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Research Article

Observation of Negative Magnetic Hysteresis Loop in ZnO Thin Films

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We report on the observation of an unusual negative magnetic hysteresis loop in ZnO thin film codoped with cobalt and aluminum (Co-Al:ZnO), while other transition-metal-doped ZnO films, such as Cu-doped ZnO and Mn-doped ZnO, exhibit normal hysteresis loops. The unusual magnetic behavior is ascribed to the presence of double magnetic layers with different magnetic moments due to the change of structural defects across the film layers. Positron annihilation measurements confirmed the presence of unique microstructural changes in the Co-Al:ZnO film. This study shows that defects in diluted magnetic semiconductors may induce not only ferromagnetism but also novel magnetic behaviors.

1. Introduction

The increasing potential of ferromagnetic materials as facilitators of spin transport electronics and applications has led to a substantial growth in diluted transition-metal-doped magnetic semiconductor (DMS) research [1–3]. Oxide-based semiconductors doped with small percentages of transition metals have shown great promise in spintronic applications by demonstrating room temperature ferromagnetism (FM) [4–6]. Dietl et al. initially predicted FM with a high Curie temperature (T_c) in p-type Mn-doped ZnO via local spin density approximation [7, 8] while simulations by Sato and Katayama-Yoshida predicted FM in V-, Cr-, Fe-, Co-, and Ni-doped ZnO, but suggested that Mn doping by itself may not be sufficient to induce FM [9], a conjecture that has been supported by local spin density approximation [10], B3LYP hybrid density functional method [11], and gradient corrected functional density theory [12]. Experimental studies on FM in DMS are often irreproducible and contradictory [13, 14], and the ambiguous nature of FM in DMS is obscured by the possible presence of transition-metal precipitates or clusters and further complicated by the magnetic dependence on growth conditions and postgrowth treatments [15–19]; this however indicates a strong correlation between intrinsic defects and ferromagnetism, a notion that is supported by observations of ferromagnetism in undoped ZnO [20, 21]. Due to this dubiety in ferromagnetic origins, a scant number of explanations have been proposed to interpret FM mediation and magnetic moment genesis, complicating the narratives of many magnetic phenomena.

In this letter, we report on the measurement of an unusual negative magnetic hysteresis loop in an aluminum-cobalt-doped zinc oxide thin film. Unusual magnetic behaviors such as reversed hysteresis have only been observed in rare cases that concern materials like GaAs-Fe hybrid structures [22] and Co-CoO nanophase systems [23]; however, we are not aware of any reversed or negative hysteresis in ZnO. We attribute the origin of such unusual magnetic behavior in the current study to the presence of film layers with different magnetic moments leading

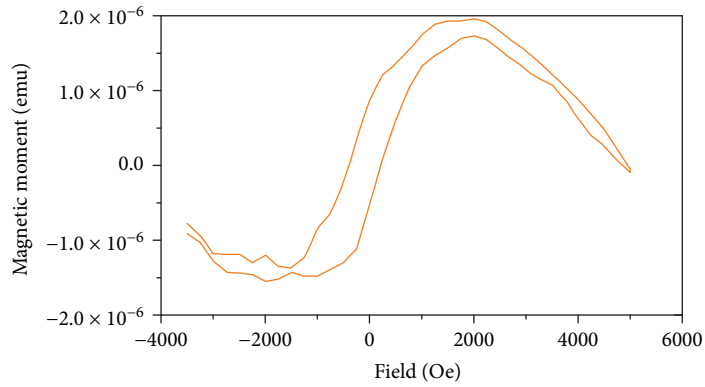

Figure 1: Out-of-plane magnetic SQUID measurements at 10K for 3% Mn:ZnO with subtracted diamagnetic behavior of quartz substrate.

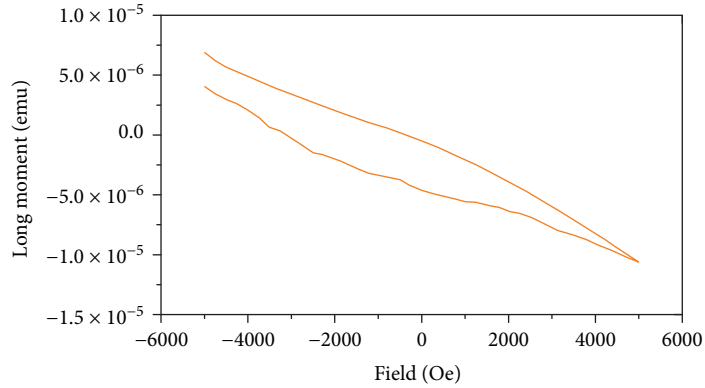

Figure 2: Out-of-plane magnetic SQUID measurements at 10K for 2% Al : 3% Co:ZnO with subtracted diagmagnetic of quartz substrate.

