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Investigation of Optical Properties of ZnO Thin Films Prepared by Sol-gel Method

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Abstract

Through this study, ZnO thin films have been deposited on a clear glass substrate by sol-gel method with and without polyethylene glycol (PEG) content and also optical properties of the deposited films have been investigated. Using PEG, with zinc acetate precursor, has enhanced the chance to obtain the porous structure of ZnO films. After annealing the films at 550^0C for 2h, optical transmittance measurements have been carried out with UV/Visible spectrometer at 200-900 wavelengths. The film are highly transparent in the visible range and the average transparency with and without PEG contented ZnO films, beyond 400nm wavelength, has been found to be of 93% and 90% respectively. A blue shift in both direct and indirect allowed band gap has been found with the addition of PEG. The direct and indirect allowed band gap of ZnO films with PEG content has been found to be of 3.24 eV and 3.14 eV respectively.

Keywords: *sol-gel, PEG content, optical properties, band gap.*

1. Introduction

Owing to the drastic developments in the fields of nanoscale science from the last few decades, study of one-dimensional (1D) materials has become one of the most interesting fields of scientific research, leading to the worldwide popularity of semiconductor nanocrystals because of their special properties in comparison with those of bulk materials [1]. In particular, Zinc oxide (ZnO) is an inexpensive n-type semiconductor which crystallizes in hexagonal Wurtzite structure (c=5.025 and a=3.249) [2]. ZnO is also a member of transparent conductive oxides (TCO) and has become one of the best options as transparent conductive electrodes for dye-sensitized solar cells due to high chemical stability, a textured surface, high conductivity and high transparency in the visible range. It is widely used for manufacturing of LEDs, OLEDs, liquid crystal displays, flat panel displays, piezoelectric transducers, surface acoustic devices, varistors, spin functional devices and UV-light emitters [3]. For photonic applications in the UV or blue spectral range [4], ZnO is the most promising material due to its wide band gap energy (3.37 eV) [5] and high exciton-binding energy (60 meV) [6] allows efficient excitonic emission even at room temperature. Moreover, ZnO technologically exhibits outstanding antimicrobial properties and exceptional UV attenuation characteristics: blocking 95% of all UV radiation that can be utilized in cosmetics, paints, varnishes, plastics and so on [7]. Last but not least, ZnO has tunable morphologies such as nanocrystals, nanowires, nanorods and nanolipsticks, nanotubes that causes to increase surface-to-volume ratio and has potential application in UV lasers, detectors, gas sensors and dye-sensitized solar cell [5][8].

ZnO thin films have been prepared by various deposition techniques, such as RF magnetron sputtering [9], spray pyrolysis [10], pulsed laser deposition [11], chemical vapor deposition [12], molecular beam epitaxy [13] and sol-gel process [14-15]. Sol-gel method is widely used for ZnO thin films fabrication over other methods for some advantages, e.g. its ability to prepare high quality of films of difficult shapes in large scale, simplicity, safety, low cost of the apparatus and raw materials [16-17]. The optical and structural properties of sol-gel derived ZnO thin films depend critically on several parameters such as annealing temperature, deposition technique, withdrawing rate, drying process, presence of polyethylene glycol (PEG) content and so on[5-6].

It has been reported that, in order to obtain high photon-to-current conversion efficiency of dye-sensitized solar cells, surface of ZnO photoanode should be porous in nature that has been accomplished by using PEG as surface modifier [5]. The present paper reports on preparation of ZnO thin films on glass substrate through conventional sol-gel method with different PEG content. The optical properties of the resulting films have been investigated and band gap energy has been determined.

