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SEM/EDX, UV-Vis-NIR spectroscopy and refractive index studies of zinc oxide thin films

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We used sol-gel via spin-coating technique to prepare zinc oxide (ZnO) thin films on glass substrates under three different conditions. SEM/EDX and UV-Vis-NIR spectroscopy characterizations were used to analyze the as-grown samples. The surface of all the films is homogeneous, has regular elongated grains and the thin films prepared consist of zinc and oxygen elements. In the wavelength region 200-800 nm, all the samples show high transparency (> 90%). The optical band gap values of the three corresponding ZnO layers were 3.2884, 3.3322 and 3.2985 eV respectively at 0.55 M, 0.75 M and 0.95 M conditions and the refractive index values are ranging from 1.982 to 2.009. These properties obtained of the ZnO thin films prepared were examined depending on the precursor concentration conditions and are attractive for use in photovoltaic applications as a buffer layer in copper indium gallium di-selenide ($Cu(In,Ga)Se_2$) solar cells.

Keywords: Spin-coating, ZnO, Band gap, Refractive index.

Introduction

In today's world, nanomaterials research has received much attention in the scientific community because of their interesting properties and applications in new electronic and optoelectronic devices [1, 2]. Most of the applications are due to the fact that matter at the nanometer scale has different properties as compared with the bulk state [2, 3]. For this reason, many research groups around the world are trying new synthesis methods of different materials at the nanoscale [4-11]. One of the most interesting and fascinating scientific research materials is zinc oxide (ZnO) due to its unique properties and applications [5, 8]. Some of zinc oxide properties are its wide direct band-gap energy (E_g) of 3.37 eV [5], large exciton binding energy (60 meV) [6], which is much larger than that of the commercial LED (light emitting diode) material GaN (25 meV), abundance and low toxicity, excellent chemical and thermal stability [4-6]. These properties make it the suitable candidate for many technological applications in transparent conducting electrodes (TCOs), UV-LEDs, catalysis and devices based on piezoelectricity, pigment in paints with ultraviolet (UV)-protective, solar cells, gas sensors [5-10]. From readings, preparation conditions, properties and devices of thin films ZnO doped and undoped have been reported [3-13]. Many deposition techniques such as spray pyrolysis [7], hydrothermal process [8], pulsed filtered cathodic vacuum arc deposition [9], sol-gel process [10, 11], plasma-assisted molecular beam epitaxy (MBE) [12], etc. have been used to produce ZnO. Among them, some are expensive growth techniques (MBE, etc...) but the sol-gel process on the other hand is a widely used technique for laboratory research activities to produce zinc oxide thin films because of relatively cheap equipment and simplified fabrication route, low temperature processing, controllability, good uniformity over wide area on large size substrates [10, 11].

Up to date, efforts have been made to study ZnO materials, doped and undoped fabrication processing, properties and applications [1-13]. As the field becomes more sophisticated, many challenges associated with this material remain, and others are to develop new approaches to make high performance ZnO materials. Therefore, research into ZnO materials still continues [1-13] and problem area exists consisting in the lack of stable and reproducible p-type conductivity since for

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LED applications both n- and p-type ZnO are necessary, the cristalline quality of ZnO which varies from one laboratory to another [7-10], etc.

To the best of our knowledge, ZnO has been widely studied in research laboratory and industries but the ideal synthesized ZnO material is missing. Furthermore, properties can vary widely with deposition conditions. Therefore, the development of ZnO films with improved properties and the cost-effective large-scale production are key challenges in the field of production in photovoltaics. In this work, spin-coating technique has been used as an alternative synthesis route for the preparation of three kinds of ZnO layers with good cristalline which could be attractive for use in photovoltaic applications as a buffer layer in copper indium gallium di-selenide ($Cu(In,Ga)Se_2$) solar cells.

Experimental procedure

As a starting material, zinc acetate 2-hydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ (Merck) was dissolved at room temperature in a mixture of ethanol and monoethanolamine (MEA, $H_2NC_2H_4OH$) yielding to three precursor concentrations respectively of 0.55 M, 0.75 M and 0.95 M. The molar ratio of MEA to zinc acetate 2-hydrate was kept at 1. Before deposition the glass substrates were cleaned with detergent solution, diluted HCl and deionized water. Further, ultrasonic cleaning was carried out for 30 min in an ultrasonic bath and then rinsed in acetone for 10 min.

