Supporting Information

Unraveling the Effect of Gd Doping on the Structural, Optical, and Magnetic Properties of ZnO Based Diluted Magnetic Semiconductor Nanorods

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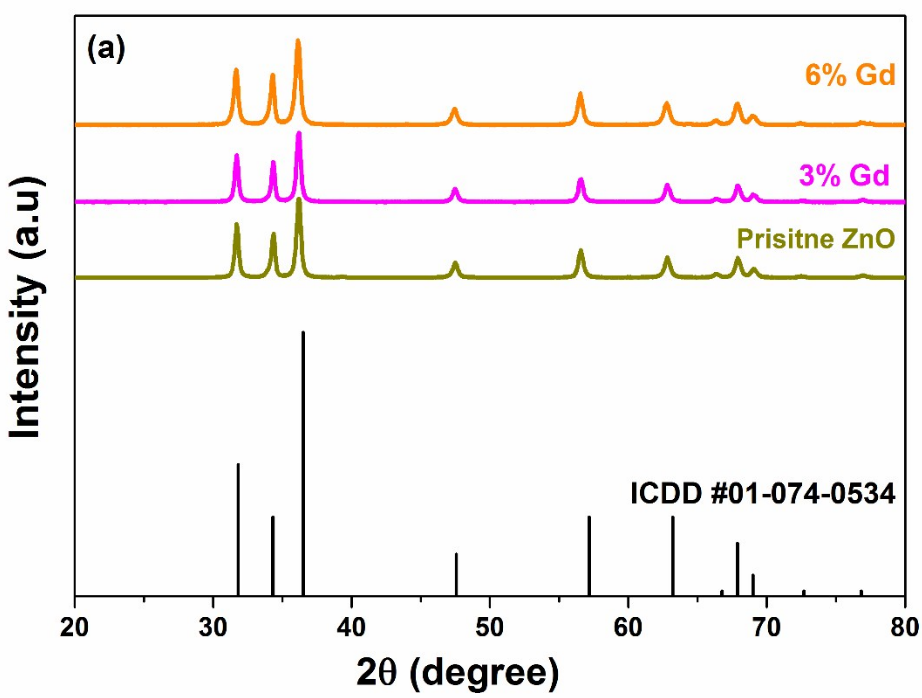


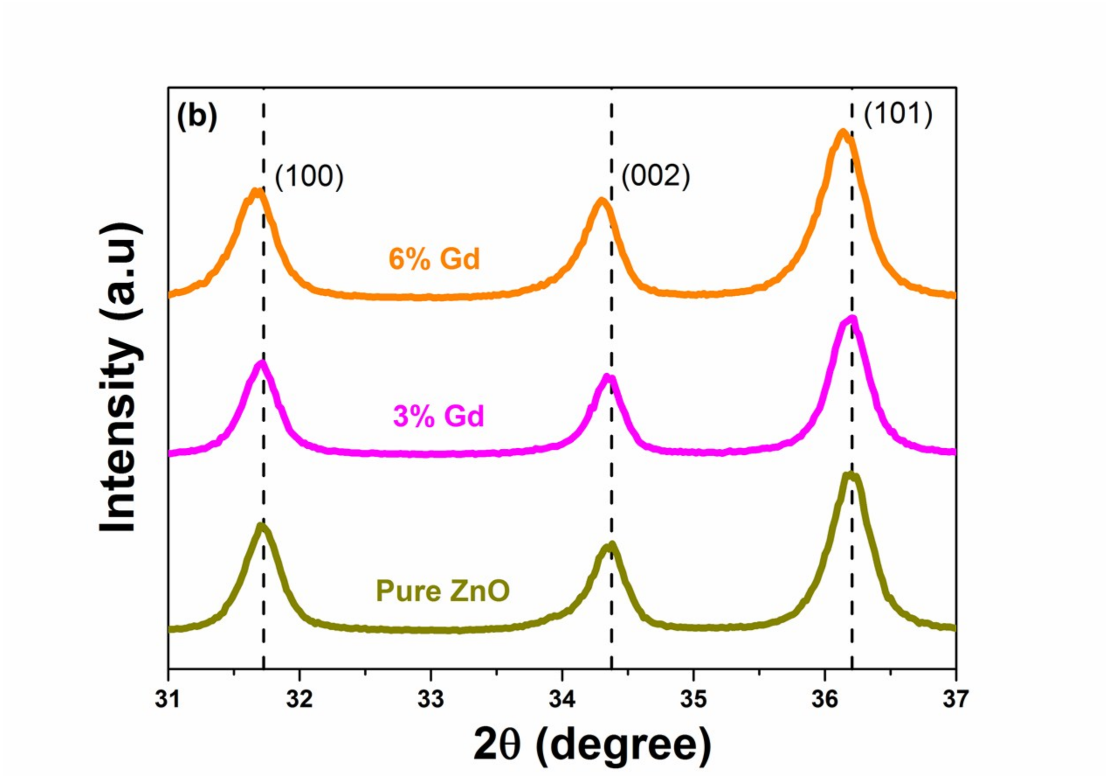


Fig. S1. (a) X-ray diffraction patterns of pristine and Gd-doped ZnO-NRs annealed at 400 °C for 1 hr and (b) shows shift of the diffraction peak along (100), (002) and (101) planes at varying doping concentrations.

