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Defect-band mediated ferromagnetism in Gd-doped ZnO thin films

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Gd-doped ZnO thin films prepared by pulsed laser deposition with Gd concentrations varying from 0.02–0.45 atomic percent (at. %) showed deposition oxygen pressure controlled ferromagnetism. Thin films prepared with Gd dopant levels (<Gd 0.112 at. %) at low oxygen deposition pressure (<25 mTorr) were ferromagnetic at room temperature. Negative magnetoresistance, electric transport properties showed that the ferromagnetic exchange is mediated by a spin-split defect band formed due to oxygen deficiency related defect complexes. Mott's theory of variable range of hopping conduction confirms the formation of the impurity/defect band near the Fermi level.
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I. INTRODUCTION

Diluted magnetic semiconductors (DMS), which are capable of spin injection and detection of selectively polarized spins of either up/down orientation, are suitable for embedding within currently successful semiconductor technologies, thereby achieving multifunctional spintronic devices.¹ ZnO is an excellent candidate for achieving such predicted multifunctionalities² due to its inherent properties, such as wide band gap, transparency, and ability to grow large high quality crystals.³ Previous literature reported that room temperature ferromagnetism (RTFM) was reported for 3d-transition metal doped ZnO.⁴ However, the origin of RTFM and optimization of conditions for reproducibility are still equivocal. Dopant segregations and/or defect-induced magnetism, achieving a high Curie temperature and high magnetic moment in doped ZnO, are the most prominent issues.⁵

Rare-earth elements (RE) possess larger magnetic moments and magneto-crystalline anisotropy compared to the 3d TM.⁶ In addition, a report on the observation of a colossal magnetic moment (4000 μ_B) upon Gd-doping in GaN⁷ has prompted efforts to investigate the magnetism in Gd-doped ZnO (Gd:ZnO). Earlier theoretical⁸ and experimental studies have brought to focus two important prerequisites to obtain long-range RTFM in Gd:ZnO: (i) optimum amount of Gd doping^{9,10} and (ii) certain density of carriers.¹¹

Intrinsic point defects, created during the sample preparation⁵ or via post-synthesis treatments, were suggested as responsible for RTFM in ZnO;¹² however, its influence on Gd:ZnO is not fully understood. Earlier report on the reversible FM in nonmagnetic Mn (Co) doped ZnO nano powders that claimed annealing under O₂ (N₂) gave rise to FM (paramagnetic) state and vice versa, suggesting that O related

defects favored FM.¹³ The motivation of the present work is to systematically study the role of Gd-doping and defects on the magnetic and transport properties of Gd:ZnO thin films prepared by pulsed laser deposition (PLD) under controlled oxygen pressure and temperature condition. For the scope of this study, we varied (i) Gd concentration (Gd%) in the PLD targets and (ii) background oxygen pressure (P_d) during the growth. In this paper, we correlate the density of localized and free electrons by magneto-transport measurements to observe RTFM in these films by invoking the relation of possible exchange mechanisms with spin splitting of the impurity/defect band.

II. EXPERIMENTS, RESULTS, AND DISCUSSIONS

Gd:ZnO thin films were prepared from ceramic targets with nominal concentrations: 0.05, 0.15, 0.25, 0.375, 0.5, and 1.0 wt. % of Gd₂O₃, on lattice matched (0.08%)¹⁴ α -plane sapphire substrates by PLD technique (KrF laser with $\lambda = 248$ nm, energy = 520 mJ, and substrate temperature = 650 °C). We set the laser energy set (520 mJ per pulse) in the laser module. This energy is decreased by 6%–7% at the target's position inside the PLD chamber. Therefore, the average effective laser energy on the target was ~ 485 mJ per pulse. Henceforth, the samples prepared from these targets are referred to as 0.02, 0.06, 0.11, 0.16, 0.22, and 0.45 at. % Gd:ZnO, respectively. Eight sets of thin films were prepared by varying Gd% and oxygen pressure (P_d) from 5 to 500 mTorr. Gd concentrations in the thin films were estimated by Rutherford backscattering spectrometry (RBS, Kobelco HRBS-V500). A typical RBS spectrum for 0.11at. % Gd:ZnO thin film revealed a close estimation of 0.15 at. % Gd,¹⁶ which confirms that a consistent cation transfer ratio¹⁵ was achieved from the ceramic targets to the thin films by the PLD.

