Electrodeposition of doped ZnO under a constant magnetic field

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Abstract

Magnetoelectrodeposition is a synthesis technique which allows to work with a superimposed magnetic field while the sample is usually electrodeposited. In this technique the magnetic field can modify the convection in the solution during the deposition via the Lorentz force convection also known as magnetohydrodynamic (MHD).

In this paper, a diluted magnetic semiconductor (DMS) material, a ferromagnetic transition metal doped with ZnO, is desired to be obtain; to determine if the superimposition of a constant magnetic field change some properties, such as its ferromagnetic properties. This type of material could be use in spintronics as well as in optoelectronics because of ZnO interesting optical intrinsic properties.

Key words : Electrodeposition, constant magnetic field, magnetohydrodynamic, diluted magnetic semiconductor, ZnO

Introduction

ZnO is one of the most used semi-conductors in a broad range of applications such as dye-sensitized solar cells or light emitting diode [1]. This hexagonal wurtzite structure material presents typically n-type electrical conductivity and a wide band gap (Eg $\sim$ 3.3 eV at 300 K). It also possesses a large exciton binding energy (60 meV) which is much higher than traditional GaN (21 meV) and ZnS (20 meV) semi-conductor [1]. Since Dietl et al. [2] have predicted room temperature ferromagnetism (RT-FM) for Mn doped ZnO (T_c >300 K) transition metals (TM)-doped ZnO are more focused. In fact, ZnO finds application in optoelectronics as well as in spintronics. Theoretically, its properties relie on charge carriers properties, but also controllable spins (contribution of the dopant), revealing ferromagnetic properties [2]. There are numerous methods, both physical and chemical to obtain zinc oxide and it can be synthesized under various forms. Magnetic properties are strongly reliant on the preparation method employed. And several reports exist about electrodeposition of ZnO with ferromagnetic properties. So, we have chosen to electrodeposit ZnO because this technique has the benefits of low cost and low temperature preparation. Furthermore, doping is direct in this approach. Here, the retained ions are cobalt II (Co^{2+}) or nickel II (Ni^{2+}), which are ferromagnetic TM. The feature of the preparation of our thin films Co-doped ZnO is with the superimposed constant magnetic field during the deposition.

The chosen substrate is titanium. Indeed, a huge number of study are performed on Indium Tin Oxide (ITO) or Fluorine Tin Oxide (FTO) substrates [3]. But some studies report these substrate materials can show ferromagnetic behavior. To avoid risks of signal contamination, we culled a diamagnetic material, titanium, which possess a $\chi_m = 2.3 \times 10^{-4}$ magnetic susceptibility. Effects of a magnetic field on an electrochemical reaction have been studied taking in account magnetohydrodynamics (MHD) convection induced by a Lorentz force. Several authors recognize that magnetohydrodynamics (MHD) induces effects on morphology and/or crystallographic orientation of the deposits [4].

The mechanism allowing diluted magnetic semiconductors to be ferromagnetic is a bit blurring. Plenty of theories, among which the most widespread concern oxygen vacancies or spin jump in interaction exchange (direct, indirect, superexchange...) are studied. Generally, if the techniques of material synthesis affect the properties of the latter, it is especially true for DMS. Several studies concerning the synthesis of doped zinc oxide (nickel or cobalt) by electrodeposition [5] have already been carried out and they have given satisfactory results regarding their magnetic properties. So here a Co or Ni-doped ZnO thin film is deposited, in order to obtain a DMS. But, at the same time, experiments are carried out under a superimposed constant magnetic field to know if the convective Lorentz force modifies some nucleation/growth process or some orbital interaction and finally on a more direct scale enhances the temperature interval of the ferromagnetism or decreases it.

Experimental details

Pure and cobalt or nickel-doped ZnO films were synthesized by electrochemical deposition on titanium substrates. First, these substrates have been clean during 5 minutes in acetone, then 5 minutes in distilled water using an ultrasonic-bath. The electrolyte consists of 0.1 mol/L concentration of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, purity 99%, Fluka) dissolved into distilled water. The average pH of the solution is around 5. The Co doping was carried out by adding cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, purity 99%, Fischer Scientific). A cobalt concentration of 0.1 mmol/L has been retained. For nickel-doped ZnO, samples have been doped up to 5 mmol/L and 0.5 mmol/L with nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, purity 96.5%). The electrodeposition was performed in galvanostatic mode using a

Versastat 4, Princeton Applied Physics potentiostat. A constant cathodic current of I = -5 mA has been applied on the 1.1 cm² surface area of the substrate (i.e. the current density is j = -4.55x10^{-3} A/cm²). The setup is a classical 3-electrodes configuration. While working electrode is a titanium one, counter electrode is a platinum wire. The reference electrode chosen is a saturated Ag/AgCl one. Experiments were done at 80 °C during 100 min. Some experiments have been carried out under a vertically downward magnetic field parallel to the substrate (from 1 to 4 T) using a Cryogenic Superconducting Magnet (SMS120C). Samples were put into the center of the magnetic field to get a constant magnetic field on the substrate.
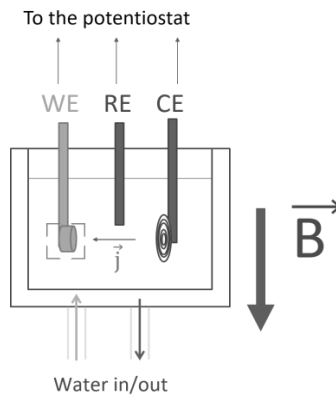

Fig. 1: Sketch of experimental setting.

