Preparation of Zinc Oxide Thin films by SILAR method and its Optical analysis

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Abstract. ZnO thin films are promising material in multipurpose applications like solar cells and piezoelectric devices manufacturing, sensors applications etc. By tailoring its electrical and optical properties, its selection in different fields could be decided. So investigations of its optical parameters play key role in its chemical and physical analysis. Different methods of preparations are adopted for ZnO thin film synthesis for its specific uses. Here we selected Successive ion layer adsorption and reaction (SILAR) for ZnO film synthesis, which is a method preferred over ordinary chemical bath method. 0.025 molar ZnO thin films is prepared for 15 dip cycles and annealed for 450°C for 1 hour. The optical property of the prepared sample is investigated with UV visible and FTIR spectrometers. Thus obtained inferences of transmittance and absorbance is used to calculate parameters like absorption coefficient, extinction coefficient, band gap energy, refractive index and reflectance. It is observed that transmittance and absorbance show lower percentage over visible range. Band gap energy and refractive index is found to be comparable with the literature values. With these obtained values and due to the simplicity of the procedure, it is suggested that SILAR is a good method for ZnO thin film synthesis.

1. Introduction
Material science is keen in developing and designing new materials, which are useful in industrial and research applications. The structural and optical analysis of materials synthesized, lead to selection of these materials according to their properties. Such a material with wide verity of applications is ZnO(1). ZnO is a bio-safe material available in the form of white powder, which is insoluble in water. Due to stoichiometric point defects like vacancies (2-3), ZnO shows its electrical properties (4-7) and it remains as an n-type semiconductor (8-12). High electron mobility (13-15), photoluminescence (16-18) and high thermal conductivity (19-21) is shown by ZnO, with its broad energy band 3.37eV (22-24) and high bond energy of 60 meV(25-27). Its high thermal and mechanical stability (28-29) at room temperature makes it a potential material for multipurpose applications. ZnO shows wurtzite(30-31) crystalline structure. Transparent metallic oxide thin films for various applications could be synthesized using different physical and chemical methods from ZnO. One of the popular methods is preparation from chemical bath (32-33). Advancement of this method was provided by Successive ion layer adsorption and reaction (SILAR) process, which is a cost effective method in thin film preparation. Good adhesions of samples on substrates, less wastage of prepared sample solution, film preparation at room temperature etc are some important features of SILAR. SILAR method is ideal method for making uniform, compact and crystalline thin films. ZnO thin film and doped ZnO thin film preparation using SILAR has been reported by many researchers over the years (34-38). Structural and optical analysis of prepared films play the key role for its selectivity in fields like solar cells (39-40), sensors (41-42), piezoelectric devices (43-44) etc. In the present work, ZnO thin films are prepared for different dip cycles. Thus obtained samples are investigated with FTIR spectrometer and UV-visible spectrometer
2. Experimental

Cationic solution is prepared using Zinc Chloride and aqueous ammonia. Zinc salt mixed with distilled water is stirred and kept at 80°C and aqueous ammonia is added drop by drop until PH value is around 9. Cationic solution is prepared for weight fraction of 0.025M. Distilled water kept as anionic solution in SILAR. Glass substrate is cleaned with acetone and then with distilled water is made to immerse alternately in cationic and anionic solutions. Dip cycles of 15 dips of 20 Sec are performed for each solution. Obtained films are annealed at 450°C for 1 hour. Optical properties of thus prepared ZnO thin films are carried out with FTIR and UV-visible spectrometers. Results obtained are discussed.

3. Result and Discussions

3.1. Transmission and Absorption spectra

![Figure 1. Optical transmission of the deposited sample](image)

| Sample      | Peak value of transmittance(T) | Optical band gap | Minimal value of Extinction coefficient(k) |
|-------------|--------------------------------|------------------|-------------------------------------------|
| 0.025M sample | 52%                            | 3.75eV           | 0.0566                                     |
Optical transmittance (T) and extinction coefficient of 0.025M sample deposited on glass substrate is shown in Fig 1 and Fig 2. It is observed that the peak value of transmittance corresponding to a wavelength of 886nm is 52%. There is a fall observed in intensity around 400nm, which may be due to band edge absorption. The conventional variation of transmittance predicts the absence of unusual reactions during the treatment. The optical band gap (Eg) is obtained by the extrapolation of the onset absorption to the energy axis. Eg is found to be 3.75 eV, which is high, compared to the theoretical value (3.3 eV) and may be due to the defect bound absorption process, which needs further clarifications. The fraction of light lost in the medium due to absorption and scattering is represented by extinction coefficient (k) in terms of absorption coefficient (α). It is given as $k = \frac{\alpha}{4\pi}$. 