X-ray diffraction (XRD) patterns show that all Gd:ZnO thin films were grown along the c -axis with peaks corresponding

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FIG. 1. XRD patterns of Gd:ZnO films showing a gradual shift of the (002) peaks with (a) increasing P_d (0.067 at. % Gd:ZnO) and (b) increasing Gd% ($P_d = 25$ mTorr). NEXAFS spectra of the Gd:ZnO thin films (a) at O K-edge and (b) Gd $M_{5,4}$ edges.

only to $\langle 0002 \rangle$ planes. Typical ϕ -scan of the $(10\text{--}11)$ planes shows its six-fold symmetry, confirming the epitaxial growth of the Gd:ZnO thin films.¹⁶ The XRD wide $2\theta < 2\theta > 90^\circ$ scan (fig. not shown), within the instrument resolution limit of ~ 2 at. %, does not reveal any secondary phases. XRD patterns of the 0.06 at. % Gd:ZnO show (Fig. 1(a)) a gradual peak shift towards higher (2θ) angles (from 34.43° to 34.56°) with increasing P_d from 5 to 100 mTorr. This shift to higher angles with increasing P_d indicates an increase in oxygen incorporation into the growth film.¹⁷ A similar shift is observed with increasing Gd concentration from 0.05 to

0.16 at. % (2θ from 34.43° to 34.59°) in Gd:ZnO thin films (Fig. 1(b)). However, this trend is counterintuitive for the direct substitution of Zn^{2+} (ionic radius $0.74 \text{ \AA}$) with Gd^{3+} (ionic radius $0.94 \text{ \AA}$). A similar shift in the peak position with increasing Gd% was already observed in Gd-doped ZnO and was attributed to tensile stress and structural defects.¹⁸ The RBS measurements indicated Gd substitution onto Zn tetrahedral sites.¹⁹ Near edge X-ray absorption fine structure (NEXAFS) spectra at the O K-edge and Gd $M_{5,4}$ -edges (Figs. 1(c) and 1(d)) also indicated substitution of Gd in ZnO.²⁰

Magnetization measurements were carried out in a SQUID-vibrating sample magnetometer (SVSM, Quantum Design). The recorded magnetization data were corrected by subtracting the diamagnetic response from the sapphire substrate. Fig. 2 shows the magnetization hysteresis loops of the Gd:ZnO thin films prepared with different Gd concentrations (Figs. 2(a)–2(c)) and at different P_d (≤ 25 mTorr), as shown in Figs. 2(c) and 2(d). Magnetization loops exhibited hysteresis in the temperature range of 5–380 K, confirming the RTFM nature of these films. The 0.11 at. % Gd:ZnO ($P_d = 5$ mTorr) exhibits the highest coercivity (H_c) and the highest carrier density (n_e) among all the samples. Fig. 3(a) shows that H_c increases as n_e increases, suggesting that the carriers play a role in mediating the exchange. Based on the RBS estimation, magnetic moment of 0.11 at. % Gd:ZnO ($P_d = 5$ mTorr) is estimated to be $\sim 5 \mu_B/\text{Gd}$ at 5 K, which is less than the free atomic moment of Gd ($7 \mu_B$). Samples deposited in higher P_d (with the same Gd%) do not exhibit FM (the figure is not shown).

Typical zero-field cooled (ZFC) and field cooled (FC) magnetization measurements (Figs. 2(e)–2(h)) show no transitions corresponding to any secondary phases, such as pure Gd ($T_C = 293$ K), GdZn or GdZn₂ ($T_C \approx 70$ K) that appeared in the ZFC-FC in Gd:ZnO thin films reported elsewhere.²¹

FIG. 2. Typical MH loops (a)–(d) of Gd:ZnO films prepared at $P_d \leq 25$ mTorr. (e)–(f) are ZFC and FC for samples (a)–(d), respectively. All measurements were done with H normal to the thin film plane.

FIG. 3. (a) Variation of H_c with carrier density (n_c) in ferromagnetic Gd:ZnO. Gd at. % are given next to the symbols. (b) Anisotropic MH loops for 0.02 at. % Gd:ZnO ($P_d = 25$ mTorr). (c) Variation of c -parameter (d) M_s , and (e) density of localized states with Gd% in Gd:ZnO thin films. P_d is given in parenthesis. Open symbols represent VA samples.

