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Obtaining strong ferromagnetism in diluted Gd-doped ZnO thin films through controlled Gd-defect complexes

I. S. Roqan,^{1,a)} S. Venkatesh,¹ Z. Zhang,¹ S. Hussain,^{1,b)} I. Bantounas,¹ J. B. Franklin,^{2,c)} T. H. Flemban,¹ B. Zou,² J.-S. Lee,³ U. Schwingenschlogl,¹ P. K. Petrov,² M. P. Ryan,² and N. M. Alford²

¹Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

²Department of Materials and London Centre for Nanotechnology, Imperial College London, London SW7 2AZ, United Kingdom

³Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

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We demonstrate the fabrication of reproducible long-range ferromagnetism (FM) in highly crystalline $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ thin films by controlling the defects. Films are grown on lattice-matched substrates by pulsed laser deposition at low oxygen pressures (≤ 25 mTorr) and low Gd concentrations ($x \leq 0.009$). These films feature strong FM ($10 \mu_B$ per Gd atom) at room temperature. While films deposited at higher oxygen pressure do not exhibit FM, FM is recovered by post-annealing these films under vacuum. These findings reveal the contribution of oxygen deficiency defects to the long-range FM. We demonstrate the possible FM mechanisms, which are confirmed by density functional theory study, and show that Gd dopants are essential for establishing FM that is induced by intrinsic defects in these films. © 2015 AIP Publishing LLC.

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Spintronic technology holds a strong promise for a new generation of electronic devices.¹ However, generating reproducible long-range ferromagnetism (FM) in wide band gap (WBG)-diluted magnetic semiconductor (DMS) materials remains a major obstacle to the fabrication of spintronic devices operating above room temperature (RT).² This has prompted significant research efforts on WBG-DMSs, doped ZnO, in particular.³ Doping ZnO with Gd has a potential to produce stronger FM, relative to that obtained from ZnO doped with transition metals, owing to the possible interaction between localized $4f$ electrons and host electrons,⁴ which remains controversial. Presently, there is no consensus on the exact exchange mechanism in such materials.⁵ FM in ZnO has been attributed to defect-induced⁶ or defect-mediated magnetism.^{7–11} Subramanian *et al.*¹² observed FM and magnetic anisotropy in polycrystalline GdZnO . However, the desirable defects that are responsible for strong reproducible long-range FM in a single-crystal GdZnO has not been identified, despite the many deposition methods/conditions used, including ion implantation and *in-situ* Gd deposition.^{12–17} The main reason behind the lack of progress using these methods/conditions, which include high Gd dopant concentrations (>2 at. %), is that deposition on lattice-mismatched substrates or through ion implantation introduces high densities of different types of *uncontrolled* defects or secondary phases. Although it is known that poor quality films have many defects that serendipitously mediate

magnetism, this approach could not identify *desirable* defects responsible for FM in such materials.¹⁸ Therefore, the origin of the reproducible long-range FM observed in GdZnO has not yet been identified. In this paper, we identify the possible mechanism that can be responsible for reproducible FM in GdZnO by controlling the density of desirable defects. We show that the material must have high structural quality with a low number of extended defects—obtained by growing on lattice-matched substrate ($\alpha\text{-Al}_2\text{O}_3$) and a low Gd (<0.9 at. % Gd) concentration—to identify the origin of the FM. Inability to control these factors may, however, result in irreproducible FM. In this work, we demonstrate deposition of epitaxial GdZnO thin films by pulsed laser deposition (PLD). We vary only the oxygen deposition pressure (P_d) to control the concentration of oxygen deficiency-related defects. Density functional theory (DFT) study is applied to explain the possible FM mechanism in this material.

For the ZnO target preparation, ZnO powder with 99.99% purity (Sigma Aldrich) was isostatically pressed into a “green” pellet measuring 25 mm in diameter and ≈ 5 mm in thickness. The pellet was sintered in air at 1000°C for 10 h at ramp rates of 5°C min^{-1} for both heating and cooling, resulting in a density of $>95\%$. For the GdZnO target, separate targets were prepared by mixing 0.1, 0.25, and 2 wt. % of high purity ($>95\%$) Gd_2O_3 (Sigma Aldrich) into the ZnO powder prior to isostatic pressing. All thin films were deposited on $5 \times 5 \times 0.5 \text{ mm}^3$ lattice-matched α -plane ($11\bar{2}0$) Al_2O_3 substrates (to reduce the formation of line defects and minimize the lattice strain mismatch between $\alpha\text{-Al}_2\text{O}_3$ and $c\text{-ZnO}$ ($\sim 0.08\%$))¹⁹ by PLD (a Lambda Physik KrF UV excimer laser operating at 248 nm) at a growth temperature of

^{a)}Author to whom correspondence should be addressed. Electronic mail: iman.roqan@kaust.edu.sa.

