

Enhanced Magnetic Properties of Gd-doped ZnO by Varying the Gd Concentration via Co-Sputtering Technique

NUR AMALIYANA Raship^{1, a}, SITI NOORAYA Mohd Tawil^{1, 2, b*} and NAFARIZAL Nayan^{3, c}

¹Department of Electrical and Electronic Engineering, Universiti Pertahanan Nasional Malaysia (UPNM), 57000 Kem Sungai Besi, Kuala Lumpur, Malaysia

²Centre for Tropicalisation, Defence Research Institute, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi 57000 Kuala Lumpur, Malaysia

³Microelectronic and Nanotechnology-Shamsuddin Research Centre (MiNT-SRC), Universiti Tun Hussein Onn Malaysia (UTHM), 86400 Parit Raja, Batu Pahat, Johor, Malaysia

^aliyanaraship@gmail.com, ^bnooraya@upnm.edu.my, ^cnafa@uthm.edu.my

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Abstract. This study reports on the effect of Gd concentrations on the properties of Gd-doped ZnO films. The films were prepared using co-sputtering method at room temperature. Characterization tools such as X-ray diffraction (XRD), atomic force microscopy (AFM), and vibrating sample magnetometer (VSM) were used to analyze the properties of the prepared films. XRD results observed that all the films are well crystalline and designated to the hexagonal wurtzite structure of ZnO with no secondary phases, which confirmed the successful of doping the Gd into ZnO. Topography analysis from AFM discovered the increase of Gd concentrations of Gd-doped ZnO films leads to the increase in grain size and rougher surface of the films. The magnetization of the films effectively depends on the Gd concentrations, which the diamagnetic behavior changed to ferromagnetic behavior upon Gd doping. A film with higher Gd doping concentration is more effective than lower Gd doping in terms of saturation magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r). These findings revealed that optimizing the Gd concentration is very crucial in enhancing the magnetic properties of Gd-doped ZnO films.

Introduction

Zinc oxide (ZnO) have been extensively researched due to their excellent combination of physical and optical properties, which offers up possibilities for a diverse range of applications such as optoelectronics, solar cells, and gas sensors [1]. Specifically, ZnO doped with various elements such as transition metal and rare-earth element have been predicted in earlier 2000's by Dietl et al., to be an effective ways in enhancing the properties especially in electrical and magnetic properties [2]. Recently, the most promising dopant is gadolinium (Gd), which categorized into rare-earth elements that have good properties of high magnetic moment and produce stronger ferromagnetism at room temperature [3]. These combination of both elements making ZnO as good material for potential applications such as spintronics, magneto-electronic, and magneto-optical devices [4][5]. Since spintronics are correlated with both manipulation and control on the spin of electron, thus enhancing the magnetic properties is very crucial to produce high degree polarization and long spin lifetimes [6]. Both characteristics benefits in producing devices such as high-speed logic, spin transistor and spin valves. Apart from doping, several studied have been reported that the synthesis method under specific conditions affecting the properties of the films and could enhanced their properties [7]. To date, variant synthesis method has been used to grow the ZnO films namely, sputtering [8], co-precipitation [9], spin coating [10], hydrothermal [11], MBE [12], spray pyrolysis [13], and chemical bath deposition (CBD) [14]. Among those synthesis methods, sputtering method is more attractive due to its value of low processing temperature, flexibility in control the dopant concentration, and able to develop good quality of film in a large area of substrate which is good for

mass-produce especially for industrial applications. The aim of this study is to investigate ways to enhance the ferromagnetism of Gd-doped ZnO by varying the composition of Gd concentration using co-sputtering method and characterized the film with different analysis method. The effect of different Gd concentration on the resulting properties of Gd-doped ZnO film was also investigated.

