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Electrical, optical and magnetoresistive behavior of nanostructured ZnO:Cu thin films deposited by sputtering

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Abstract
Copper doped ZnO (ZnO:Cu) nanostructured films with magnetoresistive behavior were produced by growing ZnO/Cu/ZnO arrays at room temperature (RT) by the sputtering technique on corning glass substrates. The arrays were made with two electrical insulating ZnO films of 50 and 105 nm, and a Cu film of 5 nm, both materials were deposited at RT by the RF- and DC-sputtering technique, respectively. The processing method involves two stages that proceed in the course of the growth process, the main one is originated by the non-equilibrium regime of the sputtering technique, and the second is the diffusion-redistribution of the intermediate Cu film towards the neighborhood ZnO layers aided by the nanocrystalline films character. The influence of applying an additional annealing stage to the arrays in N_2 atmosphere at 250 and 350 °C by periods of 30 min were studied. The resistivity of the ZnO:Cu films can be varied from 0.0034 to 2.83 Ω-cm, corresponding to electron concentrations of 1.12×10^{21} and 7.85×10^{17} cm^{-3} with carrier mobility of 1.6 and 2.8 cm^2/V s. Measured changes on the magnetoresistance behavior of the films at RT were of $\Delta R\sim3\%$ for annealed samples with electron concentration of 1.12×10^{21} cm^{-3}. The X-ray diffraction measurements show that the films are comprised of nanocrystallites with dimensions between 13 and 20 nm in size with preferred (002) orientation. The transmittance of the films in the visible region was of 83% with an optical band gap of ~3.3 eV for the low-resistivity samples.

1 Introduction

There exists a great interest to develop thin films of Diluted Magnetic Semiconductors (DMS) with high Curie temperature (Tc) to support the outstanding spintronic technology that is viewed as the link between the magnetic properties and the advanced semiconductor technology [1–3]. The Diluted Magnetic Oxides (DMO) is a subgroup of the DMS that exhibits magnetic properties at room temperature (RT) when doped with transition metal (TM) elements [4–7], or even produce magnetic properties driven by structural defects generated during the film synthesis [8, 9]. A requirement to warranty the application of the DMS or DMO films is a high Tc, whereby as reported in the literature several DMO have Tc well above RT [10–12]. As the origin of certain properties like ferromagnetism in nanostructured DMO films is still matter of discussion [13], the study of nanostructured DMO films could contribute to recognize these properties. ZnO is a relevant DMO widely investigated because their great potential for this application besides its outstanding optical and electrical characteristics, their widespread availability and low toxicity [14].

ZnO combined with different TM elements presents diverse magnetoresistance behaviors linked with the *d* shell electron interaction. According to the interaction between the *sp* hybridization and the *d* electron spin of the TM impurities different MR behavior are usually observed [7]. Cu and Ni doped ZnO produces only positive MR linear changes, however Cr, Mn and Fe doped ZnO produce negative or positive MR changes depending of the magnetic field intensity [7, 15]. However diverse results are reported in the literature in such a way that the explanations on the material properties require to include the role of the growing method, therefore more studies are required to clarify the

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influence of the material nanostructure and the processing technique. To study the influence of the films nanostructure DMO with uniform TM distribution are necessary; in this work a method to produce Cu doped ZnO (ZnO:Cu) films with the sputtering technique at room temperature is reported. Cu was chosen as ZnO dopant because is an efficient magnetizing element and the MR linear behavior of ZnO:Cu films. According to our results, the method can be extended to produce other TM doped DMO films following the described procedure. The ZnO:Cu films shown positive magnetoresistance linear changes at room temperature with percentage changes suitable to be used in spintronic devices.