High amount of Gd doping (~ 2.5 at. %) in ZnO showed segregation of a pure Gd near the film-substrate interface in the transmission electron microscopy studies.²² We did not observe such anomalies by using similar experimental analyses in the present case, suggesting that those samples are relatively free from aforementioned secondary phases.

In the present study, only those thin films prepared with $\text{Gd}\% \leq 0.11$ at. % and $P_d \leq 25$ mTorr were ferromagnetic in their as-deposited condition. On the other hand, the thin films with higher Gd concentration ($\text{Gd}\% > 0.2$) prepared at any P_d were not ferromagnetic. However, upon vacuum annealing (VA) on selected (with high (low) Gd% and low (high) P_d), non-magnetic thin films become ferromagnetic. Furthermore, undoped ZnO thin films prepared and treated under similar conditions did not show FM.²¹ We propose low P_d or vacuum annealing to introduce more defects related to oxygen deficiency (O_{defect}). We therefore believe that the combination of the low Gd concentration and high concentration of oxygen deficiency defects (due to low P_d or vacuum annealing) plays a role in establishing the FM. In addition, we carried out *in-situ* VA for the 0.22 at. % and 0.45 at. % Gd:ZnO thin films during the X-ray magnetic circular dichroism (XMCD, in BL13-1 at SSRL, USA) experiments. Initially the XMCD spectra were collected at room temperature (RT), then the samples were annealed (at 425 K)—without removing the samples—inside the chamber under a high vacuum (10^{-7} Torr) for 30 min and finally were cooled down the samples to RT. Subsequently, another set of spectra was collected. Figs. 4(a) and 4(b) show the typical NEXAF spectra of these samples before and after annealing at the Gd $M_{4,5}$ edges for 0.22 at. % ($P_d = 50$ mTorr) and 0.45 at. % Gd:ZnO ($P_d = 5$ mTorr) thin films. Figs. 4(c) and 4(d) show XMCD spectra observed for the same samples, respectively. A small XMCD signal observed is due to very diluted amounts of Gd doping in ZnO. An enhancement in the

FIG. 4. Gd $M_{5,4}$ edge NEXAF spectra for (a) 0.22 at. % and (b) 0.45 at. % Gd doped ZnO thin films. (c) and (d) show their XMCD signal. Dotted (solid) lines represent data obtained prior (after) *in-situ* VA. Enhancement of XMCD in 0.45 at. % Gd doped ZnO sample is highlighted within an oval in panel (d).

XMCD signal of 0.45 at. % Gd:ZnO ($P_d = 5$ mTorr) thin film is observed after *in-situ* VA (Fig. 4(d)), which may suggest the onset of the observed FM in this sample. Variation of n_c with H_c for VA ferromagnetic samples also follows the same trend (Fig. 3(a)). Figs. 3(c) and 3(d) show that c -parameter and M_s decrease as Gd concentration increases including for annealed samples. We therefore propose that O_{defect} is created via low Gd doping at low P_d or subsequent VA to establish a long range FM.

Anisotropic magnetization loops are observed in 0.02 at. % Gd:ZnO film (Fig. 3(b)), revealing higher M_s when the field (H) is applied parallel to c -axis relative to the perpendicular to c . As Gd is known to have strong magnetocrystalline anisotropy,²³ the magnetic anisotropy observed in these samples could arise from the Gd^{3+} ions due to its $4f$ electron that cloud experience a tetrahedral crystalline electric field in the lattice and associated spin splitting.²⁴ From the variation of c -lattice parameter and M_s (Figs. 3(c) and 3(d), respectively) with Gd%, we believe that the exchange interaction is Gd concentration dependent.²⁵

