



Performance Evaluation of ZnO Based Rare Earth Element Doped Thin Films

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ABSTRACT

In DMS materials, a small fraction of a host semiconductor cation is substituted by magnetic ions. We chose as semiconducting host the transparent ZnO, with a bandgap of 3.3 eV at room temperature. Studies on ZnO doped with 3d transition metals indicated only small magnetic moments. The more recent results for Gd in GaN, indicating high magnetic moments, motivated us to investigate ZnO thin films doped with rare earth (RE) metal ions. For the 3d transition metals, the 3d electrons are exterior and delocalized; leading to strong direct exchange interactions and high Curie temperatures, but often the orbital momentum is zero, leading to small total magnetic moments per atom. In RE metals, the 4f electrons are localized, exchange interactions are indirect, via 5d or 6s conduction electrons, but the high orbital momentum is leading to high total magnetic moments per atom, like 3.27 μ B for Nd. The Curie point for Nd is 19 K. In this paper we present the results of our study on ZnO films doped with Nd. Hall measurements are performed to investigate the electrical properties of films. Here we prepared and investigated ZnO films doped with different concentration of Nd. The films are grown on a-plane Al₂O₃ or SiO₂ substrates. Hall investigations of electrical properties revealed the presence of a degenerate, highly conducting, film-substrate interface layer for the films grown on Al₂O₃; such an effect can be avoided, for example, by using SiO₂ substrates. Magnetotransport measurements indicated no anomalous Hall effect, but a pronounced negative magneto resistance ratio that can be interpreted as a paramagnetic response of the system to the applied magnetic field. We would like to proceed with the surface sensitive techniques for investigating magnetic properties of ZnO:RE thin films.

Key words: Rare Earth, Thin Films, Hall measurements, Spintronics.

INTRODUCTION

Since last two decades there has been an explosive growth of research in the field of thin films¹⁻³. Several articles and books have been published on different aspects of elements doped thin films. These may be in the range of 10 to 1000

nm size and one can reduce the dimension in one, two or all three directions to obtain thin films, wires or dots, respectively. Note that these thin films can be of various shapes too and properties may change according to size and/or shape. One of today's challenges for the development of future technologies is the realization of devices that control

not only the electron charge, as in present electronics, but also its spin, setting the basis for future spintronics⁴⁻⁵. Spintronics represents the concept of the synergetic and multifunctional use of charge and spin dynamics of electrons, aiming to go beyond the semiconductor electronics and magnetic storage technology. The most direct method to induce spin-polarized electrons into a semiconductor is by introducing appropriate transition-metal or rare-earth dopants producing a dilute magnetic semiconductor (DMS). The DMS are semiconducting materials in which a fraction of the host cations can be substitutionally replaced by magnetic ions. These DMS are the building blocks of the future "Spintronics" devices. Hence we chose as semiconducting host the transparent ZnO, with a bandgap of 3.3 eV at room temperature. Studies on ZnO doped with 3d transition metals indicated only small magnetic moments⁶⁻⁹. The more recent results for Gd in GaN, indicating high magnetic moments¹⁰, motivated us to investigate ZnO thin films doped with rare earth (RE) metal ions. For the 3d transition metals, the 3d electrons are exterior and delocalized, leading to strong direct exchange interactions and high Curie temperatures, but often the orbital momentum is zero, leading to small total magnetic moments per atom. In RE metals, the 4f electrons are localized, exchange interactions are indirect, via 5d or 6s conduction electrons, but the high orbital momentum is leading to high total magnetic moments per atom, like 3.27 μ B for Nd. The Curie point for Nd is 19 K.

In this paper we present the results of our study on ZnO films doped with Nd. Hall measurements were performed to investigate the electrical properties of films and they revealed a non-uniform distribution of the free electrons for the films grown on Al₂O₃. Magnetotransport measurements revealed a large negative magnetoresistance (MR) in ZnO films doped with RE metals.

METHOD

For the growth of RE alloyed ZnO Pulsed laser deposition (PLD) technique is used. Pulsed laser deposition (PLD) is a thin film deposition technique where a high power pulsed laser beam is focused inside a vacuum chamber to evaporate

