Effect of solution molarity on optical properties of Al doped ZnO thin films

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Effect of solution molarity on optical properties of Al doped ZnO thin films

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Abstract. Undoped and Al-doped ZnO thin films have been prepared by the sol gel method. Zinc acetate dihydrate, ethanol and monoethanolamine were used as precursor, solvent and stabilizer, respectively. In the case of molarity study for Al-doped ZnO, aluminum nitrate nonahydrate was added to the precursor solution from 0 at. % to 6 at. % at molarity of 0.1 M, 0.2 M and 0.3 M. The optical properties were characterized using UV-Vis where the band gap of undoped ZnO increases as the annealing temperature increase and the band gap decrease as the molarity increment. Meanwhile the band gap increase upon increment of Al dopant under molarity of 0.1 M and 0.2 M due to Burstein-moss effects. Meanwhile at 0.3 M, the bandgap increase until 4 at. % of Al and suddenly decrease abruptly at 6 at. % of Al. The effect of molarity and dopant percentage on the thin film gives a different value of energy band gap.

1. Introduction

Transparent conducting oxides (TCO) a very known with their applications based on electro-optical properties especially indium tin oxide (ITO) [1]. Recently, zinc oxide (ZnO) or impurity doped ZnO are become aggressively investigate as an alternative to replace material ITO, because it is expensive and a shortage indium may occur on the future because the limited World indium reserves [2]. ZnO crucial in most applications because it has chemical stability, non-toxicity, inexpensiveness and easy availability in nature that make it can replace ITO besides has reaching high electrical conductivity and good in optical transmission as a TCO thin film [3]. They are used in solar cells, panel display, laptop screen, light emitting diode [2] and ultraviolet detection [4]. ZnO is a direct wide band-gap semiconductor which is 3.37 eV at 300K, it also have large excitation binding energy [5]. Wide bandgap semiconductors have many properties that make them attractive for high power, high temperature device applications. Molarity, annealing temperature [6] and other factors during films preparation will affect the band gap values of ZnO thin films. ZnO have wurtzite crystalline structure with constant unit cell. Aluminum doped ZnO are of interest because when ZnO thin film dope with Al it increases the conductivity of ZnO thin films [5]. Many technique and methods have been used to manufacture ZnO films like spray pyrolysis, magnetron sputtering, organometallic chemical vapor deposition, pulsed laser deposition [2], and sol-gel process. Among these methods, the sol-gel method is specializing with several benefits, such as deposition of high purity, homogeneous, and non-vacuum. Moreover, there is easy way to control solution concentration, doping level, homogeneity in sol gel procedure. In this method, thin films are made from cross-linked liquid chemical precursors through many coating like spin, drop or dip coating according to thermal decomposition [2]. In this paper, the experiment concentrate on optical properties of sol-gel derived Al doped ZnO films with different molarity of zinc acetate dehydrate which are 0.1 M, 0.2 M, 0.3 M. The percentage of dopants is varied at 0 at. %, 2 at. %, 4 at. %, 6 at. %.

2. Methodology

The ZnO precursor solution is prepared by dissolving zinc acetate dehydrate (≥98%, Sigma Aldrich) in solution of 2–methoxyethanol (99.8%, Sigma Aldrich). Solution of 2–methoxyethanol is made with concentration 0.1, 0.2 and 0.3 mol/L. Magnetic stirrer is stirred on the hot plate with temperature of 75 °C. Monoethanolamine (MEA) (≥98%, Sigma Aldrich) is added to prevent forming precipitation and stabilizer in solution. The molar ratio of MEA to zinc acetate is maintained at 1:1. For Al doped zinc oxide solution, aluminum nitrate nonahydrate (Al $(NO_3)_3 \cdot 9H_2O$) (≥98%, Sigma Aldrich) is added in the solution. Various Al/Zn ratios are used in the solution from 0%, 2%, 4% and 6%. The final solution for undoped and Al doped zinc oxide is stirred about 2 hours at the same temperature till obtain a clear and homogeneous solution. At first, glass slide is cleaned with methanol or acetone. Dip the samples with the solutions at room temperature. The deposited film is preheated at 250 °C for 15 min. Then, repeat the coating about 2 times to get uniform film. Then anneal the films at 500 °C for 1 hour for crystallization. The optical properties such as transmittance and energy band gap of Al doped ZnO thin film is characterized by using UV-Vis.

