

## Synthesis and Characterization of Gadolinium Doped Zinc Oxide Nanorods Thin Films

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**Abstract.** ZnO nanorods (NRs) arrays were synthesized by chemical solution deposition (CSD) method on commercial glass substrate with ZnO thin film act as seed layer prepared by sol-gel spin coating. The effect of annealing temperature of 150°C, 250°C and 500°C, respectively, on the structural growth was investigated. The observation reveals the structural improvement as the annealing temperature increased. The influence of gadolinium doping to ZnO NRs arrays was explored upon the structural and optical features. The FESEM imaging along with XRD, AFM and UV-Vis analysis were conducted to dissect the information gained by performing a study case on various gadolinium doping content in the range of 1 at. % to 4 at. %. Based on the results, the correlation between the doping content were drawn in details in this paper.

### Introduction

Zinc oxide (ZnO) is well known in the scientific community to possess a lot of advantages in its nature, making it as one of the most prominent material for a variety of electronic and opto-electronic applications [1]. However on the contrary, doped ZnO can hold some very different properties compared to that of pure ZnO. Group III elements, i.e. Ga, Al, and In can be used as *n*-type dopant in ZnO, have been generally recognized to influence the optical and also the electrical properties of the materials [2]. Other elements of rare earth group, i.e. Ce, Er, Eu, La, Tb, Tm, Yb, and Dy as *p*-type dopant to ZnO, have also attracted significant attention among the community due to their unique optical properties which give to intense emission peaks in the visible and near infrared range [3]. Hence, the electrical conductivity, type of conduction and band gap range, including the magnetic characteristics of the nanomaterial can be manipulated through doping. Therefore, doping effect can enhance the present properties of ZnO and provides space for new applications possible.

Presently, ZnO-based opto-electronic devices have been reported to appear as doping of ZnO began to become accessible. The facile addition of metal precursor to the solution may not be as straightforward as it seems since the metal atom might not fuse in the ZnO structure, producing a secondary phase denoted to the existence of foreign element [4]. Fabrication of stable and device-quality *p*-type ZnO, however, has not been realized regardless of a large number of publications stating successful demonstration of *p*-type [5, and reference therein]. Numerous reports on impurities doped with ZnO have been driven to minimize the resistivity and to boost the opacity of the films [6, and reference therein]. Gadolinium (Gd) metal of the lanthanum group element was selected as dopant in the work reported here based on the the Gd<sub>2</sub>O<sub>3</sub> physical properties in optical application in amendment to both the electrical and optical characteristics of the ZnO thin films.

This work is expected to provide the science and research information necessary towards the realization of the new enhanced functionality devices through the integration of photonic, electronic

and magnetic properties in a single device that will be beneficial for spin light-emitting diodes (LEDs), novel microprocesses and sensitive biological and chemical sensors. Our motivation on ZnO thin film is, therefore, to examine the structural and optical properties obtained through a feasible, toxic free, chemical solution deposition method by manipulating the Gd doping content. Comparative studies concerning the characterization of pure and Gd-doped ZnO thin films were also review in this paper.

## Experimental Setup

### *A) Deposition of seed layer template*

For the start, glass substrates of 2.5 cm X 2.5 cm in size were cleansed in ultrasonic cleaning bath in acetone for several minutes and rinsed with plenty of deionized water afterwards. Acquiring indisputable good film deposition of excellent homogeneity, quality and formation is crucial. Therefore, to certify that all the contaminants and pollutants were discard from the glass surfaces, this procedure was executed.

The deposition of seed layer was operated using the spin coater technique. The working principle of spin coater utilizes the function of high acceleration with rotary motion which governs the centrifugal force in the formation of uniform thin film on flat horizontal planar. At present, droplets of a mixture sol-gel consisting of 0.4mol of zinc acetate dehydrate, ethanolamine and 2-propanol were dripped onto glass substrate and was rotated at the required accelerations whereby the spin coater will distribute the solution thoroughly on the surface. This step was accompanied by a heat treatment of 280°C for three minutes in ensuring that all the residual solution was released from the coated substrate and simultaneously increase the film adhesion with the glass substrate as well. The procedure was replicated once again to attain the necessary thickness, dependent to the solution concentration and viscosity. Next, the substrates went through a pre-anneal process. The temperature varied from 150°C to 500°C [5].

### *B) Development of ZnO nanorods thin films*

Immerse solutions consisting of a mixing of 0.1097 g of Zinc acetate dehydrate, 0.03 ml of ethanolamine, 50.00 ml of deionized water and an equivalent amount of gadolinium (III) nitrate hexahydrate with respect to the doping percentile were prepared. Seeded substrates were placed in the prepared solution for the next three remaining hours at constant temperature of 95°C. The coated substrates were then rinsed and dried at room condition. Annealing of the grown ZnO nanorods thin films were done at respective pre-annealing temperature for another one hour in a carbolite furnace. The desired samples were then ready to be examined under the characterization tools necessary.