Table S1. Rietveld refinement results of pristine and Gd-doped ZnO-NRs annealed at 400 °C for 1 hr.

$Zn_{1-x}Gd_xO$	R_{exp} %	R_B %	R_{wp} %	GOF	Site occupancy factor (SOF)		
					Zn^{2+}	Gd^{3+}	O^{-2}
x =0	8.27	3.17	13.50	2.66	1.00000	0	0.98172
x =0.03	8.78	2.79	12.10	1.89	0.96998	0.03002	0.98912
x =0.06	7.30	2.36	12.61	2.98	0.93978	0.05989	1.00000

For stoichiometric ZnO, the atomic occupancy should be 1:1 for Zn and O. It can be seen from **Table S1** that pristine ZnO nanorods have shown oxygen deficiency. At x = 0, the oxygen occupancy is around 0.981, thus, this decrement of O occupancy in the pristine ZnO indicates the oxygen deficiency. This is lead to an intrinsic *n*-type conductivity. The results agree well with the recent published report by Dillip *et al.* [71,] but they are contradicted with the results obtained from EDX quantitative analysis and

PL analysis for pure ZnO, see **Fig. S3 and Fig. 7,** respectively. The XRD Rietveld-refined structure of pristine ZnO contains O-vacancy is presented in **Fig. S2(a).** The $Zn_{1-x}Gd_xO$ (x = 0.06) has revealed the formation of Zn vacancies via substitution Gd doping in ZnO host lattice, which leads to *p*-type conductivity of ZnO (see-**Table S1**). Therefore, the $Zn_{1-x}Gd_xO$ (x = 0.06) demonstrates higher Zn vacancies as compared to the O vacancies. This is in lines with the results obtained from EDX and PL analysis.

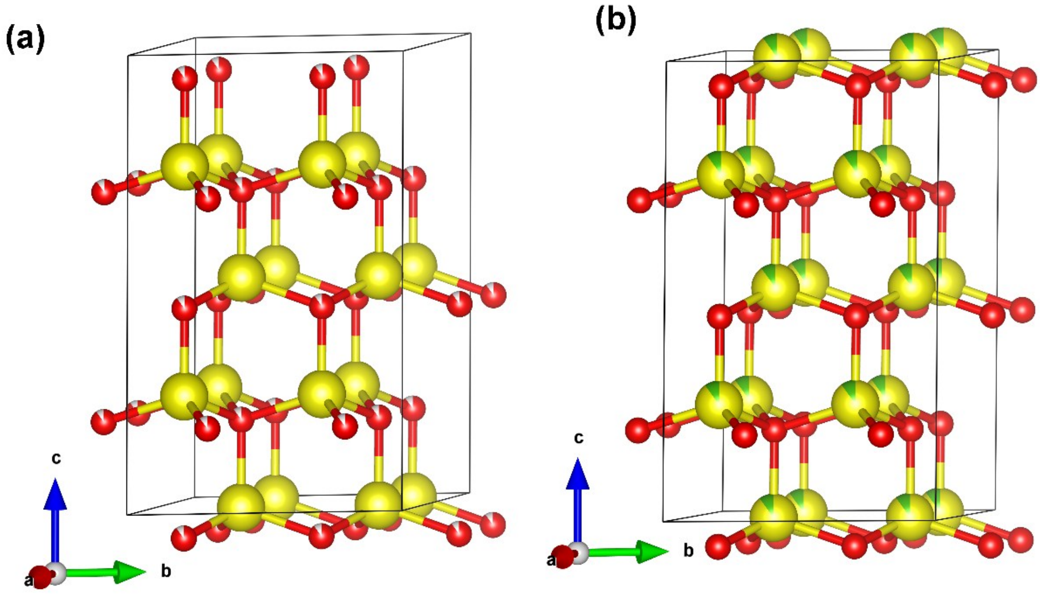
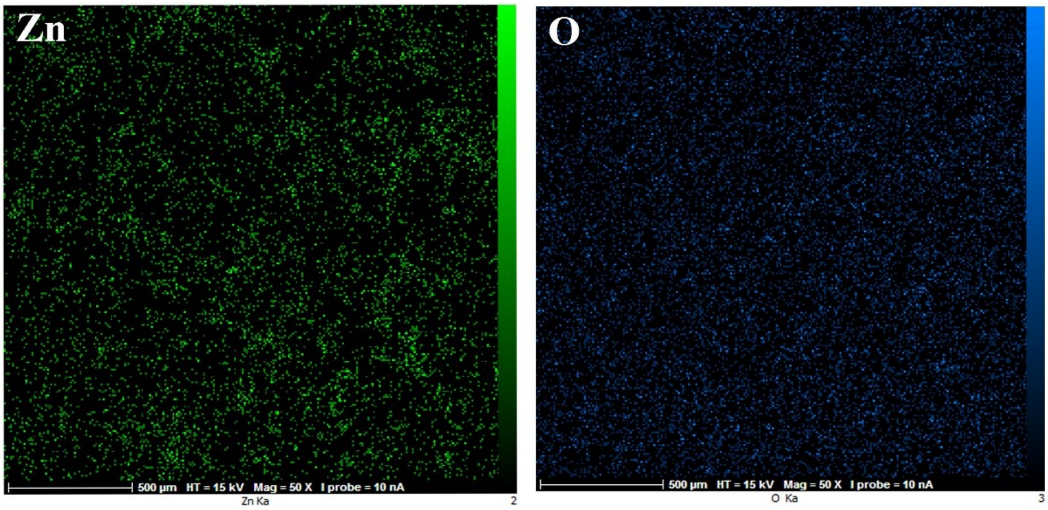
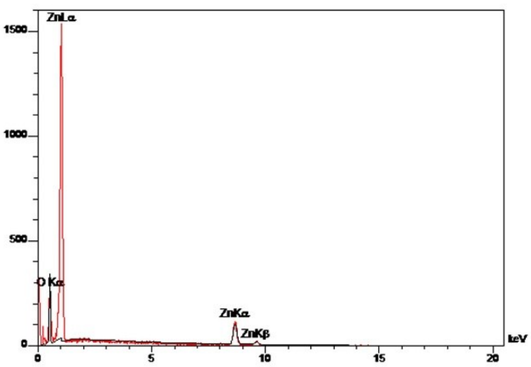