3. Results and Discussions

3.1 Effects of molarity on transmittances properties of ZnO

Figure 1(a) and Figure 1(b) shows optical transmittance spectra for Al doped ZnO at molarity of 0.1 M and 0.2 M. For molarity of 0.1 M, the transmittance's value for 0 at.%, 2 at.%, 4at.% and 6 at.% of Al was around 74.80 %, 86.00 %, 86.32% and 92.99%. Meanwhile for 0.2 M, the transmittance's value for 0 at. %, 2 at. %, 4 at. % and 6 at. % was around 79.11%, 75.61 %, 89.25% and 93.79%. The absorption edge of the samples can be found in the range from 300 to 400 nm. Blue shift of absorption edge is observed clearly with rising Al doping level. This blue shift could be attributed to the rising of band gap energy resulting from Burstein-Moss effect. With the increasing Al doping level, the optical band gap of films is growing, which causes the absorption edge shift to short wavelength region. It shows that doping of ZnO with Al^{3+} increase the intensity of optical transmittance, this can be explained by decrease of porosity in the samples. Reduction of porosity is explained by the particle size distribution where smaller particles filled in the gaps between larger particles, thus preventing the formation of pores [7]. From previous study, Inna Juhnevica et al. [7] has obtained the effect of dopant concentration by using SEM microscope image. The image shows that between the particles pores were formed. Since the samples doped with Al^{3+} had smaller particle sizes than the ZnO model, the amount of pores in these samples decreased due to the formation of particles in denser arrangement [8].

Meanwhile at molarity of 0.3 M as shown in Figure 1(c), the transmittance of undoped ZnO and doped Al at 2 at. %, 4 at. % and 6 at. % was around 36.00%, 79.51 %, 86.38 % and 77.12%. Roughly, it shows the optical transmittance also increase by doping with Al but suddenly decrease for 6 at. % of Al. The increment might be due to the grain size of the deposited films where the grain size decreases with the increment of Al dopant. The decreasing value can be related to the loss of light due to scattering at the grain boundaries [9]

