

Derivation of $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ film: the effects of Gd concentration on the structural, morphological and optical properties.

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Abstract. In recent years there has been renewed interest in zinc oxide semiconductor, mainly triggered by its prospects in optoelectronic applications. Doping ZnO with various elements has been a popular technique to gain the extrinsic properties for device applications. In this work we have studied the effect of Gadolinium (Gd) concentration on properties of sol–gel derived Gd doped ZnO films. The Gd concentration varying from 1 to 8 atomic percent (at.%). The structural, morphological and optical analyses were monitored by (XRD, Bruker D8 Advance), atomic force microscope (AFM, Tenko XE-100) and ultra violet-visible spectrophotometer (UV-Vis, Shimadzu UV 1800), respectively. Observations from the XRD results showed that all films exhibit the hexagonal wurtzite crystal structure and higher peak intensity observed at (002) peak. Based on XRD analysis, we also found that Gd concentration has a significant effect on the crystallite size and strain of the films. Moreover, the AFM analysis revealed that the surface become more uniform and denser as the Gd concentration increased. In addition, the optical transmittance spectra indicate that all films were highly transparent (>90%) in the visible range which slightly improved with increasing Gd concentration. The detail explanation on the mechanism will be discussed in detail in this paper.

Introduction

Semiconductors nanomaterials in particular seem to be important and promising for the development of the next-generation electronic applications. A lot of interest in this field due to its unique chemical, physical and electronic properties has finds potential applications in the field of optoelectronic devices. In recent years, zinc oxide (ZnO) has become one of the most promising semiconductor nanomaterials because it has a great potential in many practical applications due to its remarkable properties [1, 2]. Indeed, ZnO is intrinsic n-type oxide semiconductor material. It has a wide band gap of 3.37 eV and high exciton binding energy of ~ 60 meV (compared to GaN, ~ 25 meV) at room temperature. Moreover, ZnO can exist as a thin film as well as nanostructure in various forms (i.e nanorod, nanoparticles, nanowire, etc), which has expanded their use in many devices, such as biosensors, solar cells, transistor, etc. In order to enhance the versatility of ZnO for different application requirements, structural modifications have usually been utilized

Doping technique has been widely used for the modification of the electronic structure of ZnO films. Accordingly various types of dopants have been used to enhance the properties of the films. In the past decades, a lot of researches focused their attention on rare earth (RE) elements doped ZnO due to their unique optical properties and the promising applications in many technological fields [3]. Among them, Gd doped ZnO films have many advantageous. It has been reported that Gd ions doped into ZnO enhances hole conductivity because holes in 4f Gd are more active than electrons [4]. Besides, Gd doped ZnO has been found to have a colossal magnetic moment at room temperature [5,6] which can be used in the fabrication of ZnO based spintronic devices. Therefore, Gd doped ZnO films are believed to have significant potential in the fields of light-emitting displays and laser diode.

Various deposition techniques have been applied to prepare undoped and doped ZnO films. For example, RF magnetron sputtering [7], pulse laser deposition (PLD) [8], spray pyrolysis [9] and the sol-gel method [10]. Among them, sol-gel method represents a low-cost technique which offers great compositional control because there is a wide variety of metal oxide sols that can be created, and each can be doped and concentrated as desired. Moreover, incorporation of dopants is easier in this technique. Therefore, this technique is suitable for frontier researches.

In this work, Gd-doped ZnO ($\text{Gd}_x\text{Zn}_{1-x}\text{O}$) films were prepared by sol-gel spin coating technique. We also evaluated the effects of Gd concentration on the structural, surface morphology, and optical properties of the films. The findings were discussed in detail in the subsequent section.

Experimental procedures

Deposition of $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ films. $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ films were prepared by sol gel spin coating technique. The starting material consisted of zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, Merck], gadolinium acetate dehydrate [$\text{Gd}(\text{C}_2\text{H}_3\text{O}_2)_3\cdot x\text{H}_2\text{O}$, Sigma-Aldrich], ethanol [$\text{C}_2\text{H}_6\text{O}$, J.T. Baker] and monoethanolamine [MEA, $\text{C}_2\text{H}_7\text{NO}$, Merck] were used as a precursor, dopant, solvent and stabilizer, respectively. According to a certain proportion, zinc acetate and Gd acetate were first dissolved in ethanol at stirred for 30 min at 60 °C. After 30 min MEA was put in this solution with constant stirring for 2h at 60 °C until it become clear and homogeneous. The concentration of zinc acetate was 0.4 mol/L and the Gd atomic percentages of $[100 \times (\text{Gd})/(\text{Gd} + \text{Zn})]$, in the ZnO solution were 0, 1, 2, 4 and 8 at.% . Then, the solutions prepared were aged at room temperature for 24 h to get more stable solution.

