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# Effect of Al and Mg Doping on Optical Properties of ZnO Thin Films Prepared by Spin Coating

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**Abstract**: This paper investigated the influence of aluminum and magnesium doping on the optical and electrical properties of zinc oxide (ZnO) thin films for solar cell application. Zinc acetate dehydrates was used as starting material. Aluminum chloride and tin chloride were added to each solution to serve as dopants. X-ray diffractions were analyzed by X-ray diffraction (XRD) which revealed crystalline and hexagonal wurtzite structure. All the films showed more than 80% transparency in the visible region. The optical band gap of undoped ZnO thin film was found to be 3.12ev while that of Al-doped and Mg-doped ZnO film was estimated to be 3.16eV and 3.26eV respectively. The resistivity of the films measured were $2.51\times10^{-4}\ \Omega$ cm for Al-doped, $2.53\times10^{-4}\ \Omega$ cm for mg-doped and $2.61\times10^{-4}\ \Omega$ cm for undoped ZnO respectively. The quality of the films deposited in this work is a promising window layer component of a solar cell. The variation in the band gap observed in this work could be explained by Burstein–Moss effect which was fully explained in the discussion section of this work.

**Keywords:** Band gap, Doping, Thin films, Transmittance, Spin-coating

## 1. INTRODUCTION

Zinc oxide thin films have been intensively investigated for optical and electrical applications, such as flat-panel displays, liquid crystal displays, organic light-emitting diodes, thin-film transistors, and thin-film solar cells [1−4]. Thin films for solar cell application should have low resistivity, high transmittance in the

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visible region (400 to 800 nm), and high thermal/chemical stability [5−6] Earlier, indium tin oxide (ITO) has been widely employed as a transparent conduction oxide material because of its superb electrical and optical properties. Unfortunately, ITO has low stability, high toxicity, and high cost and is a rare material, this situation calls for search of alternatives before the supply final runs out [7]. One of the promising alternatives is zinc oxide doped with metals.

For the purpose of improving the electrical conductivity and optical transmittance of ZnO thin films, dopants are usually introduced to ZnO to make it a promising candidate for solar cell application [8]. A number of researches have been recently conducted on improving the properties of ZnO by doping with As, P, N, Al, In, B and Ga. Generally drastic change in electrical conductivity was reported with doping with metals, but there are still a number of challenges to be overcome such as unstable electrical properties, high temperature and pressure and so on. Furthermore, it was reported by various researchers that Al-doped zinc oxide films have the lowest electrical resistivity [4, 11]. Non-stoichiometric zinc oxide films have unstable electrical properties at high temperature because the sheet resistance of ZnO thin films increases under either oxygen chemisorptions and desorption [9] or heat treatment in vacuum or in ambient oxygen pressure at $300^0$C–$400^0$C [27]. Therefore, more deposition techniques are still required not only to produce quality thin films but also to overcome the shortcomings of unstable electrical properties, high temperature treatment and pressure reported by various researchers.

There are varieties of techniques for thin films deposition some of them are: DC or RF magnetron sputtering [2], electron beam evaporation [19, 20], pulsed laser deposition [21], spray Pyrolysis [22, 23], chemical vapor deposition [24] and sol–gel processing [25−34, 5]. Among them, the sol–gel spin coating method is simpler and cost effective and are sparsely reported by researchers. Films prepared by this method follow the non-alkoxide route, using metal salts such as acetates, nitrates or chlorides as precursor and dopant, respectively. [11] reported that among the zinc oxide films doped with group II elements such as barium, gallium and indium, (AZO) thin films presented the lowest resistivity. Although none of them used sol-gel spin coating technique. Among the zinc oxide films doped with group II elements such as barium, aluminum, gallium and indium, aluminum-doped zinc oxide (AZO) thin films show the lowest electrical resistivity [11]. Aluminum-doped zinc oxide (AZO) has a low resistivity of $2.4\times10^{-4}$ Ω cm [11−13], which is quite similar to that of ITO films, which is about $1.2\times10^{-4}$ Ω cm [14−16] and AZO also shows good optical transmission in the visible and near infrared (IR) regions. Thus, AZO films have been used as transparent conducting electrodes in solar cells [16, 8]. In addition to doping with Group III elements, doping ZnO with Group IV elements such as [9, 10] Ge, Sn, Ti, Si is also a good

way to obtain low resistivity transparent materials in order to replace ITO because Ge, Ti, Zr could substitute on the Zn atom site. It has been reported that the thin film deposition technique determines the quality of the thin films produced.