to net antiferromagnetic behavior. Our current study of magnetism in TM-doped ZnO thin films also revealed normal FM in Mn- and Cu-doped ZnO; however, as Cu is not a magnetic ion, it cannot provide the magnetic moment in the Cu:ZnO films. This emphasizes the crucial role of defects in producing and mediating FM in ZnO films. Thus, we performed positron annihilation spectroscopy (PAS) measurements to give insight into the presence of intrinsic defects in these films. The measurements revealed the presence of adjacent layers with different defect structures in Co-Al-doped ZnO film which may lead to different magnetic moments triggering this unusual magnetic behavior.

2. Experimental Details

Co-, Mn-, Cu-, and Al-Co-doped ZnO thin films were synthesized via the sol-gel method on quartz and sapphire substrates. Zinc acetate dihydrate was the primary precursor, and 2-methoxyethanol and ethanolamine were used as solvent and stabilizer, respectively. Cobalt acetate tetrahydrate, aluminum nitrate, manganese acetate tetrahydrate, and copper acetate were used to provide dopants for Co:ZnO, Al-Co:ZnO, Mn:ZnO, and Cu:ZnO. The solutions were heated and stirred at a constant temperature of 60°C then cooled to room temperature and deposited onto clean, etched quartz and sapphire substrates using the spin-coating method. They were then placed in an oven at 120°C for 10 minutes to evaporate the solvent. The process was repeated for each sample 16 times to obtain the desired thickness. The films were then annealed in air at 500 or 700°C to form a ZnO structure. More details concerning the synthesis of ZnO films by the sol-gel method and their structural characterization can be found in [24].

Using a superconducting quantum interference device (SQUID), ferromagnetic behavior for 3% Mn:ZnO and 2% Al : 3% Co:ZnO on quartz substrates and 1% Cu:ZnO on sapphire substrate was recorded. Doppler broadening of PAS measurements was performed using monoenergetic positron beams in the 0.2 keV to 30 keV range at the positron facility Helmholtz-Zentrum Dresden-Rossendorf (HZDR) in Dresden, Germany. The 511 keV annihilation peak for each beam energy was recorded using a high purity Ge detector, and the S and W defect parameters [25] were obtained from the annihilation peak. The structural and optical properties of the Al-Co:ZnO sample, X-ray diffraction (XRD), and ultraviolet-visible (UV-VIS) spectroscopic measurements were carried out at room temperature.

3. Results and Discussions

Out-of-plane magnetic measurements due to perpendicular magnetic field for Mn:ZnO and Al-Co:ZnO are shown in Figures 1 and 2, respectively, while Figure 3 displays in-plane magnetic measurements for Cu:ZnO [26]. No

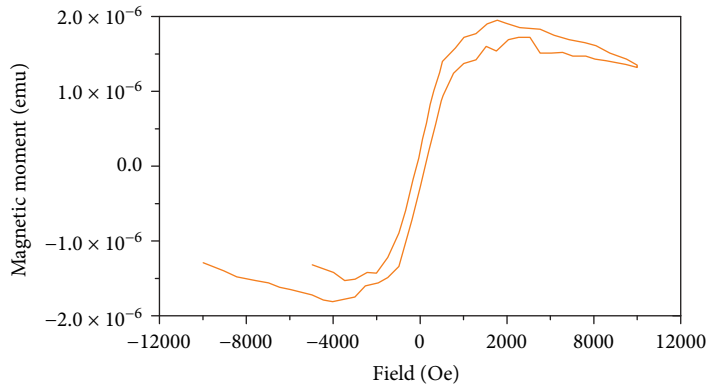

Figure 3: In-plane magnetic SQUID measurements at 10K for 1% Cu:ZnO on sapphire substrate.