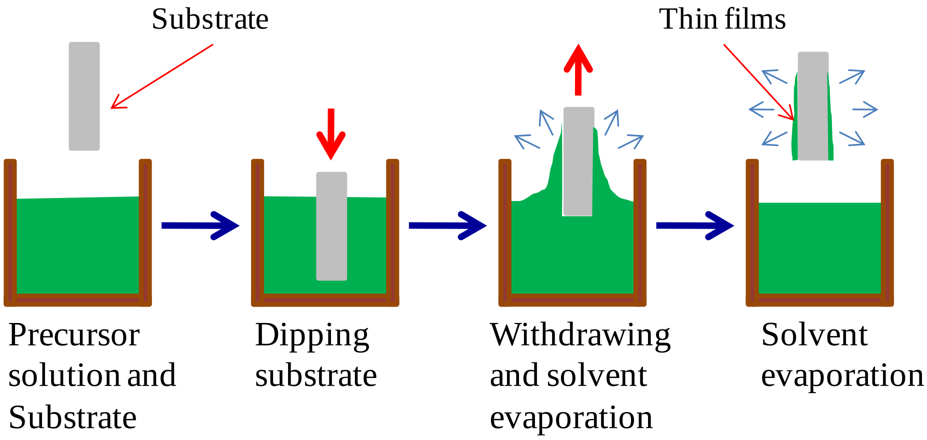

Fig.1. Different stages of sol-gel dip coating process

2. Fundamentals of Sol-gel dip coating

Sol-gel is a very well known wet chemical process, from which dense film, xerogel, areogel and ceramic fibers can be derived by using dip coating, gelling, precipitating and spinning method respectively. A sol is generally known as the molecular suspension of solid particles of ions in a solvent. When the solvent from sol begins to evaporate, ions left behind begin to join in a continuous network which is known as gel.

Fig. 1 shows the various stages of sol-gel dip coating method. At first a metal alkoxide solution, known as precursor solution, is prepared to yield sol and a substrate is cleaned on which films have to be deposited. At the second stage substrate is made to go through the solution at a suitable rate and after complete dipping is left in the solution for a while. Substrate withdrawing from the solution is the most critical point of dip coating process. In order to get uniform thickness of the films, substrate must be withdrawn vertically at a constant rate. While withdrawing, solvent from the surface of the film is evaporated and as well as draining occurs. Withdrawing rate affects the quantity of solid particles or ions left on the substrate that in turn affects the thickness. Generally, higher withdrawing rate produces milky films with increased thickness than lower rate.

2. Experimental Section

Chemical Reagents

ZnO precursor solution was prepared using absolute ethanol (M=46.07, CH_3CH_2OH, EtOH) as solvent, zinc acetate di-hydrate (M=219.50, $Zn(CH_3COO)_2.2H_2O$, ZAD) as precursor, diethanolamine (M=105.14, $[CH_2(OH)CH_2]_2.NH$, DEA) as chelating agent, polyethylene glycol (M_{av}=2000, $H(OCH_2CH_2)_nOH$, PEG) as organic template and de-ionized water.

Preparation of ZnO thin films

ZnO thin films were prepared by using conventional sol-gel dip coating method according to reference [6]. At first, in 20ml of absolute ethanol 4.39g of zinc acetate was dissolved to yield a concentration of 1.0 mol/L. The solution was then stirred thoroughly on a magnetic stirrer for 30 min and a milky solution was obtained. Then 1.93ml of DEA and 0.72ml of de-ionized water was added into the emulsion, adjusting the molar ratio of DEA/ZAD as 1:1 and that of de-ionized water/ZAD as 2:1, followed by further stirring for 20 min. Meanwhile, the emulsion became clear. Finally, PEG of 1.0g and 0.75g was separately added into above prepared sol and was continuously stirred for 2h until a transparent sol was obtained. Glass micro-slides were used as substrate for deposition of ZnO films. The substrates were cleaned ultrasonically, first in ethanol and subsequently in ion exchanged distilled water for 15 min each at 50^0C. Then using conventional dip-coating method prepared transparent sol was coated on clear glass substrate. The dipping and withdrawing rate was about 1cm/min. The coated films were kept at room temperature and after that were dried at 350^0C for 30 min each. The process above was repeated for three times and after giving the final coating, the films were kept at room temperature for 24h. Finally, the obtained as-deposited films were annealed at 550^0C at a heating rate of 20^0C/min and left at

550^{0}C for 2h.The optical properties of the deposited films were measured by UV/Visible spectrometer at 200-900 nm wavelengths using reference substrate. From transmittance spectra absorbance was determined using Beer-Lambert Law and optical band gap was found using Tauc relationship.