In this research work, we wish to investigate the optical and electrical properties of Mg-doped ZnO and Al-doped ZnO thin films using sol-gel spin coating method for solar cell applications. This technique of film deposition is sparsely reported in the literature.

## 2. EXPERIMENTAL DETAIL

Thin films were prepared by sol–gel spin-coating method. As starting materials, $AlCl_3 \cdot 6H_2O$, $Mg(NO_3)_2.6H_2O$ and $Zn(CH_3COO)_2$ were used. As solvent and stabilizer, 2-methoxyethanol and monoethanolamine (MEA) were used, respectively. Zinc acetate dehydrate was first dissolved in a mixture of methanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate dehydrate was maintained at 1.1, and the concentration of zinc acetate dehydrate was 0.3 mol/L. In order to study the influence of Al and Mg dopant concentrations on the properties of Al-doped and Mg-doped ZnO thin films, the concentrations were kept at 1.5mol% with respect to Zn. The solutions were stirred at 60°C for 60 min to yield a clear and homogeneous solution. Thereafter, glass substrates were ultrasonically cleaned in acetone; methanol and de ionized water and heated on hot plate at $60^0$C for 10 min. undoped ZnO, Al-ZnO and Mg-ZnO films were then deposited on glass substrates by sol–gel spin-coating method. Spin coating was performed at room temperature, with a rate of 4,000 rpm for 45 seconds; The films were preheated at 300°C for 15 min on a hot plate to evaporate the solvent and to remove organic residuals. The procedures from coating to drying were repeated four times. The films were then inserted into a tube furnace and annealed in air at $750^0$C for 1 hour each. The transmittance T and reflectance R data were used to calculate absorption coefficients of the films at different wavelengths. The relationship between transmittance T, reflectance R, absorption coefficient, $\alpha$, and thickness d of the film is given by equation (1).

The crystalline structures of the specimens were analyzed by X-ray diffraction (XRD) patterns. XRD $2\theta$ scans were carried out by employing a Rigaku X-ray diffractometer with a Cu-K$\alpha$ source ($\lambda$= 0.154056 nm). Optical transmittance measurements were carried out using a UV–VIS spectrophotometer. Scanning electron microscope (SEM) and Photoluminescence (PL) analysis were ignored due to inconsistency observed in the photoluminescence and SEM equipments available. Although, we hope to include these analyses in our subsequent research work.

$$T = (1 - R)\exp(\alpha d) \quad (1)$$

The absorption coefficient data was used to determine energy band gap, $E_g$, using equation (2).

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \tag{2}$$

Where $h\nu$ is the photon energy, A is a constant thus, a plot of $(\alpha h\nu)^2$ against $h\nu$ is a curve line whose intercept on the energy axis gives the energy gap. The band energy gap of the film was then determined by extrapolating the linear regions on the energy axis.

The absorption coefficient, $\alpha$, associated with the strong absorption region of the film was calculated from absorbance A and the film thickness t, using equation (3).

$$\alpha = 2.3\frac{A}{t} \tag{3}$$

The extinction coefficient k, was evaluated from equation (4)

$$k = \frac{\alpha\lambda}{4\pi t} \tag{4}$$

Where $\lambda$ the wavelength of the incident radiation and t is the thickness of the film.

The crystal phase of the films was determined by X-ray diffraction (XRD). The refractive index of the films was determined from the maxima and minima of the reflectance curve.

$$n.d = \frac{k\lambda}{4} \tag{5}$$

Where n is the refractive index, d is the film thickness (nm), $\lambda$ is the wavelength (nm) of the incident light and k is the interference order (an odd integer for maxima and even integer for minima).

