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Synthesis and characterization of nanostructured magnetoresistive Ni doped ZnO films

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ABSTRACT

We report a method to produce magnetic nanostructured semiconductor films based in ZnO doped with Nickel to control their magnetic properties. The method is based on a combined diffusion–oxidation process within a controlled atmosphere chamber to produce a uniform distribution of Ni ions in the ZnO films (ZnO:Ni). The synthesis of ZnO:Ni films is reported as well as the magnetoresistive characteristics, the used method yields films with reproducible and homogeneous properties. The films were also characterized structurally by X-Ray Diffraction (XRD) and Raman spectroscopy, and by Hall–van der Pauw measurements. The XRD measurements confirm the nanocrystalline films character. The films resulted of n-type conductivity with electron concentrations of $\sim 10^{20}$ cm^{-3} in average and carrier mobilities of 5 cm^2/V s. The Magnetoresistance (MR) behavior of the films at 300 K shows negative changes of $\Delta R \sim 0.5\%$ in accordance with the usual literature reports on samples produced by other methods.

1. Introduction

Currently, there is a great interest to develop thin films of Diluted Magnetic Semiconductors (DMS) to support the breaking through spintronic technology. The DMS enable the link between the magnetic properties and the advanced semiconductor technology [1]. A subgroup of the DMS are the Diluted Magnetic Oxides (DMO) that also exhibit magnetic properties when are doped with any transition metal (TM) [2–6] and even producing magnetic properties through structural defects caused during the synthesis of the films [7,8]. High Curie temperature (T_c) is also another requirement to improve the application of DMS films, whereby as reported in the literature the DMO are candidates to achieve high T_c [9–11]. Origin of certain properties like ferromagnetism in nanostructured DMO's is still matter of discussion [12], hence the study of nanostructured DMO doped with TM could contribute to recognize these properties. Several studies are focused in semiconductors with magnetic characteristics at room temperature, to use their physico-chemical properties in realizing and to improve important devices like spin-LED [13], spin-transistors [14], logic devices [15] and magnetic memories (MRAM) [16].

Between the distinct DMO the ZnO is widely investigated by its relevant optical and electrical characteristics. The ZnO combined with different transition metals presents peculiar magnetoresistance behaviors linked with the *d* shell electron interaction. According to the interaction between the *sp* hybridization and the *d* electron spins of the TM impurities different MR behaviors has been reported [6]. Cr, Mn or Fe

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combined with ZnO produce negative or positive MR changes depending of the magnetic field intensity. The ZnO doping with Ni or Cu produces only negative changes with the increase of the magnetic field [6,17]. The experimental results reported in the literature are not conclusive in this respect, more studies are necessary to clarify the origin of the mentioned MR behavior. With the aim to study these peculiarities DMO films with uniform TM distribution are necessary; in this work a method to produce Ni doped ZnO films is reported. ZnO:Ni films are produced and characterized but the method can be extended to produce DMO films with any other TM. The obtained films show negative magnetoresistance at room temperature with percentage changes suitable to be used in spintronic devices.

2. Synthesis method

The synthesis method is based on the use of a low temperature diffusion–oxidation process at 500 °C applied to the multilayer structure – M/ŋ/M – in controlled atmosphere conditions; M is Zinc and ŋ is the transition metal (Fe, Co, Mn, V or Ni) of the necessary volume to attain the required percentage to guarantee the semiconducting properties.

In this work the transition metal employed was nickel. The diffusion–oxidation process was realized in a resistive heated furnace with a fused quartz chamber in a constant gas flow of 1 slpm, of alternate reductive–oxidative atmosphere of hydrogen and air from the laboratory atmosphere. In the first stage pure hydrogen was employed to promote the homogenization of the metallic multilayer, after that the multilayer was exposed to atmospheric air for homogenization trough oxidization. Squared sections of silicon wafers or corning glass were used as substrates. To produce the Zn/Ni/Zn structure, Zn layers of 300 nm in thickness were deposited in a vacuum evaporator Edwards E306 system, and Ni films of 6 nm were deposited in an electron beam vacuum evaporator system, a Leybold-UNIVEX 300 of 3 kW. After the formation of the structure, the samples were introduced in the quartz chamber furnace to run the oxidation–diffusion process. After this stage, uniform, homogeneous and transparent ZnO:Ni films were produced [7,18].