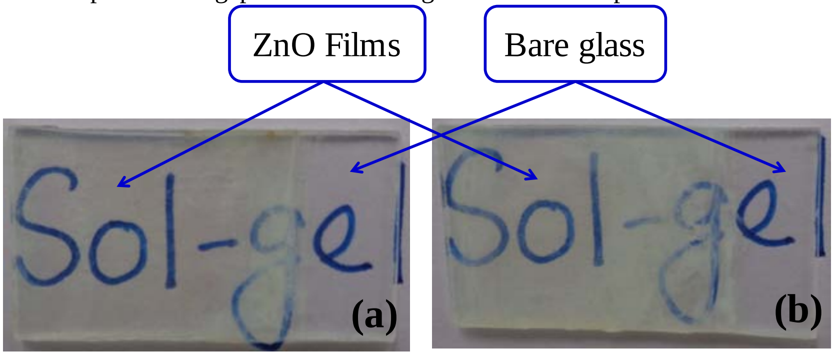

Fig. 2. Images of ZnO thin films on glass substrate with (a) with PEG, and (b) without PEG.

3. Results and discussion

Fig.2(a) and **Fig.2(b)** shows the images of ZnO thin films on glass substrate with and without PEG content respectively. It is clearly seen that, the prepared films are visually transparent. It is also to be noted that PEG-aided ZnO films are more transparent than without PEG, this may due to the fact that the generated colloidal dispersion was very stable as PEG has been added with the metal oxide solution. Measured optical properties of the films also agree with this.

Fig.3 shows the optical transmittance of ZnO thin films with and without PEG content in the wavelength (λ) range 300-900 nm. It can be observed that the films are highly transparent in the visible range of the electromagnetic spectrum with an average transmittance values up to 93% beyond the wavelength of 400 nm for PEG-aided ZnO films and presents sharp ultraviolet cutoff at approximately 370 nm. On the other hand, ZnO films without PEG content shows UV cutoff at about 360 nm with average transmittance of 90% beyond 400 nm. Transmittance for both with and without PEG ZnO films reaches to maximum value at higher wavelength. Below the wavelength of 550 nm transmittance of PEG contented ZnO films is lower than that of ZnO films without PEG. This may due to increase of interface scattering. It has been reported that use of PEG produces ZnO films porous and microring like structure and with smaller grain size [5]. Interface scattering is increased due to porous structure [18].

Fig. 4 shows the absorption spectrum of sol-gel derived ZnO films with and without PEG content. It is clearly observed that both films have a very low absorption at transparent region and high absorption at ultraviolet region. It is to be noted that, absorption at UV-region for PEG contented ZnO films is higher to that of ZnO films without PEG content. The reason is that PEG inclusion results ZnO films with smaller grain size and hence surface to volume ratio has been increased. Again ZnO films without PEG may have a smaller thickness. Due to high transparency at visible range and high absorption at UV-region, ZnO films with PEG content have the potentiality to be applicable for optical window application and UV detectors.