The lattice constants 'a' and 'c' of the Wurtzite structure of the films were calculated using the equations (6) and (7).

$$a = \sqrt{1/3}\,\lambda/\sin\theta \tag{6}$$

$$c = \lambda/\sin\theta \tag{7}$$

since four point probe and hall effect were not currently available, electrical measurements were estimated from equations (8−10)

Therefore, the resistivity of the films measured were $2.51\times10^{-4}$ Ω cm for Al-doped, $2.53\times10^{-4}$ Ω cm for Mg-doped and $2.61\times10^{-4}$ Ω cm for undoped ZnO.

$$Rs = \frac{\pi}{ln2}\left(\frac{V}{I}\right) = k\left(\frac{V}{I}\right) \tag{8}$$

K is a geometric factor which is 4.53 in the case of thin sheet material.

$R_s$ = sheet resistance

$$\rho = \frac{\pi t}{\ln 2} x \frac{V}{I} = Rsxt \tag{9}$$

t = thickness of the film

$$\sigma = \frac{1}{\rho} \tag{10}$$

Where σ is the electrical conductivity, ρ is the resistivity.

## 3. RESULTS AND DISCUSSION

The crystal structure of ZnO films were investigated through X-ray diffraction (XRD). The X-ray diffraction spectrum of undoped ZnO, Al-ZnO and Mg-ZnO film annealed at 750°C is shown in figure 1. The peaks in the XRD spectrum correspond to those of the ZnO patterns from the JCPDS data (Powder Diffraction File, Card no: 36−451) having hexagonal wurtzite structure with lattice constants a = 3.24982Å, c = 5.20661Å.The presence of prominent peaks show that the films are polycrystalline in nature.

Figure 2 shows the optical transmittance spectra of undoped ZnO, Al-ZnO and Mg-ZnO thin films in the wavelength range between 300 to 800 nm. The transparency properties of all thin films are more than 80 % at a visible wavelength of (300−800 nm). It is observed that the transmittance

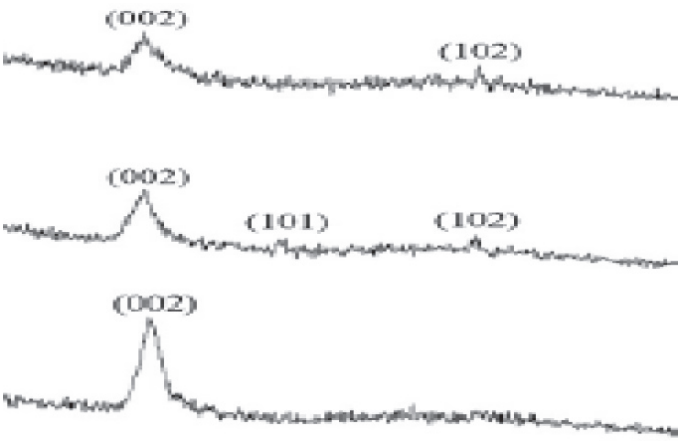


**Figure 1:** XRD patterns for (a) Mg-doped ZnO (b) Al-doped ZnO and (c) undoped ZnO films.

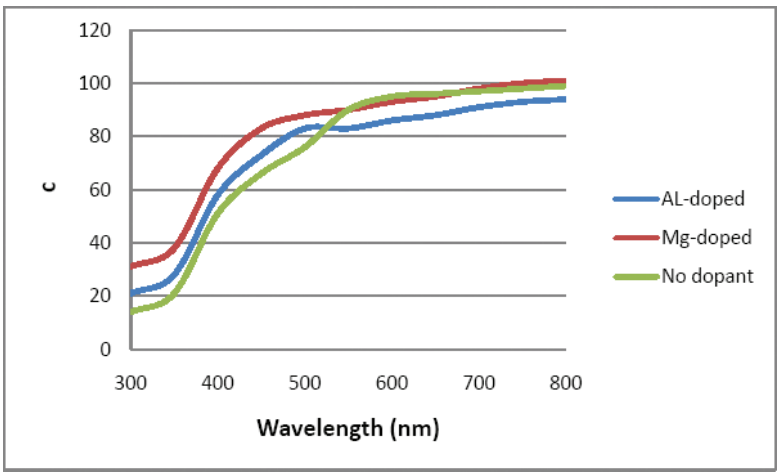


**Figure 2:** Optical Transmittance for undoped, Al-doped and Mg-doped ZnO films.

varies with aluminum doped films and magnesium doped films. The overall spectra show an emission band with two obvious peaks. The UV peak which also called the emission or near band edge emission contributed to the free exciton recombination [18]. The second broad peak, also known as the green emission corresponds to the recombination of a photon generated hole with an electron in singly ionized [18].

