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Nanopowder and Thin Films of ZnO by Sol Gel Approach

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In this work, we have studied the structural and optical properties of ZnO thin films. Pure thin films of ZnO were prepared on glass substrate by sol gel dip coating method and annealed at a temperature of 150 ºC. Similarly, 1 gm PVA capped ZnO thin film was prepared and annealed at 250 ºC and the last sample of 2 gm PVA capped ZnO thin film was prepared and annealed at a temperature of 350 ºC. The increase in sol aging time resulted in a gradual improvement in crystallinity of the hexagonal phase for all diffraction peaks. Effect of sol aging on optical transparency is quite obvious through increased transmission with prolonged sol aging time. Interestingly, 24 hour sol aging time was found to be optimal to achieve smooth surface morphology, good crystallinity and high optical transmittance which were attributed to an ideal stability of solution. The ZnO thin films have been characterized in terms of morphological, structural and optical properties by scanning electron microscopy (SEM) and ultraviolet–visible (UV–Vis) spectroscopy. The UV–Vis transmittance spectrum of synthesized sample gives the optical band gap value of 3.2 eV, 3.15 eV and 3.1 eV. Along with thin films, nanopowder is also synthesized by sol gel method and characterized by XRD, which can be potentially used in cosmetic industry. Sol-gel dip coating technique creates pure and capped ZnO films with potential for applications as transparent conducting electrodes in optoelectronic devices, such as solar cell and light emitting diodes.

Keywords: TCO, Dip coating, Structural properties, Band gap.

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1. INTRODUCTION

The application of ZnO in photovoltaics is not limited to act as electron transport material (ETM) in dye-sensitized solar cells (DSCs) and hybrid solar cells (HSCs) [1]. It can also be applied as optical spacer in polymer solar cells (tandem, hybrid and inverted organic solar cells) [2-7]. The ZnO is not toxic unlike indium tin oxide, which is one of the most currently used transparent conducting oxide (TCO) films. The direct wide band gap of ZnO, Eg = 3.37 eV, makes it transparent for a large wavelength range in the solar spectrum. Other advantages of the use of ZnO as layers in photovoltaic cells concern its high chemical and physical stability, thermal stability in hydrogen plasma atmosphere, large excitons binding energy of 60 meV, high electrical conductivity and finally, its low cost price.

ZnO thin films have been prepared using several deposition techniques such as pulsed laser deposition [8], magnetron sputtering [9], spray pyrolysis [10] and sol-gel [11]. Compared to other techniques, sol gel is simple, non-vacuum and inexpensive method. Moreover, it is useful for producing large scale films. The quality and physical properties of films prepared using the sol gel dip coating technique depend on different deposition and post-deposition conditions, such as the nature and concentration of precursor, substrate temperature, dipping and annealing. In these parameters, substrate temperature usually plays a crucial role in growth of ZnO films. It has been revealed that these conditions have a significant effect on properties of ZnO based TCO films.

In the present work, we have studied the nanopowder and thin films obtained by sol gel method and characterized the deposited thin films by XRD, SEM and Spectrophotometer.

2. EXPERIMENTAL DETAILS

2.1 Preparation of ZnO Nanoparticles by Sol-gel Method: Our Methodology

Zinc oxide nanoparticles were synthesized by sol-gel method using zinc acetate and ethanol as precursors. In the preparation, 16 gm of zinc acetate was dissolved with 8 gm of NaOH with distilled water and add 112 ml of ethanol. Also, we added some capping agent to control the size of nanoparticles, i.e. (PVA). After 10 min magnetic stirring at room temperature the resultant solution was subjected to gelatin for one-day constant stirring for 2 hours, from which the zinc oxide nanomaterial in the form of powder was obtained. The resultant powder was annealed at 80 ºC for 15 min. After that, we repeated the same process to prepare zinc oxide thin films by dip coating process.

2.2 Preparation of ZnO Thin Films by Sol-gel Process through Dip Coating

In our experiment, the sol-gel method was used for preparing thin films by dip coating. In a typical procedure, 12.6 gm of zinc acetate dihydrate (as a precursor) was added to 400 ml of distilled water with constant stirring to dissolve zinc acetate completely. Then the solution was heated at 50 °C, and 600 ml of absolute alcohol was added drop-wise to the vessel and then mixed using a magnetic stirring. After this, 6 ml of H_2O_2 was added drop-wise to the vessel and mixed with magnetic stirring to get almost a clear solution. We prepare two solutions: one is pure H_2O_2 and other with capping agent H_2O_2. Both solutions were incubated for one day.

After that, a sol thick solution was prepared and dip coating was done. In pure sample we dipped slides 2-3

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times and for capping agent solution we dipped slides 5 times. Then the layers were formed on the slides, and we started heating from 80 °C to 350 °C in hot air oven. After that, we found that there was a film formed on the slides. Similarly, we prepared another sample i.e. pure and with capping agent PVA. Final obtained thin films were transparent and were further processed for characterization.

