SOL-GEL PREPARATION AND OPTICAL PROPERTIES OF RARE-EARTH DOPED ZNO THIN FILMS SUITABLE FOR SOLAR CELL APPLICATION

NOOR JANNAH AWANG[1], MADZLAN AZIZ, ABDULL RAHIM MOHD YUSOFF

[1]Chemistry Department, Faculty of Science,

Universiti Teknologi Malaysia,

81310 Skudai, Johor

Malaysia

Corresponding author email: madzlan@kimia.fs.utm.my and njannah@ukm.my

Tel: +607 553 7863, Fax: +603 553 7811

ABSTRACT

Owing to the superior chemical stability, ZnO has a potential as a host lattice for doping several luminescence centers and show versatile application. In this study, the optical properties of rare-earth doped ZnO were studied. Europium doped zinc oxide (ZnO:Eu) and terbium doped zinc oxide (ZnO:Tb) thin films were prepared by sol-gel dip-coating process on glass substrates. The content of terbium and europium in the sol was varied from 5% to 15%. Synthesis parameters such as annealing temperature and concentration of doped ions on the highly oriented crystal growth were studied. The coating was characterized by defuse reflectance UV-visible (DRUV) and fluorescence spectrophotometer. The crystalline ZnO thin films were obtained following an annealing process at temperatures between 300 ^{o}C to 500 ^{o}C for 2 h. ZnO:Eu and ZnO:Tb thin films are transparent in near ultraviolet and visible region. From luminescence analysis, energy transfer from the ZnO host to the doped Eu^{3+} and Tb^{3+} has occurred. Band gap energy of rare-erath doped ZnO suggest that the absorption edge has moved to the longer wavelength with increasing amount of doping, hence decreasing the optical band gap of films. From the optical properties, lowering of band gaps of the rare-earth doped ZnO has high potential in solar cell applications.

Keywords: Sol-gel; ZnO; rare-earth; thin film; solar cell

INTRODUCTION

ZnO is a II-VI semiconductor with important wide and direct band gap semiconductor of 3.3 eV band gap at room temperature which crystallizes in the hexagonal wurtzite structure [1,2]. Its exceptional luminescent properties in ultraviolet (UV) and visible region have been studied [3]. Beside that, ZnO has a potential as a very attractive host lattice for doping several luminescence centers and show versatile application. ZnO is useful in various technological domains such as transparent electrodes, solar cell, gas sensors, light emitting diodes, active channel in thin films transistor and opto-electronic devices. High quality II-VI semiconductor nanocrystals can also become materials for doping of optically active impurities. Generally, the II-VI semiconductor nanocrystals doped with luminescence centers exhibit efficient luminescence even at room temperature. P. Che *et al.* had reported that the luminescence of ZnO:Eu films was observed due to energy transfer from ZnO host to the Eu^{3+} ion in highly oriented c-axis ZnO films [4]. Moreover, rare-earth complexes have the ability to absorb light at shorter wavelength and emit at a longer wavelength. The high energy region of the solar spectrum which could not be utilized by conventional Si solar cells can be shifted to a longer wavelength region [5].

There are many studies on the fabrication and optical properties of II-VI semiconductor nanocrystals doped with luminescence centers such as transition-metal ions, rare-earth ions and donor-acceptor pairs. Numerous deposition techniques for instance radio-frequency magnetron sputtering [6], spray pyrolysis [7], chemical bath deposition [8], sol-gel process [9], chemical vapor deposition [10] and thermal evaporation [11] were developed and employed to deposit ZnO on various substrates. Among the deposition techniques, sol-gel process has received an increasing attention because of the capability of large area coating and the high degree of film homogeneity without using any complicated instrument. H. Li *et* employed sol-gel processing to ZnO film on silica glass substrates. They used 2-methoxyethanol and monoethanolamine as starting material and stabilizer respectively [12]. H. Zhou *et al* utilized sol-gel method to prepare Al doped ZnO thin film. From their review, dip coating technique were used to prepare thin film where alkali free glass were used as substrates [13].

