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Room temperature ferromagnetism in ZnO films due to defects

Qingyu Xu,[1,a)] Heidemarie Schmidt,[1] Shengqiang Zhou,[1] Kay Potzger,[1] Manfred Helm,[1] Holger Hochmuth,[2] Michael Lorenz,[2] Annette Setzer,[2] Pablo Esquinazi,[2] Christoph Meinecke,[2] and Marius Grundmann[2]

[1]*Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Dresden-Rossendorf e.V., Bautzner Landstraße 128, 01328 Dresden, Germany*

[2]*Institut für Experimentelle Physik II, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany*

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ZnO films were prepared by pulsed laser deposition on *a*-plane sapphire substrates under N_2 atmosphere. Ferromagnetic loops were obtained with the superconducting quantum interference device at room temperature, which indicate a Curie temperature much above room temperature. No clear ferromagnetism was observed in intentionally Cu-doped ZnO films. This excludes that Cu doping into ZnO plays a key role in tuning the ferromagnetism in ZnO. 8.8% negative magnetoresistance probed at 5 K at 60 kOe on ferromagnetic ZnO proves the lack of *s-d* exchange interaction. Anomalous Hall effect (AHE) was observed in ferromagnetic ZnO as well as in nonferromagnetic Cu-doped ZnO films, indicating that AHE does not uniquely prove ferromagnetism. The observed ferromagnetism in ZnO is attributed to intrinsic defects. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2885730]

The search of diluted magnetic semiconductor is a subject of current interest due to the possibility to control spin and charge simultaneously for future spintronics. Mn-doped GaAs is a successful diluted magnetic semiconductor (DMS), however, the highest Curie temperature T_C is only 173 K, far below room temperature.[1] Magnetic doped ZnO was intensively studied after the theoretical predication of room temperature ferromagnetism in Mn-doped, *p*-type conducting ZnO.[2] Because of good solubility into ZnO, most of the magnetic doping were 3*d* transition metals, such as Mn, Co, Fe, Ni, etc.[3] However, ZnO is intrinsically *n*-type conducting. Diverse magnetic properties were observed, for example, ferromagnetism, paramagnetism, antiferromagnetism, etc.[4] The observed ferromagnetism in magnetic doped ZnO is in general very weak[5] and, therefore, an extrinsic origin due to magnetic impurities could not be excluded.[6]

Gacic *et al.* reported that the magnetic properties in Co-doped ZnO consist of two parts, strong temperature dependent paramagnetism which follows the Brillouin function and temperature independent ferromagnetism, while x-ray magnetic circular dichroism measurements only revealed a paramagnetic behavior of the active Co-dopant atoms,[7] in contrast to similar measurements on similar samples reported earlier.[8] These results indicate that a specific parameter is not yet well controlled.

Recently, we have reported ferromagnetic properties in Mn-doped ZnO prepared under N_2 atmosphere.[9] These results indicate that the observed ferromagnetism might not originate from the active magnetic dopant atoms, but from vacancies in the ZnO lattice, as other results in undoped ZnO (Refs. 10 and 11) as well as in other oxides such as TiO_2 already indicate.[12,13] In this paper, we prepared undoped ZnO films under N_2 atmosphere that show clear room temperature ferromagnetic signals from defects. The importance of defects in triggering magnetic order in otherwise diamagnetic materials appears to be a key issue, as the main ferromagnetic paradigm, namely graphite, already demonstrated.[14]

ZnO films were grown from a ZnO ceramic target on 10×10 mm^2 *a*-plane sapphire substrates by pulsed laser deposition (PLD) using a KrF excimer laser in N_2 atmosphere (0.3 mbar) with substrate temperature T_s of 570 °C. The deposition conditions (N_2 pressure and substrate temperature) were selected to prepare conducting films. The film thickness was controlled by the number of laser pulses with an energy density of 2 J cm^{-2} and *ex situ* determined by modeling spectral ellipsometry data measured in the energy range from 1 to 4 eV. The composition of the films was determined by combined Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE) measurements. The crystal structure of the films was characterized by x-ray diffraction (XRD) measurements with θ-2θ scans using a Cu Kα source. The XRD pattern (Fig. 1) shows the *c*-axis orientation without impurity phases within the resolution. Magnetization *M* versus temperature *T* from 5 to 300 K and versus magnetic field *H* from 0 to 60 kOe was measured with a superconducting quantum interference device magnetometer with the magnetic field applied in the film plane. The *a*-plane sapphire substrates, which show sometimes weak ferromagnetic signals, were measured separately after etching off the film by an HCl dip.[15,16] Magnetotransport measurements with the field applied parallel to the *c* axis were performed in van der Pauw configuration between 5 to 290 K.

