Optical properties of pure ZnO Thin films prepared by the sol-gel method

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Abstract:

Zinc oxide (ZnO), a direct, wide band gap and n-type metal oxide semiconductor, is being anticipated as the next generation functional nano-material towards remarkably diversified sensing applications. ZnO and its composites have revealed a new era in the fabrication of sensors owing to their excellent opto-electronic, physicochemical, electrical properties such as low dielectric constant, plentiful Zn-O bonds, high luminous transmittance, good physicochemical stability, huge excitation binding energy, non-toxicity, biocompatibility, large surface area to volume ratio and so on.

In this work, nanostructured thin films of pure zinc oxide (ZnO) were deposited on a glass substrate using a sol-gel spin coating technique. All deposited films were characterized by UV-Visible Spectroscopy and Photoluminescence spectroscopy etc. From the optical absorption spectra measured using UV–Visible spectroscopy, it is clearly observed that the average transmittance of all prepared films in the visible region is 90%. The energy band gap of prepared thin films is found to be 3.22 eV. The photoluminescence spectrum gives two emission peaks. This work can provide a low-cost, environment friendly and a good film of zinc oxide for optical sensing.

Keywords: ZnO, sol – gel, spin coating, optical properties.

I] Introduction:

Zinc oxide is an important element as it is used in many areas such as medical applications, electronics, sunscreens, cosmetics, UV protection, electrodes in solar cells, piezoelectric elements, etc.

Currently, there is a growing demand for the development of ZnO nanoparticle semiconductors due to their significant electrical and optical properties. An interesting feature is the wide direct band gap of 3.37 eV and the large binding energy of 60 meV of ZnO material [1-6]. The wide band gap and having large binding energy makes ZnO potentially useful in various optoelectrical applications such as optical sensors, light emitters, solar cells, etc. ZnO nanoparticles are promising candidates for various applications such as nanogenerators [7], gas sensors [8], biosensors [9], photodetectors [10], and photocatalysts [11].

ZnO thin films were prepared by various techniques such as chemical vapor deposition [12], molecular beam epitaxial [13], spray pyrolysis [14] and sol-gel process [15-18]. Among these methods, the sol-gel process using spin-coating techniques is attractive for its simplicity, flexibility, easy doping, the possibility of preparing a large area, and acceptable costs [19]. In our work, optical properties of pure ZnO thin films prepared by the sol-gel spin coating technique were investigated.

II] Experimental Details:

A. Chemical Reagent:

The ZnO precursor solution was prepared using, zinc acetate di-hydrate (M=219.50, Zn $(CH_3COO)_2.2H_2O$, ZAD) as a precursor, diethanolamine (M=105.14, [CHH2(OH)CH2]2.NH, DEA) as a chelating agent and de-ionized water.

B. Preparation of ZnO Films

Pure ZnO films were prepared by the sol-gel method on a glass substrate. In this work, ZnO films were deposited for zinc acetate concentration with 10 number of coatings. ZnO precursor solution was prepared in the following way. At first, 2.195 g of zinc acetate was dissolved in 25 ml of 2 – methoxy ethanol to yield 1.0 mol/L concentration of precursor solution and then magnetically stirred for 30 min. A milky solution was obtained were with a molar ratio of DEA/ZAD as 1:1, 5 ml of DEA was added into the

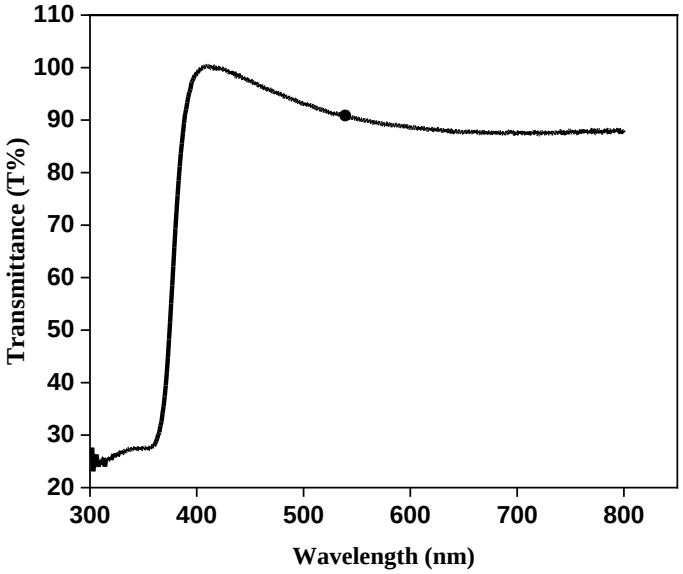
solution. The solution was again stirred and a clear solution was obtained after a certain period. All of the solutions were then aged at room temperature for 6 hrs before coating.

Glass substrates are used for the deposition of ZnO films. The substrates were cleaned with chromic acid, acetone, and distilled water. After that solvents from the surface of the substrate were swept away by using an air compressor. Then, on such clean substrate of 2 cm length a thin film was spin coated with the prepared sol using sol- gel process. ZnO thin films were deposited by using above prepared solution by using spin coater (2000 rev/min for 30 s). A specially designed two-stage spin coater was used for coating. The coated films were heated at 350^0 C in air for 1 h to decompose the precursor film to ZnO. After that another deposition cycle was carried out. The process was repeated 10 times to obtain the desired thickness.