3. RESULTS AND DISCUSSION

To evaluate a material quality of the semiconductor thin films a wide variety of characterization techniques were used. The structural properties of the polycrystalline films were studied by the (SEM) and the crystalline phase was determined by the XRD. The optical properties of the films were studied by UV-Vis spectroscopy by using transmission measurements.

3.1 X ray Diffraction Analysis

The phase purity and composition of particles is obtained by a sol gel process which is examined by XRD. Diffraction from as prepared and annealed ZnO nanoparticles sample is based on the Bragg's equation $n\lambda = 2d\sin\theta$, where n is an integer, d is the interplanar spacing and λ is the wavelength. The crystallinity of powder is determined by X-ray powder diffraction (XPRD). Analysis was done by diffractometer equipped with a $CuK_{\alpha 1}$ radiation source, maintaining applied voltage of 45 kV and current at 1000 Ma. About 0.5 gm of dried ZnO particles were deposited as an oriented powder into a sample container, and XRD pattern was recorded between the 20 ° to 80 ° angles with speed 10 deg/min. We used Scherrer equation to determine the crystalline diameter obtained by XPRD peaks [12].

$$D = K\cdot\lambda/\beta\cos\theta,$$

where λ is the X-ray wavelength ($\lambda = 0.15418$ nm with CuK_α radiation), β is the full width at half maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is the Scherrer constant of the order of unity for usual crystal and thin films.

In this work, ZnO nanoparticles show typical XRD pattern, the phase purity and the compositions of the particles obtained by sol gel process, which is examined by XPRD as shown in Fig. 1. A number of Bragg reflections with 2θ values of 31.74°, 35°, 36.83° and 47.62° are observed to corresponding planes (100), (101) and (102). The size of nanoparticles is determined as 59.3 nm from the width of dominate peak (100), (002) and (101) reflections according to the Debye- Scherrer equation. Diffraction peaks are indexed according to hexagonal phase since no peaks of impurity except ZnO are found good crystalline in the sample. We also observed that the intensities of Bragg peaks of annealed ZnO sample is sharp and narrow compared to as prepared ZnO nanoparticles, it confirms that the sample exhibits good crystallinity and increased particle size. But some small peak was shown in XRD graph which indicates that impurities exhibit in sample. However, the XRD pattern of ZnO powder sample annealed at 80 °C for 15 min shows a small peak $2\theta \sim 26.25°$ corresponding to sample holder such that it has no relation of wurtzite hexagonal phase of ZnO. The ZnO nanoparticles also exhibit several diffraction peaks which can be indexed as hexagonal wurtzite ZnO lattice parameters as $a = 3.224$ Å and $c = 5.1904$ Å. The broadening of peaks in the XRD pattern shows small particle size of the synthesized ZnO [13].

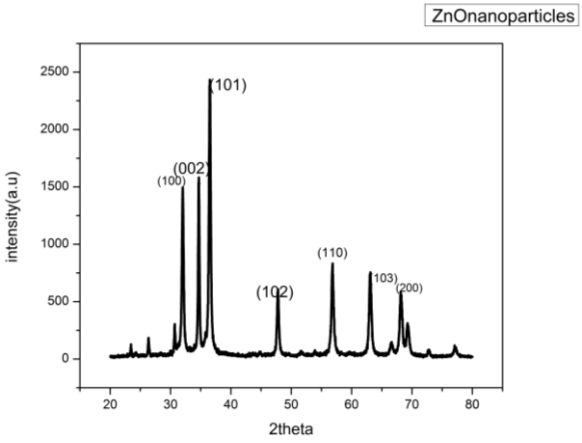


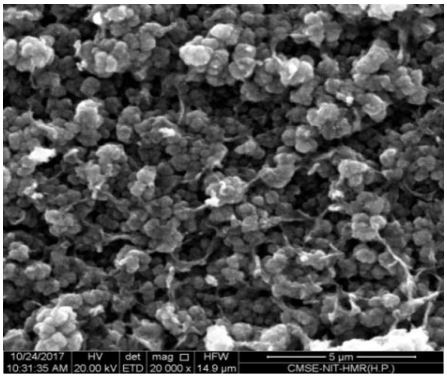
Fig. 1 – XRD pattern of ZnO nanoparticles sample prepared by sol-gel method