The process, based on the multilayer arrangement was performed according to the time–temperature schedule shown in Fig. 1c. To guarantee safe processing conditions, a nitrogen gas flow was utilized between both processing stages to purge the hydrogen content previous to the introduction of air in the process chamber. Due to the processing method and the nanometric thickness of the metallic layers arrangement, nano-crystalline features were expected. The crystal structure of the distinct films was characterized by X-Ray Diffraction (XRD) and Raman spectroscopy. The XRD pattern was performed in PANalytical X'Pert Powder X-ray Diffractometer system with Cu Kα radiation (λ=1.540598 Å). Raman scattering spectra was obtained at room temperature using a Horiba-Jobin Yvon spectrometer model LabRAM HR800 with a He–Ne laser (λ=632.8 nm) as excitation source. The electrical

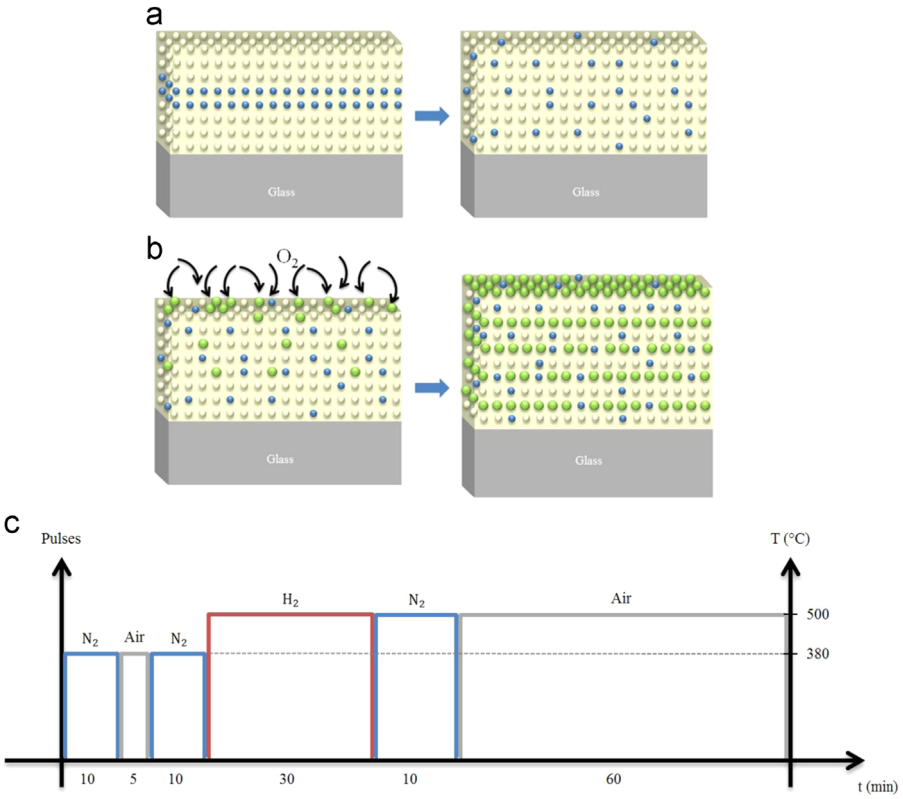

Fig. 1. Scheme depicting the homogenization of the Zn/Ni/Zn structure (a) by diffusion of Nickel interlayer, (b) the formation of ZnO:Ni by thermal oxidation in O_2 atmosphere, and (c) temperature and pulses of thermal oxidation.