Journal of the Arkansas Academy of Science

Volume 66 Article 17

2012

# Synthesis and Optical Properties of Sprayed ZnO and ZnO:Ga Thin Films

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# Synthesis and Optical Properties of Sprayed ZnO and ZnO:Ga Thin Films

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## Abstract

Characteristics and optical constants of pure and Ga-doped ZnO thin films have been studied. Pure and Ga-doped zinc oxide thin films were deposited onto glass substrates using the spray pyrolysis technique. Optical absorption studies in the wavelength range of 300–900 nm showed a peak near 450 nm for different doped films (in addition to the peak for un-doped ZnO). Increasing the doping concentration of Ga to 7% induced an increase in the optical constants of films. This increase is attributed to the formation of charge-transfer complexes. ZnO thin films doped with Ga have improved the optical transmittance in the visible region. The addition of Ga also induced an obvious increase in the optical band gap of these films; the optical band gap of Ga-doped films was slightly higher than that of undoped samples (3.1 eV). This study also found that the highest band gap ($E_g$=3.4 eV) occurred for the film deposited with a doping concentration of 5% gallium.

**Keywords:** Spray Pyrolysis technique, Transparent Conducting Oxide (TCO), Optical Constant, ZnO:Ga

## Introduction

Zinc oxide (ZnO) is one of the most multifunctional semiconductor materials used for the fabrication of optoelectronic devices operating in the blue and ultraviolet region, owing to its direct wide band gap (3.37 eV) at room temperature and large excitation binding energy of 60 meV (Myoung et al. 2002). In addition, it is one of the best potential materials for use as a transparent conducting oxide (TCO) because of its high electrical conductivity and high transmission in the visible region (Fortunato et al. 2009). Group III elements, such as aluminum (Benhaliliba et al. 2010), indium (Singh et al. 2010), and gallium (Fortunato et al. 2008), are usually used as dopants to improve the electrical and optical properties and stability of ZnO-based films (Zi-qiang et al. 2006). Knowledge of optical properties is essential in that they govern the device performance. Doped and undoped ZnO are currently used in the copper indium gallium diselenide (CIGS, or Cu (In, Ga)$Se_2$) thin-film solar cell production (Wellings et al. 2008, Romeo et al. 2004) .

Various deposition methods have been used to prepare ZnO thin films, such as pulsed laser deposition (Suzuki et al. 1996), molecular-beam epitaxy (Ko et al. 2002), DC magnetron sputtering (Kon et al. 2002, Ma et al. 2007), vacuum evaporation (Minami et al. 2003), chemical-vapor deposition (Li et al. 1997), successive ionic layer adsorption and reaction SILAR (Lindroos and Leskela 2000), and chemical spray pyrolysis techniques (Ramakrishna et al. 2002). Out of these, chemical spray pyrolysis (CSP) is an inexpensive and safe method for producing highly transparent and conductive zinc oxide film. In the present study, undoped and Ga-doped ZnO thin films were prepared by the CSP technique.

## Methods

Thin films of zinc oxide were prepared by a chemical pyrolysis (CSP) method. The spray pyrolysis is accomplished with a laboratory- designed glass atomizer, which had an output nozzle of approximately 1 mm. The films were deposited on preheated glass slide substrates (2.5x 2.5 cm) at a temperature of 400°C. The aqueous starting solution, containing 0.1M $Zn(CH_3COO)_2.2H_2O$ (Merck chemicals) with 0.1M $GaCl_2$ (BDH chemicals), was used as the doping agent with concentrations of 2%, 5% and 7%v/v. These materials were dissolved with de-ionized water/ethanol (25/25) to forming the spray solution. A total volume of 50 mL was used in each deposition. The optimized conditions were as follows: spray time was 10 sec and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of $10^5\,Nm^{-2}$, the distance between nozzle and substrate was about 29 cm ±1 cm. The solution flow of rate was 5 ml/min. Sample thickness was measured using the weight difference method (Habubi et al. 2009) and was found to be approximately 350 nm.

