

## Influence of Gd doping on the Structural and Optical Properties of ZnO

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**Abstract.** Doping transition metal or rare-earth metal ion are one of the most popular topics in semiconductors. In this work, gadolinium (Gd) doped zinc oxide thin films was prepared using the spin - coating technique with different concentrations in atomic percent (at. %). The influences of rare-earth ions doped into the zinc oxide films were studied. The effects on the physical and optical properties of the films were investigated by field emission scanning electron microscope, x-ray diffraction, atomic force microscopy and ultraviolet-visible spectrophotometer. It was found that the properties of zinc oxide can be tuned by changing the concentration physical and optical of Gd.

### Introduction

Zinc oxide (ZnO) has recently attracted enormous attention among researchers due to their wide band gap energy of 3.37 eV and higher exciton binding energy of 60 meV at room temperature, which makes it a promising candidate for many applications such as electronic, optoelectronic, and information technology devices including sensors and solar cells [1-4]. Besides that, it has special properties such as long-term stability, low cost, environmental friendliness, excellent resistance radiation, and etc. Furthermore, ZnO is an excellent material when doped with a suitable dopant for a variety of photonic applications [5]. Doping is a popular technique for tuning the optical properties of ZnO system because they show a lot of absorption transitions in the visible region. Rare-earth, such as Gd may introduce extra functionality to the material system since a combination of magnetic and optical properties may be possible to fabricate combine functional devices on a single chip [6-7].

The thin films can be deposited by a number of different techniques such as sputtering, metal chemical vapor deposition (MOCVD), pulsed laser deposition (PLD) and sol-gel method [8]. Among this technique, sol-gel has advantages for its simplicity, low-cost, not required a vacuum, capable to produce large area of coating and good uniformity of thickness [9]. In this study, sol-gel spin-coating technique was used in the synthesis of Gd doped ZnO films on a glass substrate using different concentration. The effects of different concentrations were studied in details.

### Experimental Procedure

#### A. Solution Preparation

Gd doped ZnO films were deposited onto a microscope glass substrate by sol-gel spin-coating techniques. As a starting material, zinc acetate dehydrate (ZAD), gadolinium acetate dehydrate, and 2-methoxyethanol and monoethanolamine (MEA) were used as a dopant, solvent and stabilizer, respectively. In this work, five different concentrations in atomic percentages which are 0%, 1%, 2%, 4% and 8% were prepared. An aqueous solution containing same molarity of 0.4 mol ZAD and MEA, followed by different Gd concentration for each solution was diluted in 30 ml of

2-methoxyethanol. The mixed solution was then vigorously stirred at 60 °C for 30 min. Then, MEA was added drop by drop in this solution with constant stirring for 2h until it becomes clear and homogeneous. All solutions prepared were aged at room temperature for 24h before deposition process.

### B. Film Deposition

After 24h, each of the solutions was spin-coated by putting a few drops onto the glass substrates. Subsequently, the samples were preheated at 250 °C on the hot plate for 3 min to evaporate the solvent. The process was repeated 10 times to obtain a thick film on an appropriate thickness. Lastly, all samples were annealed in the furnace at 500 °C for 1h to remove organic residuals.

### C. Characterization Technique

The surface topologies of the films were investigated using atomic force microscopy (AFM, Park System, XE-100). Meanwhile, the morphology of the films was measured using a field-emission scanning electron microscopy (FESEM, Joel, JSM-7600) and the crystallinity of the films were characterized using an X-ray diffractometer (XRD, PANalytical, xpert<sup>3</sup>-pro). The films were optically characterized using an ultraviolet-visible spectrophotometer (UV-Vis, Shimadzu UV 1800).

## Result and Analysis

### A. Morphological Analysis

Fig. 1 represents the surface morphologies of the films. Generally, we can see that the size of the nanoparticles is homogeneous, but there is porous granular surface caused by different concentration [2, 10]. As can be seen in Fig. 1 (a), the size of the nanoparticles forming virtually a sphere. When Gd concentration was increased, the size of the nanoparticles turned into smaller cluster grains and it is shown in Fig. 1 (b-e).