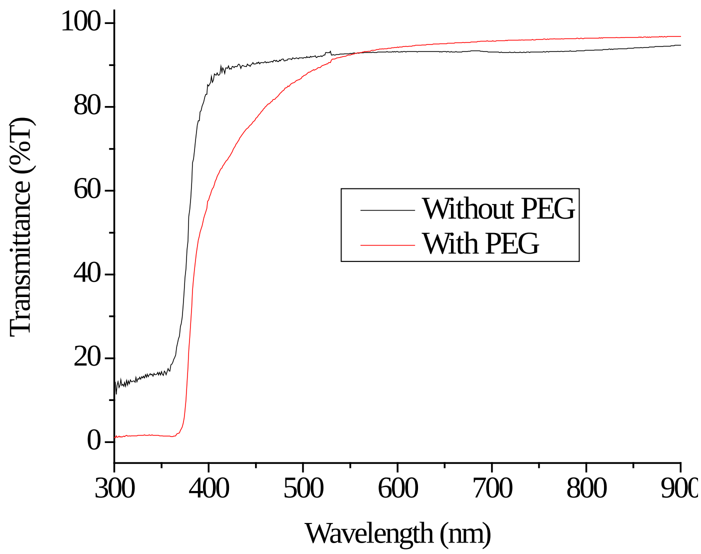

Fig. 3. Optical transmittance ZnO thin films

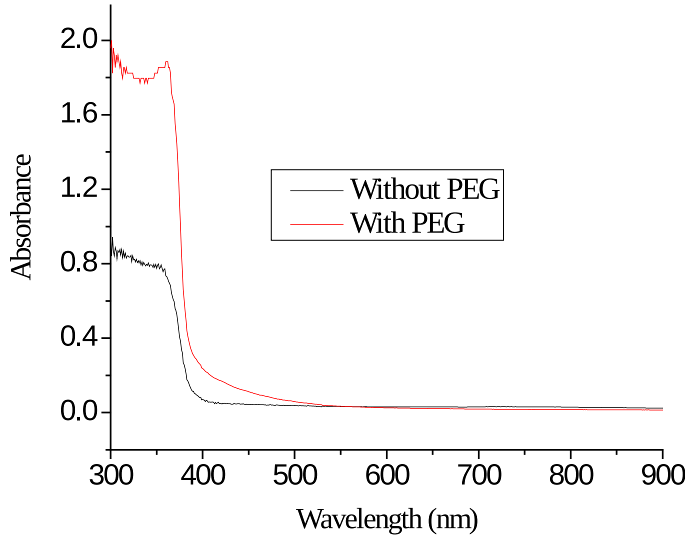

Fig. 4. Optical absorbance of ZnO thin films

The direct and indirect allowed optical transitions between valance and conduction bands can be evaluated by fitting a straight line in strong absorption spectral region using the Tauc relationship. According to Tauc law dependence of absorption co-efficient (α) on photon energy (hν) can be given by [19]

$$(\alpha h\nu) = A(h\nu - Eg)^{r} \quad (1)$$

Where α is the absorption co-efficient, A is the edge width parameter, and hν is the photon energy, and r is a constant, for direct allowed transition r equals ½ and for indirect allowed transition equals 2.
Fig. 5 shows the plot of $(\alpha h\nu)^2$ vs. hν of prepared ZnO films grown with and without PEG content. The optical band gap for direct allowed transition of the films have been determined from the extrapolation of the linear portion of $(\alpha h\nu)^2$ vs. hν at α= 0. Direct transition band gap is found to be of 3.03eV for without PEG that has been shifted to UV-region with a value of 3.24 eV when PEG has been added. Although this value is smaller than the bulk value of 3.37 eV but still it is in good agreement with previously reported data of ZnO thin films [20].

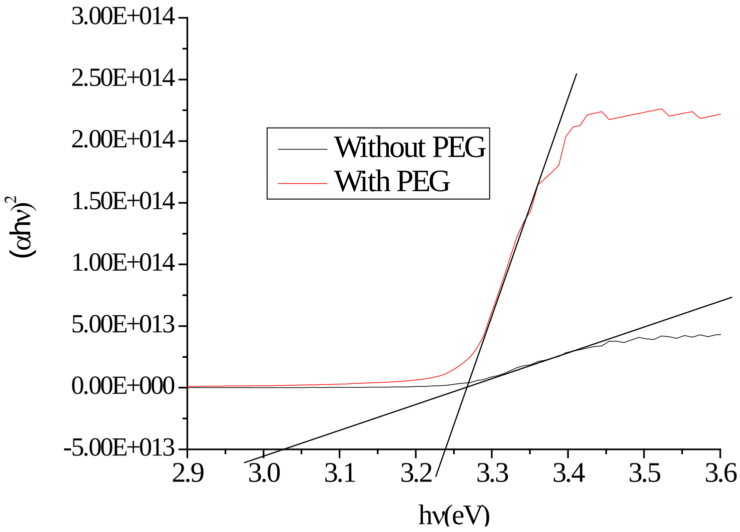

Fig. 5. Plot of $(\alpha h\nu)^2$ vs. hν of ZnO thin films.