In the present study, we deposited rare-earth doped ZnO onto glass substrates using sol-gel technique where Eu^{3+} and Tb^{3+} were utilized as dopant. In addition, the optical properties of the thin films in term of luminescence and band gap energy were studied in details.

EXPERIMENTAL DETAILS

Preparation of sols

The sol was prepared using zinc acetate dehydrate (ZnAc), diethanolamine (DEA), and absolute ethanol. DEA was first dissolved in absolute ethanol. Zinc acetate dihydrate was then added under stirring and heated for 1 h at temperature 70 ^{o}C. Europium nitrate pentahydrate was dissolved in ethanol, and then added to the above-mentioned solution. 1 g polyethylene glycol (PEG) was added to the solution. The molar ratios of dopant in the solution, [Eu/Zn] and [Tb/Zn] were varied from 5 % to 15 %. The molar ratio of DEA to ZnAc was maintained at 1.0. The solution was stirred at 70 ^{o}C for 2 h to yield a clear and homogenous solution, which served as the coating solution after cooling to room temperature. The coating was usually made 1 day after the solution was prepared. The procedures were repeated for ZnO:Tb coating solution.

Preparation of films

ZnO:Eu and ZnO:Tb films were prepared by dip-coating using quartz glass substrates (25mm x 25mm). Those substrates were cleaned with soap and distilled water and dried in an oven 100 ^{o}C for 15 min. The glass substrates were dipped into the coating solution and dried at room temperatures for 10 min to evaporate the solvent. The procedures from coating to drying were repeated five times.

Film annealing

As prepared films were heat treated in a furnace (Carbolite Chamber, ELF 11/6B) at 300 ^{o}C to 500 ^{o}C for 2 hours in air to remove the organic residuals. A heat ramp of 15 ^{o}C min^{-1} was used and samples were kept in the furnace and cooled to room temperature. Finally, ZnO:Eu and ZnO:Tb thin films were characterized.

Characterization

The optical properties were investigated using LS 55 Luminescence Spectrometer (Perkin Elmer-LS50B) equipped with a 450 W xenon (Xe) lamp as the excitation source at room temperature. In

addition, band gap energy of films were examined through defuse reflectance ultra violet visible (DR-UV) (Perkin Elmer-Lambda 900) with slit of 2.0 nm and scan speed of 200 nm/min.

RESULT AND DISCUSSION

Optical Properties

Fig. 1 (a) shows the excitation spectrum of ZnO:Eu thin films annealed at 500 ^{o}C with different concentration of doped ions (5 %, 10 % and 15 %) where the detection wavelength was 610 nm, corresponding to the $^{5}D_{0}\rightarrow{}^{7}D_{0}$ transition of Eu^{3+} ions. Only one pronounced peak at 445 nm, which is related to the $^{5}F_{0}\rightarrow{}^{7}D_{2}$ transition of Eu^{3+} ions was observed. Fig. 1 (b) shows the emission spectra of ZnO:Eu thin films with different concentration of dopants, excited by the 445 nm light. The result showed multi-peak fitting of the emission spectrum for the thin films annealed at 500^{o}C. It is possible to distinguish two emission bands centering at 590 nm and 612 nm corresponding to the transitions of
$^{5}D_{0}\rightarrow{}^{7}F_{j}$ (J = 1, and 2) respectively. In addition, both of the excitation and emission intensities increase with increased concentration of Eu^{3+} ions. This result indicates energy transferring from ZnO host to Eu^{3+} has occurred [14].