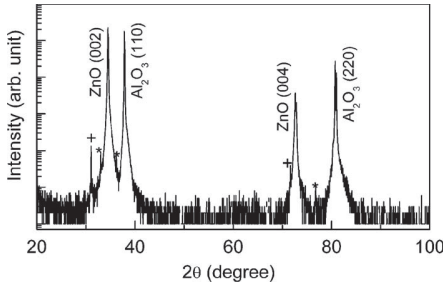

FIG. 1. XRD pattern of a ZnO film prepared under N_2 atmosphere on *a*-plane sapphire substrate. The weak diffraction peaks corresponding to Cu Kβ and W Lα are labeled by "+" and " *" respectively.

[a)]Author to whom correspondence should be addressed. Electronic mail: xuqingyu_1974@yahoo.com.

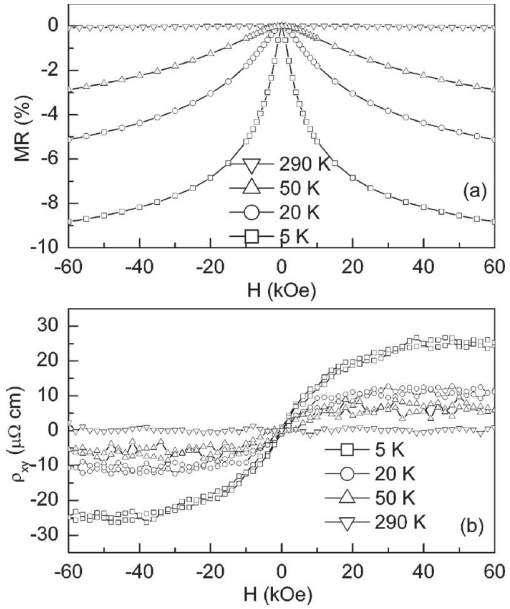

FIG. 2. The field dependent (a) MR and (b) anomalous Hall resistivity of the ZnO film from Fig. 1.

Figure 2 shows the magnetotransport properties of the ZnO film prepared under N_2 atmosphere. Due to the lack of *s-d* exchange interaction, in contrast to magnetic doped ZnO,[17] negative magnetoresistance (MR) {defined as $[R(H)\text{-}R(0)/R(0)]$} of 8.8% at 5 K under 60 kOe was observed and the MR effect decreases with temperature [Fig. 2(a)]. The negative slope of the Hall curves shows the *n*-type conductivity from 5 to 290 K. After subtraction of the ordinary Hall effect (OHE) (the slope of the Hall curve at high field), anomalous HE (AHE) was observed [Fig. 2(b)].

Figure 3 shows the magnetic properties of ZnO films after the subtraction of the magnetic signal from substrate. Figure 3(a) shows the *M-H* loops of a ZnO film at 5 and 290 K. Clear hysteresis loops were observed at 5 and 290 K. The coercivity fields at 290 and 5 K are 50 and 67 Oe, respectively. The difference between the saturation magnetization at 5 and 290 K is small, suggesting that the ferromagnetism in ZnO remains much above 290 K. The inset of Fig. 3(a) shows the high field part of the *M-H* curve up to 60 kOe at 5 K. Contrary to the strong paramagnetic signals (which follow the usual Brillouin function at high fields) obtained in the magnetic-doped ZnO prepared under similar condition,[7] no obvious paramagnetic contribution was observed in the undoped ZnO film, as the temperature dependent magnetization curves also indicate [see Fig. 3(b)]. The difference between field cooled (FC) and zero-field zero-field cooled (ZFC) curves decreases with temperature, resembling partially the temperature dependence of the small hysteresis.