2 Methodology

The methodology is based on experimental results that demonstrate the fabrication of films with controllable properties produced when forming multilayers of nanometric thicknesses by the sputtering technique taking advantage of their non-equilibrium character. In our previous report [16] the nickel diffusion from the ZnO/Ni/ZnO array was observed during the multilayer formation with the sputtering technique. The Ni distribution towards the adjacent ZnO layers can be explained by the high concentration of structural defects such as the surface vacancies or grain boundaries at the interfaces according to the microstructure of the forming layers. In this work ZnO:Cu magnetoresistive layers were produced by assembling ZnO and Cu films of nanometric thickness in ZnO/Cu/ZnO arrays deposited on corning glass substrates. The first ZnO film was included to dismiss the influence of the glass substrates on the characteristics of the produced layers. The thickness of the Cu and ZnO films were chosen to provide a copper atomic percentage of 3% in the produced ZnO:Cu layers. The arrays were deposited on corning glass substrates according to the method reported elsewhere [16], using ZnO and Cu targets of 5N chemical purity with 2 inches in diameter from Kurt J. Lesker at a working pressure of 2.5×10^{-3} Torr in Ar gas atmosphere. The corning glass substrates were formerly cleaned using the chemical cleaning conventional procedures. The ZnO/Cu/ZnO array were build following the next sequence: initially a ZnO film of 50 nm in thickness was deposited by RF-sputtering with a ZnO target at a power of 100 W in Ar flow of 40 sccm during 60 min; afterwards a metallic Cu film of 5 nm in thickness was deposited by DC sputtering with a power of 25 W in Ar flow of 40 sccm; finally the array was completed with a second ZnO film of 105 nm deposited with the same growth conditions as the first one, for a total thickness of the multilayer structure of 160 nm (Sample V2).

To observe the effects of post grown processes the arrays were thermally annealed under inert N_2 atmosphere at 250 °C (Sample V2-250) and 350 °C (Sample V2-350). The electrical properties of the ZnO:Cu films were measured by the Hall-van der Pauw method with a magnetic field of 0.55 T. Magnetoresistance (MR) measurements were done using the same Hall-van der Pauw system; the samples were placed in normal direction to the magnetic field in a variable field electromagnet (0 to 0.55 T). The morphological characteristics of the films were studied with a field emission scanning electronic microscopy (FE-SEM) JEOL JSM-7401F equipped with an EDS microprobe. The structural characteristics of the films were obtained with an X-ray diffraction system PANalytical X'Pert PRO MRD, using Cu $k\alpha$ radiation (1.5406 Å). Raman scattering spectra was obtained at room temperature using a Horiba-Jobin Yvon spectrometer model LabRAM HR800 with a He–Ne laser ($\lambda = 632.8$ nm) as excitation source. The optical transmittance of the layers was obtained using a UV–VIS Spectrophotometer, Jasco V-670.

3 Results and discussion

The surfaces of the as-grown arrays have mirror like appearance with highly transparence at the naked eye. Figure 1 shows FE-SEM microphotographs of the films surface after the thermal annealing stage at 350 °C with two magnifications (Fig. 1a, b). Figure 1c contains the information of the chemical composition by EDS analysis showing that zinc and oxygen are the main elements; the copper content was less than 2% atomic. FE-SEM microphotographs taken on as-grown surfaces and annealed samples indicate that the samples consist of uniform spheroidal-like particles with diameters of ~ 30 nm in average. For the samples annealed at 350 °C by periods of ~ 30 min the particle borderlines are better defined in comparison with the as-grown samples or single ZnO films, possibly by the existence of the distributed but non-oxidized copper within the array. As is well known the annealing processes of un-doped ZnO under inert atmosphere conditions can lead to electrically insulating material according to the chemical purity of the used atmosphere. For example in absolute dry N_2 atmosphere conditions negligible electrical changes are observed, but in N_2 atmosphere conditions with minute oxygen or water vapor content a tendency to reach stoichiometric conditions can be observed producing insulating films. In our case the existence of minute copper content makes easy the sample surface observation by FE-SEM. When the annealing process was extended by periods greater than 30 min the surface observation by FE-SEM was difficult probably by the copper oxidation.

The electrical characteristics of the produced arrays measured by the Hall-van der Pauw method at room temperature are detailed in the Table 1. To provide a reference on the electrical characteristics, non-doped single crystalline n-type ZnO sample measured with the same equipment