The optical absorbance spectrum measured within the wavelength range of 300−800 nm using a Shimadzu Spectrophotometer is shown in figure 3.

Approximately, the band gap alteration of the thin film can be deduced from Figure 3. Here, it shows that changes in the absorption edges are in parallel with types of dopant in the thin film. In order to appropriately estimate the optical band gap, equation (2) was used. The presence of a single slope in the plot suggests that the films have direct and allowed transition. It is also well known that ZnO is a direct band-gap material [1] and the energy gap ($E_g$) can thus be estimated by assuming direct transition between conduction band and valance bands. Theory of optical absorption gives the relationship between the absorption coefficients $\alpha$ and the photon energy $h\nu$ for direct allowed transition as shown in (2) The direct band gap determined using this equation when linear portion of the $(\alpha h\nu)^2$ against $h\nu$ plot is extrapolated to intersect the energy axis at $\alpha = 0$. Plot of $(\alpha h\nu)^2$ against $h\nu$ for undoped, Al-doped ZnO and Mg-doped films are shown in figure 3. The optical band of pure ZnO is 3.12eV while the band gap for Al-doped ZnO and Mg-doped films are 3.16e V and 3.26e V respectively.

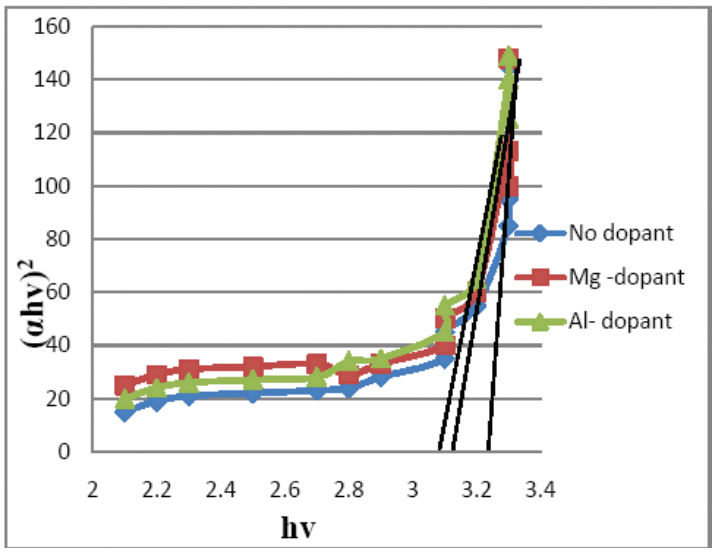


**Figure 3:** Plot of $(\alpha hv)^2$ vs photon energy for Al-doped, Mg-doped and undoped ZnO thin films.

## 4. CONCLUSION

Transparent conducting thin films (ZnO, Al-ZnO and Mg-ZnO) have been deposited by sol–gel spin coating technique. The result obtained is very similar to those obtained using different techniques. No doubt, the optical and electrical properties of the films could be improved if deposition parameters such substrate temperature can be varied while spin coating. It is observed that the transmittance varies with dopant types i.e. aluminum and magnesium. The optical band of pure ZnO was 3.12 eV while the band gap for Al-doped ZnO and Mg-doped films were 3.16 eV and 3.26 eV respectively. The variation of optical band gap with doping is well described by Burstein–Moss effect [2–5]. For AZO films, compared to pure ZnO films, the contribution from $Al^{3+}$ ions on substitution sites of $Zn^{2+}$ ions and Al interstitial atoms determines the widening of the band gap caused by increase in carrier concentration. This is the well-known Burstein–Moss effect and is due to the Fermi level moving into the conduction band. Since doping increases the carrier concentration in the conduction band, the optical band-gap energy increases [2]. Enhancement of band gap thus also ensures that doping was successfully carried out in the ZnO thin films. It is further observed in our present work that an increase in band gap occurs

in Mg- doped film as compared with undoped ZnO and Al-ZnO thin films. The absorption properties of the films in UV range are due to the behavior of ZnO intrinsic optical band gap energy. An absorption coefficient in the UV region significantly varies with types of dopant used.

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