### B. Surface Topologies Analysis

Fig. 2 shows the three-dimensional (3-D) surface topology images of the samples. A scanning probe microscope was used to observe the surface topologies of the films in a scan size of 5μm x 5μm by non-contact mode. Based on Fig. 2 (a), (c) and (d), they have non-uniform grains and relatively rough surface. However, for Fig. 2 (b) and (e), we can see that the surface is quite smooth and more uniform grains. Therefore, it is concluded that different concentration has a substantial effect on the surface topology and the roughness of the samples. The root-mean-square average (RMS) roughness [11], as determined from the AFM measurement shows that the lowest surface roughness (1.302 nm) has been observed for 8% of Gd concentration and the highest surface roughness (2.778 nm) for 0% of Gd concentration.

### C. Structural Analysis

Fig. 3 shows the XRD spectra of Gd doped ZnO films deposited onto a glass substrate using different concentration. It was found that the ZnO growth is preferential of (0 0 2) orientation, whereas other peak such as (1 0 0), (1 0 1) and (1 0 3) with comparatively lower intensity were also observed for all film. When Gd concentration was increased, the intensity of the XRD peak at (0 0 2) was degraded. The results are in accordance with the FESEM findings where we can see that in XRD results, the existence of peak (1 0 3) at 0%, 1% and 2%, is higher than 4% and 8%. This also indicates, that the samples are non-uniform and relatively rough surface. The increasing of the crystallite size is indicated by the enhancement of the crystallinity and c-axis orientation of the films [12].