Optical transmittance and absorbance were recorded in the wavelength range 300-900 nm using a UV-visible spectrophotometer (Shimadzu Company Japan). Optical transmittance and absorbance are reported to illustrate the effect of doping on the parameters under investigation.

## Results and Discussion

As ZnO is a direct transition semiconductor, the optical band gap can be determined by extrapolation of the linear region from the $(\alpha h\upsilon)^2$ versus $h\upsilon$ graph near the onset of the absorption edge to the energy axis. Figure 1, which shows the results of this measurement for the undoped ZnO film, indicates that the optical band gap is 3.1 eV. This value increased slightly with increasing Ga doping concentration (Figures 2 and 3). The highest optical band gap, 3.4 eV, was achieved in the ZnO thin films doped with 5% Ga. The extrapolated absorption onset is lightly blue shifted on increasing the Ga doping concentration . This is associated with the increase in carrier concentration which blocks the lowest state in the conduction band , and is known as the Burstein–Moss effect (Kon et al. 2002). There are numerous reports on electrical and optical properties of Ga-doped ZnO thin films, with many choosing 4% Ga-doped ZnO targets , and some others choosing 2, 3, or 5% Ga-doped ZnO to obtain thin films, which have excellent electrical and optical properties (Jung et al. 2010, Miyake et al. 2008, Nagarani and Sanjeeviraja 2011).

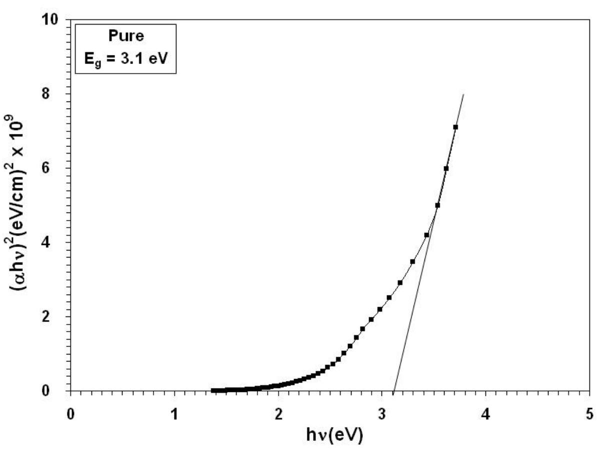


Figure 1. $(\alpha h\upsilon)^2$ versus photon energy for undoped ZnO thin films.

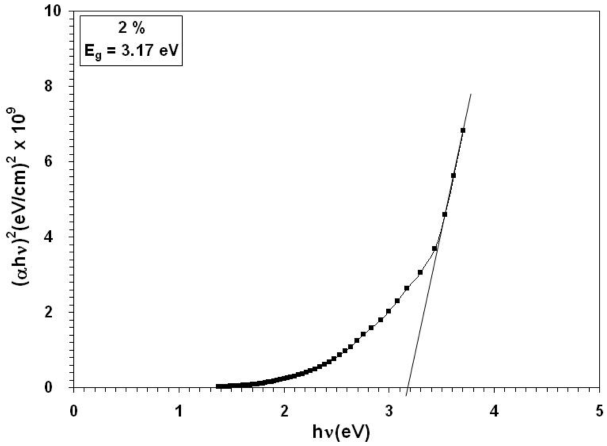


Figure 2. $(\alpha h\upsilon)^2$ versus photon energy for ZnO:Ga thin films.

