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Magnetic and electrical properties of undoped and holmium doped ZnO thin films grown by sol-gel method

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Abstract. Undoped and holmium-doped ZnO thin films were obtained, using the sol-gel method. The films were characterized by scanning electron microscopy (SEM), Hall effect measurements, electron paramagnetic resonance (EPR) spectroscopy and superconducting quantum interference device – vibrating sample magnetometry (SQUID-VSM). The Hall effect measurements have indicated a n-type conduction with a resistivity of about 3.2 Ω.cm for the undoped ZnO and of about 4.5 Ω.cm for the 5 at. % Ho-doped ZnO thin films. The EPR measurements have indicated the presence of interstitial zinc in the undoped ZnO and the presence of zinc vacancies in 5 at. % Ho-doped ZnO. Ho (5 at. %)-doped ZnO films exhibit superparamagnetism at 5 K, while a low paramagnetic behavior was observed at room temperature.

Introduction

ZnO is a promising material for many applications such as optoelectronic or spintronic devices, solar cells, transparent conductors, sensors, especially due to its wide direct band gap (3.37 eV) [1-2]. Lately, ZnO-based diluted magnetic semiconductors (DMSs) have been of great interest because of some theoretical predictions of room temperature ferromagnetism [3]. So far, doping ZnO with transition metals like Co, Fe, Mn, Ni was usually employed in order to obtain ferromagnetic properties in ZnO [4-12]. However, the origin of the ferromagnetism is already controversial. Some studies indicate no ferromagnetism in transition metal doped ZnO [13], while others detected metal clusters in the ZnO matrix, the origin of the ferromagnetic properties being associated with defects in the ZnO matrix [14]. According to recent studies, a ferromagnetic behavior has also been observed in some undoped ZnO samples, as well and was usually attributed to the presence of defects, especially interstitial zinc and oxygen vacancies [15]. Rare earths (RE) doped ZnO with has also attracted considerable interest due to their 4f shells [16-21]. The 4f electrons are localized and the exchange interactions are indirect via conduction electrons, which result in high total magnetic moments per atom owing to its high orbital momentum [16]. Rare earths such as Gd [16, 22-24], Tb [19, 25], Er [17], Eu [26], and Sm [20] were used as dopants in order to modify the ZnO magnetic properties.

In this paper, we have prepared undoped and Ho-doped ZnO thin films, using the sol-gel method. Holmium has the highest magnetic moment (10 μ_B) of all naturally occurring elements and grants ferromagnetism below 19 K [27]. The influence of holmium in the ZnO host matrix on magnetic properties is relatively poor debated in literature [28-29]. Therefore, a special attention is devoted to the magnetic and electrical properties of these materials in this study.

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Experimental part

Sample preparation. The thin films were obtained using a precursor solution of 0.7 M zinc acetate dihydrate (ZnAc) (Merck, 99,5%) and holmium nitrate pentahydrate (Aldrich, 99,99%) - 1, 3 and 5 at. % Ho in ZnO, in absolute ethanol (ETOH) (Alfa Aesar, 99%). Monoethanolamine (MEA) (Alfa Aesar, 98%) was added as a complexing agent, to increase the ZnAc dissolution rate in ethanol. The as-obtained solution was aged under stirring for about 15 h. Fused quartz (Alfa Aesar) substrates were used for the thin films deposition. Prior to the deposition, the substrates were cleaned successively in ethanol / acetone / ethanol for 5 minutes each solvent in an ultrasonic bath. The coating solution was deposited on the substrates by spin-coating (3000 rpm/30 s), using a VTC 100 spin-coater. The films were deposited in 3 layers and subsequently pre-heated at 300 °C for 2 minutes. The final thermal treatment was performed at 500 °C for 2h.

Sample characterization. The morphology and the thicknesses of the films were determined using a JEOL JSM 6700F scanning electron microscope (SEM).

The room temperature electric properties were carried out using an Ecopia Hall effect equipment. The Hall coefficient and the resistivity (ρ) are experimentally determined and then related to the electrical parameters through the following relations (for the *n*-type conduction):

$$R_H = \frac{r_H}{n \times e} \quad (1)$$

$$\mu_H = \frac{r_H}{\rho} \quad (2)$$

where n is the free-electron concentration, e is the unit electronic charge, μ_H is the Hall mobility, and r_H is the Hall scattering factor which is dependent on the particular scattering mechanism. The transport properties reported in literature, mostly based on Hall effect measurements, assume the Hall scattering factor to be unity [30].