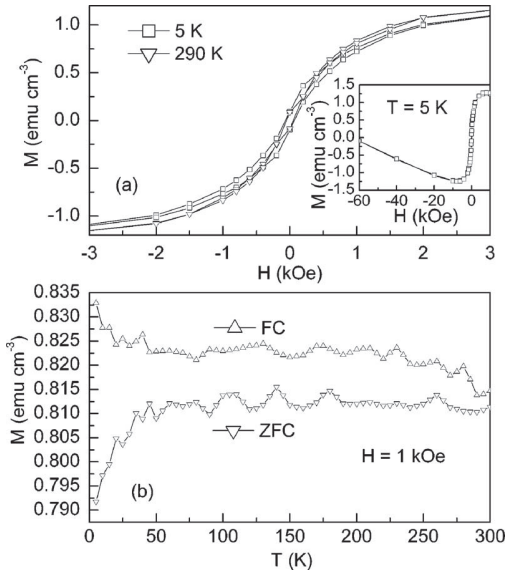

FIG. 3. (a) The *M-H* loops, (b) ZFC and FC *M-T* curves of the ZnO film from Figs. 1 and 2. The sample was cooled under 1 kOe for FC curve.

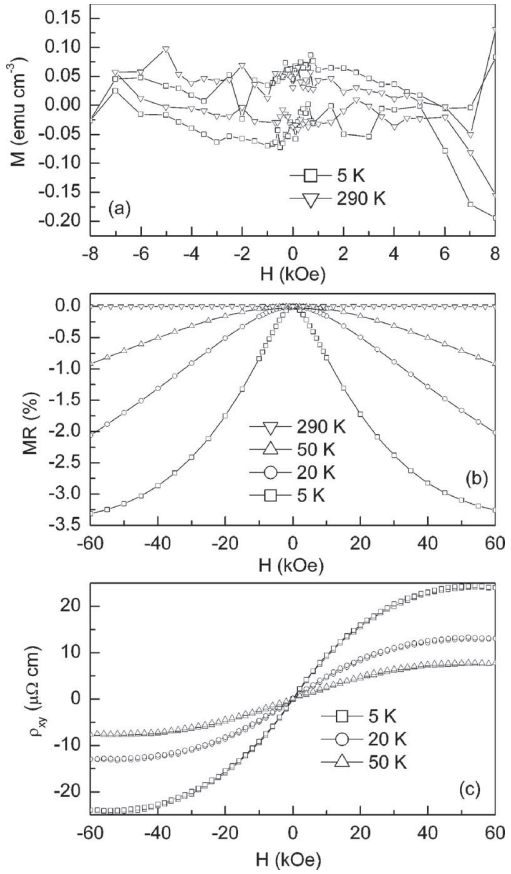

FIG. 4. The *M-H* loops (a), the field dependent MR (b) and anomalous Hall resistivity (c) of $Zn_{0.985}Cu_{0.015}O$ film.

RBS/PIXE were done to check the impurities. The measured impurities are S 0.03%, Cu 0.12%, Ca 0.06%, Fe 0.01%, and (Ti) 0.01%. The N concentration is less than the RBS (N is not detectable in PIXE for our setup) detection limit (less than 0.11 atoms in the ZnO molecule). The influence of the small amount of nonmagnetic impurities like S, Ti, and Ca can be excluded. The measured amount of Fe was always observed in our previous ZnO and doped ZnO and showed no influence on the ferromagnetic properties.[18]

Recently, room temperature ferromagnetism was reported in Cu-doped ZnO.[19] To check the influence of Cu impurities, Cu was intentionally doped into ZnO films under N_2 atmosphere by PLD. The composition of the prepared films was $Zn_{0.985}Cu_{0.015}O$ with 0.01% Fe impurity inside. The XRD spectrum of $Zn_{0.985}Cu_{0.015}O$ film shows similar structure as the ZnO film (Fig. 1) without impurity phases. Figure 4(a) shows the *M-H* loops of $Zn_{0.985}Cu_{0.015}O$ at 5 and 290 K. A linear background was subtracted from the *M-H* loops. Figure 4(a) shows that no clear ferromagnetism was