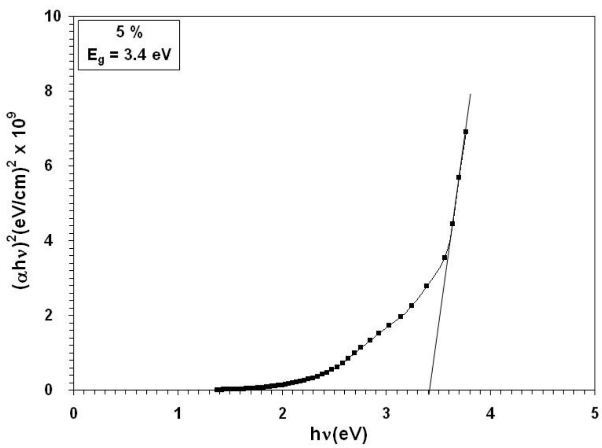


Figure 3. $(\alpha h\upsilon)^2$ versus photon energy for ZnO:Ga thin films.

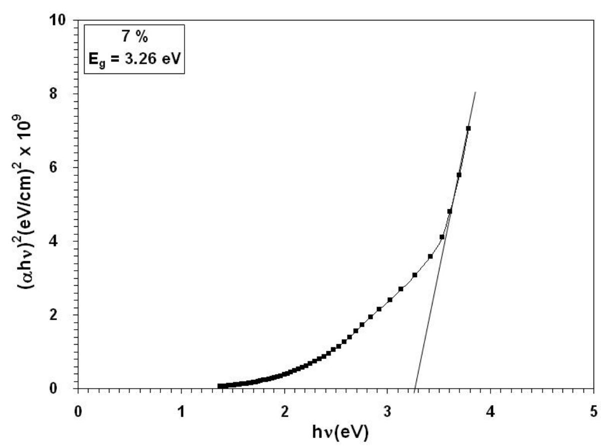


Figure 4. $(\alpha h\upsilon)^2$ versus photon energy for ZnO:Ga thin films.

The refractive index is an important parameter for optical materials and their applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation (Islam and Podder 2009):

$$n = [1 + R/1 - R] + [4R / (1-R)^2 - k^2]^{1/2} \quad (1)$$

where k ($k = \alpha\lambda/4\pi$) is the extinction coefficient. The n and k values dependence on wavelength are shown in Fig. 5 and 6 respectively. As seen in those figures, the n and k values increase with increasing doping ratio in the visible region. The average refractive index of the films in the visible range was found to be about 2. This result was reported earlier by Khoshman and Kordesch (2007)

The real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of the dielectric constant were obtained using the formula as shown below (Buet et al. 1991):

$$\varepsilon_1 = n^2 - k^2 \quad (2)$$

$$\varepsilon_2 = 2nk \quad (3)$$

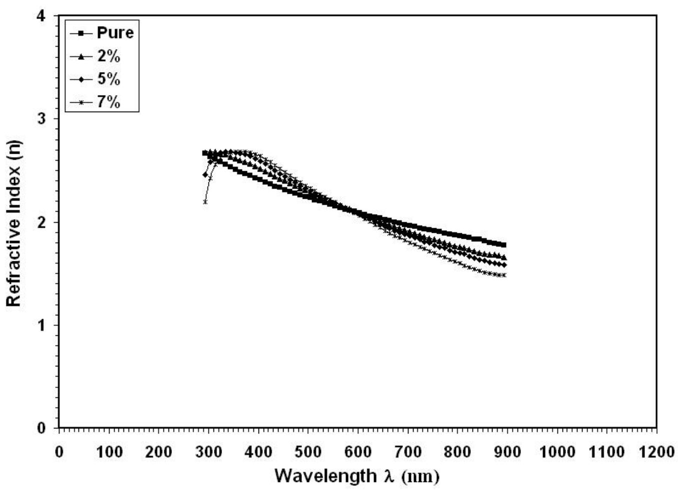


Figure 5. Refractive index versus wavelength for the ZnO and ZnO:Ga thin films.