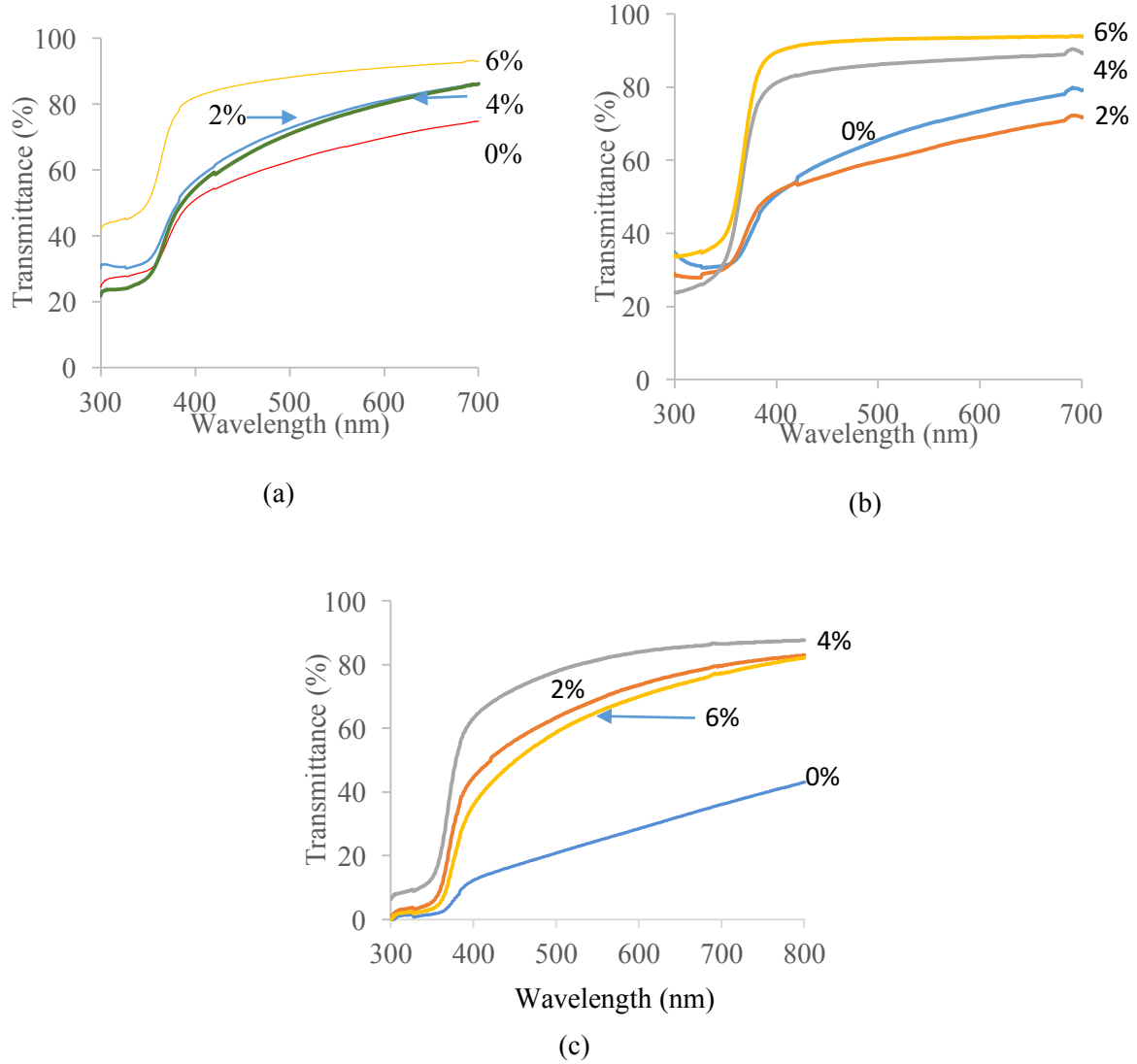

Figure 1. Optical transmittance of undoped ZnO and ZnO doped with 2 at. %Al, 4 at. %Al, 6 at. %Al at molarity of (a) 0.1M, (b) 0.2M and (c) 0.3M

Figure 2 shows the optical transmittance of undoped ZnO with molarity of 0.1 M, 0.2 M and 0.3 M. The transmittance of the samples with molarity of 0.1 M, 0.2 M and 0.3 M was around 74.80 %, 79.11 % and 36.00 %. It shows the optical transmittance spectra decrease with increase ZnO thin film concentration. This is because the grain size of thin film increase when the concentration increase. The size of grain affects the optical transmittance spectra to pass through the sample. In addition, a decrease in defect concentration due to increased transmittance, thus a reduction in grain boundaries, caused by rising grain size, serves to improve transmittance. Scattering photons by grain boundaries may result in a decrease in transmittance.

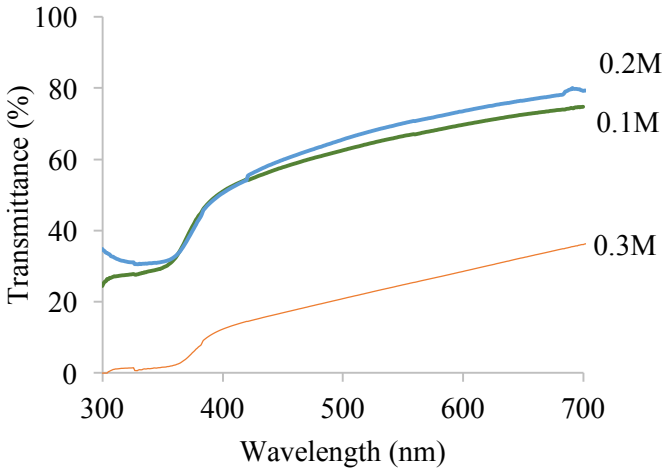

Figure 2. Optical transmittance of undoped ZnO at molarity of 0.1 M, 0.2 M and 0.3 M