A MPMS SQUID–VSM (Quantum Design) magnetometer in a temperature and field ranges of 5 - 300 K and 0 - 7 T, respectively, was used to determine the magnetic properties of the samples.

EPR measurements of the thin films were carried out on a Bruker E-500 ELEXSYS X-band spectrometer at room temperature. The spectra processing was performed by Bruker Xepr software.

Results and discussion

Morphological characterization. The SEM images are shown in Fig. 1. The films present an homogeneous morphology in undoped ZnO and 1 and 3 at. % Ho-doped ZnO. Small bumps in the Ho-doped ZnO thin films morphology can be observed. The thicknesses of the films vary between 200 - 250 nm.

Electrical characterization. The resistivity and the Hall mobility as function of Ho doping is shown in Fig. 2. One can remark a small increase of the resistivity by increasing the holmium concentration from 0 to 5 at. %. Seemingly, the enhancement is slightly accentuated in the 5 at. % Ho-doped sample, as compared with the trend observed for the rest of the samples. S. Singh *et al* [28] have also reported the increase of the resistivity when doping the ZnO nanoparticles with Ho. The Hall mobility exhibits a decrease when the Ho concentration raised from 0 to 3 at. % and further increased when the Ho concentration reaches 5 at. %. These materials show a *n*-type conductivity, having a carrier concentration as high as 1.8×10^{19} cm^{-3} for the undoped ZnO, while the highest carrier concentration of the Ho-doped ZnO series was 3.2×10^{19} cm^{-3} for the 3 at. % Ho-doped sample.