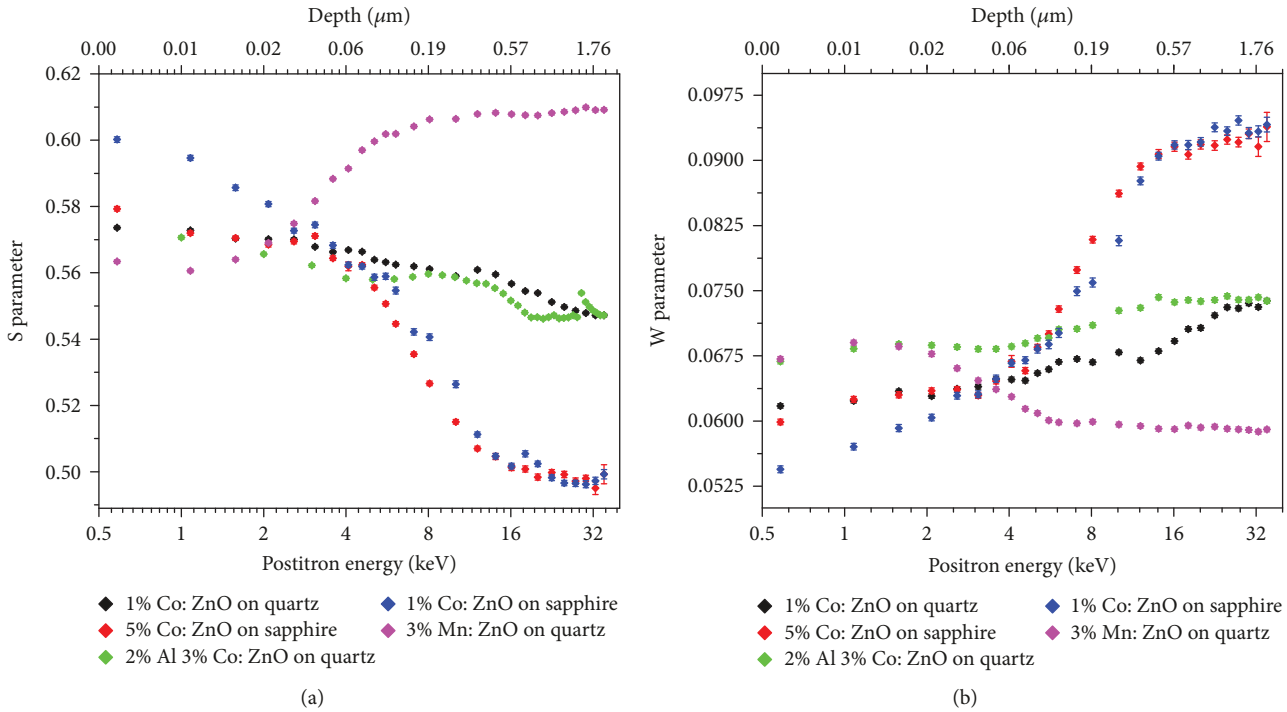

Figure 4: S parameter (a) and W parameter (b) of depth-resolved positron annihilation spectroscopy by Doppler broadening for sol-gel grown transition-metal-doped ZnO thin films.

ferromagnetic behavior was observed in the 1% or 5% Co:ZnO films. In all cases, the diamagnetic behavior of the substrates was accounted for. The hysteresis loops in Figures 1 and 3 indicate the presence of ferromagnetism in the Mn:ZnO and Cu:ZnO films. Although FM has been predicted and observed experimentally in Mn:ZnO, a discord exists in the reported justifications [25, 26]. Likewise, the origins of ferromagnetism in Cu:ZnO remain unidentified as neither Cu nor ZnO is intrinsically magnetic, meaning that one defect type must exist to induce the magnetic moments and another to mediate them.

The focus of this work is the unusual negative hysteresis loop observed in the Al-Co:ZnO sample (Figure 2). Treatment of the film as a simplified two-layer system, in which the bottom layer has a magnetic moment and coercivity different from that of the upper layer, offers a possible explanation for the reversed hysteresis [27]. These magnetic moments are probably associated with different defects, the plausibility of which is supported by the unique behavior of the S parameter [28] in the depth-resolved Doppler broadening of PAS measurements of the Al-Co-doped ZnO film explained below. Doppler broadening of PAS has been established as an effective technique in identifying neutral or negatively charged vacancy-type defects in semiconductors and dielectrics [28–35]. Due to a lack of positive ion cores, these vacancies form attractive potentials that trap positrons, resulting in characteristic changes in the measured positron annihilation parameters.