3.2 Effects of molarity on band gap of undoped ZnO and Al doped ZnO

The optical band gap of Al doped ZnO films were calculated by using the relation $(\alpha hv)^2$ vs photon energy where α is the absorption coefficient as shown in Figure 3. The energy band gap for Al doped ZnO with 0 at. %, 2 at. %, 4 at. % and 6 at. % of Al at molarity of 0.1 M was around 3.14 eV, 3.21eV, 3.20 eV, 3.30 eV as shown in Figure 3(a). At molarity of 0.2 M, the energy band gap of 0 at. %, 2 at. %, 4 at. % and 6 at. % of Al was around 3.07 eV, 3.15eV, 3.31 eV and 3.34 eV as shown in Figure 3(b). The band gap of the ZnO thin films increases as the Al doping content increases from 0 at.% to 6 at.%, respectively which is in good agreement to other former published work [10]. In addition, the ideal band gap of pure ZnO is 3.3 eV and that of Al_2O_3 is 8.7 eV [11]. The feature regarding the increase of optical bandgap with increasing doping concentration may be attributed to the truth that Al dopant may increase the carrier concentration of the film resulting in the carrier-induced wideness of bandgap, well-known as Burstein-Moss effect [12]. The other possible mechanism taking responsibility on this widening of the bandgap is the quantum size effect of the nanocrystalline structure of the films [13].

Meanwhile Figure 3(c) shows the band gap Al doped ZnO at 0 at. %, 2 at. %, 4 at. % and 6 at. % with molarity of 0.3 M which was around 3.16 eV, 3.30eV, 3.32 eV and 3.25 eV. The energy band gap increase when the percentages of Al dopant increase. The band gap at 6 at. % of Al decrease which might be due to over doping Al content causing the ease of formation and segregation of Al_2O_3 in the ZnO thin film and the molarity of precursor solute is high which is 0.3 M. The reduction of band gap when ZnO doped with Al is also obtained by A.R.A. Rashid et al. [14,15].