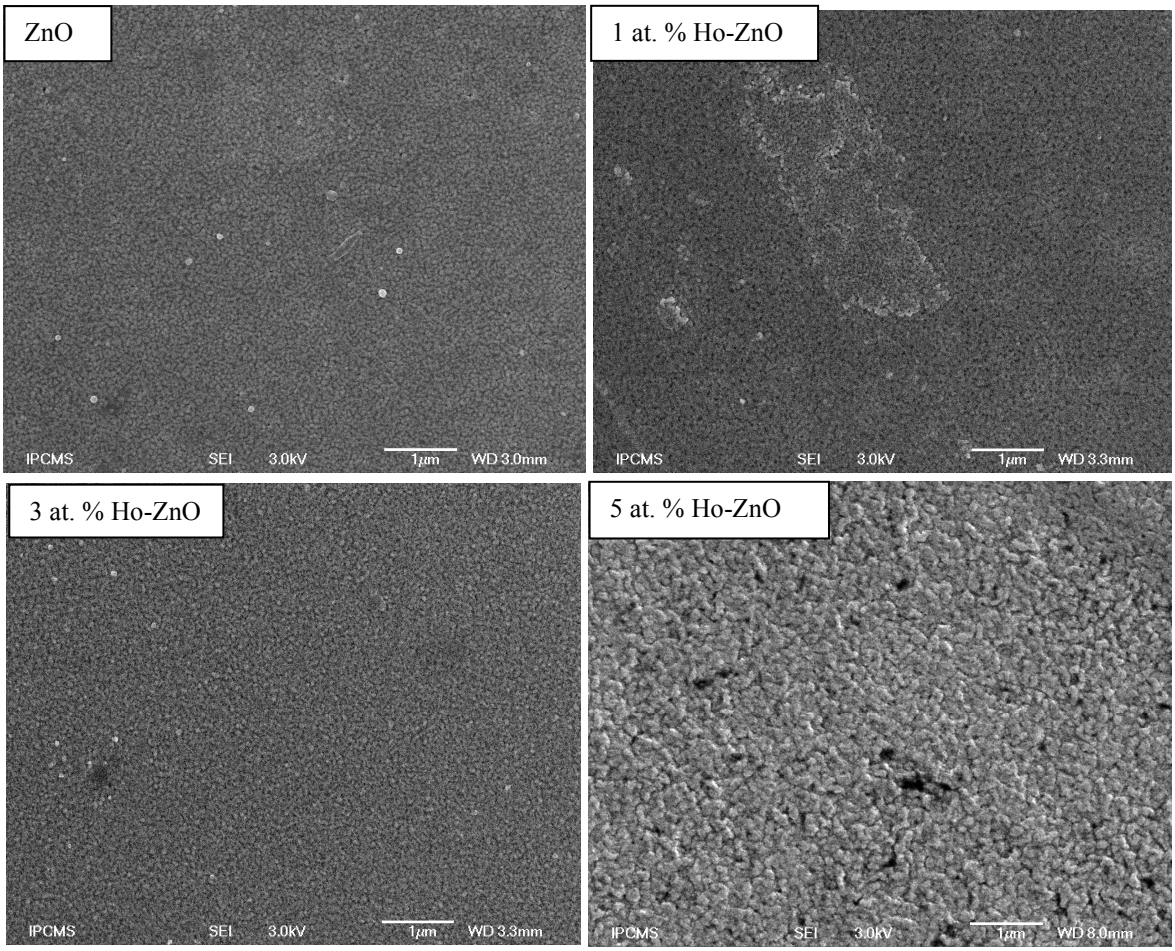


Fig. 1. SEM images of undoped and 1, 3 and 5 at. % Ho-doped ZnO thin films.

Undoped ZnO with a wurtzite structure naturally is confirmed as an *n*-type semiconductor due to the presence of intrinsic or extrinsic defects, which were generally attributed to native defects, such as the Zn-on-O antisite (ZnO), the Zn interstitial (Zn_i), and the O vacancy (V_o) [30].

EPR spectroscopy is a sensitive technique to characterize paramagnetic centers, impurities, and other types of defects in any material. Fig. 3 presents the EPR spectra of ZnO and 5 at. % Ho-doped ZnO thin films. The EPR spectrum corresponding to the ZnO thin films shows a low and broad signal centered at g = 2.019. In literature, this signal has been attributed to Zn vacancies [31]. For the 5 at. % Ho-doped ZnO thin films, the EPR spectrum exhibits two sharp signals at g = 2.14 and g = 2.75. The intense resonance at g = 2.14 has been assigned to Zn vacancy [31-32].The origin of the resonance at g = 2.75 is not known. As expected, no resonance signal corresponding to Ho^{3+} ions was observed at room temperature.

The electrical properties of the undoped ZnO thin films prepared by sol-gel are comparable with those reported in literature [33-35], while the Ho-doped ZnO resistivities seem to be higher than those of Sm-doped ZnO thin films, considering a thickness of about 200 nm [20]. In the undoped ZnO, the trapped carriers in the grain boundaries could be responsable for the increase of the resistivity [34]. In the Ho-doped ZnO series, the insertion of the holmium ions in the ZnO matrix is expected to be rather difficult due to the higher ionic radius of the Ho^{3+} ions (0.904 Å) as compared with the Zn ionic radius (0.704 Å). The rare earths could be located at the ZnO grain boundaries, probably as oxides or as REZnO unknown compounds [36], increasing the number of surface defects in the ZnO matrix. Hence, the electrical resistivity of ZnO is reduced as the concentration of holmium in ZnO is increased.

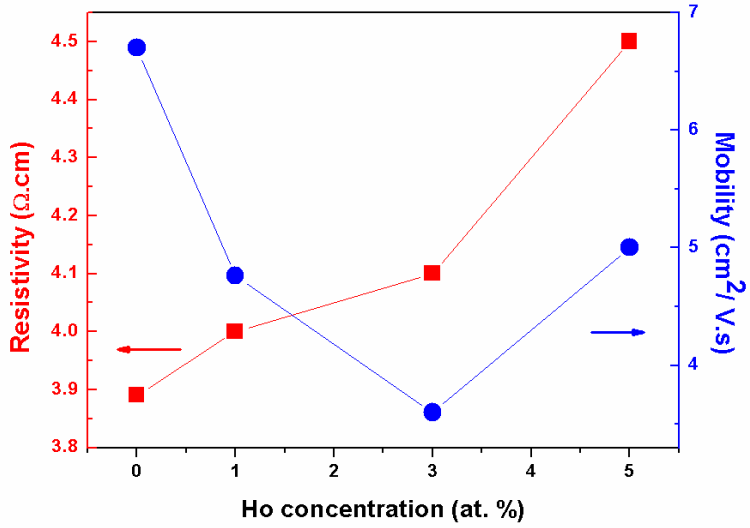


Fig. 2. Resistivity and Hall mobility dependences on Ho concentration in the ZnO thin films.