material from a target of the desired composition and deposited as thin film on a substrate. The physical phenomena of laser-target interaction and film growth are quite complex (for more details see reference¹³⁻¹⁵). The laser pulse is absorbed by the target and energy is first converted to electronic excitation and later on into thermal, chemical and mechanical energy, which result in evaporation, ablation and plasma formation¹⁶. The ejected species expand into the surrounding vacuum/ambient in the form of a plume containing many energetic species including atoms, molecules, electrons, ions and particles, before depositing on the typically hot substrate¹⁶. Wurtzite ZnO films, doped with 0.01, 0.1 or 1% Gd or Nd, have been grown on 10 \times 10 mm² a-plane Al₂O₃ or SiO₂ substrates by pulsed laser deposition (PLD). For the growth of RE alloyed ZnO, the PLD target are sintered with a defined RE concentration by intermixing ZnO powder with RE-oxide powder¹⁷⁻¹⁸. As alternative two different metal foils are used for RE:ZnO growth¹⁶, whereas one is a Zn foil and the other one is RE dopant foil. The laser is then screened over both foils. As for pure ZnO growth a partial oxygen pressure of some tenth mbar is applied and the substrates are heated to about 500°C. Thereby most work groups use a-plane (11 $\bar{2}$ 0) or c-plane (0001) sapphire as substrates. Some films were also doped with 0.1%–0.5% Al. Films with thicknesses between 20 nm and 1 μ m were grown at substrate temperatures (TG) between 500 and 850-C, applying oxygen partial pressures

Table 1.

Property	Characteristics/values
Group	II-VICompound
Crystal structure	Wurtzite(B3)
Atomic weight	81.38 amu
Lattice Constant	4.580 Å ⁰
Density	5.67 gm/cm ³
Eg(300K/0K)	3.35eV/3.42eV
Band Gap Type	Direct
Electron mobility	200 cm ² /Vs
Hole mobility	180 cm ² /Vs
Effectivemass m*/m ₀	0.27
Intrinsic carrier Conc.n _i	7.0X10 ¹⁶ cm ³
Donors	Al, Ga,In,Cl,I
Acceptors	Li,Na,K,Co,N,P,As

(pG) between 3×10^{-5} and 0.15 Torr. The properties of ZnO¹⁰⁻¹¹ are shown in table 1.

Electrical and magnetic properties

The electrical properties of RE-doped ZnO

films with different thicknesses were investigated by Hall effect measurements as shown in figure1, using the van der Pauw geometry as shown in figure 2. For Hall measurements in vander Pauw geometry¹⁹⁻²⁰, four Au contacts are evaporated, of

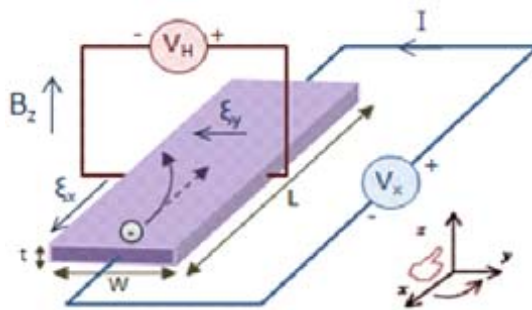


Fig. 1: Hall measurement

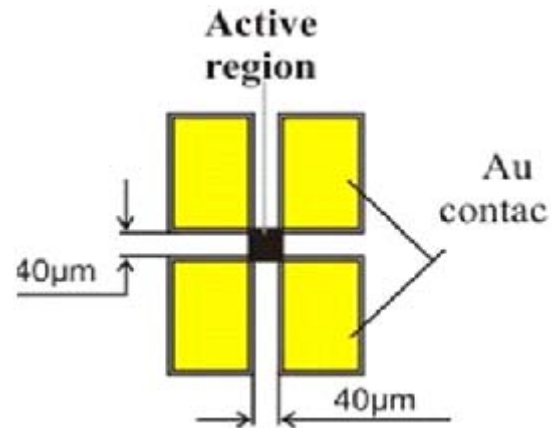


Fig. 2: Working vander Pauw geometry

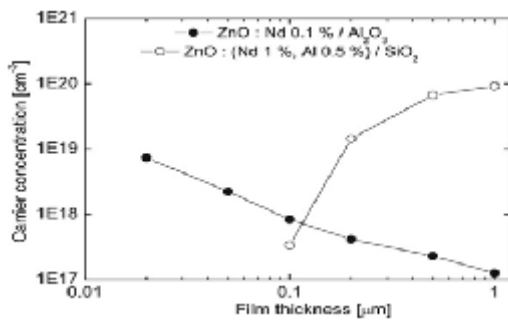


Fig. 3: Hall results for ZnO:Nd films with varying thickness grown on Al₂O₃ or SiO₂ substrates

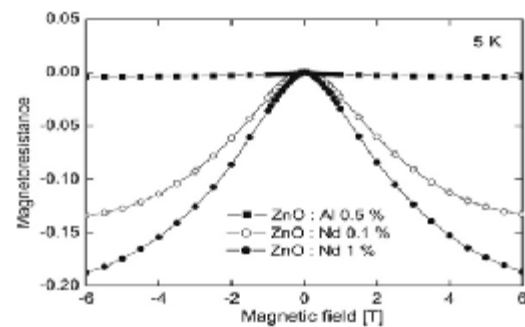


Fig. 4: MR for ZnO films with different dopings grown on Al₂O₃. A much higher ratio is observed in ZnO:RE compared to ZnO:Al