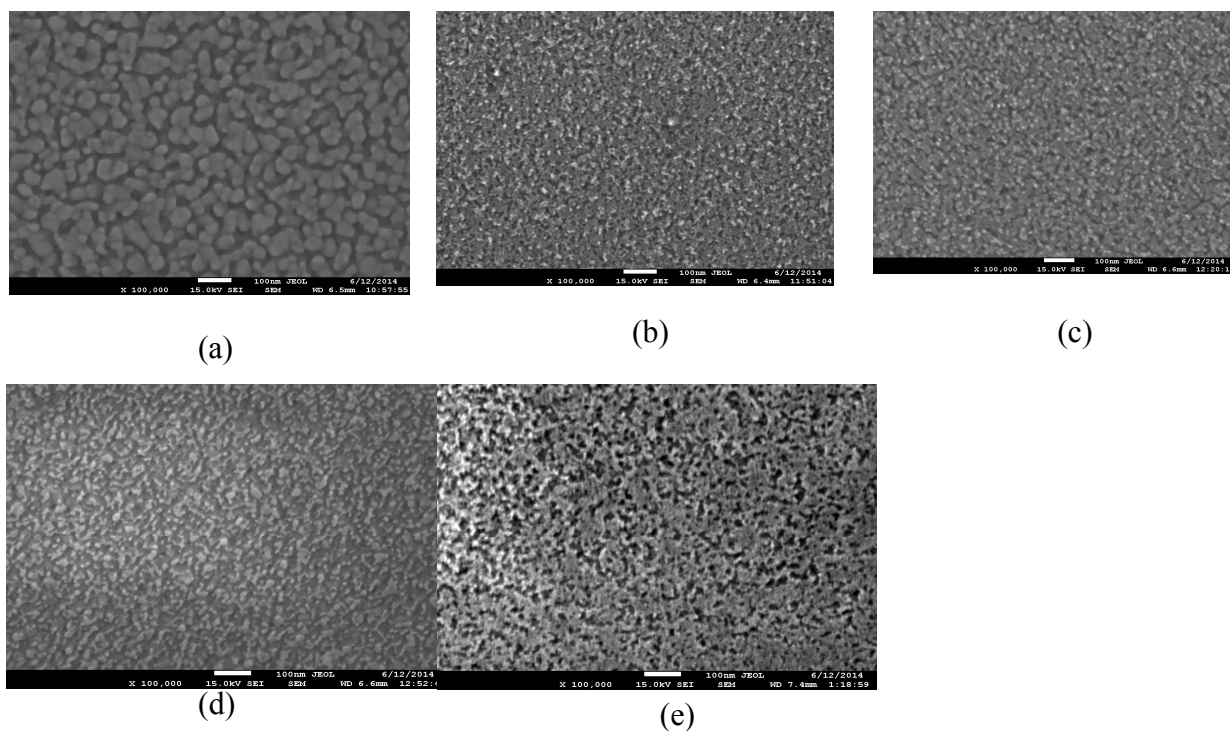


Fig. 1. FESEM image for Gd doped ZnO nanostructure at different concentration in atomic percentages (at. %); (a) 0%, (b) 1%, (c) 2%, (d) 4% and (e) 8%, respectively

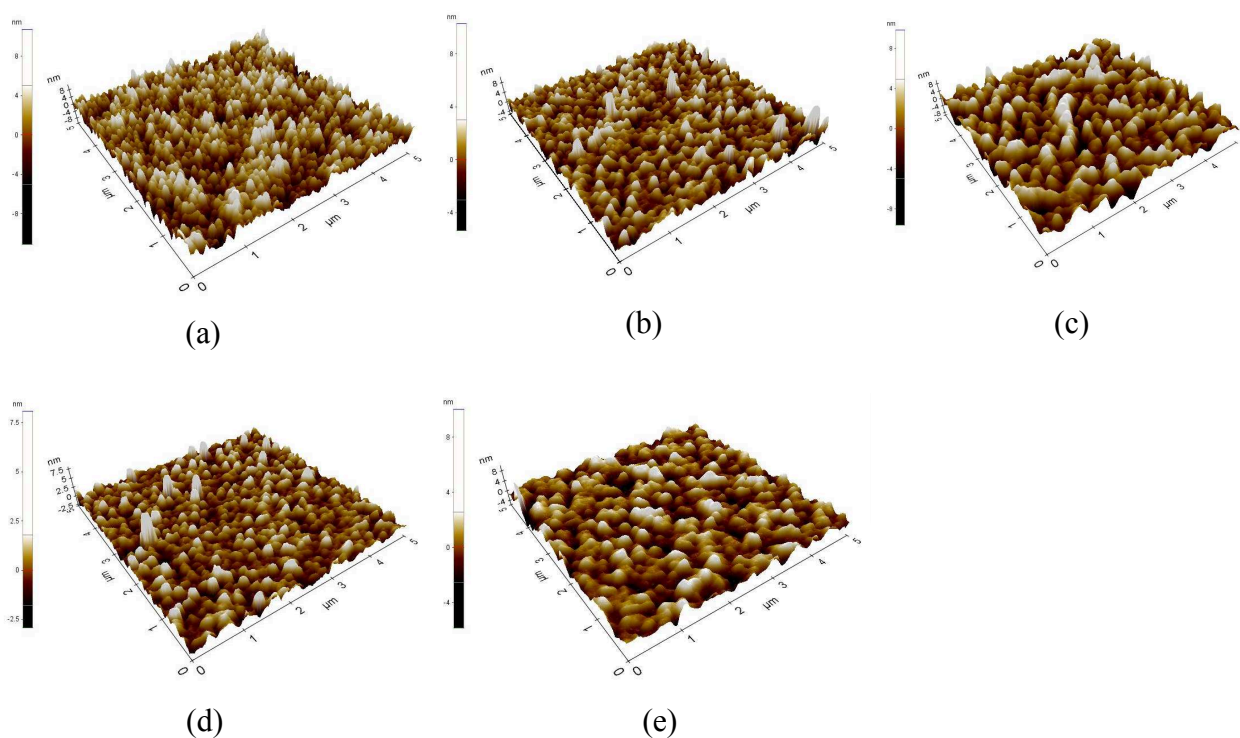


Fig. 2. AFM topologies image for Gd doped ZnO films at different concentration in atomic percentages (at. %); (a) 0%, (b) 1%, (c) 2%, (d) 4% and (e) 8%, respectively