## Results and Discussion

In general, this section reports on the results of the synthesized Gd-doped and pure ZnO nanorods thin films. Analysis reports attained through all four characterization tools, namely the field emission scanning electron microscope (FE-SEM), X-Ray diffractometer (XRD), atomic force microscope (AFM) and ultraviolet – visible spectrophotometer (UV-Vis), were discussed.

### *A) Structural properties of ZnO nanorods thin films*

The investigation on the fabrication of pure ZnO nanorods thin films at different temperature parameter conducted explores a significant impact on the structural morphology. Fig. 1 represents the diffractogram of an XRD analysis. Appearance of the following peaks of (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) confirmed the existence of hexagonal wurtzit ZnO structure with a dominant orientational growth on the *c*-axis. As seen from the figure, it is evident that ZnO nanorods film corresponds to (a) recorded the sharpest symmetrical peaks distribution as compared to (b) and (c). This statement is supported by the FE-SEM images as portrayed in Fig. 2.

The films show an improvement to the surface morphology as the annealing temperature increased. Fig. 2(a) demonstrates a dense uniform grain distribution with smaller grain size. In contrast to Fig. 2(a), Fig. 2(b) and Fig. 2(c) result in larger grain gap with inconsistency in size and surface distribution. The grain size and film distribution can be verified through the AFM analysis as depicted in the Fig. 2 insets. From there, we proved that the increase in annealing temperature had resulted in reduced roughness values from 12.81 nm to 6.04 nm for ZnO nanorods films annealed at 150°C and 500°C, respectively. Hence, the annealing temperature of 500°C has been selected as the optimum temperature for ZnO nanorods film growth.

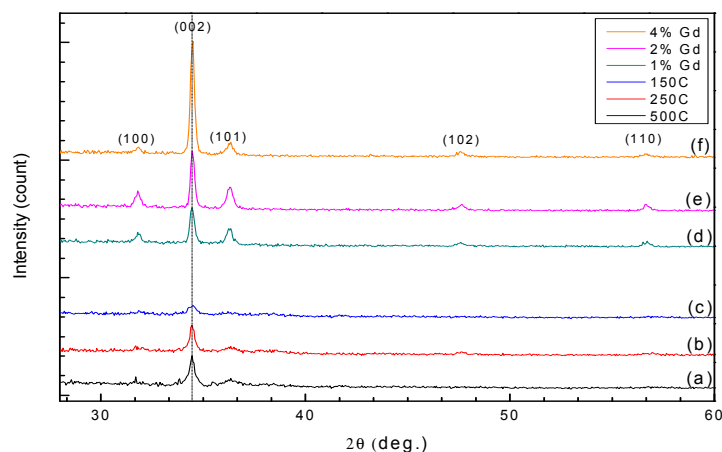


Fig. 1 X-ray diffractogram patterns of the ZnO nanorods thin films grown at various annealing temperature and Gd concentration.

From the observation in Fig. 2(d-f) insets, the morphological differences can be observed by performing an AFM study on different Gd concentration of 1 at. %, 2 at. %, and 4 at. %, correspondingly. The descending roughness readings occur because of the temperature and the doping content of Gd which resulted in smoother and denser surface. These images show a noticeable variation on the homogeneity of the films with large nanorods formation. The presence of diffraction peaks indicates that the films were polycrystalline in nature with preferential orientation growth along the (0 0 2) plane. The XRD diffractogram illustrated in Fig. 1 also proved no formation of other phase in the samples. From FE-SEM images as pictured in Fig. 2, it was observed that the average particle size increased with the increased in doping concentrations.