Fig. S2. The XRD Rietveld-refined structures of pristine ZnO (a) and $Zn_{0.94}Gd_{0.06}O$ (b). The ZnO shows oxygen deficiency (O-gray in colour for vacancies). The $Zn_{0.94}Gd_{0.06}O$ reveals higher Zn vacancies compared to the O vacancies. The deficiencies are noticeably seen in the right side figure (Zn-green in color for vacancies). If we consider the total area of a Zn atom as 1 in the $Zn_{0.94}Gd_{0.06}O$ (bearing in mind that the Zn atoms are expected as circles in a 2D plane), then the area of the green portion is approximately 6% of the total area (because the corresponding Zn-occupancy is about 0.94, *SOF*. **Table S1**). This indicates that, in a unit cell of $Zn_{0.94}Gd_{0.06}O$, 6% of the Zn-sites will be vacant (which would eventually be occupied by Gd-atoms via substitutional doping), and only 94% of the Zn sites will be occupied by Zn atoms.

Table S2. Structural parameters of pristine and Gd-doped ZnO-NRs annealed at 400 °C.

$Zn_{1-x}Gd_xO$	W-H plot		Scherrer	Lattice constant a (c) (Å)	c/a	R	Cell volume (Å)	Bond length Zn-O (Zn-Zn) (Å)	ρ 10^{-4} $(nm)^{-2}$
	Size (nm)	$<\varepsilon^2>^{1/2}$ (10^{-4})	Size (nm)						
x =0	29.8	9	23.23	3.2483(5.2084)	1.6034	1.0184	47.5933	1.986(3.2483)	11.26
x =0.03	31.6	6	26.72	3.2475(5.2058)	1.6030	1.0186	47.5456	1.987(3.2475)	10.01
x =0.06	28.9	10	19.9	3.2475(5.2073)	1.6034	1.0184	47.5595	1.991(3.2475)	11.97





Element	Wt %	At %
O (Ka)	26.62	59.71
Zn (Ka)	73.38	40.29

Fig. S3. EDX elemental mapping and spectrum of un-doped ZnO.

Table S3. Calculated results for optimized defect-bearing structures; formation energy $\Delta E_{O,\ Zn}$ in O-rich and Zn-rich conditions, minimum value of the energy band gaps (E_{gap}). Characters of [↑], [↓], [d] and [i] denote for spin-up, spin-down, direct and indirect band gap, respectively, magnetic moment per supercell (μ) (NM is for nonmagnetic systems).

	ZnO	$Zn_{15}GdO_{16}$	$Zn_{15}GdO_{16}$ + V_{Zn}	$Zn_{15}GdO_{16}$ +V_O
ΔE_{Zn} (eV)	-	−2.48	−2.05	−2.33
ΔE_O (eV)	-	−3.17	−3.43	−2.33
E_{gap} (eV)	3.38 [d]	3.26 [d]	3.70 [↑] 0.39 [↓]	1.36 [i]
μ (μ_B)	NM	7.007	8.00	7.04

References

73 Dillip, G., Banerjee, A. & Joo, S. Conductivity inversion of ZnO nanoparticles in ZnO-carbon nanofiber hybrid thin film devices by surfactant-assisted C-doping and non-rectifying, non-linear electrical properties via interfacial trap-induced tunneling for stress-grading applications. *Journal of Applied Physics* **125**, 175106 (2019).