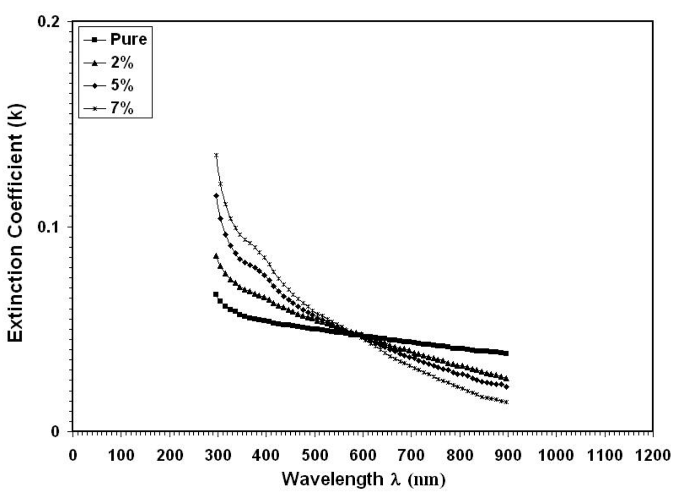


Figure 6. Extension coefficient versus wavelength for the ZnO and ZnO:Ga thin films.

The variation in the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric constant for different Ga contents are shown in Figures 7 and 8. The values of the real part are higher than those of the imaginary part.

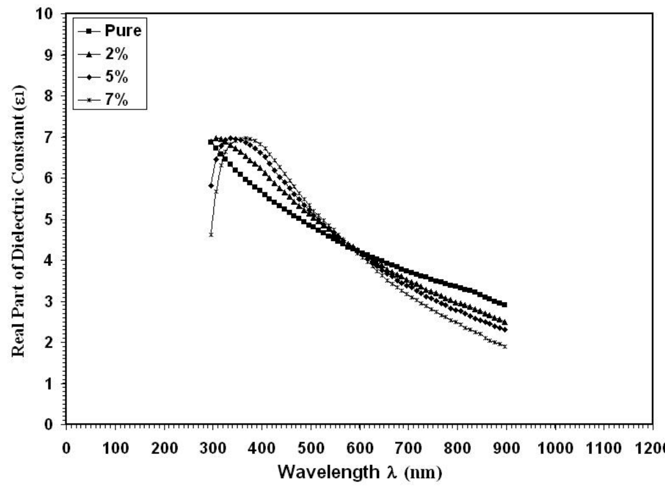


Figure 7. The spectra of the real ($\varepsilon_1$) part of the dielectric constant of ZnO and ZnO:Ga thin films.

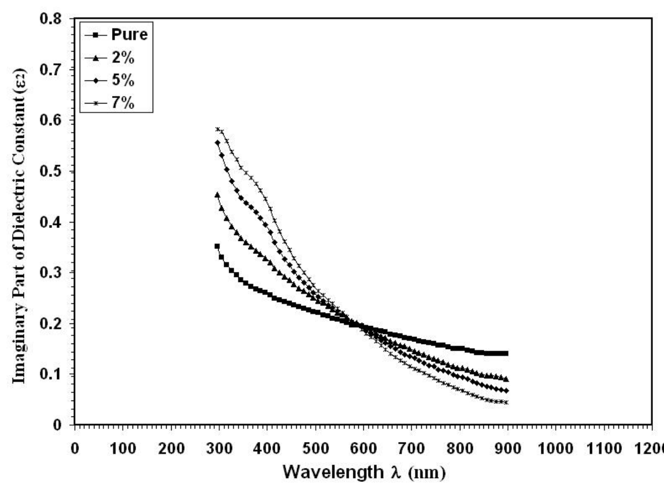


Figure 8. The spectra of the imaginary part of the dielectric constant of ZnO and ZnO:Ga thin films.

## Conclusion

Our results indicate that Ga can be effectively used to dope ZnO thin films for the purpose of enhancing optical properties, and increasing their band gap optical band gap increase due to doping. The highest band gap (Eg= 3.4 eV) was observed for the film deposited with a doping concentration of 5% gallium. Generally, both

ZnO and gallium-doped ZnO showed high transmittance in the visible range. Optical parameters tended to increase with increasing doping concentration. The UV-visible spectra of pure and doped ZnO showed peak maxima that were found to be red shifted as the amount of Ga increase.

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