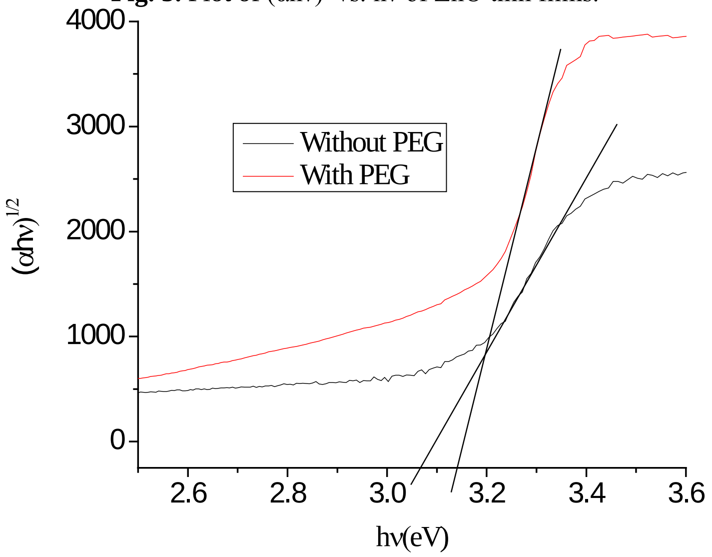

Fig. 6. Plot of $(\alpha h\nu)^{1/2}$ vs. hν of ZnO thin films.

Fig. 6 shows the plot of $(\alpha h\nu)^{1/2}$ vs. hν and band gap for indirect allowed transition has been determined by extrapolating the straight line portion of the spectrum at α= 0. Here blue shift in the band gap has also been seen but smaller with compared to direct transition. Indirect band gap for ZnO films without and witho PEG has been found to be of 3.07 eV and 3.14 eV respectively that are greater than the previously reported indirect band gap of ZnO [21].

4. Conclusion

ZnO thin films were successfully prepared on glass substrate, with PEG as organic template, by simple and effective sol-gel dip coating technique using zinc acetate as precursor. In order to obtain crystal structure of ZnO, as-deposited films were calcined at 550^0C for 2h. The results have revealed that, ZnO thin films with PEG content show better optical performance than ZnO thin films without PEG content. It was found that, both direct and indirect band gap for ZnO films with PEG content was higher and was of 3.25 eV and 3.16 eV respectively. Higher transmittance in the visible region and higher absorption in the UV-region has made the films potentially able for the application as transparent conductive oxide (TCO).

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11. References

[1] Z.L. Wang, "Zinc oxide nanostructures: growth, properties and applications", *J. Phys.: Condens. Matte.*, vol.16, pp. 829-858, 2004.

[2] C.Y. Tsay1, M.C. Wang, and S.C. Chiang, "Effects of Mg Additions on Microstructure and Optical Properties of Sol-Gel Derived ZnO Thin Films", *Materials Transactions*, Vol.49, No.5, pp. 1186-1191, 2008.

[3] F.K. Shan, B.I. Kim, G.X. Liu, Z.F. Liu, J.Y. Sohn, W.J. Lee, B.C. Shin and Y.S. Yu, "Blueshift of Near Band Edge Emission in Mg Doped ZnO Thin Films and Aging," *Journal of Applied Physics*, Vol.95, No.9, pp. 4772-4776**,** 2004.

[4] A.B. Djurisˇic´ and Y.H. Leung, " Optical Properties of ZnO Nanostructures", *small,* vol.2, No. 8-9, 944 – 961, 2006.

[5] M.F. Hossain, S. Biswas, M. Shahjahan, and T. Takahashi, "Study of sol-gel derived porous ZnO photoelectrode for the application of dye –sensitized solar cells," *J. Vac. Sci. Technol. A*, vol.27, No.4, pp.1047-1051, 2009.