The S and W parameters for Co-, Al-, and Mn-doped ZnO on quartz and sapphire substrates are shown in Figures 4(a) and 4(b) and are plotted as functions of incident positron energy and mean implantation depth. The

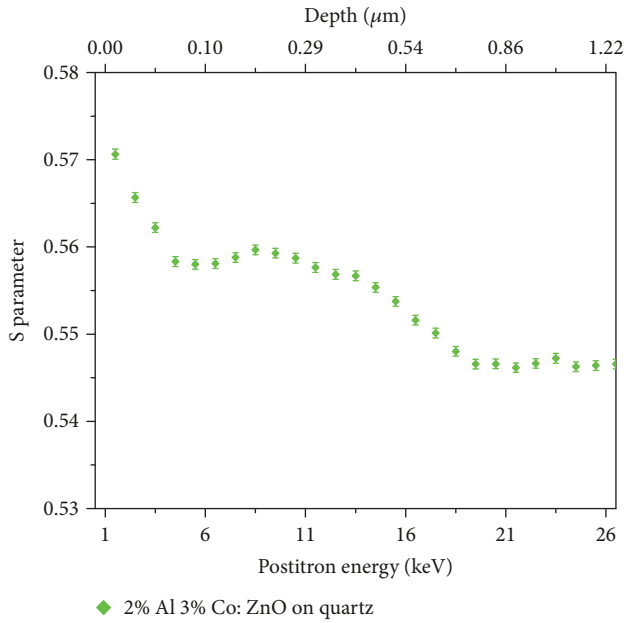

Figure 5: S-parameter of PAS measurements for Al-Co:ZnO thin film.

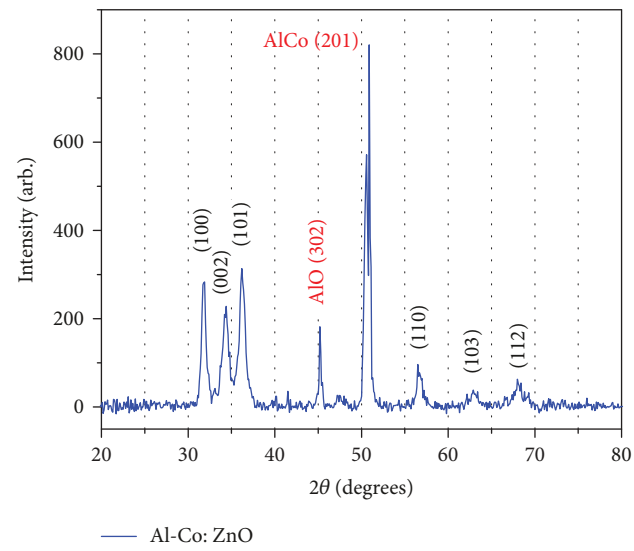

Figure 6: XRD pattern of Al-Co:ZnO thin film, indicating polycrystalline phases of hexagonal wurtzite ZnO as well as AlO and AlCo phases.

parameters S and W represent the fractions of positron annihilation with valence and core electrons, respectively, and provide information about defect structures and densities. We obtain the S and W parameters, respectively, by dividing the counts in the center of the 511 keV peak, and the counts in the wings of the peak, by the total counts. The attractive potential induced by neutral or negatively charged vacancies is likely to trap positrons at these defect sites, causing annihilation with low momentum valence electrons, leading to an increase in the S parameter and a decrease in the W parameter. In Figures 4(a) and 4(b), positron annihilation at the surface of the films takes place within the first 10–20 nm (0-1.5 keV) and positron annihilation within the substrate begins near the film-substrate interface past 10 keV at roughly 270 nm. The large variation in S parameter by positron energy past 10 keV is due to positron annihilation within the substrates. The film of 3% Mn:ZnO was grown on quartz of nanocrystalline fused silica substrate while the other films were grown on sapphire or quartz of crystalline silica substrates. This explains the higher S parameter for the sample of 3% Mn:ZnO on quartz. Between the regions of 1.5 keV to 10 keV, positrons interact in the bulk of the films and the high S parameter in this region indicates a high concentration of defects in all the films. The S parameter of the Al-Co:ZnO replotted in Figure 5 displays an unusual behavior in which the initial decrease in the S parameter, characteristic of compositional transitions (from film to substrate for example), briefly plateaus near 5 keV and then increases until 8 keV before it tapers off as per usual substrate typicality. This behavior suggests a microstructural dissimilarity between the Al-Co:ZnO film and the other TM-doped films; it indicates film layers with different defect types and may substantiate the above-proposed two-layer model for the negative magnetic hysteresis loop measured in the Al-Co:ZnO film.