^{b)}Present address: UGC-DAE CSR, Kalpakkam Node, TN 603104, India.

^{c)}Energy Research Institute @ Nanyang Technological University (ERI@N), Cleantech One, 1 Cleantech Loop, Singapore 637141.

TABLE I. The magnetic properties of GdZnO samples.

GdZnO thin film (wt. %)	Estimated average Gd concentrations (at. %)	Magnetization (μ_B/Gd)		Coercivity (Oe)		Magnetic saturation (emu/cc)	
		300 K	5 K	300 K	5 K	300 K	5 K
0.1	~ 0.04	10.53	12.35	120.5	85.8	1.91	1.62
0.25	~ 0.11	4.97	5.82	114.7	82.7	2.45	2.1
2.0	~ 0.87	0.31	0.44	113.2	62.2	1.46	1.03

650 °C and variable P_d . The deposition consisted of 20 000 pulses to produce a film thickness of ≈ 400 nm for all films (measured by a Zygo white-light microscope-based interferometer). The Gd concentrations in all films were estimated by the wavelength dispersive X-ray spectroscopy (WDS) to be ≈ 0.04 , ≈ 0.11 , and ≈ 0.87 at. % for GdZnO targets with 0.1, 0.25, and 2 wt. % Gd_2O_3 , respectively (Table I). This implies good cation transfer ratios, as is expected from the chosen PLD method. The WDS (Gd-L_{α} , Zn-K_{α} , and O-K_{α}) was performed using a Cameca electron probe microanalyzer (EPMA), operating with a 40 mA, and 10 keV electron beam to avoid penetrating into the substrate based on the Monte Carlo Electron-trajectory Simulation.²⁰ For the purpose of comparison, different films with the same Gd concentration deposited at high P_d were used (50 and 500 mTorr). All samples were handled with plastic tweezers to avoid any ferrous contamination that could potentially affect the magnetic response. During all stages of processing, care was taken to avoid any cross-contamination. As a control, undoped ZnO thin films, for which the target was prepared using the same pellet dies, were used and did not show any FM.

X-Ray diffraction (XRD) data were collected using a Bruker D8 x-ray diffractometer with Cu K_{α} radiation to study the structural properties of the films. No secondary phases are observed by the wide XRD 2θ scan measurements (as shown in Fig. 1), within the detection limit of the technique. FEI high resolution-transmission electron microscopy (HR-TEM, Titan) measurements of GdZnO thin films reveal that all have single crystal form and exhibit growth along the c -axis of the ZnO wurtzite structure (Figs. 1 and 2(a)). The HR-TEM analyses of all samples showed no evidence of secondary phases. A low Gd concentration (< 0.9 at. %) was selected to avoid formation of segregation or clusters.

Secondary phases can also be confirmed by the X-ray absorption spectroscopy (XAS) measurements, as it is much

more sensitive compared to TEM and thus better suited for detecting the secondary phases.²¹ The electronic structure and the local environment of the GdZnO films were investigated by XAS measurements both at the O K -edge (resulting from O $1s \rightarrow 2p$ dipole transitions) and at the Gd $M_{4,5}$ -edge ($3d \rightarrow 4f$ dipole transition) to explore the hybridization between Gd and O. All XAS measurements were carried out at BL 8-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) under an ultra-high vacuum of $\sim 1 \times 10^{-9}$ Torr. XAS spectra were collected in the total electron yield mode, providing a maximum sample probing depth of approximately 5–10 nm. The photon polarization of the X-rays (98% polarized) was tuned by rotating the incidence angle, with 90° corresponding to the polarization parallel to the sample surfaces. The O K -edge spectra of ferromagnetic GdZnO films (~ 0.04 and ~ 0.1 at. % Gd) agree with those obtained for the undoped ZnO (Fig. 2(b)); however, the peak at 531 eV is weaker in undoped ZnO. The two sharp peaks at ~ 531 eV and ~ 535 eV in the GdZnO spectrum represent the electron transitions from an O $1s$ fully occupied state to an O $2p_z$ partially occupied state (π -bonding along the c -axis) and an O $2p_{x+y}$ state (σ -bonding perpendicular to the c -axis), respectively.²² The peaks are pronounced in GdZnO films due to strong O $2p$ state hybridization with the Gd $4f$ and Zn $3d$ states.²³ The intensity of these peaks increases with Gd concentration, confirming that they arise from hybridization and are associated with a decrease in the occupation of O $2p$ states. This is related to the higher electronegativity of Gd relative to Zn.^{24,25} These results are in line with our theoretical calculations.²⁶ The Gd valence state measured at the Gd M_5 -edge ($3d_{5/2,3/2} \rightarrow 4f$ transitions) is consistent with the 3+ oxidation state of Gd, as shown in Fig. 2(c).^{27,28} The intensities of the peaks and the shoulders at 1186 and 1190 eV, which are characteristic of Gd^{3+} , are enhanced with Gd concentration.¹² No change in the spectral features is observed, as no peak related to pure Gd cluster and Gd_2O_3 is visible at