Excitation spectrum of ZnO:Tb thin films annealed at 500 ^{o}C with different concentration of doped ions (5 %, 10 % and 15 %) is shown in Fig. 2 (a) with excitation peaks at 335 nm and 393 nm respectively. The excitation spectrum showed an intense peak at 335 nm. Fig. 2 (b) shows the emission spectrum for ZnO: Tb thin films. Two emission peaks were observed at 454 nm and 514 nm correspond to the transition of Tb^{3+} from $^{5}D_{4}$ to $^{7}F_{J}$
(J = 3 and 4) and the strongest peak transition appear at 514 nm same as repeated elsewhere [15]. Furthermore, the excitation and emission intensity increase with increased concentration of Tb^{3+} ions. Excitation into the ZnO band gap at 335 nm, the $^{5}D_{4}\rightarrow{}^{7}F_{4}$ transition can also be observed for ZnO:Eu thin films. The result indicates energy transferring from ZnO host to Tb^{3+} has occurred.
From the PL spectra obtained rare-earth complexes had potential to absorb light at shorter wavelength and emit at longer wavelength. The high energy region of the solar spectrum is shifted to longer wavelength because the emitted light matches with higher sensitivity region of the basic Si solar cell [16].

Determination of thin films band gap

The band gap, E_g values were calculated using UV-Vis spectra from the following equation [17]:

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

Where α is the absorption coefficient, hν is the photon energy and m=1 for a direct transition between bands. The wavelength of absorption edges was determined by extrapolation of the linear part to part to the x-axis [18]. From Fig. 3(a) to 3(c) the band gap is calculated by extrapolating a straight line to the abscissa axis. When α is zero, then

$E_g = h\nu$. The values calculated from this equation are shown in Table 1.

From the UV-Vis spectra obtained, band gap energy of undoped ZnO is a 3.3eV which is consistent with corresponding literature. Band gap energy of rare-earth doped ZnO showed the absorption edges moved to the longer wavelength with increasing amount of doping, consequently decreasing the optical band gap of films. The blue shift of the absorption edges with increasing of Eu^{3+} and Tb^{3+} content is mainly attributed to the Burstein-Moss effect resulting from increasing of carrier concentration [19]. Thus, the trace doping of rare-earth ions (Eu^{3+} and Tb^{3+}) gives a significant effect on the band structure of host semiconductor oxides. From the result described above, it can be concluded that rare-earth ions are good dopant for the fabrication of doped ZnO for solar cell application. Rare-earth doped ZnO thin films could be considered as a solar cell material in spite of the large gap compared to the band gap of the conventional Si solar cell. Theoretically, a gap at least 3.5 eV is needed for thin films in most anticipated optoelectronic application and the films prepared in this study have achieved this requirement [20].

Visible transmittance

The results of transmittance test in Fig. 4 that all the undoped ZnO and rare-earth doped ZnO thin films were transparent in visible spectra region approximately between 60 to 85%. The transmittance of doped ZnO films was higher than that of the undoped films. In addition, the transmittance of the doped film with 5 % molar for Eu^{3+} and Tb^{3+} was higher than 80% for wavelength over than 400nm, and these are higher than the doped films with 15% and 10% molar doping. This is owed to the fact that the film with 5% molar doping contain more voids compare to the films with 10% and 15% molar doping, due to optical scattering may lead to decrease.

CONCLUSION

Rare-earth doped ZnO were successfully deposited onto glass substrates using sol-gel process. Band gap of bulk ZnO could be improved by adding some impurities or doping. In this study, rare-earth ions of Eu^{3+} and Tb^{3+} results in reducing the band gap energy of films significantly. Energy transfer from ZnO host to Eu^{3+} and Tb^{3+} and the complexes have the ability to absorb light at shorter wavelength and emit at longer wavelength. The results of the present work suggest that the properties of rare-earth doped ZnO films have high potential in solar cell applications.

ACKNOWLEDGEMENTS

The authors would like to thanks the Research Management Center (RMC) of Universiti Teknologi Malaysia (UTM) and Ministry of Science, Technology and Innovation, MOSTI with VOT No. 79078 for financial supports.

REFERENCES

[1] D.C. Look, Mater. Sci. Eng. B 80 (2001) 383.

[2] D.C. Reynolds, D.C. Look, B. Jogai, C.W. Litton, G. Cantwell, W.C. Harsch, Phys. Rev. B 60 (1999) 2340.