After each deposition, samples have been washed with distilled water to remove Zn^{2+} and Co^{2+} left from the solution. The structural characterization of the material was investigated using X-ray diffraction (XRD) D8 Advance, Bruker. A glancing angle of 3°, a step size of 6 sec /0.06° with CuK$_\alpha$ (1.542 Å) radiation and a 2 θ ranging from 20 to 70° have been used. Morphologic characterization was mainly performed with scanning electron microscope (SEM) JEOL JSM 6460LA or with a JEOL7900F and chemical compositions were determined by an EDS JEL 1300 Microprobe coupled with the SEM. A micro-Raman spectrometer was used for the characterization of the Co-doped ZnO samples. The magnetic characteristics have been studied with SQUID and VSM measurements. The diamagnetic signal of the capsule was directly subtracted for M-H loop on ZnO samples. In order to determine chemical bounding and elemental constituents FTIR PerkinElmer Uatr Two has been used.

Results and discussion

The structure of Co-doped ZnO and pure ZnO thin films has been determined using X-ray diffraction. Fig. 1 (a) shows XRD spectra of ZnO:Co thin films prepared on titanium substrate from 30 to 70°. Some peaks from the substrate are noticeable and marked with a star. Other peaks result directly from the ZnO phase (JCPDS 36-1451, *c/a*: 1,5871) and no other phase is present. Films are (002) oriented.

(a)   (b)

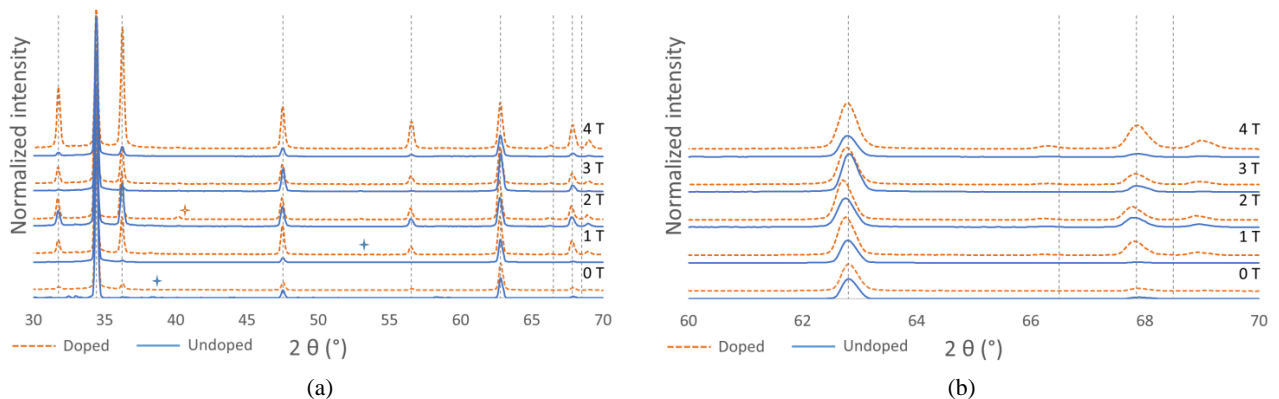Fig. 2: (a) XRD pattern of pure and Co-doped ZnO under different magnetic field intensities (b) a zoom between 60-70°.