The XRD spectrum in Figure 6 indicates a polycrystalline structure matching the hexagonal wurtzite structure of ZnO [26]. The peaks at $2\theta = 45.2^\circ$ and 50.8° represent the (302) phase of AlO and the (201) phase of AlCo, respectively. These phases do not induce FM and thus cannot contribute to the ferromagnetism in the films. Furthermore, the absence of cobalt oxides and clusters in the XRD spectrum indicates no secondary magnetic phases in the films. The optical absorption spectrum for the Al-Co:ZnO films is shown in Figure 7 and indicates good transparency in the visible range. The optical band gap can be estimated from the absorption spectrum using a Tauc extrapolation [36, 37], in which the linear portion of $(\alpha \mathrm{hv})^2$ versus hv is extrapolated to $(\alpha \mathrm{hv}) = 0$ to approximate the band gap, where α is the absorption coefficient and hv is the energy in electron volts (eV). For direct allowed transitions, the band gap of the Al-Co:ZnO film was 3.15 eV, which is consistent with the band gap of ZnO. The presence of layers with different defect structure did not affect the band edge of ZnO; however, it affects the tail of the absorption curve as shown in Figure 7. It should be mentioned that the ferromagnetic films were highly resistive; therefore, investigation of carrier concentration and type via Hall effect measurements was not possible. This may indicate that charge carriers are not the primary mediators of ferromagnetism in these samples. We anticipate that magnetic proximity effects that take place in heterostructures with magnetic layers are responsible for the unusual negative magnetic behavior.

We should consider the possible role of grain boundaries on inducing FM, as our structural characterization of the sol-gel-doped ZnO films [24] indicates a small grain size of about 20 nm. According to a previous work by Hsu et al. [38], FM occurs in polycrystalline ZnO films at high grain boundary densities. Another recent work revealed that ZnO films with

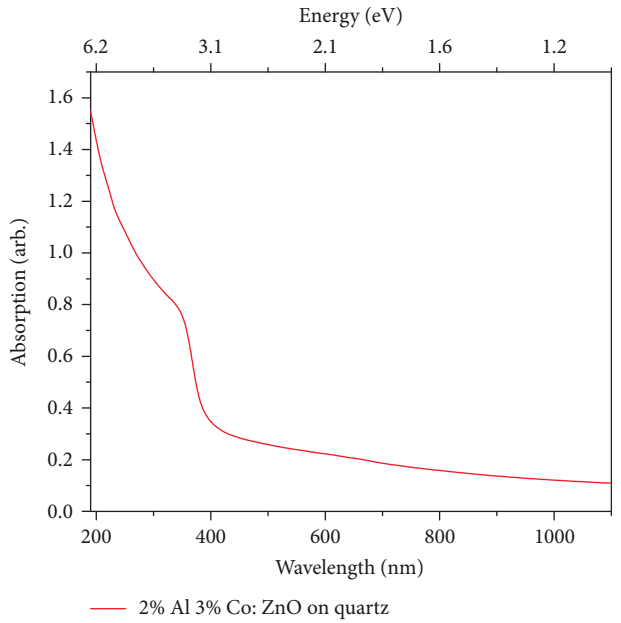

Figure 7: UV-VIS absorption spectra of 2% Al : 3% Co:ZnO film.

strong texture have FM behavior whereas untextured films are nonmagnetic [39]. Two factors related to the grain boundaries may affect FM in our films. The solubility of dopant or impurity may increase with decreasing grain size in polycrystalline films as the impurity dissolves in both the grain boundaries and the bulk; this would enhance the concentration of magnetic ions [18, 40]. The other factor is associated with the Co-Al:ZnO film as the codoping of ZnO films can induce defects in the grain boundaries which may enhance FM in the films and affect their magnetic behavior. This represents another possible explanation for the unusual hysteresis loop in Co-Al:ZnO film.

4. Conclusions

Ferromagnetic transition-metal-doped ZnO thin films were grown by the sol-gel method and investigated by magnetic SQUID measurements and depth-resolved positron annihilation spectroscopy. High concentrations of defects were observed in all the samples, indicating the possible role of defects in inducing magnetic moments and mediating ferromagnetism. An interesting, negative magnetic hysteresis loop indicating antiferromagnetic behavior was measured in the Al-Co-doped zinc oxide film and interpreted via a two-layer model where the film consists of layers with two different magnetic moments and substantiated by the unique behavior in the S parameter of the Co-Al:ZnO film arising from layers with different defect structures. The XRD spectrum verified hexagonal wurtzite ZnO structure as well as phases of AlO and AlCo which may produce various defects with different magnetic moments, while optical spectroscopy indicated variations in the absorption tail indicating high defect concentrations. Defects have been already predicted to be behind FM in ZnO and other DMS; however, this study reveals that defects may also induce novel magnetic behavior in DMS thin films.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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