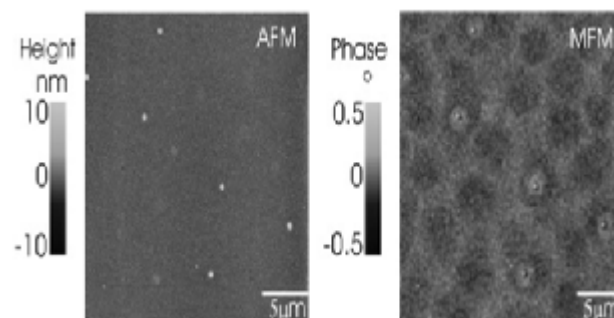


Fig. 5: Bubble-like magnetic domains on a ZnO film doped with 0.1 at% Nd

which the I(V) characteristics exhibits an ohmic behaviour and have resistances ranging from 100 Ω to 1 k Ω determined by Hall measurement in which magneto transport measurements are performed in two point geometry with a magnetic field H perpendicular to the sample plane as shown in figure 1. They depend on the film composition, oxygen partial pressure, and substrate temperature during the growth process.

Our investigations revealed that the free electron concentration, n , is independent of temperature over the investigated range 20–320 K. Measurements for films with different thicknesses revealed that for films grown on Al_2O_3 substrates the carrier concentration is decreasing with increasing film thickness, contrary to our expectations. This behaviour was observed in ZnO films grown on Al_2O_3 substrates and is explained by the presence of a thin, degenerate, highly conducting interface layer between substrate and film. The results for films grown on SiO_2 show that the carrier concentration is increasing with increasing film thickness (Fig.3). This allows us to assume that most carriers in the highly conducting interface layer for the films grown on Al_2O_3 are produced by Al diffusion from the substrate. RBS has a sensitivity for Al as low as 3%, not allowing the investigation of Al depth profile in our films.

The magnetic behavior of the films was investigated by magnetotransport measurements at different temperatures. We investigated the MR behaviour in different magnetic fields. Negative MR ratio was detected in ZnO:RE films. In Fig. 4 we present results obtained at 5 K for ZnO films doped with different Nd contents or Al. A much pronounced negative MR is detected in ZnO:RE as compared to ZnO:Al, meaning that the signal from the ZnO:RE films is given by the RE incorporated into the ZnO lattice. The carrier concentration in the ZnO:Al film is $2 \times 10^{20} \text{ cm}^{-3}$ while for the ZnO:RE films is in the range 1×10^{17} to $1 \times 10^{19} \text{ cm}^{-3}$. With increasing temperature, MR approaches zero very quickly. No anomalous Hall effect was detected, even at low temperatures. The negative MR can be interpreted as a paramagnetic response of the RE ions to the applied magnetic field [6], meaning the RE ions do not interact via exchange mechanisms. This statement is also supported by the lack of

anomalous Hall effect. We should remark that the films presented in Fig. 4 have thicknesses around 20 nm, meaning only degenerate layers. For thicker films attention must be paid, because the path of the current through the film cannot be easily established, the results being difficult to interpret. It could happen that current passes only through the thin degenerate layer near the film–substrate interface.

Other methods are used to investigate the local magnetic properties on film surface. Magnetic force microscopy (MFM), for example, is used to detect the presence of magnetic domains on the film surface. As an example, this technique revealed bubble like magnetic domains with diameters around 4 μm on a ZnO:RE film containing 0.1 at.% Nd, grown at 639 $^\circ\text{C}$ and 0.012 Torr on a-plane Al_2O_3 (Fig. 5). Such domains are characteristic for films with uniaxial magnetic anisotropy, the easy axis being perpendicular to film surface. The homogenous distribution of magnetic domains in Fig. 5 indicates that the signal is not due to clusters eventually formed during the growth process.

CONCLUSIONS

We prepared and investigated ZnO films doped with different contents of Nd. The films were grown on a-plane Al_2O_3 or SiO_2 substrates. Hall investigations of electrical properties revealed the presence of a degenerate, highly conducting, film–substrate interface layer for the films grown on Al_2O_3 ; such an effect can be avoided, for example, by using SiO_2 substrates. Magnetotransport measurements indicated no anomalous Hall effect, but a pronounced negative magnetoresistance ratio that can be interpreted as a paramagnetic response of the system to the applied magnetic field. We would like to proceed with the surface sensitive techniques for investigating magnetic properties of ZnO:RE thin films.

Future Work

This section recommends additional experiments and characterization techniques that would extend the information obtained in the present study. Thin film samples with dopant concentrations slightly higher and lower than 3 atomic % should be fabricated in parallel with

investigation of post annealing effects on observed paramagnetism. The effects of oxygen partial pressure during deposition should also be studied. Another very useful study would be to attempt to deposit very smooth and very thin films by varying the deposition rate and substrate temperature while also studying growth on conductive substrates. This

would allow for characterization of magnetic field dependent electrical properties.

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