The coating solutions were then spin-coated on glass substrates at room temperature with a rate of 3000 rpm for 30sec. After each layer deposition, the gel layers were heat-treated at 300 °C for 10 min to evaporate the solvent and remove organic residuals. All the samples were subsequently annealed at 550 °C for 2 hrs. Finally three kinds of samples denoted $S_{0.55M}$, $S_{0.75M}$ and $S_{0.95M}$ were fabricated.

Different analytical techniques were employed to characterize the ZnO thin films prepared. The surface morphology of the grown thin films was analyzed using scanning electron microscopy (SEM, JSM- 6490LV) and their elemental composition was evaluated by energy dispersive X-ray (EDX) analysis. The optical properties were investigated by Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) transmittance in the wavelength range of 350-2500 nm which were measured using a Perkin Elmer Scan-Lambda 750 spectrophotometer. All measurements were carried out at room temperature.

Results and Discussion

Figs. 1(a-b) show the SEM images of the as-prepared products synthesized at three different precursor concentrations respectively of 0.55 M, 0.75 M and 0.95 M. The obtained SEM images reveal that all the ZnO thin films consist of nanoparticles. Homogeneous

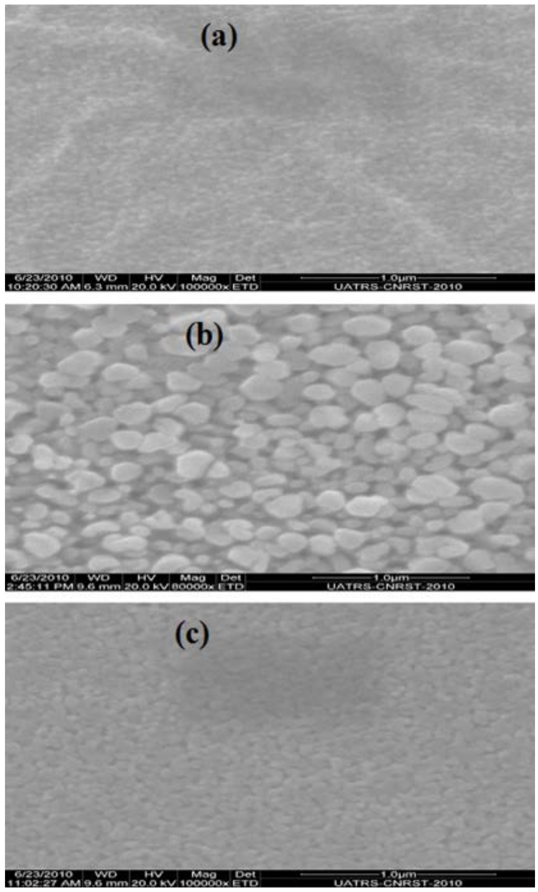

Fig. 1. SEM micrographs of thin films at different concentrations (a) 0.55 M, (b) 0.75 M and (c) 0.95 M.

surface, regular elongated grains and hexagonal grains were observed in all the samples. The different degrees of brightness of the grains indicate the presence of multiple layers of ZnO on the substrates. The brighter grains represent the upper layer of the thin films and the darker grains represent the lower layer of the thin films [6, 10].

In order to check for chemical composition, EDX measurements were performed. The EDX spectra presented in Figs. 2(a-c) confirm that the products are composed of both peak zinc (Zn) and peak oxygen (O) [10, 11] with other signals like Mg, Al, Si and Ca appeared due to the glass substrates [9]. The EDX / SEM results show that the different concentrations used in the preparation of ZnO solution strongly affect the surface of the ZnO thin films.