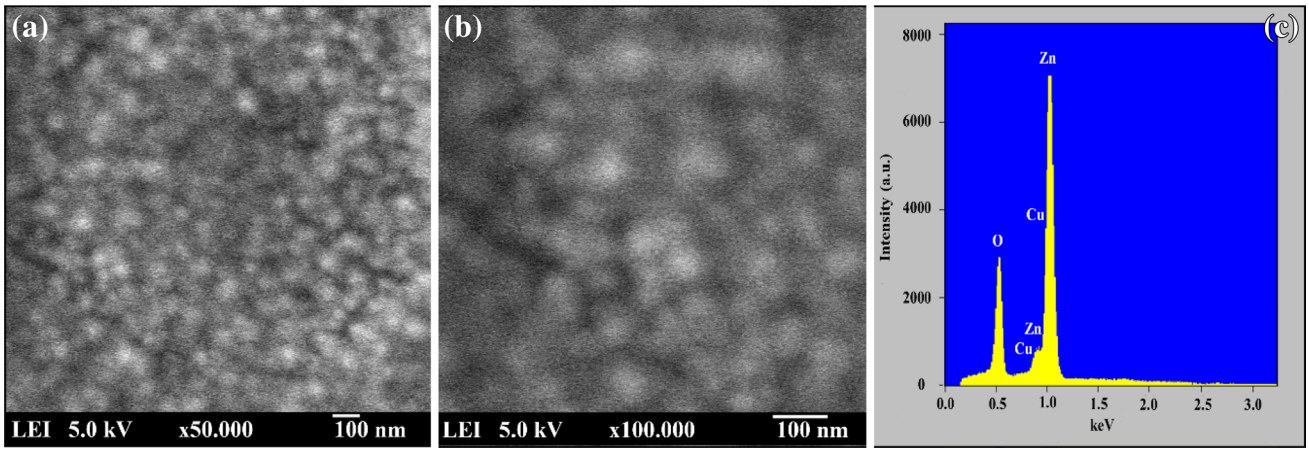

Fig. 1 Field emission scanning electronic microscopy (FE-SEM) images at distinct magnification of a ZnO:Cu film annealed in N_2 atmosphere at 350 °C for 30 min

Table 1 Electrical properties of the ZnO:Cu measured by the Hall-van der Pauw method with a magnetic field of 0.55 T

Sample	Resistivity (Ω-cm)	Mobility ($cm^2/V\ s$)	Electron concentration (cm^{-3})
V2	6.69×10^{-3}	0.367	-2.53×10^{21}
V2-250	3.47×10^{-3}	1.60	-1.12×10^{21}
V2-350	2.83	2.80	$-7.85\times1\ 0^{17}$
$ZnO_{Crystal}$	1.4×10^{-3}	177	-2.35×10^{15}

is also included in the Table 1 ($ZnO_{crystal}$). Furthermore, assuming that the Cu film of the array were non-affected during the growth process the carrier concentration measured on the sample V2, should be similar to the electron concentration for a metallic copper film [17], however the carrier concentration was of $\approx10^{22}$ cm^{-3}. Using the carrier mobility as a quality feature of the layers it can be seen that when the annealing temperature was increased the electron mobility shown a significant increment accompanied by a decrease on the electron concentration. This finding can be explained as a reduction on the carrier scattering produced by the crystallization during the annealing stage accompanied by the grain growth.

The Fig. 2 shows the results of the magnetoresistance (MR) measurements for an as-grown sample and one annealed at 250 °C (V2). It is clear that the as grown array ZnO/Cu/ZnO (V2) does not shown MR changes, however, a clear variation on the MR was observed for the annealed sample. Furthermore, after applying the annealing processes of 350 °C in N_2 atmosphere conditions by 30 min no changes in MR were observed. Undetectable changes on the MR can be explained because the applied annealing process produced a reduction in the electron concentration in two orders of magnitude. Additionally, the carrier

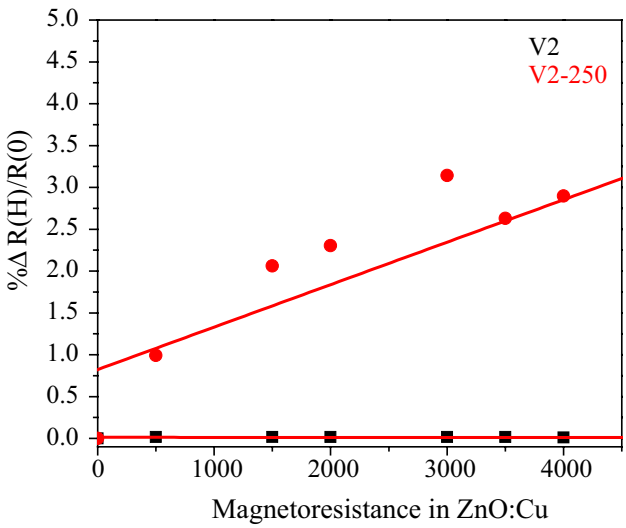

Fig. 2 Magnetoresistance measurements of the ZnO:Cu films at sample V2 (squares dots) and sample V2-250 (dots)

reduction can be related to the ensuing oxidation of the copper atoms during the annealing process produced by the minute oxygen and water vapor contents in the N_2 gas annealing atmosphere [18].