Experimental Details

Co-sputtering method with two targets of the sputtering system were used to prepared Gd-doped ZnO films. A 99.999% purity of ZnO target was connected to RF source whereas 99.99% purity of Gd target was connected to DC source. All the prepared films were deposited simultaneously on top of glass substrate. The glass substrate was first cleaned before it was placed on the substrate holder inside the sputtering chamber. The substrate cleaning was done as stated in previous research report [15]. The sputtering chamber was warmed up for 15 minutes by running the rotary pump. The chamber was then evacuated until the base pressure reached 7×10^{-6} Torr. Argon gas was brought into the chamber as a process gas and the flow of the argon gas was fixed at 29 sccm. The working pressure was set constant at 10 mTorr, whilst source power of ZnO target was kept at 100 W. Other conditions such as target to substrate distance, and speed of substrate rotation were also kept constant at 13.5 cm and 9 rpm, respectively. The variable parameter of Gd concentrations, which varied from 0 at% to 5 at% were achieved by tuning the source power of Gd target. The complete deposition process for Gd-doped ZnO films was done for 1 hour at a room temperature without any heat element supplied throughout the process.

Gd-doped ZnO films were characterized to further study the structural properties, surface topography and magnetic properties. For structural analysis, the X-ray diffractometer (XRD) of PANalytical X-Pert Powder was used and the films was examined at angle of incidence between 20° to 80° along with $\text{CuK}\alpha$ radiation ($\lambda = 0.1540$ nm). The atomic force microscope (AFM) from Park system (XE-100) was used to figure out the surface roughness and grain size of the films, while the characterization of magnetic properties examined at a room temperature using a vibrating sample magnetometer (VSM, LakeShore 7404, Carson, CA, USA).

Results and Discussion

Structural Analysis. The crystal structure as well as phases of the films determined from the XRD analysis. The XRD diffraction spectra of Gd-doped ZnO films deposited from various amount of Gd doping concentration is shown in Fig. 1. Two peaks have been recognized from XRD spectra at 2 Theta of 34.1° and 62.4° that corresponded to (002) and (103) crystal planes, respectively. All the observed XRD peaks are well crystalline and correlated to the ZnO phase structure referring to hexagonal wurtzite (ICSD 98-018-6243). According to the XRD spectra, (002) diffraction peaks dominating for all the films regardless of different Gd concentration. No secondary phases related to Gd clustering were noticed for all the films, indicating the films produced were single phase. This also denotes the substitution of Gd ions into ZnO sites [16]. Additionally, there is moderately shifting of diffraction peak facing lower angle with increasing of Gd concentrations. This is because of the different ionic radii between Gd and ZnO where bigger ionic radii of Gd (0.096 nm) substitute smaller ionic radii of Zn (0.074 nm) [17][18]. The average crystallite size of all Gd-doped ZnO films was deriving out of the full width at half maximum (FWHM) from (002) peak by use of Debye-Scherrer equation [19][20]. The evaluated result was tabulated in Table 1. As presented in Table 1, the average crystallite size decreases with increasing of Gd concentrations while the FWHM showed the opposite trend.

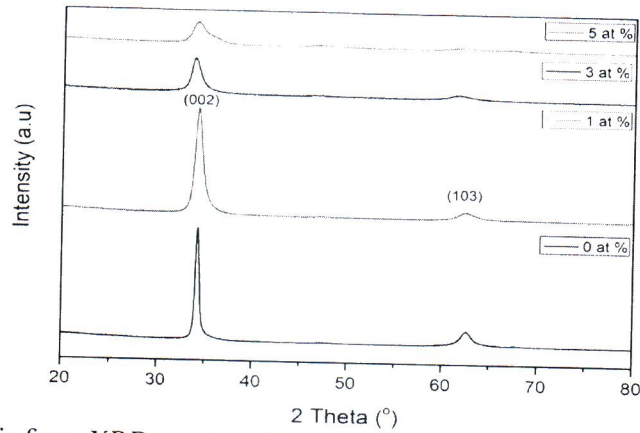


Fig. 1. Peak analysis from XRD spectra of various Gd concentrations of Gd-doped ZnO films

Topography Analysis. The surface topography analysis is one of the important properties contributes in enhancing the ferromagnetism of the film. The value of surface roughness as well as grain size of the film determines the magnetic properties of the films [21][22]. The 3D AFM images in Fig. 2 illustrates the changes in surface topography with the varying amount of Gd concentration. The grain structures look uniform and distribute cover over the surface of the substrate. However, the changes of the grain size was observed, which the grain size getting bigger when the Gd concentrations of the films are increased. The arrangement of the grains for undoped ZnO is tightly packed with small grains as shown in Fig. 2(a). When the films are doped with Gd in Fig. 2(b) to Fig. 2(d), the grains grows bigger with combination of both smaller and larger size of grains.