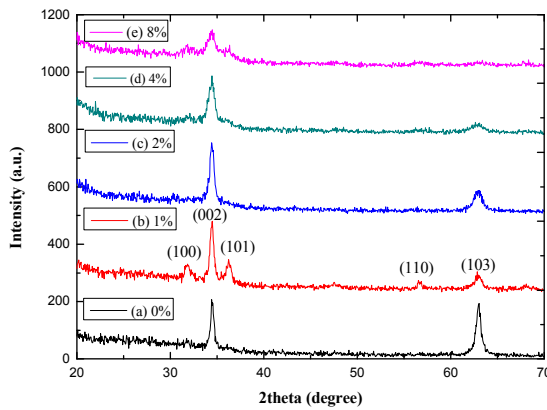


Fig. 3. XRD spectra of Gd doped ZnO films deposited using different Gd concentration; (a) 0%, (b) 1%, (c) 2%, (d) 4% and (e) 8%, respectively

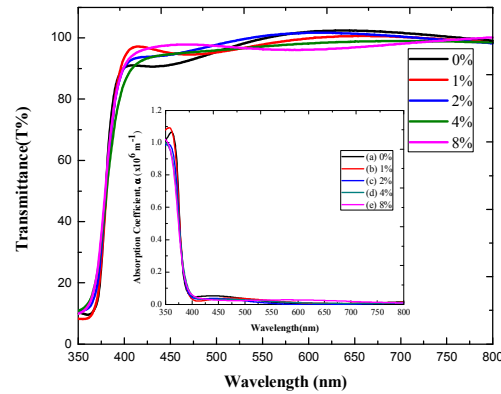


Fig. 4. Transmittance spectra of Gd doped ZnO films deposited using different Gd concentration. The intersect shows the absorption coefficient of Gd doped ZnO; (a) 0%, (b) 1%, (c) 2%, (d) 4% and (e) 8%, respectively

#### D. Optical Properties Analysis

Fig. 4 presents the optical transmittance and intersect of absorption coefficient spectra of Gd doped ZnO films deposited using different concentrations measured at room temperature with wavelength ranging from 350 - 800 nm. The transmission decreased sharply near the ultraviolet region at approximately 390 nm [1]. All films exhibit good transparency in the visible spectral range with an average transmission of approximately 94%. Based on Fig. 4, we can see that for Gd concentration at 1% and 2%, the signal is bouncing similarities with ZnO film, which indicates the film is highly crystalline whereas for 4% and 8%, the films have a very nice slope which revealed the crystallinity is lower compared to the previous Gd concentration.

The absorption coefficient,  $\alpha$ , can be calculated based on the thickness of the thin films and transmittance data using Lambert's Law based on the relation (1):

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (1)$$

Where  $t$  is the thickness of the thin film and  $T$  is the transmittance of the thin film. The gradient of the absorption edge is an identification of the good crystallinity of the films. As reflected in the result, at 1%, the film is highly crystalline because the signal is bouncing more than 1.0 of absorption coefficients compared to the other Gd concentration. Thus, the use of different Gd concentration affects the physical of the film, which causes the change in the optical properties.

#### Conclusion

In conclusion, Gd doped ZnO films have successfully deposited onto a glass substrate by sol-gel spin-coating techniques. Consequently, we have studied the effect of five different Gd concentration which is 0%, 1%, 2%, 4% and 8%, respectively on the properties of Gd doped ZnO films. The FESEM studies show that when the Gd concentration was increased, the structures of the films are porous and the size of nanoparticles eventually became smaller cluster grains. Meanwhile, the XRD result shows that the intensity of the XRD peak at (0 0 2) was degraded when Gd concentration is changing. The AFM result revealed that Gd concentration which is 1% and 8% has a quite smooth with fine structure and uniform grains. However, for 0%, 2% and 4%, they have non-uniform grains and relatively rough surface. Based on UV-this result, the films are highly crystalline when Gd

concentration reached 1% and 2% similar to ZnO film, whereas 4% and 8% the crystallinity is lower. Generally, when transmittance is high, the absorption coefficient is lower. The results show that the use of different Gd concentration on the preparation of the solution affects the structure of the Gd doped ZnO film which causes a change in the properties of the films.

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