The UV-Vis-NIR transmission and absorbance spectra of the prepared zinc oxide thin films at three different concentrations are presented in Figs. 3(a-c). We can clearly observe that the ZnO thin films absorb the light of the wavelength less than 400 nm. This absorption occurred mainly in the UV region. From the transmission spectra, it is observed that the ZnO films were transparent and exhibited significant diffuse scattering of light. An exception was observed with ZnO sample fabricated in the precursor concentration

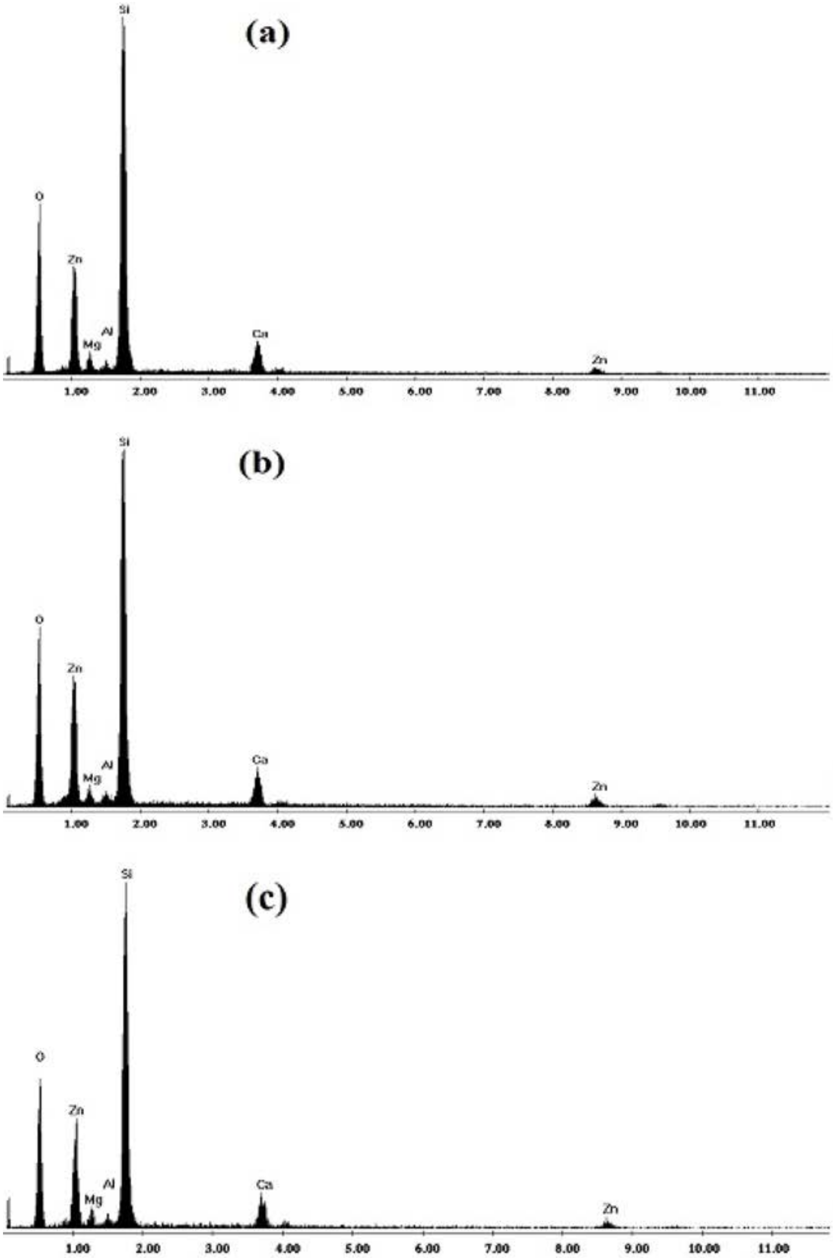

Fig. 2. EDX analysis of ZnO samples at (a) 0.55 M, (b) 0.75 M and (c) 0.95 M conditions.

with 0.75 M condition which was transparent significantly. The average transmittance in the visible range (400-800 nm) reached T = 95%, and the transparency of the samples grown depended on Zn^{2+} precursor condition. Also we can observe an absorption edge around 370 nm which indicates that all the samples are able to absorb ultra violet light [14, 15].

ZnO crystal is a direct semiconductor and its absorption coefficient (α) and incident photon energy (hυ) can be written as [16]:

$$(\alpha h\upsilon)=A(h\upsilon-E_g)^{\frac{1}{2}} \quad (1)$$

Where A is the optical absorption coefficient for direct transition [16], h is the Planck's constant, υ is the frequency of the photon and E_g is the direct band gap.