Meanwhile, the surface roughness of the films also shows the same behavior as grains size. The surface roughness was rougher upon higher concentration of Gd doping. As can be seen in the AFM images in Fig.2(b) to Fig. 2(d), the outcome surface topography appears bumpy with different heights of grains, causing the surface topography of the film to be rougher. This result supported by the result reported from Hashim *et al.*, which doping produce large grain, enlarge the porosity and increasing the surface roughness [23]. Overall, varying the quantity of Gd concentrations give significant effects to the resulting surface roughness as well as grain size of the films and the data was tabulated in Table 1.

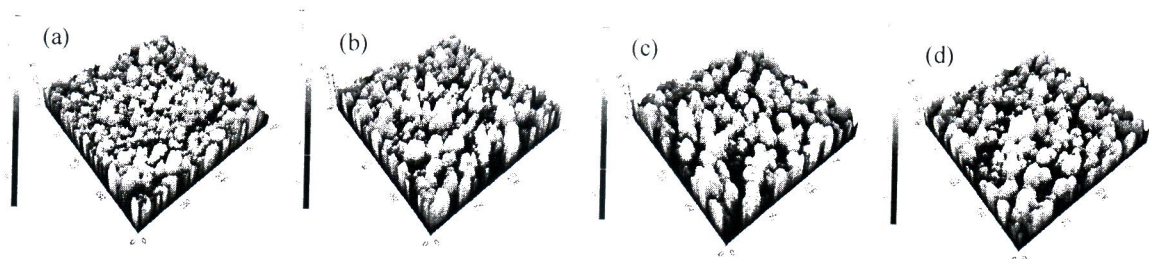


Fig. 2. Topography of AFM images of Gd-doped ZnO films at various Gd concentrations (a) Undoped ZnO (0 at%), (b) 1 at%, (c) 3 at%, and (d) 5 at%

Table 1. Properties of average crystallite size, FWHM value, surface roughness and grain size of Gd-doped ZnO films at various Gd concentrations

Gd concentration	Average crystallite size (nm)	FWHM (°)	Average roughness, R_a (nm)	Average grain size (nm)
Undoped ZnO	21.01	0.4133	2.35	29.91
1 at%	19.60	0.4428	2.63	35.14
3 at%	12.24	0.7085	2.69	43.53
5 at%	10.49	0.8266	3.07	44.13

Magnetic Properties. The magnetic properties of Gd-doped ZnO films at various Gd concentrations were measured using VSM measurement at room temperature. Fig. 3 shows the graph of M-H curves with respect to the applied magnetic field for Gd-doped ZnO films at various Gd concentrations. The diamagnetic effects from glass substrate were subtracted for all the films. Based on M-H curves in Fig. 3, it was observed that undoped ZnO film indication a diamagnetic behavior. This is due to the film itself is non-magnetic which is 0 at% of Gd. Upon Gd doping from 1 at% to 3 at%, the films exhibit clear hysteresis curve with ferromagnetic behavior. This ferromagnetism observed in Gd-doped ZnO films is induced by the magnetic coupling mechanism, where the exchange interaction occurred among $4f$ and $6s$ electrons in Gd ions [24]. The coupling between both f and s electrons result in polarization of s electrons and influencing the direction of f electrons spin [25]. Thus, this exchange interaction between Gd ions significantly affects the changes of magnetic behavior in Gd-doped ZnO films. Additionally, it was verified that the ferromagnetism did not arise from Gd clusters or any oxide precipitates, which has been confirmed through XRD analysis that no secondary phases were identified.