[6] M.F. Hossain, Z.H. Zhang and T. Takahashi, "Novel micro-ring structured ZnO photoelectrode for dye-sensitized solar cell," *Nano-Micro Lett*., vol.2, pp. 53-55, 2010.

[7] D.S. Carr, B. Baum, "Zinc Oxide/Synegist systems provide improved UV control", *Modern Plastics,* pp. 64-68, 1981.

[8] M.F. Hossain, T. Takahashi, S. Biswas, "Nanorods and nanolipsticks structured ZnO photoelectrode for dye-sensitized solar cells", *Electrochemistry Communications*, vol. 11, pp. 1756-1759, 2009

[9] Y.R. Park, D. Jung, K.C. Kim, S.J. Suh, T.S. Park and Y.S. Kim, "Physical Properties of Transparent Conducting Indium Doped Zinc Oxide Thin Films Deposited by Pulsed DC Magnetron Sputtering," *Journal of Electroce- ramics*, Vol.23, No.2-4, pp. 536-541, 2009.

[10] S. Ilican, Y. Caglar, M. Caglar and B. Demerci, "Poly- Crystalline Indium-Doped ZnO Thin Films: Preparation and Characterization," *Journal of Optoelectronics and Advanced Materials*, Vol.10, No.10, pp. 2592- 2598, 2008.

[11] N. Naghavi, A. Rougier, C. Marcel, C. Gueary, J.B. Leriche and J.M. Tarascon, "Characterization of Indium Zinc Oxide Thin Films Prepared by Pulsed Laser Deposition Using a $Zn_3In_2O_6$ Target," *Thin Solid Films*, Vol.360, No.1-2, pp. 233-240, 2000.

[12] J.H. Lee and B.O. Park, "Transparent Conducting ZnO:Al, In and Sn Thin Films Deposited by the Sol-Gel Method," *Thin Solid Films*, Vol.426, No.1-2, pp. 94-99, 2003.

[13] A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda and Y. Segawa, "Mg_xZn_{1-x} O as a II-VI Widegap Semiconductor Alloy," *Applied Physics Letters*, Vol.72, No.19, pp. 2466-2468, 1998.

[14] M. Rezaee, R. Abadi, M. Behdani, H. Arabshahi and N. Hosseini, "Indium-Doped Zinc Oxide Thin Films by Sol- Gel Method," *International Review of Physics*, Vol.3, No.4, pp. 219-223, 2009.

[15] E. J. L. Arredondo, A. Maldonado, R. Asomoza, D.R. Acosta, M.A.M. Lira and M. de la L. Olvera, "In- dium-Doped ZnO Thin Films Deposited by the Sol-Gel Technique," *Thin Solid Films*, Vol.490, No.2, pp. 132-136, 2005.

[16] F.E. Ghodsi and H. Absalan, "Comparative Study of ZnO Thin Films Prepared", *Acta Physica Polonica A*, Vol.118, No.4, pp. 659-664, 2010.

[17] A.J. Hurd and C.J. Brinker, "Optical sol-gel coatings : ellipsometry of film formation", *J. Phys. France*, Vol.49, pp. 1017-1025, 1988.

[18] C.X. Xu, G.P. Zhu, X. Li, Y. Yang, S.T. Tan, X.W. Sun, C. Lincoln and T.A. Smith, "Growth and Spectral Analysis of ZnO Nanotubes," *Journal of Applied Physics*, Vol.103, No.9, 2008.

[19] Z. Liu, J. Li, J. Ya, Y. Xin, and Z. Jin, "Mechanism and characteristics of porous ZnO films by sol-gel method with PEG template". *Materials Letters*, Vol.62, pp. 1190-1193, 2008.

[20] N. Shakti, P.S. Gupta, "Structural and Optical Properties of Sol-gel Prepared ZnO Thin Film", *Applied Physics Research*, Vol.2, No.1, pp. 19-28, 2010.

[21] W.R. Saleh, N.M. Saeed, W.A. Twej, M. Alwan, " Synthesis sol-gel derived highly transparent ZnO thin films for optoelectronic applications", *Advances in Materials Physics and Chemistry*, vol.2, pp. 11-16, 2012.