The Fig. 3 shows the X-ray diffraction (XRD) patterns for the as-grown film V2, and for two samples annealed at 250 °C, sample V2-250, and 350 °C, sample V2-350, accompanied by the XRD pattern of ZnO powders. The diffraction lines for the films can be indexed as (002), (101), (102) and (013) of the hexagonal (würtzite) phase of ZnO according to database ICSD #98-002-9272. The strong (002) peak, besides the weak line at (102) and (103) shows their polycrystalline character but also illustrates that the film crystallites possesses preferential orientation along c-axis.

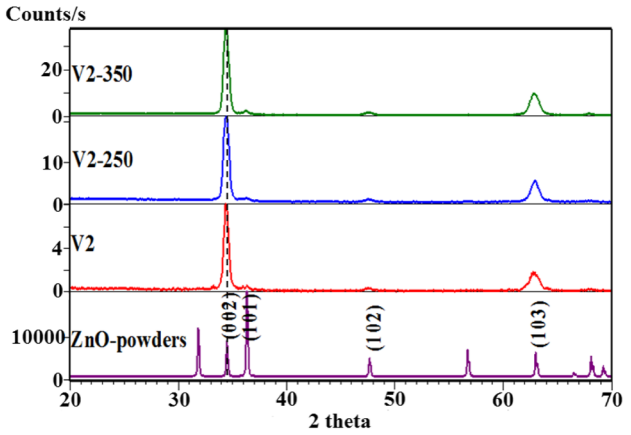

Fig. 3 XRD diffraction patterns corresponding to the as-grown ZnO:Cu structure (V2), and two distinct annealed samples at 250 °C (V2-250) and 350 °C (V2-350) during 30 min in N_2 atmosphere at atmospheric pressure conditions. The XRD pattern for ZnO powders is also included

Table 2 Structural parameters of ZnO:Cu films

Sample	2θ	Grain size	Lattice constant **c**	Strain, ξ_{zz} (%)
ZnO 30 nm	34.013	8.711	5.2714	1.4493 [20]
V2	34.495	17.8	5.20890	0.2668
V2-250	34.493	15.5	5.20908	0.2702
V2-350	34.4924	15.4	5.20924	0.2733

The main peak corresponding to the (002) planes intensifies as the annealing temperature was increased. The (002) line also shows a consistent broadening as the annealing temperature was increased suggesting that the produced ZnO films are composed by oriented nanocrystallites. These results demonstrate the crystallization produced either by the annealing process but also by the presence of the intermediate copper films, it must be noticed that there exists any diffraction peak associated with Cu metal or copper oxide phases. These results suggest that the Cu atoms are incorporated in interstitial position in ZnO lattice or as substitutional ion in Zn site, during the growth process of the array.

Calculated values of the lattice constant ***c*** for the films are shown in the Table 2. Films with lattice constant ***c*** greater than the theoretical value have positive stress, while those with small values have negative stress or compressive [17, 18]. The values of the lattice parameter *c* obtained for our films are greater than the theoretical value, this means that the unit cell is elongated along the c axis after being deposited and is in a condition of tensile stress (Tables 2, 3).

To study the effects of the annealing process on the microstructure and vibrational properties of the ZnO/Cu/ZnO arrays Raman spectroscopic analysis were done on a complete set

Table 3 Optical properties of samples the ZnO:Cu

Sample	n	α	Thickness (nm)	E_g (eV)
V2	2.01	0.469	385.47	3.28
V2-250	2.09	0.419	329.37	3.27
V2-350	2.08	0.419	332.15	3.27

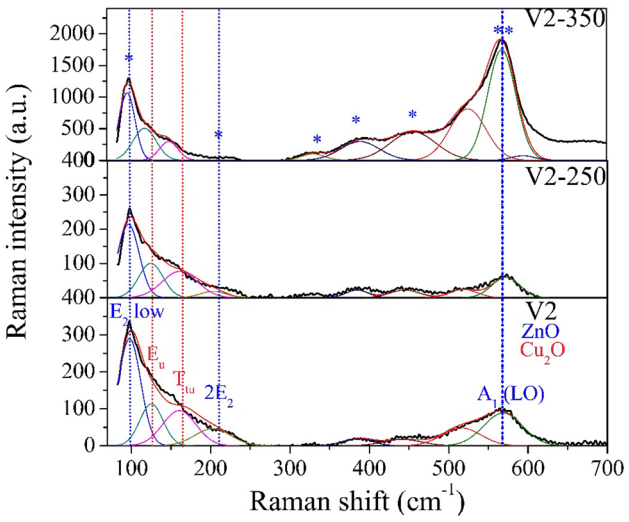

Fig. 4 Room-temperature Raman spectra corresponding to an as-grown ZnO:Cu structure (V2) and two distinct annealed samples at 250 °C (V2-250) and 350 °C (V2-350) during 30 min in N_2 atmosphere at atmospheric pressure conditions