The saturation magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r) were extracted from the hysteresis curve and all the data was tabulated in Table 2. There is enhancement of saturation magnetization from 5.63×10^{-4} emu/cm³ to 8.51×10^{-4} emu/cm³ when more Gd concentration is added. These results were consistent with results reported by Obeid *et al.* [26], in which more substitution of Gd ions into ZnO provides a greater magnetic moment. The long-range spin polarization of the ZnO by Gd explains this increment in magnetic moment. Moreover, it was discovered that the coercivity value rises with increasing Gd concentration but continue to decrease with further doping of Gd concentration up to 5 at%. This indicates that Gd-doped ZnO films exhibit hard ferromagnetic behavior at higher Gd concentrations while soft ferromagnetic behavior represents lower Gd concentrations. The remanent magnetization increased gradually from 9.6×10^{-6} emu/cm³ to 1.7×10^{-5} emu/cm³ upon increasing Gd doping concentrations. As a consequence, the magnetism of the samples is highly influenced by the amount of Gd and doping of Gd induces the room temperature ferromagnetism.

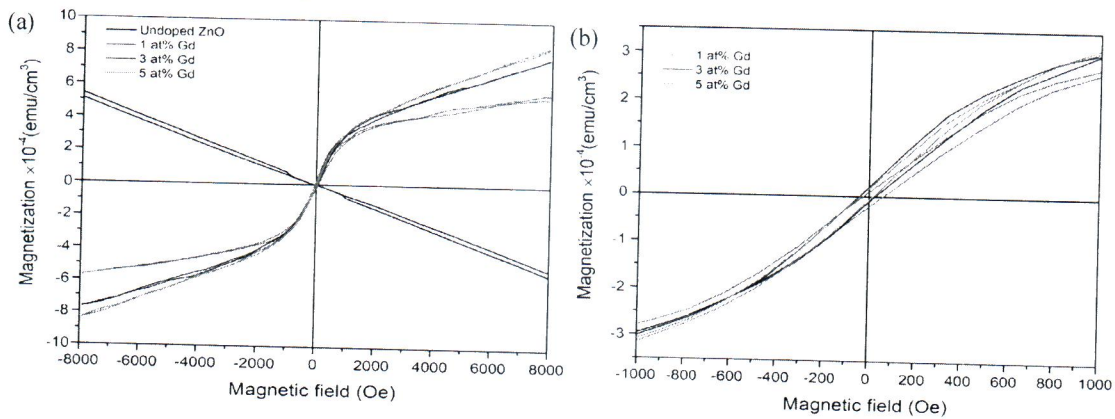


Fig. 3. M-H curves of Gd-doped ZnO films at various Gd concentrations at (a) Magnetic field range from -8 kOe to $+8$ kOe and (b) Magnetic field range from -1 kOe to $+1$ kOe

Table 2. The magnetic properties of undoped ZnO and Gd-doped ZnO films at various Gd concentrations

Gd concentration (at %)	Saturation magnetization (M_s), emu/cm ³	Coercivity (H_c), Oe	Remanent magnetization (M_r), emu/cm ³
Undoped ZnO	NA	NA	NA
1	5.63×10^{-4}	25.88	9.653×10^{-6}
3	7.81×10^{-4}	43.85	2.084×10^{-5}
5	8.52×10^{-4}	37.98	1.708×10^{-5}

Summary

Various Gd concentrations from 0 at % to 5 at% of Gd-doped ZnO films were successfully synthesized by a method of co-sputtering. It has been discovered that Gd doping concentration plays a vital role in enhancing the magnetism where the result of the structural analysis, surface topography and magnetic properties are corroborated with each other. The structural analysis from XRD result showed that Gd ions are totally incorporated inside host of ZnO lattice with a single phase. The Gd concentrations also give significance effects to the topography analysis where the surface roughness and grain size of Gd-doped ZnO films increasing with higher doping of Gd. Additionally, the magnetism of the samples is highly influenced by the amount of Gd doping showing that high dopant concentration enhanced the (M_s), coercivity (H_c) and remanent magnetization (M_r) of Gd-doped ZnO films. Thus, it can be concluded that varying the Gd concentration induced the ferromagnetism at room temperature, which change the diamagnetic behavior to ferromagnetic behavior upon higher doping of Gd.

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