After completing 10 deposition cycles the films were annealed at 350^0 C.

The optical properties of above prepared films were measured by UV/Visible spectrometer for 300-800 nm wavelengths using a reference substrate. From UV spectroscopy transmittance spectra and absorbance spectra were obtained. The optical band gap was found using the Tauc relationship from absorbance spectra. PL spectroscopy was used to study the luminescence property at room temperature.

III] Result and Discussions:



Optical transmittance of prepared ZnO Thin films

Fig. 1 shows the optical transmittance of ZnO films for 10 coatings in the wavelength range 300-800 nm. It is clearly seen that in the visible range of the electromagnetic spectrum the films are highly transparent with an average transmittance value of 90 % beyond the wavelength of 400 nm and present sharp ultraviolet cut-off at approximately 360 nm. Transmittance reaches to its maximum value at a higher wavelength.

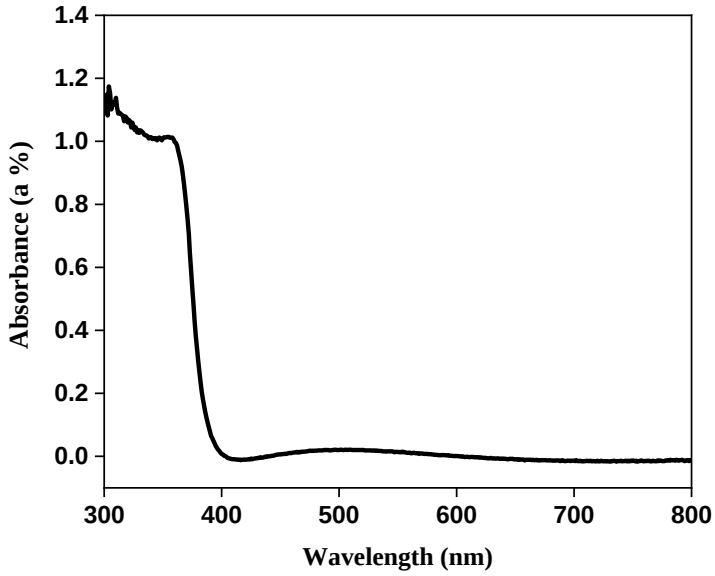


Fig. 2 : Optical Absorbance of prepared ZnO Thin films

Fig. 2 shows the absorption spectrum of sol-gel-derived ZnO for 10 coatings. It is clearly observed that the films have a very low absorption at transparent region and high absorption at the ultraviolet region.

The direct and indirect allowed optical transitions between the 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 coefficient (α) on photon energy (hϑ) can be given by [20],

$$\boldsymbol{\alpha h\vartheta = A(h\vartheta - Eg)^{r}} \ldots\ldots\ldots\ldots\ldots\ldots \textbf{(1)}$$

where α is the absorption co-efficient, A is the edge width parameter, hϑ is the photon energy, and r is a constant, for direct allowed transition r equals ½ and for indirect allowed transition equals 2.

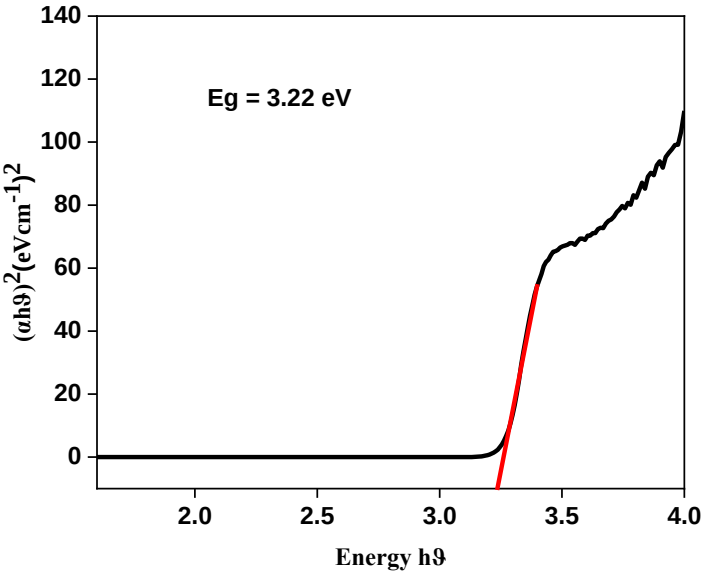


Fig. 3: Plot of $(\alpha h\vartheta)^2$ vs. $h\vartheta$ of ZnO Thin films

Fig. 3 shows the plot of $(\alpha h\vartheta)^2$ vs. $h\vartheta$ of prepared ZnO films of 10 coatings. The optical band gap for the direct allowed transition of the films has been determined from the extrapolation of the linear portion of $(\alpha h\vartheta)^2$ vs. $h\vartheta$ at α= 0. Direct transition band gap is foound to be of 3.22eV.