FIG. 1. (Log scale) The XRD 2θ scan of the undoped and Gd doped ZnO samples, showing ZnO growth oriented along the $[0001]$ direction. No peaks related to secondary phases are observed.

FIG. 2. (a) HR-TEM image of GdZnO sample with (0.87 at. % Gd). The image contrast is due to the thickness variation. (b) The XAS spectra at the O K -edge and (c) Gd M_5 -edge after subtracting the background.

FIG. 3. (a)–(c) M-H loops and (d) ZFC-FC magnetization for GdZnO samples deposited at 5 mTorr (Top inset: high temperature (380 K) M-H loops for GdZnO samples with ~ 0.04 at. % Gd (~ 0.1 wt. %) deposited at low P_d (25 mTorr); and (e) M-H loops of GdZnO samples grown at high P_d and after vacuum annealing. (Bottom inset: Magnetization measurements of undoped ZnO films deposited at high oxygen pressure (50 mTorr) after vacuum annealing).

1183 eV.^{27,28} This indicates that no modification in the Gd valence state occurs, apart from the Gd orbital symmetries due to the hybridization between Gd 4f and O 2p states, which is in line with the O *K*-edge results. Therefore, XAS findings show that no secondary phases and Gd segregation in these films within the instrumentation detecting limit.

Magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer and a SQUID vibrating sample magnetometer. The magnetization data were subtracted from those pertaining to the diamagnetic substrate. Figs. 3(a)–3(c) show the magnetization (*M*) per cm³ as a function of magnetic field *H* (M-H loops) for samples grown at low P_d , indicating FM with magnetic saturation at 5 and 300 K. The undoped ZnO films deposited under the same conditions showed diamagnetism. The GdZnO sample grown with 0.04 at. % Gd shows the maximum coercivity (H_C) and a very high magnetic moment of $12.35 \mu_B$ per Gd³⁺ ion (Table I). Increasing the Gd concentration by an order of magnitude reduces the magnetic moment to $0.44 \mu_B/\text{Gd}^{3+}$ (Table I). For the temperature dependence measurements, the samples were initially cooled down from RT to 5 K without applying any field. A field of 100 Oe was applied and the magnetic data were recorded (Zero field-cooled (ZFC)) as a function of temperature, which increased to 300 K before cooling to 5 K, under the same applied field (field-cooled (FC)). Fig. 3(d) shows the ZFC-FC curves for the same GdZnO films without any magnetic phase transitions or blocking temperature (T_B). Superparamagnetic behavior is characterized by the blocking phenomena in the ZFC-FC, whereby a peak near T_B pertains to finite size FM clusters. We do not observe such hump in the ZFC-FC within the temperature range (5–300 K) employed in our measurements. All the films are also ferromagnetic above 300 K (top inset). Films deposited by PLD with high Gd concentrations (~ 2.6 at. %) showed secondary phases and nano-segregation of other GdZn phases (shown by HR-TEM)²⁹ such as Gd ($T_C = 293$ K), GdZn ($T_C = 268$),³⁰ or GdZn₂ ($T_C = 68$ K).³¹ The magnetism measurements of these phases can affect magnetic hysteresis by

inducing superparamagnetic loops and blocking phenomena.²⁹ Such behavior has been reported by Murmu *et al.*¹⁴ for Gd (2.5 at. %)-implanted ZnO films. This behavior is not observed in our ferromagnetic films. Superparamagnetism is typically characterized by an unsaturated MH behavior with negligible coercivity (ideally zero). In the present case, we have observed non-zero coercivity for all the samples at room temperature, as shown in Figs. 4(a)–4(c). Furthermore, *M* vs. *H*/*T* curves (Figs. 4(d)–4(f)) do not show superimposing universality for 5 K and 300 K, which also excludes superparamagnetism.³² A comparison of results obtained at 300 K and 380 K reveals similar behavior. Therefore, based on this evidence, we can exclude the superparamagnetic contribution in these films and the possibility that the FM of our films is due to segregation. Next, we carried out X-ray magnetic circular dichroism (XMCD) measurements for ferromagnetic samples with ≤ 0.1 at. % Gd, which could not be