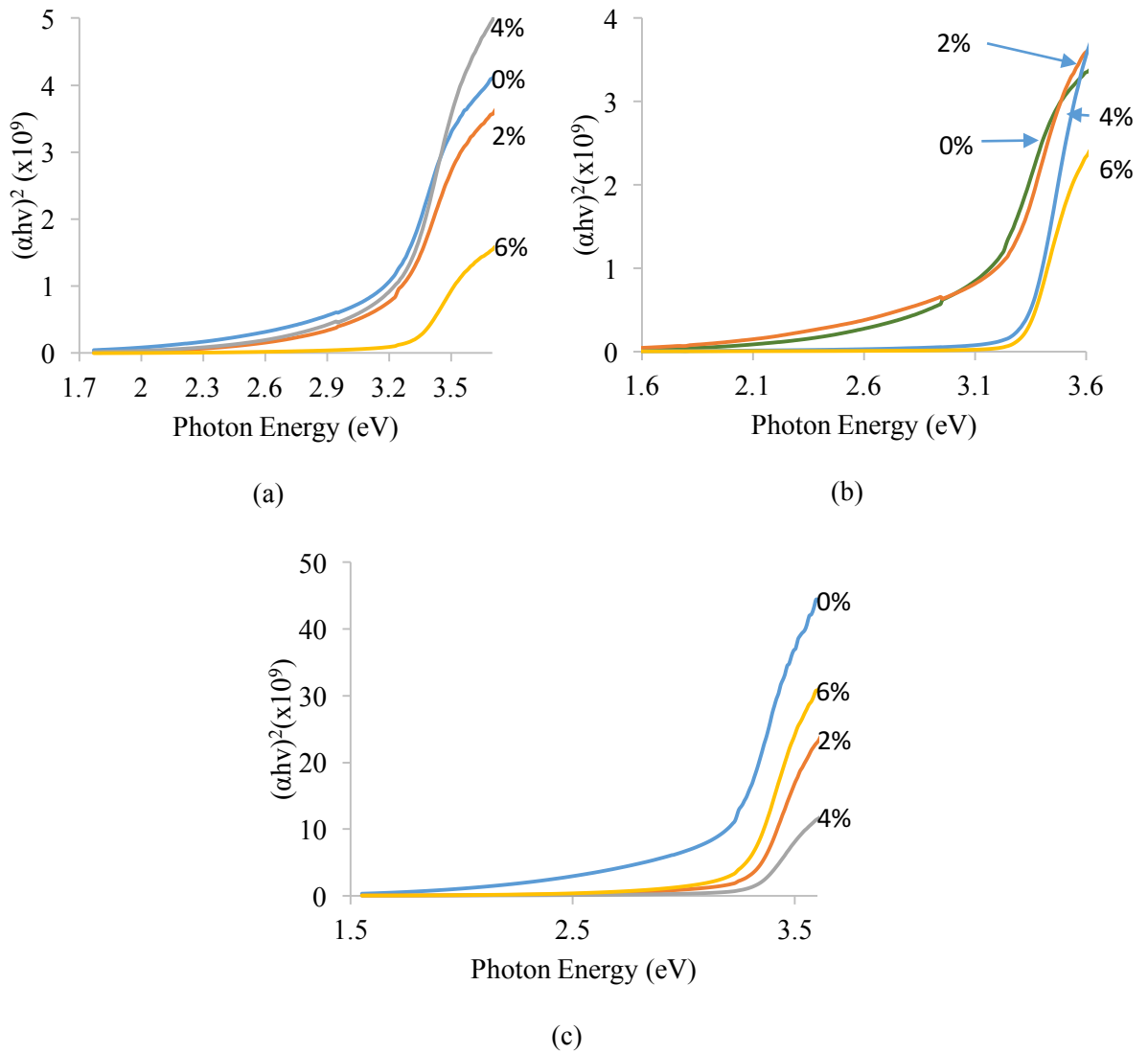

Figure 3. $(\alpha hv)^2$ versus hv plots of undoped ZnO and ZnO doped with 2 at. % Al, 4 at. %Al, 6 at. % Al at molarity of (a) 0.1 M, (b) 0.2 M and (c) 0.3 M

4 Conclusions

Results prove that molarity of precursor solution and percentage of Al dopant give significant effect to the optical properties and energy band gap value of ZnO thin films. The energy band gap value increasing when the percentage of Al dopant increase at molarity of 0.1 M and 0.2 M, due to Burstein Moss effect that relate the dependence energy gap on carrier concentration. At higher concentration 0.3 M, the band gap increase when Al is added but suddenly decreased at 6 at. % of Al which may due to segregation of Al_2O_3 in the ZnO thin film.

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References

[1] Mozibur Rahman, M., Khan, M.K.R., Rafiqul Islam, M.A. Halim, M. Shahjahan,M-A'Hakim, Dilip Kumar Saha and Jasim Uddin Khan. 2012. *J. Mater. Sci. Technol.* **28** (4):329-335.
[2] Kondratiev, V.I. Kiok, I., Romanov, A.E. 2013. *Materials Physics and Mechanics*. l7:38-46.
[3] Nanda Shakti and P.S. Gupta. 2010. *Applied Physics Research*. **2**(1): 1-10.
[4] A.R.A. Rashid, P.S. Menon, S. Shaari. 2013. *Journal of Nonlinear Opticl Physics & Materials*. **22**(3): 1350037.
[5] Nsimama, PD and Samiji, ME. 2012. *Tanz. J. Sci* **38**: 1-14.
[6] Affa Rozana Abd Rashid, Tuan Nur Hazwani e tal. 2018. AIP Conference Proceedings **1972**, 030006 (2018).
[7] Inna Juhnevica, Marija Masonkin, Gundms Mezinskis and Alona Gabrene. 2015. *Material Science and Applied Chemistry*. **31**(2015): 33-37
[8] Shankar Prasad Shresthq, Rishi Ghimire, Jeevan Jyoti Nakarmi, Young-Sung Kiro, Sabita Shrestha, Chong-Yun Park and Jin-Hyo Boo. 2010. *Bull. Korean Chem. Soc*.**31**(1): 112-115.
[9] Bangbai, Chatpong, Krisana Chongsri, Wisanu Pecharapa and Wicharn Techitdheera.2013. *Sains Malaysiana* **42**(2):239-246.
[10] Emin Bacaksiz, Serdar Aksu, Salih Yılmaz et al. 2010. *Thin Solid Films* **518** (2010) 4076–4080.
[11] Banerjee P, Lee WJ, Bae KR, Lee SB, Rubloff GW. *J Appl Phys*. 2010;108:043504.
[12] J. G. Lu and S. Fujita. 2007. *Journal of Applied Physics* **101**, 083705 (2007).
[13] Marotti, r.E., Giorgi, P., Machado, G. & Dalchiele, E.A. 2006. *Solar Energy Materials and Solar Cells* **90**: 2356-2361.
[14] A. R. A. Rashid, P. S. Menon, S. Shaari. 2013. *Optoelectronics and Advanced Materials – Rapid Communication* **7**(11-12): 835-839.
[15] S. Shaari, A. R. A Rashid, P. S. Menon, N. Arshad. 2013. *Advanced Science Letters* **19** (3): 816-819.