Before spin-coating process, the glass substrates were cleaned thoroughly. After that, the aged solution was spin coated using 3-step program (1000 r.p.m (5s), 3000 r.p.m (30s), 1000 r.p.m (5s)). After each spin-coating, the samples were preheated at 300 °C in hot plate for 5 min to evaporate the solvent. This process was repeated several times to increase the thickness of the film. Finally, all samples were annealed in annealing furnace at 500°C for 1 hour.

Characterization Techniques. The crystallographic of $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ films were characterized by means of the X-ray diffraction (XRD, Bruker D8 Advance) with $\text{CuK}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$. The surfaces topographic of the $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ films were analyzed by atomic force microscope (AFM, XE-100 Park System). In the meantime, the optical properties of films were examined through measuring the transmittance spectra using violet-visible spectrophotometer (UV-Vis, Shimadzu UV 1800) in the wavelength range of 350–800 nm.

Results and Analysis

Structural Properties Analysis. Figure 1 shows the XRD spectra of undoped and $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ films with different Gd concentrations. In general, we can say that when the ZnO films was doped with Gd the (0 0 2) peak degrades sharply and increasing the Gd concentration up to 8 at% reduced the intensity (0 0 2). This indicates that the structural properties of ZnO films changed by Gd doping. However, other peaks such as (1 0 0), (1 0 1), (1 0 2) and (1 0 3) still appear but did not much significant different. Based on the XRD results, the average crystallite size D , the strain and the lattice constant ' a ' and ' c ' of the (002) orientation can be calculated. The crystallite size D could be calculated by Scherrer's formula [9]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where λ , θ and β is the X-ray wavelength (0.154 nm), Bragg's diffraction angle in degrees and full width at half maximum (FWHM) of the peak corresponding to the θ value in radians, respectively. The average crystallite sizes of the films are listed in Table 1. It may be noted from Table 1 that crystallite sizes decrease with increasing Gd concentration. This may due to the fact that Gd ions could disturb the ZnO crystal lattice and influence the crystal growth.

The lattice constants 'a' and 'c' of the wurtzite structure can be calculated using the relations (2) and (3) as given below:

$$a = \frac{2}{\sqrt{3}} d_{002} \quad (2)$$

$$c = 2d_{002} \quad (3)$$

Meanwhile, the strain along the c-axis of the films was calculated by the following formula:

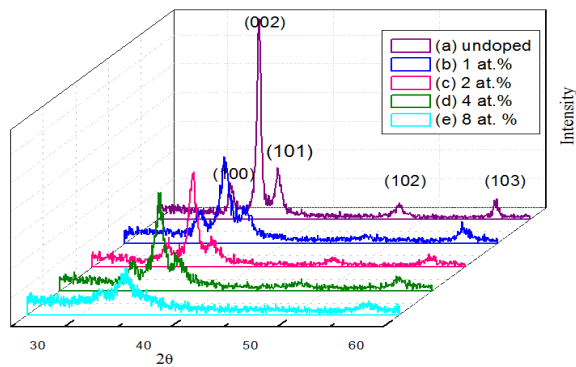
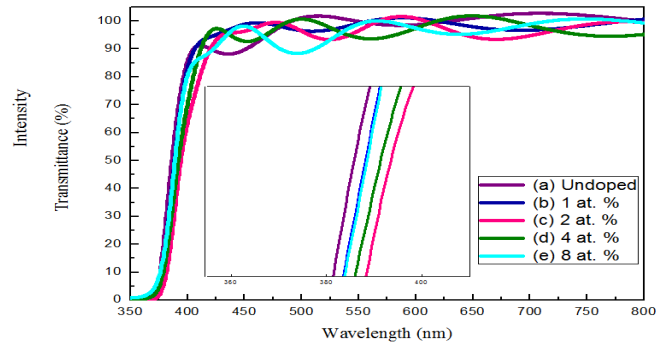
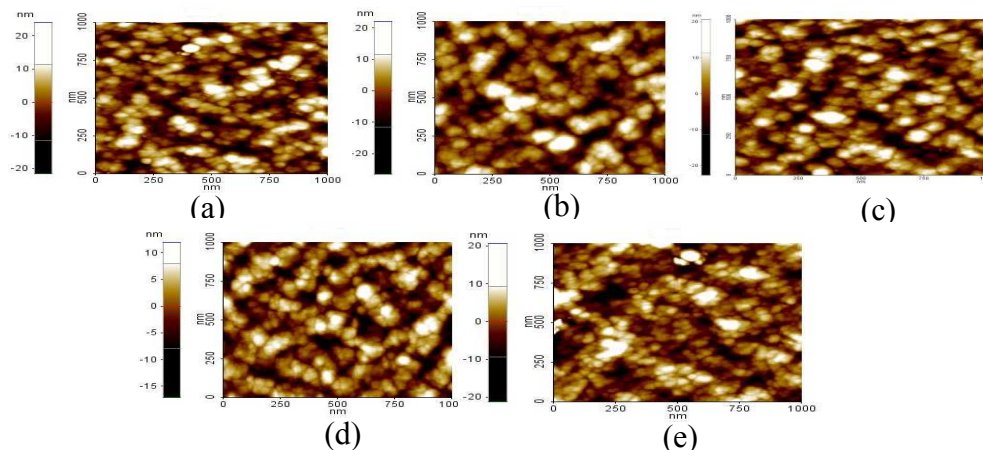
$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (4)$$