of samples as is shown by Fig. 4. The characteristics Raman frequencies for würtzite ZnO constitutes the main visible frequencies [19, 20]: the E_2 (low) at 99 cm^{-1}, $2E_2$ (low) at 202 cm^{-1}, E_2 (high)-E_2 (high) at 333 cm^{-1}, the A_1 (TO) mode at 378 cm^{-1}, E_2 (high) at 438 cm^{-1} and the two intense lines A_1 (LO) at 574 cm^{-1} and E_1 (LO) at 590 cm^{-1}. Within the Raman spectra the frequencies at 125 and 160 cm^{-1} correspond to the E_u and T_{1u} modes related to the copper oxide (Cu_2O) [20, 21], however these two lines almost disappear in samples annealed at 350 °C. This result is in line with the XRD studies that shown a negligible content of copper oxide phases in the produced films.

Finally, the Fig. 5 includes the optical transmittance spectra for the set of samples showing that the arrays conserve their characteristic optical transparency. From the experimental spectra the calculated refractive index and the thickness of the layers are included in the Tables 2, 3.

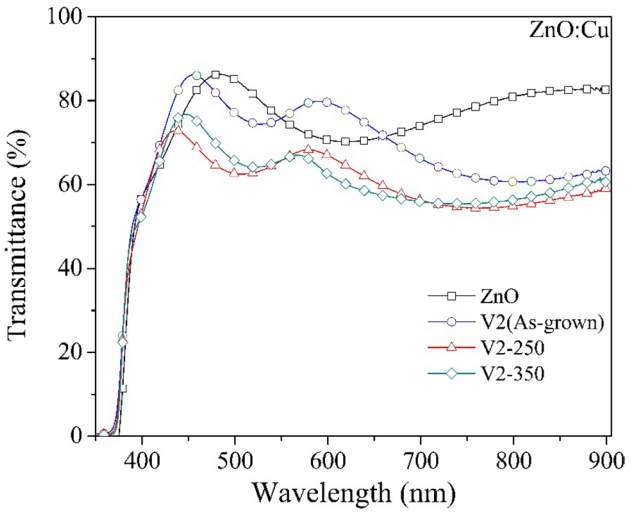

Fig. 5 Transmission spectra corresponding to a single ZnO films, an un-annealed array V2 and for annealed arrays at 250 and 350 °C during 30 min

4 Conclusions

ZnO:Cu films with magnetoresistive properties were produced by a process that takes advantage of the peculiarities of the sputtering technique and the solid state diffusion enhanced by the nanocrystalline character of the films producing the ZnO/Cu/ZnO arrays grown by sputtering. The consistence of the measured magnetoresistance (MR) behavior with the XRD and Raman characterizations of the ZnO:Cu films demonstrates the capability of the used method to produce ZnO based DMO films.

The morphological characteristics of the as-grown ZnO:Cu samples shown that the films are constituted by uniform islands conformed by nanocrystallites produced in the course of the growing process. On the other hand, when the produced arrays were annealed at 350 °C an enhancement on the layer homogeneity was observed.

The XRD characterization shows that the ZnO:Cu thin films are nanocrystalline with preferred orientation (002). The detailed XRD characterization of the films demonstrates that Cu atoms do not induce the formation of any copper oxide phase. Therefore, the Cu atoms are probably incorporated as interstitials in the ZnO lattice or as substitutional zinc anti-sites.

The Raman spectra of the films revealed the prevalence of the ZnO phonon modes. The observed modes were the E_2 (low) at 99 cm^{-1} and a wide line that represent the A_1 (LO) and E_1 (LO) modes at 438 and 590 cm^{-1}, respectively.

The variation of the transmittance response shown that their variation on the optical properties can be attributed to the presence of the Cu film and by its influence as a crystallization center aided by the applied annealing processes.

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Compliance with ethical standards

Conflict of interest The authors declare that we have no conflicts of interest.

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