An important feature of Gd distinguishing it from other RE atoms is the partially filled $5d$ and $4f$ levels, which could activate inter- and intra-ion exchange interactions.²⁶ The magnetic coupling mechanism responsible for the RTFM in Gd:ZnO could be: (i) inter-Gd ions (i.e., between neighboring Gd ions) via $5d$ - $5d$ exchange and intra-Gd ions via $4f$ - $5d$ exchange, (ii) Gd-Zn (f - s), and (iii) Gd-O (f - p). In addition, s - f exchange can be stronger than f - f or f - p exchange.^{8,27} One of the concerns here is related to the location of the Fermi level (E_F) and $4f$ levels in the band, which is required to establish such magnetic exchange. Earlier theoretical studies showed that the $4f$ levels lie inside the conduction band (CB) (spin-down) and valence (spin-up) bands in Gd:ZnO.²⁷ For pure ZnO, E_F lies in the ZnO band gap and introduction of intrinsic donor defects such as $\text{V}_{\text{O}}/\text{Zn}_i$ ^{2,28} does not shift (E_F) into the CB. However, doping ZnO with Gd shifts the E_F into the CB.^{21,29} Therefore, the location of E_F inside the CB can assist in establishing the magnetic exchange interaction

between donor states (defect states or states of impurity-defect complexes). This impurity/defect band formed near the CB can be due to $[\text{Gd-O}_{\text{defect}}]$ complexes or intrinsic O_{defect} donors, which facilitate long range exchange interaction. As the Gd 5d electrons contribute to the bottom of the CB,³⁰ s-d exchange between Gd^{3+} ions can be mediated via impurity/defect band located close to the CB edge.³⁰ This defect band has been reported to have spin-split due to the s-d exchange.³¹ In addition, FM originating from the vacancy related defects in the grain boundaries³² and associated dangling bonds³³ in the present case cannot be completely excluded because spin-split can be due to the result of an exchange interaction between these intrinsic defects.³³ If the spin-splitting is larger than the band width, long range spin-polarization could be realized.³⁴

The formation of a defect band and its spin-splitting can be envisaged via electrical transport studies. Therefore, we carried out magnetoresistance (MR) and Hall effect experiments for the Gd:ZnO thin films in a physical property measurement system (PPMS, Quantum design). All the samples were 'n' type, with carrier concentrations varying from 8.4×10^{17} to $1.9 \times 10^{19} \text{ cm}^{-3}$ (Fig. 3(a)). Therefore, it is essential to study the effect of the density of defect states on the magnetic exchange. Temperature dependence of resistivity of all thin films in the present study was typical of a semiconductor, whereby an exponential increment of resistivity as the temperature was decreased. At high temperatures ($T > 180 \text{ K}$), a thermally activated $\rho(T) = \rho_0 \exp(\Delta E/k_B T)$ -type conduction (fitting not shown) is dominant in all the films. However, at low temperatures, the temperature dependency of resistivity of these FM thin films followed Mott's *variable range of hopping* (VRH) due to localization behavior of carriers below a metal insulator transition (MIT).³⁵ According to VRH theory, localized carriers form an impurity band and the low temperature conductivity is governed by a phonon-assisted hopping of carriers between localized states and the density of localized states at E_F ($N(E_F)$) can be calculated by³⁵

$$\rho = \rho_0 \exp \left[\left(\frac{T_0}{T} \right)^{1/4} \right], \quad (1)$$

where T is temperature, $\rho_0 = (3e^2 V_{\text{ph}})^{-1} (N(E_F)/8\pi\alpha k_B T)^{-1/2}$, $T_0 = (\lambda\alpha^3/k_B N(E_F))$, k_B is Boltzmann constant, ν_{ph} is phonon frequency at Debye temperature ($\approx 10^{13} \text{ s}^{-1}$), α^{-1} is the localization length, and λ is a dimensionless constant (≈ 16).³⁶ Fig. 5(a) shows linear $T^{1/4}$ dependence of $\ln(\sigma T^{1/2})$ at low T . The best fit (residual sum of squares < 0.02) to the function given in Eq. (1) confirms VRH conduction³⁵ in the Gd:ZnO thin films. With respect to confirming the Mott's VRH mechanism, the figure of merit should be satisfied: (i) αR value should be more than the unity ($\alpha R > 1$), and (ii) the hopping energy W should be larger than $k_B T$.³⁷ These values are fulfilled for our samples ($3.24 < \alpha R > 2.25$ and $1.86 < W > 1.29$), which indicate the formation of an impurity/defect band³⁸ near E_F . The location of the E_F within the band of localized carriers is controlled by Gd dopants as shown in a previous theoretical study.²⁹ A

FIG. 5. (a) $T^{-1/4}$ variation of conductivity showing VRH conduction P_d is given within parenthesis; open symbols represent post deposition VA samples. MR fit for (b) 0.067 at. % and (c) 0.11 at. % Gd:ZnO thin films.

comparison of the density of localized states $N(E_F)$ (deduced from the fitting shown in Fig. 5(a) and Eq. (1)), c -lattice parameter, and M_S (Figs. 5(a) and 5(b)) shows a monotonic decrement with increasing Gd, thus confirming the relation between the impurity/defect band and the observed FM.