A focus between 60 and 70° on Co-doped ZnO samples (Fig. 1 (b)) shows a slight wide angles shift depending on magnetic field intensity. The affected angles are (103), (200), (112) and (201). This offset seems to be inexistent for undoped samples. The shift is not steady with the increasing of the field. It first goes toward the small angles and from 2 T until 4 T, it returns to its initial place. Magnetic field seems to slightly influence the structural properties of the samples (doped and undoped).
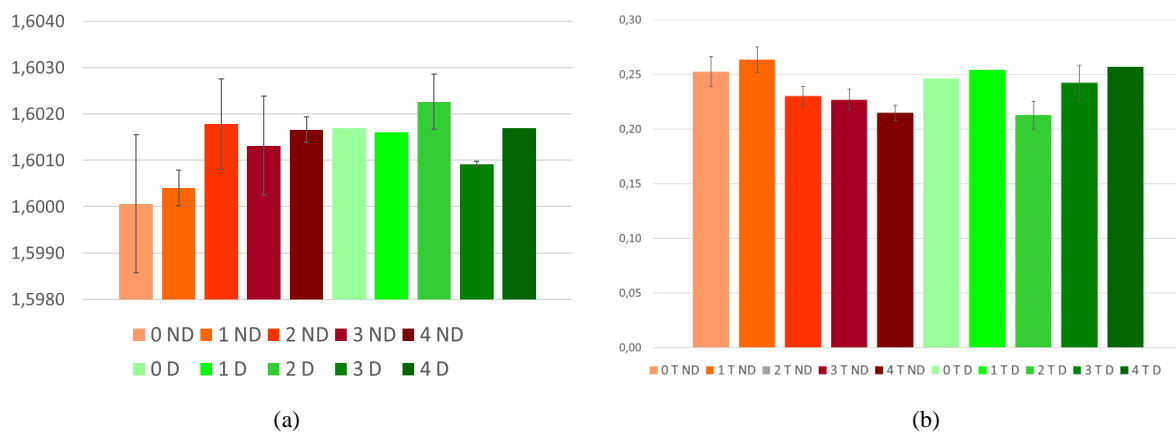

(a)

(b)

Fig 3: (a) ZnO hexagonal c/a ratio and (b) full width at half maximum (FWHM) of Co-doped ZnO (D) and undoped ZnO (ND) samples depending on magnetic field intensity.

Looking at c/a ratio where c and a (a=b, because of hexagonal structure) are the lattice parameters which define the unit cell geometry, doping does not seem to affect the ratio but the magnetic field seems to do it. The same inference can be made with the full width at half maximum. Co-doped and undoped samples in terms of FWHM behave the same way. Sample surfaces are not completely homogeneous and hence there is some uncertainty on measurements which are visible on XRD error bars.
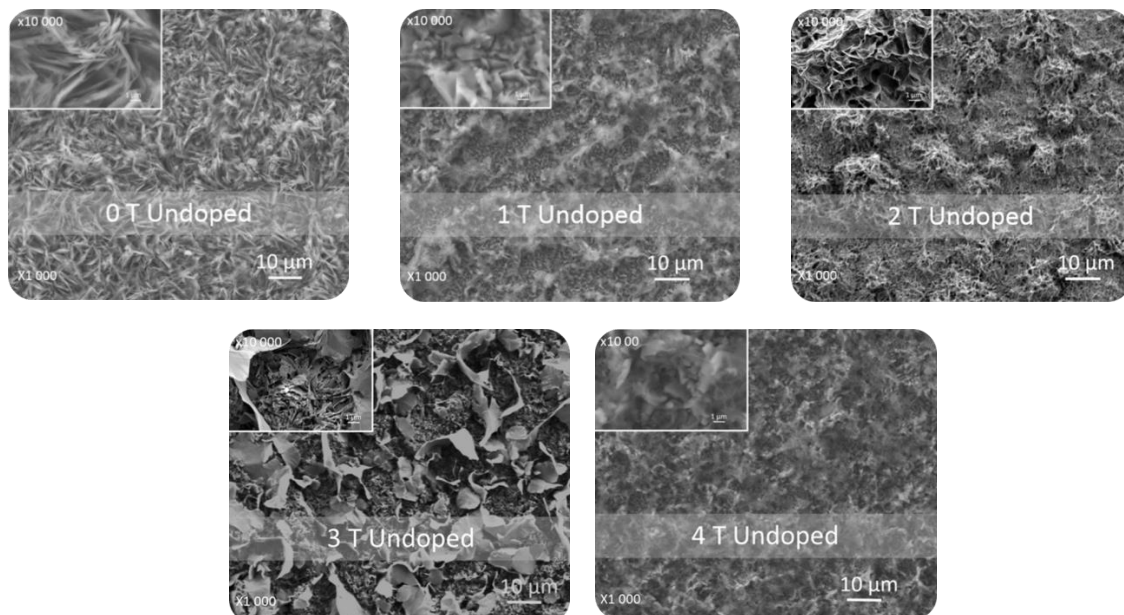

Fig. 4: SEM images of ZnO samples under a constant 1, 2, 3, 4 T magnetic field or not, at several magnifications (x1000 and inset (x10000).

Even if their surfaces are not homogeneous, here, SEM shots (Fig. 3) depict the behavior of most of samples. Those morphologies of pure ZnO under different magnetic field amplitudes are different. As before, the field seems to act on deposit, but in a not linear mode. The morphology goes to slips to big leaves.

Conclusion

Based on this these measurement, magnetic field seems to play a part in the growth process of the deposit since morphological and structural modifications are noticeable. This is a first step in understanding the influence, if any, of the magnetic field on doped ZnO deposits.

Acknowledgment

References

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