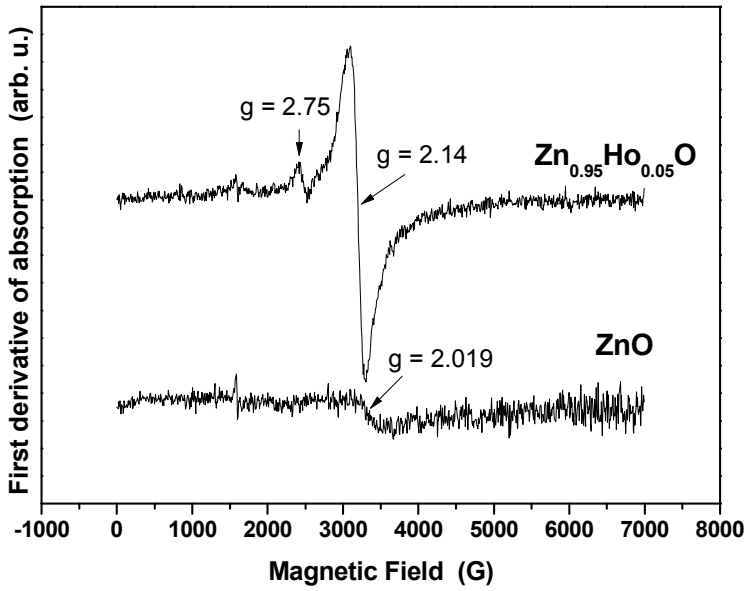
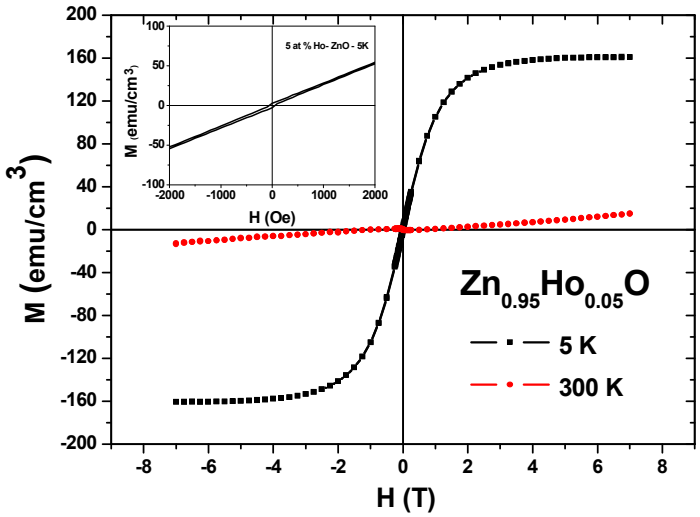


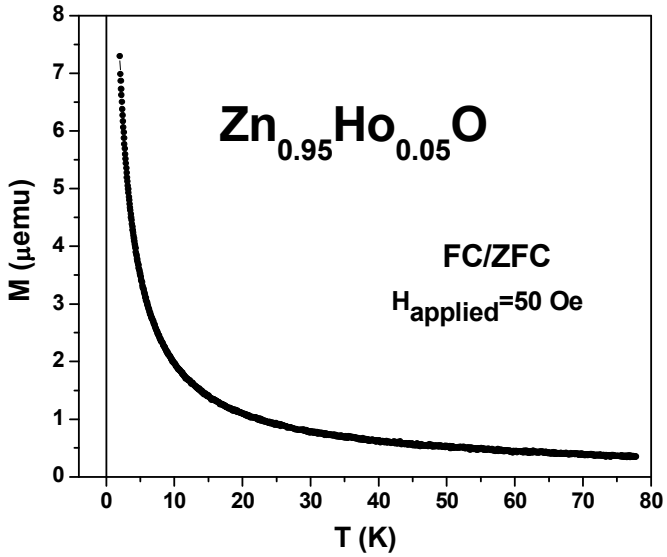
Fig. 3. EPR spectra of the as-deposited undoped and 5 at. % Ho-doped ZnO thin films at room temperature.