[3] Ishizumi, I., Taguchi, Y., Yamamato, A. and Kanemitsu, Y. 486 (2005) 50-52.

[4] Chen, P., Ma, X. and Yang, D. J. of Alloys and Compounds. 431 (2007) 317-320.

[5] E. Fortunato, A. Goncalves, A. Marques, A. Viana, H. Aguas, L. Pereira, I. Ferreira, P. Vilarinha, R. Martins, Surf. Coat. Technol. 180 (2004) 20.

[6] N.Y Shishkin, L.M Zharsky, L.G. Lugin and V.G. Zarafin, Thin Solid Films, 48 (1998) 403-408.

[8] N. Oleynik and M. Adam, Journal of Crystal Growth, 248 (2003) 14-19.

[9] Z. Hong-ming, Y. Dan-qing, Yu-Zhi-ming, X. Lai-rong and L. Jian, Thin Solid Films, 515 (2007) 6909-6914.

[10] N.K Zayer, R. Greef, K. Rogers, A.J.C Grellier and C.N Pannell, Thin Solid Films, 353, (1999) 179-184.

[11] S. Sandhu, T. Sen and A. Patra, Chemical Physic Letter, 440 (2007)121-124.

[12] Li, H., Wang, J., Liu, H., Yang, C., Xu, H., Li, X. and Cui, H.. Vacuum. **77** (2004) 57-62.

[13] Zhou, H.M., Yi, D., Yu, Z., Xiao, L. and Li, J. Thin Solid Films. 515 (2007) 6909-6914.

[14] P.Che, J.Meng and L.Guo, Journal of Luminescence, 122-123 (2006) 168-171.

[15] J. Zhang, H. Feng, W. Hoa and T. Wang, Materials Science and Engineering, 425, (2006) 346-348.

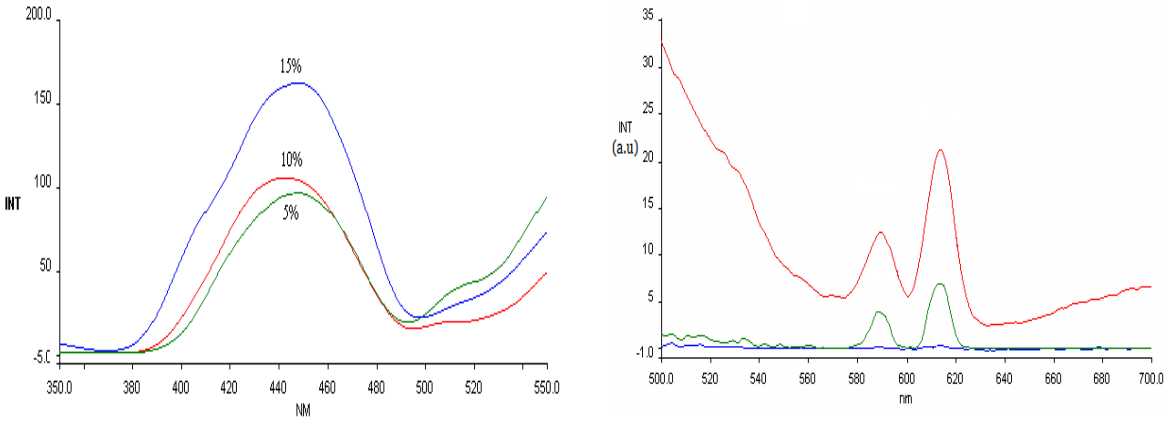
[16] K. Kawano, K. Arai, H. Yamada, N. Hashimoto and R. Nakata, Solar Energy Mater. & Solar Cells, 48 (1997) 35-41.

[17] M. Girtan, G. Folcher, Surf. Coat. Technol. 172 (2003) 242-250.

[18] E. Sanchez and T. Lopez, Matt. Lett. 25 (1995) 271-275.