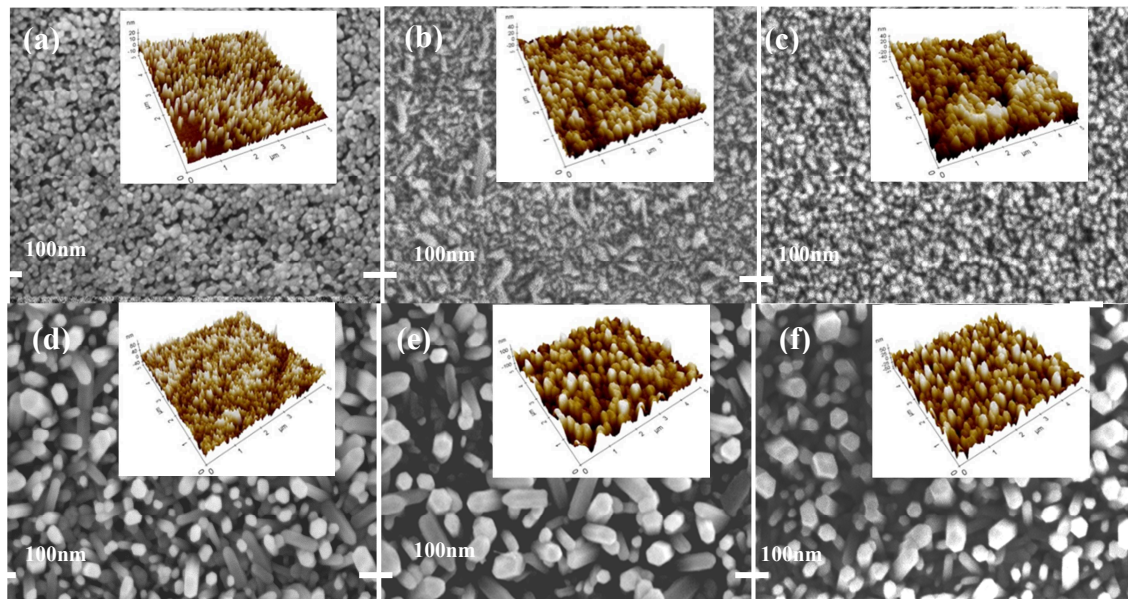


Fig. 2FESEM images of ZnO thin films attained at various annealing temperature (a) 500 °C, (b) 250 °C, (c) 150 °C; and at various Gd impurity concentrations (d) 1 at. %, (e) 2 at. %, and (f) 4 at. %, respectively. (Insets were the topographical image attained from AFM analysis of the corresponding samples.)

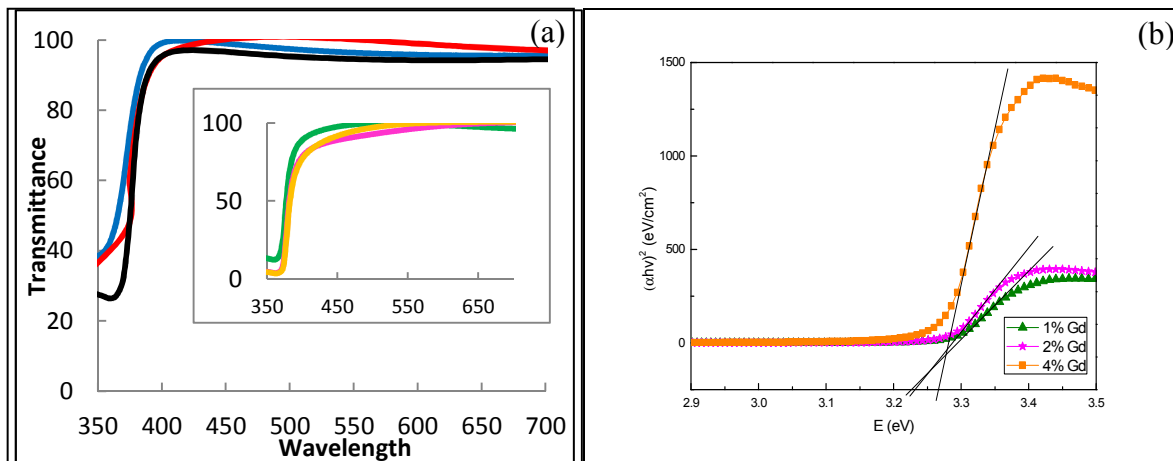


Fig. 3 (a) Graph depicted the transmittance spectra of the corresponding samples; and (b) plot of  $(\alpha h\nu)^2$  as a function of photon energy against for Gd-doped ZnO thin films.

#### B) Optical properties of pure and Gd-doped ZnO nanorods thin films

Fig. 3 shows the transmittance and band gap of pure and Gd-doped ZnO nanorods thin films. From the transmittance graph, it shows that the visible transparency is above 80% in average. It was likely to see that the visible transparency of 500 °C was more excellent compared to that of 150 °C and 250 °C samples. Therefore, from the optical analysis, the optimum temperature of 500 °C is suitable to be chosen. We could also be able to identify that the transmittance of Gd-doped ZnO films responded positively to the increased doping concentration of 4 at. % Gd as oppose to that of 1 at. % and 2 at. % Gd concentrations. The absorption analysis, on the other hand, has been increasing from 2 and 4 at. % Gd, whistle at 1 at. % Gd the absorption decreased. The optical band gap was found to be 3.22 eV and 3.23 eV for Gd-doped ZnO thin films at 1 at. % and 2 at. % Gd concentrations and it increased to 3.27 eV for 4 at. % Gd doping.

### Conclusion

The optimum temperature of two steps annealing of 500 °C has been selected as the optimum temperature for the doping of gadolinium to ZnO nanorods thin film samples. The role of Gd-doped ZnO can be clearly seen throughout the increase of doping concentrations. These also provided evidence that resulted in decreasing of roughness values as measured from AFM. This was the resultant of the temperature and the doping of Gd element, which has been causing the molecular structure of the hexagonal wurtzite to be deformed through the replacement of Gd atom on the Zn site through substitutional doping and hence resulting in a more smooth and dense upper surface of the films. The FESEM images depicted the increased in size and compact growth of the nanorods structure with respect to the increased in Gd concentration. The optical analysis as a measure of the visible transparency reported that 4 at. % of Gd concentration to be the best followed by 2 at. % and 1 at. % was observed. Meanwhile for the absorbance, the absorption of light has been increasing from 2 to 4 at. % Gd concentration, while at 1 at. %, the absorption decreased.

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