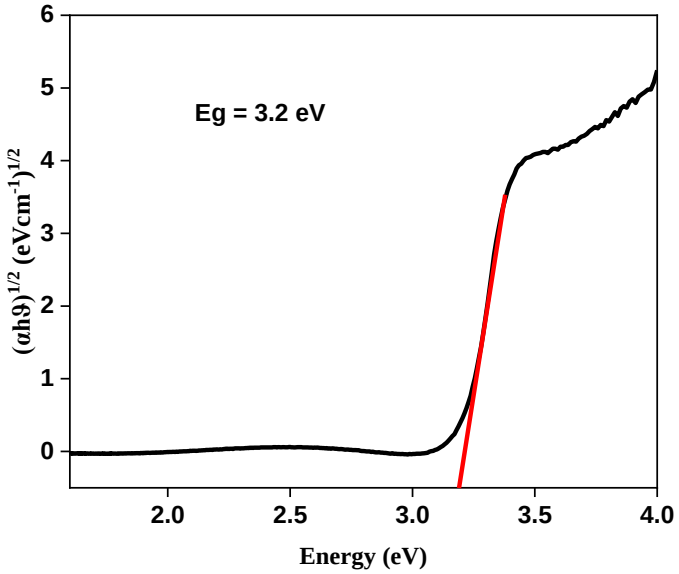


Fig. 4: Plot graph of $(\alpha h\vartheta)^{1/2}$ vs. $h\vartheta$ of prepared ZnO Thin film

Fig. 4 shows the plot of $(\alpha h\upsilon)^{1/2}$ vs. $h\upsilon$ of ZnO films of 10 coatings and band gap for indirect allowed transition has been determined by extrapolating the straightline portion of the spectrum at α = 0. The indirect allowed band of prepared ZnO thin films has been found to be of 3.19 eV.[21]

Photoluminescence:

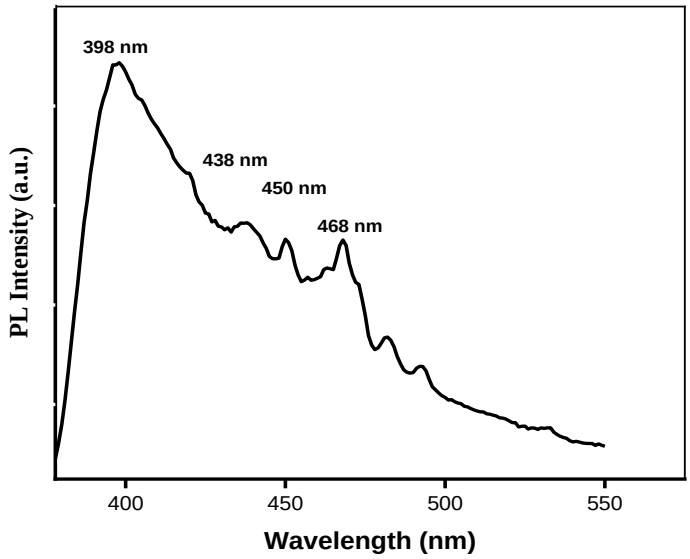


Fig. 5: Photoluminescence of prepared ZnO Thin filmFig. 1 :

Photoluminescence studies have been performed on the prepared ZnO thin film. Particularly, the sol - gel method can be an appropriated route to maximize the luminescent properties of the ZnO films. Room temperature luminescence emission spectra of pure ZnO nanoparticles synthesized by sol – gel method is shown in fig.5. The excitation wavelength of ZnO was 350 nm. This PL spectrum shows strong peak observed at 468 nm corresponding to blue luminescence.

However, at 398 nm a UV peak may be obtained due to intrinsic defects such as zinc interstitials, oxygen vacancies etc. [22, 23]. N'Konou et al. [24] reported the dominant UV peak of ZnO originated from the free excitons emission.

IV] Conclusions:

ZnO thin films can be successfully prepared on glass substrate by using sol-gel method with zinc acetate as precursor. Also ZnO thin films can be prepared with 10 numbers of coatings. In order to obtain crystal structure of ZnO, as-deposited films were annealed at 350 ^{0}C. The results have revealed that, ZnO films prepared by sol-gel method are highly transparent i. e more than 90 % at visible region.

Direct and indirect allowed band gap has also to be found with satisfactory value. Higher transmittance in the visible region and higher absorption in the UV-region has made the films potentially able for optical window applications and also as transparent conductive oxide (TCO). The photoluminescence spectrum shows the major peaks observed in the blue emission region. Zinc oxide has been an important industrial material for centuries and is currently the subject of considerable new interest. As luminescent material, it has potential technological applications such as in the construction of printed electronics such as organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs). With no a doubt, the sol-gel method is a friendly route to obtain uniform and stable zinc oxide films with high optical quality. Further improvement in the band gap can be obtained with suitable doping at the time of preparation and the prepared doped ZnO film can be act a suitable candidate for optical sensing devices such as solar cells.

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