FIG. 4. (a)–(c) Non-zero coercivity of M-H loops for the same GdZnO samples deposited at 5 mTorr and (d)–(f) *M* as a function of *H*/*T*, exhibiting FM behavior without any superparamagnetic phases.

used for estimating the magnetic moment per Gd atom since the signal was extremely weak.

All samples deposited at $P_d \leq 25$ mTorr show FM, whereas samples deposited at higher P_d (>25 mTorr) with similar Gd concentrations are diamagnetic, as indicated in Fig. 3(e) of a GdZnO sample deposited at 500 mTorr (Gd ~ 0.07 at. %). To demonstrate that FM could be induced in these films under oxygen-deficient conditions, these non-magnetic films were annealed under vacuum (7.5×10^{-4} mTorr) at 350°C (above the oxygen binding energy in ZnO (Ref. 33)), after which they became ferromagnetic (Fig. 3(e)). Undoped ZnO deposited and annealed under similar conditions exhibited a diamagnetic response (bottom inset). These results confirm that FM in these films is reproducible and mediated by a defect complex associated with oxygen deficiency. Moreover, we show that low Gd concentration is necessary for this FM.

In order to explore the types of defects present in the thin films, low-temperature photoluminescence (PL) measurements were performed under vacuum at different temperatures by using the 325 nm line of a ~ 8 mW He–Cd laser. PL measurements were performed to investigate the defect roles. The band-edge emission (~ 369.1 nm peak) of undoped ZnO is dominant (Fig. 5(a)) and shows an orange-red band at 587 nm (2.11 eV), which is attributed to oxygen interstitials (O_i), as confirmed by deep level transient spectroscopy (DLTS).³⁴ The spectra of GdZnO films (grown at low P_d) show a dominant broad green PL band centered at 495 nm (2.50 eV). This band was attributed to oxygen vacancy (V_O), whereas the weak blue band was attributed zinc interstitial (Zn_i) as confirmed by DLTS,^{34,35} electron paramagnetic resonance,³⁶ optically detected magnetic resonance.^{35,37} PL measurements of the GdZnO (Fig. 5(a)) suggests that at low P_d , Gd dopants in ZnO films increase the density of oxygen deficiency defects due to crystal distortion.

For samples deposited at high P_d (>25 mTorr), the green band disappears and a red emission at 690 nm (1.80 eV) develops. As can be seen in Fig. 5(b), the samples (shown in Fig. 3(e)) produce a dominant red band attributed to a combination of the O_i and V_Zn emissions at 587 nm (2.11 eV) and 775 nm (1.60 eV), respectively.^{34–37} The spectrum of this film obtained after vacuum annealing shows green emission (2.50 eV), accompanied by decreased red emission intensity (Fig. 5(b)). These findings confirm that the reproducible FM in low P_d GdZnO films can be associated with V_O or Zn_i .

FIG. 5. (a) The PL spectra of the samples grown at low P_d (shown in Figs. 2(a)–2(c)) and (b) the PL spectra of the sample grown at high P_d (shown in Fig. 2(e)) before and after annealing.

To support this premise and identify the possible mechanism of this strong FM, we investigated the effect of Gd dopants and intrinsic defects in ZnO by first-principles DFT calculations. The calculations were performed using the Vienna *Ab-initio* Simulation Package (VASP),^{38,39} with projector augmented wave (PAW) potentials and a plane-wave expansion of 400 eV and $2 \times 2 \times 2$ for k-meshes for structural relaxations. The exchange and correlations were treated within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). All configurations were fully relaxed until the forces per atom declined below 0.02 eV/Å. For the localized Zn 3d and Gd 4f states, Hubbard U correction was taken into account with $U_\text{eff} = 5$ eV for Zn 3d and 6 eV for Gd 4f states, respectively. The energy convergence was set to 5×10^{-5} eV, at the k-mesh of $4 \times 4 \times 4$, as it provides slightly higher accuracy than the relaxation criterion.