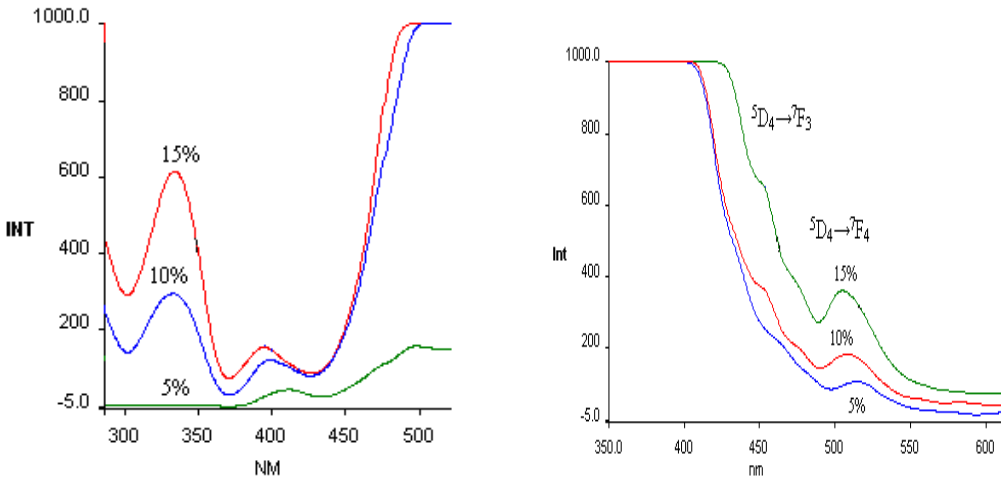
[19] N.Wang, X. Li, Y. Wang, Y. Hou, X. Zou and G. Chen, Matt. Lett. 62 (2008) 3691-3693.

[20] T. Minami, T. Yamamoto and T. Miyata, Thin Solid Films, 366 (2000) 63-68.



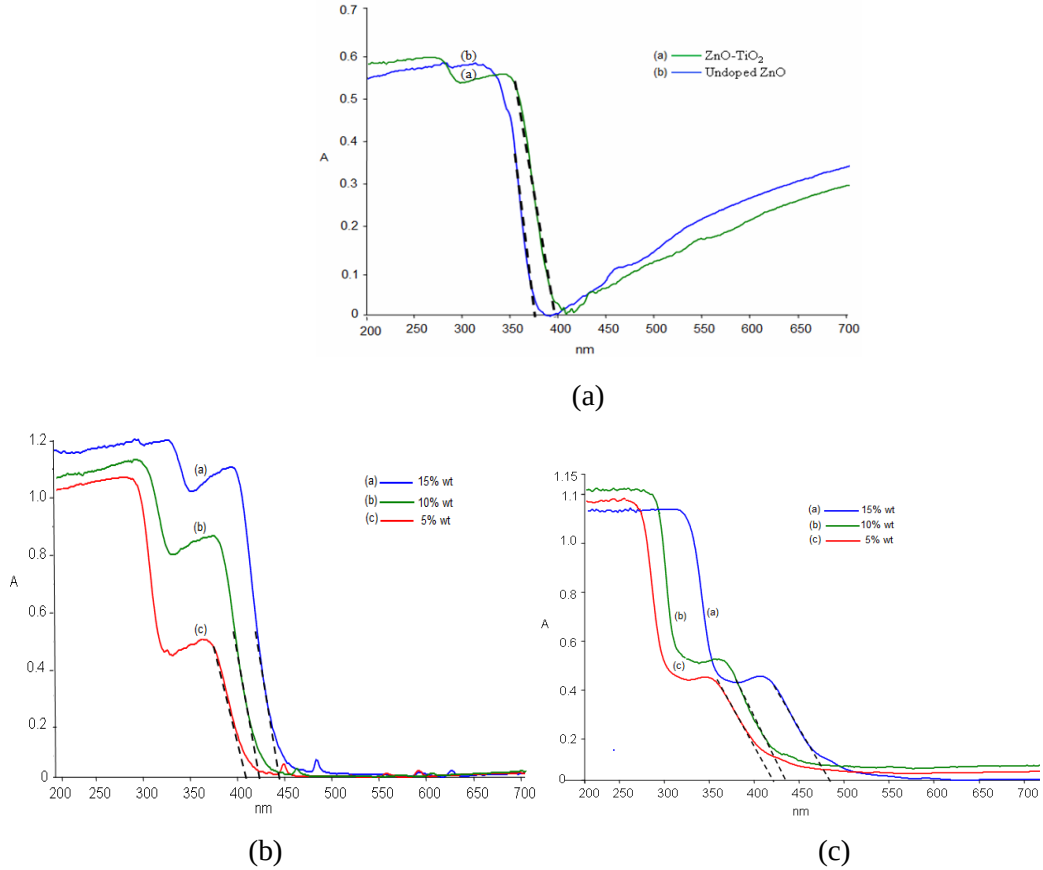
(a) (b)

