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Ferromagnetic transition metal implanted ZnO: A diluted magnetic semiconductor?

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ABSTRACT

Recent theoretical works have predicted that some semiconductors (e.g. ZnO) doped with magnetic ions are diluted magnetic semiconductors (DMS). In DMS, magnetic ions substitute cation sites of the host semiconductor and are coupled by free carriers, resulting in ferromagnetism. One of the main obstacles in creating DMS materials is the formation of secondary phases because of the solid–solubility limit of magnetic ions in semiconductor hosts. In our study transition metal ions were implanted into ZnO single crystals with the peak concentrations of 0.5–10 at.%. We established a correlation between structural and magnetic properties. By synchrotron radiation X-ray diffraction (XRD) secondary phases (Fe, Ni, Co and ferrite nanocrystals) were observed and have been identified as the source for ferromagnetism. Due to their different crystallographic orientation with respect to the host crystal, these nanocrystals in some cases are very difficult to be detected by a simple Bragg–Brentano scan. This results in the pitfall of using XRD to exclude secondary phase formation in DMS materials. For comparison, the solubility of Co diluted in ZnO films ranges between 10 and 40 at.% using different growth conditions pulsed laser deposition. Such diluted, Co-doped ZnO films show paramagnetic behavior. However, only the magnetoresistance of Co-doped ZnO films reveals possible s–d exchange interaction as compared to Co-implanted ZnO single crystals.

1. Introduction

Diluted magnetic semiconductors (DMS) are materials that simultaneously exhibit ferromagnetic and semiconducting properties [1,2]. They are usually common semiconductor materials containing a few atomic percent of transition metal (TM) ions substituted onto the cation sites. The ferromagnetism in DMS is driven by free charge carriers, and can be controlled by an electrical field. DMS materials could fundamentally change the functionality of traditional semiconductor devices, therefore, have been intensively investigated over the last decades. Among ferromagnetic semiconductors, the (Ga,Mn)As DMS is the most well understood and promising for application in spintronics. The main obstacle is that the highest Curie temperature of (Ga,Mn)As is reported to be 173 K [3], far below room temperature. Nevertheless, spin-related devices based on (Ga,Mn)As, namely spin-polarized light emitter (spin-LED) [4], spin FET [5] and spin-valve [6], have been demonstrated at low temperature. In order to increase the Curie temperature of (Ga,Mn)As, one has to increase the concentration of Mn. However, phase separation, i.e. ferromagnetic MnAs precipitates, easily occurs when the Mn concentration is larger than 7% [7]. In parallel, considerable effort is dedicated to search for alternative materials, which are expected to be DMS with Curie temperature well above room temperature.

Dietl et al. [8] proposed a mean-field Zener model to understand the ferromagnetism in DMS materials. It has been successful in (Ga,Mn)As and (Zn,Mn)Te materials. This model predicts that wide bandgap semiconductors doped with Mn exhibit critical temperatures above 300 K, if a sufficiently large hole density can be achieved (10^{20} cm^{-3}). Sato et al. calculated the properties of n-type ZnO doped with 3*d* TM ions (V, Cr, Mn, Fe, Co, and Ni) [9]. The ferromagnetic state, with a T_C of around 2000 K, is predicted to be favorable for V, Cr, Fe, Co, and Ni in ZnO while Mn-doped ZnO is predicted to be anti-ferromagnetic. These predictions largely boosted intensive experimental activities on transition metal doped ZnO. A large number of research groups have reported the

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experimental observation of ferromagnetism in TM (from Sc to Ni) doped ZnO [10–15] fabricated by various methods including ion implantation. For a comprehensive review, see Ref. [16]. However in these reports the magnetic properties using the same magnetic dopant vary considerably. For example, the saturation moment and Curie temperature for Mn doped ZnO ranges from 0.075 μ_B/Mn, 400 K [11] to 0.17 μ_B/Mn, 30–45 K [17], respectively. In contrast to these publications, other groups reported the observation of antiferromagnetism [18–20], spin-glass behavior [21, 22], and paramagnetism [19,23–25] in TM-doped ZnO. Recently it was also found that nanoscale precipitates can contribute to the ferromagnetic properties substantially. In Table 1, we list the ferro(ferri)-magnetic nanoclusters found in transition metal doped ZnO materials.

The controversy regarding the magnetic properties of ZnO-based DMS, as stated above, might partially be due to the insufficient characterization of the samples [35–37]. Particularly, a careful correlation between structure and magnetism should be established by sophisticated methods. Synchrotron radiation based X-ray diffraction (SR-XRD) is a powerful tool to detect small precipitates, e.g. metallic TM nanocrystals (NC) in ZnO [26]. On the other hand, element selective measurements of the magnetic properties, e.g. X-Ray Magnetic Circular Dichroism (XMCD) [38] and Mössbauer spectroscopy [26,39], address the origin of the measured magnetism directly.

Among the methods used in the study of ZnO based DMS materials, ion implantation is a non-equilibrium doping method and can overcome the solid–solubility limit of the dopant in substrates. The major drawback of ion implantation is the generation of structural defects in the host lattice. However, in several studies it has been demonstrated that ZnO exhibits a high amorphization threshold. Therefore ion implantation is widely used to dope ZnO with transition metal ions. Ref. [40] gives a review on transition metal ion implantation into ZnO. In this paper, we review our activities on ion implanted ZnO, and scrutinize the formation of secondary phases by a careful correlation between structure and ferromagnetism. Moreover, we compare the preparation method of ion implantation with another non-equilibrium one, pulsed laser deposition (PLD).