These calculated values of the strain along the c-axis are tabulated in Table 1. The peak position is shifted in accordance with the strain value, resulting in a variation in lattice constant *c*. It is because of the Gd ion replaces Zn ion or inserts into the interstitial site of ZnO lattice, which resulted in change of original lattice. The increasing in the *c* parameter clearly indicates that the smaller Zn ions (ionic radius 0.74 nm) are substituted by the larger Gd ions (ionic radius 0.938 nm) in the hexagonal wurtzite ZnO structure. Hence there is an increase in lattice parameter *c* values. This increase in lattice constant *c* leads to a decrease in diffraction angle 2θ for the (002) peak. Although the estimation of the crystallite size at the highest doping level is less accurate due to the low peak intensity and large peak width, the tendency of crystallite size decreased with increasing extrinsic doping level is clearly visible.

Table 1 Values of peak position, FWHM value, lattice parameters, strain, crystallite size, grain size and surface roughness.

Gd concentration	2θ	FWHM (10^{-3} rad)	ε (10^{-3})	c (Å)	a (Å)	D_{XRD} (nm)	D_{AFM} (nm)	Sq (nm)
Undoped	34.58	0.00733	1.750	5.184	2.993	19.58	50.132	6.028
1	34.32	0.0148	3.535	5.222	3.015	9.692	56.389	5.959
2	34.48	0.0136	3.247	5.198	3.001	10.55	53.263	5.414
4	34.42	0.0127	3.033	5.207	3.006	11.30	58.445	4.923
8	34.26	0.0229	5.471	5.230	3.019	6.263	52.539	4.836

Surface Topological analysis. Fig. 2 displays the two-dimensional (2-D) surface topology image of $\text{Gd}_x\text{Zn}_{1-x}\text{O}$ films with different Gd concentration. From the figure, it can be seen that all films have uniformly distributed spherical and the particle topology significantly change with increasing the Gd concentration. The root-mean-square (RMS) values of roughness have been calculated using XEI's Park System software. The calculated values of RMS surface roughness and the grain sizes are summarized in Table 1. It has been observed that RMS value decreases from 6.028 to 4.386 nm with increasing Gd concentration in the solution which ascertains that the surface becomes slightly smooth and grain size decreases. Thus it is consistent with the XRD results that the grain size of the film decreases with the increase of Gd concentration. However, the grain size observed by AFM is larger than the values of the size of the crystallite size obtained from the XRD analysis. The significant difference in grain size is probably due to the reason that AFM measures the grain size on the surface only and grain may contain several crystals aligned in the same direction, i.e., have same orientation, and two grains are separated by grain boundaries because of misalignment of the crystals by differing their orientation. While, XRD gives the crystallite size as the X-rays determine the crystal structure by determining the close pack planes and distance between two atoms. In other words, one grain may contain sub-grains with the same alignment to form crystals with larger crystallite size.

Fig. 1, XRD spectra for $Gd_xZn_{1-x}O$ filmsFig.3, Optical transmittance spectra for $Gd_xZn_{1-x}O$ films. (The inset shows the magnified band edge)Fig. 2, AFM topologies image for $Gd_xZn_{1-x}O$ films

Optical properties analysis. Figure 3 shows the optical transmission spectra for the $Gd_xZn_{1-x}O$ films in the wavelength region of 350-800 nm. For all films, they have transmittance approximately higher than 90% above in the visible range and transmission increase sharply with increasing Gd concentration. That is to say that the additional of Gd concentration in ZnO films gives little effect on the transmittance of the films in the visible range. This attributed to decrease in free carrier absorption due to the elevated carrier mobility of the film.