To determine the values of direct band gap, we plot $(\alpha h\upsilon)^2$ versus the photon energy hυ and extrapolating the tangential line to the photon energy ($h\upsilon$) to $\alpha = 0$ from the linear region [17]. The intercept of the tangent to the plot gives the values of the direct band gap energies of the samples (Fig. 3(a)). The optical energy gaps of the ZnO thin films was within 3.2-3.4 eV. These values agree well with the published data for bulk zinc oxide samples and values reported [18]. However, band gap values obtained are little lower than the band gap value of bulk zinc oxide semiconductor (3.37 eV) [16]. This reduction is attributed to the structural and electronic defects such as little interstitials and vacancies created during the synthesis process [18].

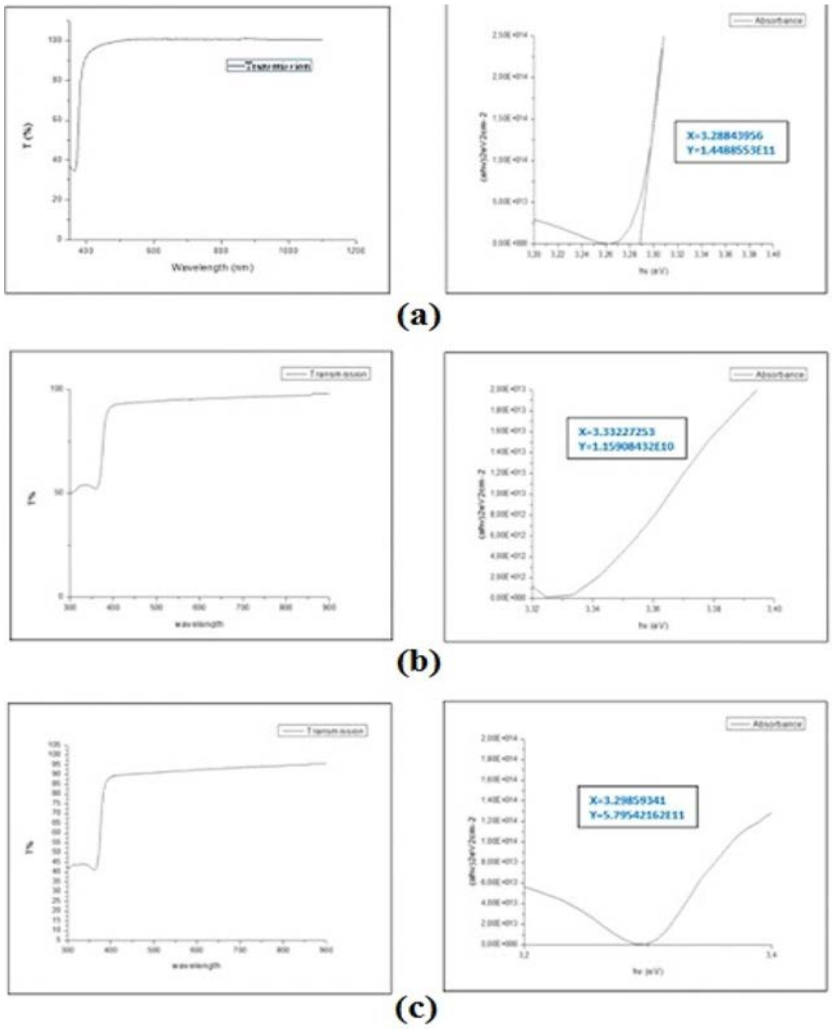

Fig. 3. Transmittance and absorbance spectra of ZnO films prepared at (a) 0.55 M, (b) 0.75 M and (c) 0.95 M conditions.

Table 1. Calculated refractive indices and optical dielectric constant of ZnO samples.

Sample	n	ε_∞
$S_{0.55M}$	2.009	4.036
$S_{0.75M}$	1.982	3.928
$S_{0.95M}$	2.003	4.012

To measure the transparency to the incident photons, we calculate the refractive index of the ZnO samples prepared. In solid physics, the refractive index is considered as an important physical parameter for semiconductor materials [19]. So, a proper design of optoelectronic device needs an accurate knowledge of refractive indices of materials. Refractive index is closely related to the electronic properties and band structure of the material according to Ravindra [19]. One of the popular empirical relations available in literature between refractive index n and energy gap Eg is given by the well known Ravindra approximation [19]:

$$n = \alpha + \beta \, Eg \tag{2}$$

Where $\alpha = 4.048$ and $\beta = -0.62$ eV^{-1}.