Fig. 1: Excitation (a) and emission (b) spectra of ZnO:Eu thin films annealed at 500^{o}C with different concentration of doped ions (5%, 10% and 15% at wt).



(a) (b)

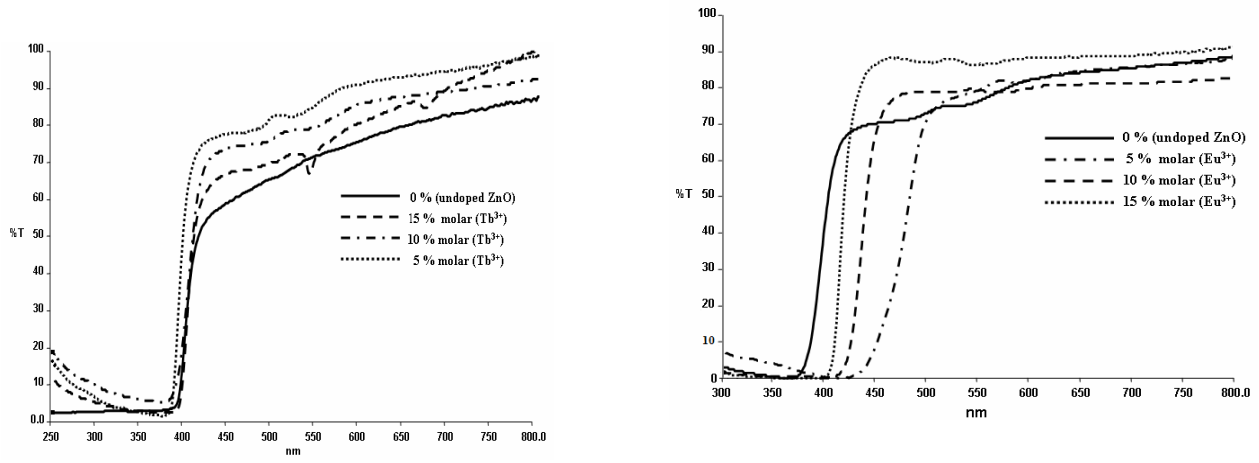
Fig. 2: Excitation (a) and emission (b) spectra of ZnO:Tb thin films annealed at 500°C with different concentration of doped ions (5%, 10% and 15% at wt)



(a)

(b) (c)

Fig. 3**:** UV-Vis spectra of ZnO-TiO2 and undoped ZnO (a), ZnO:Eu (b) and ZnO:Tb (c)



(a) (b)

Fig. 4: Optical transmittance spectra of ZnO:Eu (a) and ZnO:Tb (b) thin films at 500°C with different doping concentration.

Table 1

Band gap (E_g) values for the undoped ZnO, ZnO-TiO_2 and rare-earth doped ZnO thin films.

Films	λ (nm)	E_g (eV)
Undoped ZnO	375	3.30
ZnO-TiO_2	400	3.10
Europium doped ZnO		
5 % at wt	410	3.03
10% at wt	428	2.89
15% at wt	443	2.80
Terbium doped ZnO		
5 % at wt	425	2.92
10% at wt	435	2.85
15% at wt	480	2.58