**FIGURE 2.** Variation of Extinction coefficient

**FIGURE 3.** $(\alpha\varepsilon)^2$ vs energy for the sample
$k$ is found as reducing to 0.07 for a wavelength range greater than that of 650nm. The variation of $k$ with wavelength is represented in Fig3. The minimal value of $k$ is observed as 0.0566.

**Infra-Red analysis**

![FTIR spectrum of ZnO film](image)

**FIGURE 4. FTIR spectrum of ZnO film**

Figure 4 shows the infrared absorption characteristics of the deposited film. From the absorption spectra, the characteristic zinc-oxygen stretching vibration was found to be at 467 cm$^{-1}$, well agreement with the theoretical suggestions.
Calculation of refractive index

The reflectance (R) using $\alpha$ is obtained by the relation

$$R = \frac{\exp(-\alpha T) \sqrt[2]{\exp(-3 \alpha T) + \exp(-2 \alpha T) + \exp(-\alpha T)}}{\exp(-2 \alpha T) + \exp(-2 \alpha T)}$$

Variation of R with wavelength is shown in fig.5. Reflectance variation with wave length is found to be decreasing from a wavelength of 200nm to 300nm but then remain constant up to 900 nm. ZnO thin films exhibit low reflectance, with lesser than that of 10% for wave length greater than that of 300nm. It is confirming the transparency of ZnO thin film in this wavelength range.

Thus obtained values of reflectance are used for calculating the refractive index (n) of the thin film as,

$$n = \frac{\sqrt{R} + 1}{\sqrt{R} - 1}$$

The unusual variation of refractive index with wave length is be suggested due to the increased roughness of the sample due to comparatively longer time of annealing. The volumetric incensement of voids due to annealing in the film surface will attribute as roughness and may be the reason for decrease in reflectance and refractive index of the film. The optimum value of refractive index is calculated as 1.707.

4. Conclusions

SILAR method is adopted for the synthesis of 0.025M ZnO thin film. Transmission and absorption spectra of the film is investigated and parameters like transmittance (T), Optical band gap energy ($E_g$), Extinction coefficient (k), FTIR absorption characteristics, reflectance (R) and Refractive index (n) are determined. It is observed that these parameters are comparable with the literature values. Since the method of synthesis by SILAR in obtaining these values is simpler comparative to other methods, SILAR is suggested to be a good preparatory method for ZnO thin films.

References

[1] Qi, Kezhen, Bei Cheng, Jiaguo Yu, and Wingkei Ho. *J. Alloys and Compounds* (2017).
[2] Wang, Jing, Yi Xia, Yan Dong, Ruosong Chen, Lan Xiang, and Sridhar Komarneni. *App Catalysis B: Env* 192,8-16 (2016)
[3] Kayaci, Fatma, SeshaVempati, InciDonmez, NecmiBiyikli, and Tamer Uyar. *Nanoscale* 6, no.
[4] Ammaih, Youssef, AbderrazakLafakir, BouchaibHartiti, AbderraoufRidah, Philippe Thevenin, and MeryaneSiadat. *Opt. Quantum Electron* 46, 229-234. no. 1 (2014)

[5] Saravanan, R., T. Prakash, V. K. Gupta, and A. Stephen. *J. Mol. Liquids* 193,160-165 (2014).

[6] Chen, Cheng-Ying, Ming-Wei Chen, Jr-Jian Ke, Chin-An Lin, José RD Retamal, and Jr-Hau He. *Pure Appl Chem* 82, 2055-2073. 11 (2010)

[7] Cheun, Hyeunseok, Canek Fuentes-Hernandez, Yinhua Zhou, William J. Potscavage Jr, Sung-Jin Kim, Jaewon Shim, Amir Dindar, and Bernard Kippelen. *J. Phys Chem C* 114, 20713-20718. 48 (2010)

[8] Ong, Khuong P., David J. Singh, and Ping Wu. *Phys Review B* 83, 115110, 11 (2011)

[9] Lu, J. G., S. Fujita, T. Kawaharamura, H. Nishinaka, Y. Kamada, T. Ohshima, Z. Z. Ye et al. *J Appl Phys* 101, 083705. 8 (2007)