The optical dielectric constants (ε_∞) can be fitted to the well known relation [20]:

$$\varepsilon_\infty = n^2 \tag{3}$$

The calculated refractive index and optical dielectric constants for the three kinds of samples are given in Table 1. Values are close to ordinary bulk values [21, 22] indicating good crystalline quality of ZnO thin films prepared.

Conclusions

In this study we have shown that ZnO thin films deposited on glass substrates can have good optical quality and uniform surface. The EDX measurement shows the purity of the ZnO particles and indicates that the products consist of zinc and oxygen elements. SEM images reveal that the surface is homogeneous and has regular elongated grains and confirm significantly higher quality in 0.75 M condition. In the visible region, the average transmittance is in the range of 95%. Measured optical energy gaps were 3.2884, 3.3322 and 3.2985 eV respectively for precursor concentrations 0.55 M, 0.75 M and 0.95 M. The refractive indices of zinc oxide (ZnO) thin films were measured and ranged from 1.982 to 2.009.

The best crystalline structure and the transparency of all the grown samples prove that they are attractive for use in photovoltaic applications.

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References

1. X. Li and Y. Wang, J. Alloys Compd. 9 (2011) 5765- 5768.
2. A.E. Morales, and U. Palb, Curr. Appl. Phys. 11 (2011) 525-531.
3. G. Murugadoss, J. Mater. Sci. Technol. 28 (2012) 587-593.
4. D.S. Kim, D. Lee, J.H. Lee, and D. Byun, J. Korean Phys. Soc. 64[10] (2014) 1524-1528.
5. X. Li, J. Song, Y. Liu, and H. Zeng, Curr. Appl. Phys. 14 (2014) 521-527.
6. K.K. Kim, and I.K. Park, J. Ceram. Process. Res. 18[6] (2017) 435-439.
7. E. Muchuweni, T.S. Sathiaraj, and H. Nyakotyo, Ceram. Int. 42 (2016) 10066-10070.
8. L.Z. Pei, H.S. Zhao, W. Tan, H.Y. Yu, Y.W. Chen, Q.-F. Zhang, Mater. Charact. 60 (2009) 1063-1067.
9. E.Ş. Tüzemen, H. Kavak, and R. Esen, Phys. B: Condens. Matter 390 (2007) 366-372.
10. Munirah, Z.R. Khan, A. Aziz, M.S. Khan, and M.U. Khandaker, Mater. Sci-Poland, 35 [1] (2017) 246-253.
11. Q. Li, X. Li, and J. Zhang, J. Alloys Compd. 572 (2013) 175-179.
12. D. Adolph, T. Tingberg, T. Andersson, and T. Ive Front. Mater. Sci. 9[2] (2015) 185-191.
13. M. Caglar, S. Ilican, and Y. Caglar, Thin Solid Films 517 (2009) 5023-5028.
14. D. Chhikara, M. SenthilKumar, and K.M.K. Srivatsa, Superlattices Microst. 82 (2015) 368-377.
15. S. Chen, G. Carraro, D. Barreca, and R. Binions, Thin Solid Films 584 (2014) 316-319.
16. J. Tauc, R. Grigorovici, and A. Vancu, Phys. Stat. Sol. 15 (1966) 627-637.
17. R.Vettumperumal, S. Kalyanaraman, and R.Thangavel, Superlattices Microst. 83 (2015) 237-250.
18. J. Hu, and R.G. Gordon, J. Appl. Phys.71 (1992) 880-890.
19. N.M. Ravindra, S. Auluck, and V. K. Srivastava, Physica Status Solidi b 93[2] (1979) K155-K160.
20. G. A. Samara, Physical Review B 27[6] (1983) 3494-3505.
21. W.L. Bond, J. Appl. Phys. 36[5] (1966) 1674-1677.
22. G.E. Jellison, Jr. and L.A. Boatner, Phys. Rev. B 58 (1998) 3586.