All Gd-doped ZnO samples showed n-type conductivity. Therefore, in our theoretical analysis, we focus on the effect of the Gd complexes with intrinsic defects that introduce donor electrons, such as V_O and Zn_i , which are the most stable defects in ZnO.^{40,41} It is known that FM occurs when the Fermi level should be near the band edge and overlaps with the impurity level, allowing it to be partially occupied by the donor electrons, thus facilitating the magnetic exchange coupling between the host carriers and impurity states.^{4,42} Fig. 6(a) shows that introducing V_O is insufficient for moving the Fermi level near the conduction band (CB) minimum (CBM). On the other hand, introducing Gd impurities shows a remarkable shift of the Fermi level above the CBM, as shown in Fig. 6(b). Unlike Gd-doped GaN, here, the Gd d -electron from Gd does not contribute to the bond and can thus contribute to the magnetic moment.⁴³

Figs. 6(c) and 6(d) show Gd complex with V_O and Zn_i , respectively, which suggest three possibilities for the observed FM in GdZnO deposited at oxygen deficiency conditions (low P_d): (i) Gd induced FM through s - f or s - d coupling. However, this interaction cannot take place in this case; as Fig. 6 shows that the f state is buried inside the CB. Furthermore, the overlap between the Fermi level and the Gd d -state is very slight. Therefore, s - d interaction is unlikely to be the reason for the strong FM in GdZnO films. Our previous DFT prediction showed that Gd complex with intrinsic defects does not induce FM in Gd-doped ZnO,⁴⁴ which is in line with the results yielded by the XMCD experiments.¹⁵ (ii) The other possibility is defects-induced FM, which requires the defect band and the CBM located near the Fermi level. In this case, Gd- Zn_i complex shows a shallow donor band located below the Fermi level (Fig. 6(d)). Here, the role of Gd is to stabilize the desirable defects and shift the Fermi level above the CBM to allow magnetic coupling between the host and donor levels and induce FM. Recently, we found that, in Zn-based semiconductors, the magnetic exchange took place between the electrons of two singly charged anion vacancies and that of a neutral anion vacancy, thus establishing FM coupling.⁴⁵ A similar mechanism can take place with Zn_i or V_O defect complexes. (iii) The third possible mechanism is Gd-mediated FM, whereby FM is induced by the defects and Gd stabilizes and mediates the exchange coupling between the defect state and host s electrons. Such

FIG. 6. The DOS of (a) a V_O defect, calculated using the PBE + U ; (b) a substitutional Gd (Gd_{sub}); (c) Gd + V_O , calculated using hybrid functional HSE06 ($\alpha = 0.25$ for the Hartree-Fock exchange); and (d) $2Gd_{sub} + Zn_{int}$, calculated using the PBE + U .

behavior was reported for Gd-doped GaN when the FM (due to intrinsic defects) increased to several tens of μ_B by Gd dopants.⁴³ This mechanism is realistic when the density of state (DOS) of ZnO shows a band broadening (formed by intrinsic defects) that is resonant with Gd f states, to establish FM exchange interaction.⁴³ Figs. 6(c) and 6(d) show that V_O and Zn_i (minority spin) added additional band broadening that is resonant with the Gd f state (minority spin) in the CB. Furthermore, Fig. 6(d) shows that Zn d -state is also hybridized with the Gd f -state (majority spin) in the valence band (VB). The resonance between these defects can be the reason for the observed FM in this material at low P_d conditions. Further theoretical studies are necessary to consider neutral and charged Zn_i and V_O complexes in Gd-doped ZnO, in order to investigate the magnetic coupling in more detail and examine the energy gain due to the FM interaction. The aim of this paper was to show that Gd dopants are essential for stabilizing long-range reproducible FM at poor oxygen conditions. The last two mechanisms are confirmed by our recent magnetoresistance studies in GdZnO thin films grown at low P_d , in which the application of Mott's theory of variable range of hopping conduction allowed us to confirm the formation of the oxygen deficiency defect band located near the Fermi level that mediated the FM through spin splitting of the defect band.⁴⁶

In conclusion, we confirmed our initial postulate that strong reproducible long-range FM in GdZnO thin films arises from Gd-defect complexes related to oxygen deficiencies. We have demonstrated that it is possible to “switch on” DMS properties in GdZnO films deposited by vacuum annealing. We also found that Gd is necessary to establish the observed long-range RT-FM in Gd doped ZnO at oxygen poor conditions. The possible FM mechanism was confirmed by the theoretical calculations, the results of which indicated that Gd dopants assist in stabilizing the RT-FM in Gd-doped ZnO. Our approach provides a transferable methodology for

the design of other WBG-DMS systems and functional oxides.

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