2. Experimental methods

Commercial ZnO bulk crystals were implanted with ^{57}Fe, Co, and Ni ions at an elevated temperature of 623 K with fluences from 0.4×10^{16} to 8×10^{16} cm^{-2}. The implantation energy was 180 keV, which results in a projected range of $R_p \sim 89 \pm 29$ nm, and a maximum atomic concentration from 0.5% to 10% (TRIM code [41]).

Structural analysis was achieved both by synchrotron radiation XRD (SR-XRD) and conventional XRD. SR-XRD was performed at the Rossendorf beamline (BM20) at the ESRF with an X-ray wavelength of 0.154 nm. Conventional XRD was performed with a Siemens D5005 equipped with a Cu-target source. In XRD measurements, we use 2θ–θ scans to identify crystalline precipitates, and azimuthal φ scans for determining their crystallographical orientation.

The lattice damage induced by implantation was evaluated by Rutherford backscattering/channeling spectrometry (RBS/C). χ_{min} is the channeling minimum yield in RBS/C, which is the ratio of the backscattering yield at channeling condition to that for a random beam incidence [42]. Therefore, χ_{min} indicates the lattice disordering degree upon implantation.

The magnetic properties were measured with a superconducting quantum interference device (SQUID, Quantum Design MPMS) magnetometer in the temperature range of 5–350 K. Field dependent magnetization (hysteresis loops) was measured at 5 K and 300 K. Temperature dependent magnetization was measured after zero field cooling and field cooling (ZFC/FC) [31]. Note that SQUID magnetometry is an integral method, which measures the total magnetic response from the sample, including substrate and possible contaminations from previous processing [43,44]. On the other hand, conversion electron Mössbauer spectroscopy (CEMS) is an element specific method, which was used to investigate the ^{57}Fe lattice sites, electronic configuration and corresponding magnetic hyperfine fields.

The Co-doped ZnO films were grown by pulsed laser deposition (PLD) using a KrF excimer laser. Different substrate temperatures, oxygen pressure and film thickness were chosen to control the electron concentration in the intrinsically n-type conducting ZnO by several orders of magnitude [45].

Table 1
Second phases observed in TM-doped ZnO and their magnetic properties.

Secondary phase	Magnetism	Curie temperature (K)	References
Fe	Ferromagnetic	800	[26]
$ZnFe_2O_4$ (inverted)	Ferrimagnetic		[27,28]
Co	Ferromagnetic	1373	[29,30]
Ni	Ferromagnetic	630	[31]
$(Zn,Mn)Mn_2O_4$	Ferrimagnetic	40	[32]
Mn_3O_4	Ferromagnetic	43	[33]
$Mn_{2-x}Zn_xO_{3-\delta}$	Ferromagnetic	980	[33]
CoZn	Ferromagnetic	400–450	[34]

Curie temperature (for ferro- or ferrimagnetic material) of these secondary phases in bulk form is given.

3. Results

3.1. Fe implanted ZnO

We pick out the ZnO single crystals implanted with Fe as an example to show the possible misinterpretation of the observed ferromagnetism. Fig. 1a shows the magnetization measurement on the sample implanted with Fe, with the field along the sample surface. The implantation temperature is 623 K and the Fe fluence is 4×10^{16} cm^{-2}. At 5 K and 300 K, the sample shows ferromagnetism. However, with increasing temperature, its coercivity and remanence are decreased drastically: from 360 Oe at 5 K to 10 Oe at 300 K, and 0.14 μ_B/Fe to 0.01 μ_B/Fe, and this is a strong indication of superparamagnetism, which has been confirmed by the measurement of ZFC/FC magnetization. The inset of Fig. 1a shows ZFC/FC curves with an applied field of 50 Oe. A distinct difference in ZFC/FC curves was observed. ZFC curves show a gradual increase (deblocking) at low temperatures, and reach a broad peak with a maximum, while FC curves continue to increase with decreasing temperature. The broad peak in the ZFC curves is due to the size distribution of Fe NCs.

Fig. 2b shows symmetric 2θ–θ scans for the sample performed by conventional XRD and by SR-XRD. Obviously no secondary phases could be detected by conventional XRD, where the sharp peaks, at $2\theta \sim 34.4^\circ$ and $2\theta \sim 72.6^\circ$, are from bulk ZnO. In contrast to conventional XRD, SR-XRD has the advantages of larger source intensity and signal-background ratio. In the SR-XRD 2θ–θ scan, a rather broad and low intensity peak at $2\theta \sim 44.5^\circ$ originating from α-Fe(110) with a theoretical Bragg angle of $2\theta = 44.66^\circ$ occurs. Apart from α-Fe, no other Fe-oxide (Fe_2O_3, Fe_3O_4, and $ZnFe_2O_4$) NC are detected. For comparison, the peak intensities for both scans are normalized at the same level. It is clear that the signal-background ratio in SR-XRD is larger than that in conventional XRD by three orders of magnitude. By combining the magnetic and structural measurements, it is reasonable to conclude that metallic α-Fe NC have formed during implantation at 623 K with the fluence of 4×10^{16} cm^{-2}, and they are responsible for the ferromagnetism. The saturation moment at