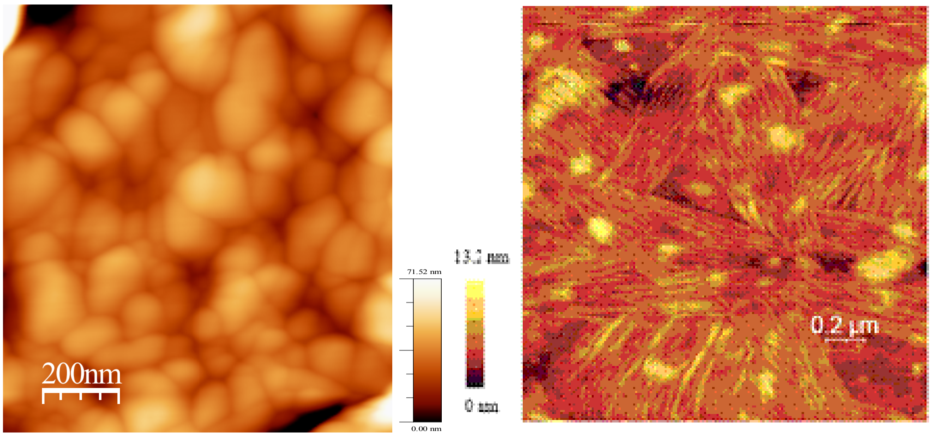


Figure 1. XRD patterns of $Zn_{0.88}Mn_{0.05}Fe_{0.07}O$ and $Zn_{0.86}Mn_{0.1}Sn_{0.04}O$ thin films on sapphire substrate.

To determine the surface morphology of the codoped films, AFM analysis was performed for several samples. AFM image corresponding to $Zn_{0.85}Li_{0.09}Mn_{0.06}O$ film deposited by RF sputtering on glass substrate is shown in Figure 2a. This image indicates that the surface roughness of the $Zn_{0.85}Li_{0.09}Mn_{0.06}O$ film is very high with a root mean square roughness (Rms) of 4.3 nm. In contrast, for codoped $Zn_{0.93}Mn_{0.03}Sn_{0.04}O$ film AFM image shown in Figure 2b suggests of more complicated surface morphology. There is clear evidence for the formation of elongated clusters which in turn consist of nanowires. The estimated length of nanowires is about 3-4 µm, and average diameter is about 10 nm. The observed nanostructures are oriented mainly along the surface plane.



a b

Figure 2. AFM micrographs (topography in dynamic mode) of $Zn_{0.85}Li_{0.09}Mn_{0.06}O$ (a) and $Zn_{0.93}Mn_{0.03}Sn_{0.04}O$ (b) thin films on glass substrate.

Electrical and magnetic characteristics of the studied single doped and codoped films are summarized in Table 1. Undoped ZnO films as a rule exhibit n-type conductivity which can be explained by inner defects. Among the codoped materials we would like to focus on $Zn_{0.88}Mn_{0.05}Fe_{0.07}O$ and $Zn_{0.85}Fe_{0.1}Al_{0.05}O$ thin films which exhibit p-type conductivity and ferromagnetic behavior. On the other hand, the codoped $Zn_{0.86}Mn_{0.1}Sn_{0.04}O$ and $Zn_{0.85}Fe_{0.1}Al_{0.05}O$ thin films are characterized n-type conductivity and paramagnetic behavior. The presence of room temperature magnetism in $Zn_{0.9}Fe_{0.1}O$ and the first couple of codoped materials can be associated with influence of Fe dopant.

Table 1. Electrical and magnetic characteristics of oxide thin films

Film compositions	Type of conductivity	Conductivity $(\Omega\ cm)^{-1}$	Magnetic state
ZnO	n	10^{-7}	diamagnetic
$Zn_{0,97}Mn_{0,03}O$	n	10^{-6}	paramagnetic
$Zn_{0,9}Fe_{0,1}O$	p	2×10^{-7}	ferromagnetic
$Zn_{0,86}Mn_{0,1}Sn_{0,04}O$	n	1.6×10^{-4}	paramagnetic
$Zn_{0,88}Mn_{0,05}Fe_{0,07}O$	p	2×10^{-6}	ferromagnetic
$Zn_{0,85}Fe_{0,1}Al_{0,05}O$	p	5.5×10^{-4}	ferromagnetic
$Zn_{0,85}Mn_{0,06}Li_{0,09}O$	n	10^{-6}	paramagnetic

Optical transmission spectra for several samples of the codoped oxide SMS are shown in Figure 3. They have typical form in spectral range near energy band gap. The absorption edge is broadened because of disordering effect for quaternary SMS. In addition, the absorption edge is shifted towards the lower wavelength side with the increase of Mn, Fe, Sn, Al and Li content. In Figure 4 magnetic field dependence of Faraday rotation is shown demonstrating ferromagnetic behavior for codoped $Zn_{0,88}Mn_{0,05}Fe_{0,07}O$ film.

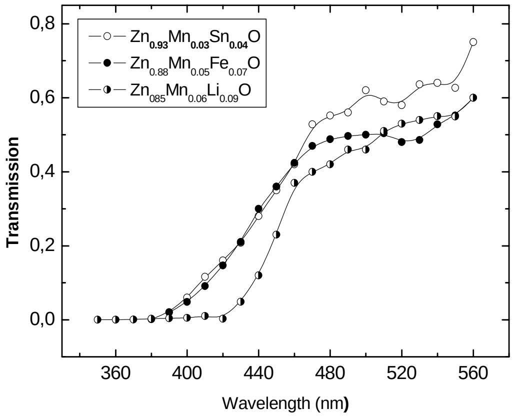


Figure 3. Transmission spectra of codoped oxide SMS thin films.

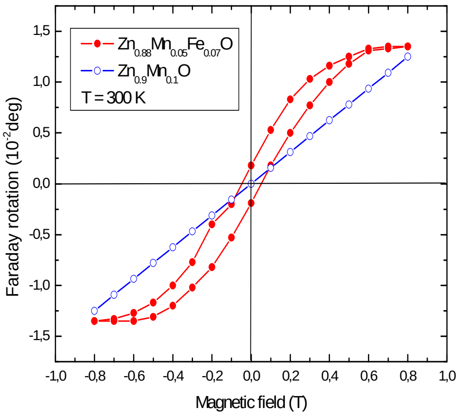


Figure 4. Faraday rotation vs magnetic field for single doped and codoped thin films.

4. Conclusion

Thin films of SMS oxides were grown by PLD and RF sputtering techniques. XRD analysis has not revealed secondary phases. AFM images demonstrate different surface morphology depending on growth conditions and film compositions. Optical and magneto-optical spectra are typical for SMS materials. The obtained results confirm possibility to induce ferromagnetism in ZnO-based SMS by codoping.

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