In addition, the variation of the absorption band edges of the film can be deduced from the inset Fig. 2. As we can see the band edge were observed at 381, 383, 388, 386 and 384 nm for undoped, 1 at.%, 2 at.%, 4 at.% and 8 at.%, respectively. The small shift in the absorption band is due to the doping of Gd into ZnO. Meanwhile, the optical band gap (E_g) of the films was determined using the following formula:

$$E_g = \frac{hc}{\lambda} \quad (5)$$

Where h , c , and λ is plank's constant, velocity of light, and wavelength, respectively. Therefore, the band gap of undoped ZnO films was found to be 3.26 eV while $Gd_xZn_{1-x}O$ films was found to be 3.24, 3.20, 3.22 and 3.23 eV nm for 1 at.%, 2 at.%, 4 at.% and 8 at.%, respectively.

Conclusion

Gd-doped ZnO ($Gd_xZn_{1-x}O$, $x=1, 2, 4$, and 8 at.%) films have successfully deposited by sol-gel spin coating technique and investigated the effect of Gd concentration on the material properties. The XRD result revealed that the crystal structure of ZnO is highly affected by Gd doping. The intensity of (002) peak of undoped sample decreases with increasing gd doping concentration as a result of deterioration the film crystallinity. Meanwhile, from AFM image, it was observed that surfaces of doped Gd films exhibited uniform particle-like and granular topologies and were affected by the Gd incorporation. Increased doping concentrations up to 8 at.% have decreased the grain sizes in

Gd_xZn_{1-x}O films. In addition Gd_xZn_{1-x}O, films exhibited better transparency than undoped ZnO film with highly transparency in the visible region. In conclusion, doping of gd into ZnO films with specific dopant concentration will find wide applications in the future because of their good transparent properties integrated with their beneficial effect of improving optical and structure properties.

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Reference

- [1] A. Mashkoo, and Jing Zhu. "ZnO based advanced functional nanostructures: synthesis, properties and applications." *Journal of Materials Chemistry* 21, no. 3 (2011): 599-614.
- [2] O.Uemit, D.Hofstetter, and H.Morkoc. "ZnO devices and applications: a review of current status and future prospects." *Proceedings of the IEEE* 98, no. 7 (2010): 1255-1268.
- [3] Liu, Yongsheng, Wenqin Luo, Renfu Li, and Xueyuan Chen. "Optical properties of Nd 3+ ion-doped ZnO nanocrystals." *Journal of nanoscience and nanotechnology* 10, no. 3 (2010): 1871-1876.
- [4] L. Liu, P.Y. Yu, Z. Ma, S.S. Mao *Physical Review Letters*, 100 (2008), p. 127203
- [5] Potzger, S. Zhou, F. Eichhorn, M. Helm, W. Skorupa, A. Mcklich, et al. *Applied Physics Letters*, 99 (2006), p. 063906
- [6] M. Ungureanu, H. Schmidt, Q. Xu, H. Wenckstern, D. Spemann, H. Hochmuth, et al. *Superlattices and Microstructures*, 42 (2007), p. 231
- [7] Lin, Wei, Ruixin Ma, Wei Shao, and Bin Liu. "Structural, electrical and optical properties of Gd doped and undoped ZnO: Al (ZAO) thin films prepared by RF magnetron sputtering." *Applied Surface Science* 253, no. 11 (2007): 5179-5183.
- [8] J.W. Kim, H.S. Kang, S.Y. Lee *J. Electr. Eng. Technol.*, 1 (2006), p. 98
- [9] Mariappan, R., V. Ponnuswamy, P. Suresh, R. Suresh, and M. Ragavendar. "Nanostructured GdxZn1-x O thin films by nebulizer spray pyrolysis technique: Role of doping concentration on the structural and optical properties." *Superlattices and Microstructures* 59 (2013): 47-59.
- [10] Kim, Kyoung-Tae, Gwan-Ha Kim, Jong-Chang Woo, and Chang-Il Kim. "Characteristics of Nickel-doped Zinc Oxide thin films prepared by sol-gel method." *Surface and Coatings Technology* 202, no. 22 (2008): 5650-5653.