Typical MR for the Gd:ZnO (with 0.06 at. % and 0.11 at. % Gd:ZnO) thin films prepared at $P_d = 25 \text{ mTorr}$ are shown in Figs. 5(b) and 5(c), respectively. A large negative MR was observed for the 0.11 at. % Gd:ZnO ($P_d = 25 \text{ mTorr}$) and a positive MR component was also found to coexist with negative components above 100 K (Fig. 5(b)). Negative MR in the doped semiconductors is generally attributed to the presence of localized magnetic moments,^{39,40} impurity band conduction, or degenerate semiconducting states (when E_F is located inside the CB).⁴¹ In order to understand the MR behavior, we fit MR data using an empirical model proposed by Khosla-Fischer⁴² given by

$$\frac{(R_H - R_{H=0})}{R_{H=0}} = -a^2 \ln(1 + b^2 B^2) + \frac{(c^2 B^2)}{1 + d^2 B^2}, \quad (2)$$

where $a = (\langle A_1 J \delta_F [S(S+1) + \langle M^2 \rangle] \rangle)$ and $b = (\langle [1 + 4S^2 \pi^2 (\frac{2J\delta_F}{g})^4] (\frac{g\mu_B}{\alpha_1 k_B T})^2 \rangle)$ are negative and positive scattering parameters, respectively,⁴³ B is magnetic field, c is a conductivity-dependent parameter, d is carrier-mobility-dependent parameter, A_1 is spin-scattering amplitude, J denotes an exchange parameter, δ_F corresponds to density of states at E_F , S is spin of the localized moment, $\langle M \rangle$ refers to an average effective magnetic moment, g is Landé g -factor, μ_B denotes as Bohr magneton, and α_1 is a constant (0.1 to 10). Parameters ' c ' and ' d ' in Eq. (2) are dependent on the conductivity and mobility of the electrons under the influence of Lorentz force. The first term in Eq. (2) indicates negative MR,^{44,45} which accounts for the spin-dependent scattering of localized electrons in the impurity band and weaken as the field-induced spin-polarization progresses. Therefore, negative MR shows the presence of an impurity band in these films.^{44,45} The second term accounts primarily for the positive MR, which is related to two-band conduction (via CB and impurity- O_{defect} band).⁴²

The negative scattering is found to be dominant in all the thin films below 50 K, which is an indication of spontaneous spin-polarization of localized spins at the isolated paramagnetic ions⁴⁶ (Gd^{3+} in the present case). Using Eq. (2) and the expression for 'a,' it can be established that the magnitude of negative MR is proportional to the square of the average effective magnetic moment of the localized spins.⁴⁷ Therefore, we attribute the large negative MR (14%) and higher M_s found in 0.22 at. % Gd:ZnO ($P_d = 25$ mTorr) thin film to the largest spin-splitting of the impurity- O_{defect} band states. Therefore, we conceive that appropriate concentration of Gd, carriers (n_e), and oxygen deficient defects are requisite conditions for strong ferromagnetic coupling in Gd:ZnO thin films.

In summary, we found that Gd (<0.11 at. %) doped ZnO thin films prepared by PLD at low oxygen pressures exhibited ferromagnetic behavior at RT. Gd doping is essential for moving E_F inside the CB, which may cause spin-splitting in the band. Based on the negative magnetoresistance and low temperature hopping conduction studies, we conclude that a spin-split defect band mediates the FM exchange formed due to either O_{defect} or defect-Gd complexes. Our study confirms that appropriate concentration of Gd, defects associated with oxygen deficiency, and localized carriers are prerequisites to achieving RTFM in Gd-doped ZnO.

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