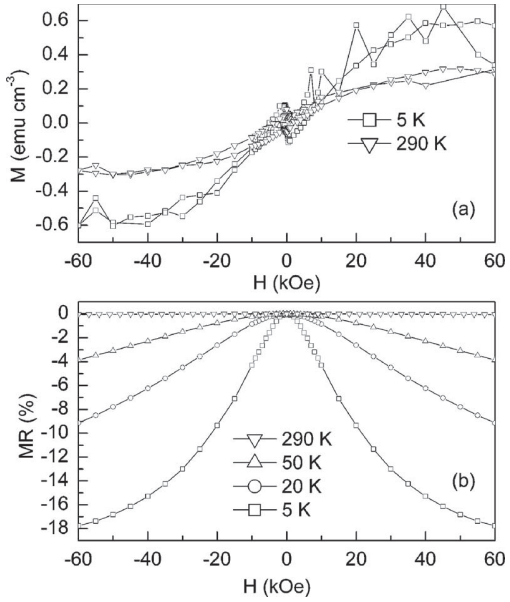

FIG. 5. (a) The *M-H* loops and (b) field dependent MR of ZnO film prepared under higher substrate temperature (655 °C).

observed for the Cu-doped film excluding Cu impurities as the reason for the ferromagnetism in ZnO. Similar negative MR was observed from 5 to 290 K, as shown in Fig. 4(b). Interestingly, clear AHE was also observed in $Zn_{0.985}Cu_{0.015}O$, as shown in Fig. 4(c), after the subtraction of the OHE part, indicating that AHE should not be used as an indication of intrinsic ferromagnetism in DMS.

The origin of the ferromagnetism in pure ZnO was attributed to oxygen vacancies[10] or to defects on Zn sites.[11] Recent theoretical calculations indicate that the ferromagnetism in ZnO might originate from Zn vacancies and not from oxygen vacancies.[20] Deep level transient spectroscopy (DLTS) on ferromagnetic Mn-doped ZnO prepared under N_2 atmosphere showed that Zn vacancies were present.[9] Thus, it is reasonable to attribute the observed ferromagnetism to Zn vacancies in ZnO films.

Another undoped ZnO film was prepared under 0.3 mbar N_2 but at a higher substrate temperature (655 °C). This ZnO film showed a better crystal structure with fewer defects, as the increase in the resistivity from 0.08 Ω cm (T_s=570 °C) to 2 Ω cm (T_s=655 °C) suggests. Figure 5(a) shows the *M-H* loops at 5 and 290 K. A linear background was subtracted from the *M-H* curves. No clear ferromagnetic hysteresis loop can be observed, indicating that the observed ferromagnetism in undoped ZnO originates from defects. Larger MR values are obtained for this film prepared at high-substrate temperature [see Fig. 5(b)]. Note the difference in the field dependence of the MR curves between the samples [see Figs. 2(a), 4(b), and 5(a)], especially in the low field region. This difference indicates the difference in the magnetic contributions between the samples.[21] Further extensive experimental and theoretical studies on the influence of defects in ZnO are needed to understand their magnetic contributions and how to control them in ZnO to obtain room or even higher temperature magnetic order.

In summary, ZnO films were prepared under N_2 atmosphere by PLD. Clear hysteresis loop was observed up to 290 K in ZnO prepared with lower substrate temperature. The extrinsic impurity origin was excluded. The absence of ferromagnetism in ZnO film produced at higher substrate temperature indicates that defects in ZnO should play an important role in triggering magnetic order. Our results further show that AHE cannot be used as an indication of intrinsic ferromagnetism. Our results suggest that a careful control of defects in ZnO and not the doping with magnetic ions might be a possible, better way to obtain reproducible intrinsic, homogeneous room temperature ferromagnetism in ZnO.

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