[10] Ágoston, Péter, KarstenAlbe, Risto M. Nieminen, and Martti J. Puska. *Phys review lett* 103, 245501. 24 (2009)

[11] Kim, Yong-Sung, and C. H. Park. *Phys review let t* 102, 086403. 8 (2009)

[12] McCluskey, M. D., and S. J. Jokela. *Physica B: Cond Mat* 355-357, 401 (2007)

[13] Tiwana, Priti, Pablo Docampo, Michael B. Johnston, Henry J. Snaith, and Laura M. Herz. *ACS nano* 5, 5158-5166. 6 (2011)

[14] Yang, Jing-Jing, Qing-Qing Fang, Wen-Han Du, Ke-Ke Zhang, and Da-Shun Dong. *Chinese Phys B* 27, 037804. 3 (2018)

[15] Caglar, Mujdat, and Serif Ruzgar. *J. Alloys and Compounds* 101-105. 644 (2015)

[16] Rakhesh, V., and V. K. Vaidyan. *J. optoele.bio mat* 1, 281-290. 8 (2009)

[17] Kaviyarasu, K., C. Maria Magdalane, K. Kanimozh, J. Kennedy, B. Siddhardha, E. Subba Reddy, Naresh Kumar Rotte et al. *J Photochem .Photobio B: Bio* 466-475. 173 (2017)

[18] Soepriyanto, Syoni, AkhmadArdianKorda, and SuponoAdiDwiwanto. *Mat Rese Expr* 5, 036517. 3 (2018)

[19] Scamehorn, John F., T. Muto, C. H. L. Ribeiro, J. R. Ferrere, and J. L. Zacharias. *In Zinc Oxide*, pp. 1-6. Springer, Berlin, Heidelberg, 2010.

[20] Lee, Kian Mun, Chin Wei Lai, Koh Sing Ngai, and JoonChing Juan. *Water research* , 428-448. 88 (2016)
[32] Sreedev, P., V. Rakshesh, and N. S. Roshima. In *IOP Conference Series: Materials Science and Engineering*, vol. 377, no. 1, p. 012086. IOP Publishing, 2018.

[33] Shaikh, Shahin K., Sumayya I. Inamdar, Vinayak V. Ganavle, and Kesu Y. Rajpure. *J. Alloys and Compounds*, 242-249. 664 (2016)

[34] Patil, Vithoba L., Sharadrao A. Vanalakar, Pramod S. Patil, and Jin H. Kim. *Sens and Actuat B: Chem*, 1185-1193. 239 (2017)

[35] Ramirez, Sara E., Luis A. García-Cerda, and Luis A. González. *Superlattis .Microstruct*, 409-417, 100 (2016)

[36] Shei, Shih-Chang, Shoou-Jinn Chang, and Pay-Yu Lee. *J. Electrochem.Society* 158, H208-H213. 3 (2011)

[37] Shei, Shih-Chang, Pay-Yu Lee, and Shoou-Jinn Chang. *Appl Surf Scie* 258, 8109-8116. 20 (2012)

[38] Kumar, K. Deva Arun, S. Valanarasu, V. Ganesh, MohdShkir, A. Kathalingam, and S. AlFaiify. *J. Elect. Mat* 47, 1335-1343. 2 (2018)

[39] Sun, Yanming, Jung HwaSeo, Christopher J. Takacs, Jason Seifter, and Alan J. Heeger. *Adva Mat* 23, 1679-1683. 14 (2011)

[40] Barceló, Irene, Teresa Lana-Villarreal, and Roberto Gómez. *J.Photochem. Photobiol A: Chem* 220, 47-53. 1 (2011)

[41] Singh, Gaurav, AnshulChoudhary, D. Haranath, Amish G. Joshi, Nahar Singh, Sukhvir Singh, and RenuPasricha. *Carbon* 50, 385-394. 2 (2012)

[42] Patil, Vithoba L., Sharadrao A. Vanalakar, Pramod S. Patil, and Jin H. Kim. *Sens .Actu B: Chem* 1185-1193. 239 (2017)

[43] Pan, C. T., Z. H. Liu, Y. C. Chen, and C. F. Liu. " *Sens . Actuat A: Phys* 159, 96-104. 1 (2010)

[44] Hu, Guofeng, WenxiGuo, Ruomeng Yu, Xiaonian Yang, Ranran Zhou, Caofeng Pan, and Zhong Lin Wang. *Nan. Ener* 27-33. 23 (2016)