Magnetic characterization. The magnetic properties of the samples have also been determined. As expected, the quartz substrate is diamagnetic in the temperature range 5 - 300 K. After substracting the diamagnetic background arising from the substrate, a low paramagnetic behavior has been observed in the undoped ZnO thin films (not shown). The M(H) curves of the 5 at % Ho-doped ZnO thin film, measured at 5 and 300 K, respectively, are shown in Fig. 4 a). A very weak hysteretic comportment can be observed at 5 K. (inset Fig. 4 a)). Room temperature measurements reveal a small paramagnetic behavior, comparable with that of the undoped ZnO sample. The magnetic behavior at 5 K is however difficult to be customized. Rai *et al* [29] have observed a room temperature ferromagnetic behavior in the 5 at % Ho-doped ZnO thin films, detecting a coercive field of $H_C \sim 54$ Oe and a saturation magnetization of 0.339 emu. However, Singh *et al* [28] have also reported a "S"-like hysteresis at 5 K, in the Ho-doped ZnO nanoparticles, where the superparamagnetism below blocking temperature (T_b) was not excluded (at 5 K, T_b was not

observed experimentally in our case). The ferromagnetism in Ho-doped ZnO was attributed to the substitution of Zn^{2+} with Ho^{3+} ions and was explained as a mediated exchange interaction between the 4f Ho^{3+} ions (magnetic moment about 10 μ_B and S = 2) and the free delocalized carriers of the 5d ions [29].



a)



b)

Fig.4. a) Magnetization vs. magnetic field for the 5 at. % Ho-doped ZnO thin film at 5 and 300 K; in the inset, a zoom of the hysteresis recorded at 5 K (inset) and b) The field cooled (FC) and zero field cooled (ZFC) curves for the 5 at. % Ho doped ZnO thin film.

The low hysteretic behavior observed at 5 K makes us believe that a weak ferromagnetic phase might exist in our samples. However, some small Ho_2O_3-ZnO heteroparticles or some individual Ho_2O_3 nanoparticles (more likely smaller than 10 nm) are probably responsible of the rather paramagnetic behavior that we observed. The temperature dependence of the magnetic properties was investigated by zero field cooled – field cooled (ZFC-FC) measurement, performed by applying a magnetic field of 50 Oe (Fig. 4 b). As can be seen, the ZFC and FC curves are overlapped, having a sharp decrease of the magnetization below 10 K. The magnetization was furthermore reduced when the measurement temperature increased above 10 K. A similar ZFC-FC pattern was observed by Subramanian *et al* [24] in Gd-doped ZnO thin films, except for the overlapping of the two curves

which took place only at around 300 K. The overlapping of the ZFC-FC curves was also observed by W. Van den Heuvel *et al* [37] in $Er_{0.3}Pb_{0.7}F_{2.3.}$ In combination with other observed magnetic properties, the authors noticed that the investigated nanoparticles are not superparamagnetic but simply paramagnetic, i.e., described by independent dynamics of individual magnetic moments of Er^{3+} ions.

Obviously, the electric and magnetic behaviors of the Ho-doped ZnO compositions could be particularly related to how the Ho ions interact with the ZnO host matrix. Therefore, an extended study in this way is specially required.

Conclusion

Undoped and Ho-doped ZnO thin films were synthesized by the sol-gel method in order to determine their morphological, electrical and magnetic properties. The SEM images have revealed an uniform structure for the undoped and 1 and 3 at. % holmium-doped ZnO thin films and a distinct structure for the 5 at. % Ho-doped ZnO. The electrical properties, as determined from the Hall effect measurements, indicate an increase of the resistivity by increasing the Ho concentration from 0 to 5 at. %. The highest resistivity was of 4.5 $\Omega \times$ cm, in the case of the 5 at. % Ho-doped ZnO. The Hall mobility decreased by doping with 1 and 3 at. % Ho and increased again for the 5 at. % Ho doped ZnO. The carrier concentration was about 3.2×10^{19} cm^{-3} in the 3 at. % Ho doped ZnO and of about 1.8×10^{19} cm^{-3} in the undoped ZnO. The presence of interstitial zinc in the undoped ZnO and zinc vacancies in the 5 at. % Ho doped ZnO thin films was observed by EPR spectroscopy. The magnetic measurements performed on the 5 at. % Ho doped ZnO thin films exhibited a rather paramagnetic behavior at 5 K and reduced paramagnetism at room temperature.

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