3.2 SEM Analysis

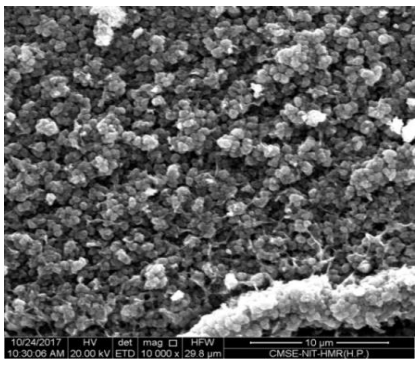
Fig. 2 shows SEM images of ZnO thin films annealed on glass substrate at a temperature of 150 °C which is homogeneous and continuous [14]. Surface morphology of thin film is important tool to search microstructures of thin films. SEM micrographs reveal that the thin films are found to be crack free, having uniform texture the substrate and the films found to be spherical like structure. The average diameter of the rods for the thin film deposited and annealed at 250 °C in Fig. 3 was found to be approximately 0.61-2 μm. We found that the average diameter of the fibers increases with annealing temperature and the fiber structures become thicker in diameter [15]. Due to addition of capping agent PVA and annealing at different temperatures there is a great influence on the diameter of spiral structure. In Fig. 4, ZnO thin films with different zinc concentration 0.35 M and 0.64 M and with the capping agent PVA show non-uniform surface morphology as compared to other thin films [16]. The image reveals good adhesion properties because there is no crack and voids in figure. The thin film deposited on the glass substrate showed the spherical, spiral, granular particle shape and the average particle size near about 1-2 μm. The SEM images of ZnO thin film were taken at the ×20,000 and ×10,000 magnification. SEM images of ZnO thin film with different magnification at different temperatures show various kinds of morphology structures [17]. By scanning the sample, the image in SEM is produced with a focused electron beam and detecting the secondary or backscattered electrons. Electrons during their passage through specimen determine different information about the sample. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications that are easily adjusted from ~ 10 to over 100,000. Not only does the SEM produce topographical information as optical microscopes produce, but it also provides the

chemical composition information near the surface. It is clear from later images (Fig. 4) that surface morphology is considerably affected by sol aging time. Effectively, as-prepared thin film produces the appearance of granular structures composed of small grains that appear somehow aggregated with porosity around.

We observed that the size of samples can be controlled by capping agent.



a



b

Fig. 2 — SEM images of ZnO thin film samples prepared at 150 °C

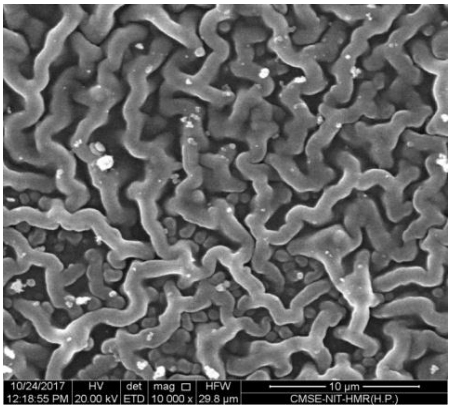


Fig. 3 — SEM images of ZnO thin film sample prepared at 250 °C with capping agent (1 gm PVA)

3.3 UV-Visible Spectroscopy

UV-Vis absorption spectroscopy is a powerful technique for the optical properties of semiconductor nanomaterials. The optical properties of bulk materials and thin films are very important for optoelectronic applications and the properties of absorbance (*A*), transmittance

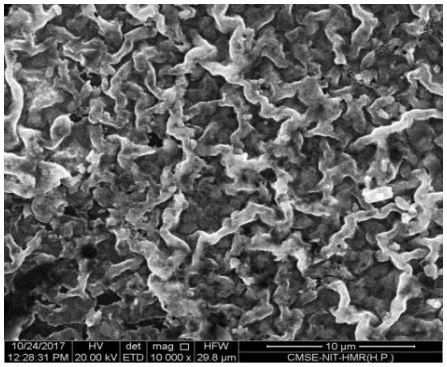


Fig. 4 — SEM images of ZnO thin film sample prepared at 350 °C with capping agent (2 gm PVA)

Table 1 – Shape and size of samples prepared at 150 °C (a), 250 °C (b) and 350 °C (c)

№	Sample details	Shape	Size
1	Thin film sample prepared at 150 °C	Spherical shape	1.30 μm
2	Thin film sample prepared at 250 °C (with capping agent of 1 gm)	Spiral shape	1.07 μm
3	Thin film sample prepared at 350 °C (with capping agent 2 gm)	Granular shape	0.61 μm

(*T*), reflectance (*R*) characterize the interaction of incident radiation with a coating of material. These properties are also related to intrinsic properties of thin film. To investigate optical properties of ZnO thin films prepared at different temperatures, the transmittance was measured as wavelength between the range of 300-800 nm. The samples were prepared by dip coating method, two samples are in pure and the other two with capping agent. The samples show optical transparency ranging from 70 % to 80 % approximately [18]. As we know, the high transmittance of the deposited thin films mainly results in low thickness. If the thickness of samples was increased, the transmission goes on decreasing. The decrease in transmittance may be due to increase in optical scattering caused by increase in grain boundary density. In the visible region of solar spectrum, transmission spectra show sinusoidal behavior; this may be layered structure of thin film at different annealing temperatures. The value of band gap is calculated from absorption edge of thin films [19, 20]. For direct transitions, the absorption coefficient is given as:

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

where A is the constant, υ is the frequency of the incident radiation and E_g is the energy gap. It is evident that surface defects control the transmittance and hence the desired transparency can further be obtained by engineering such defects.

Band gaps are one of the most important properties of semiconductors. To develop the electronic band structures of thin film of a material, it is necessary to determine band gap energy Eg. The most common method was to determine the band gap of semiconductor by optical absorption and transmission measurements [21, 22].

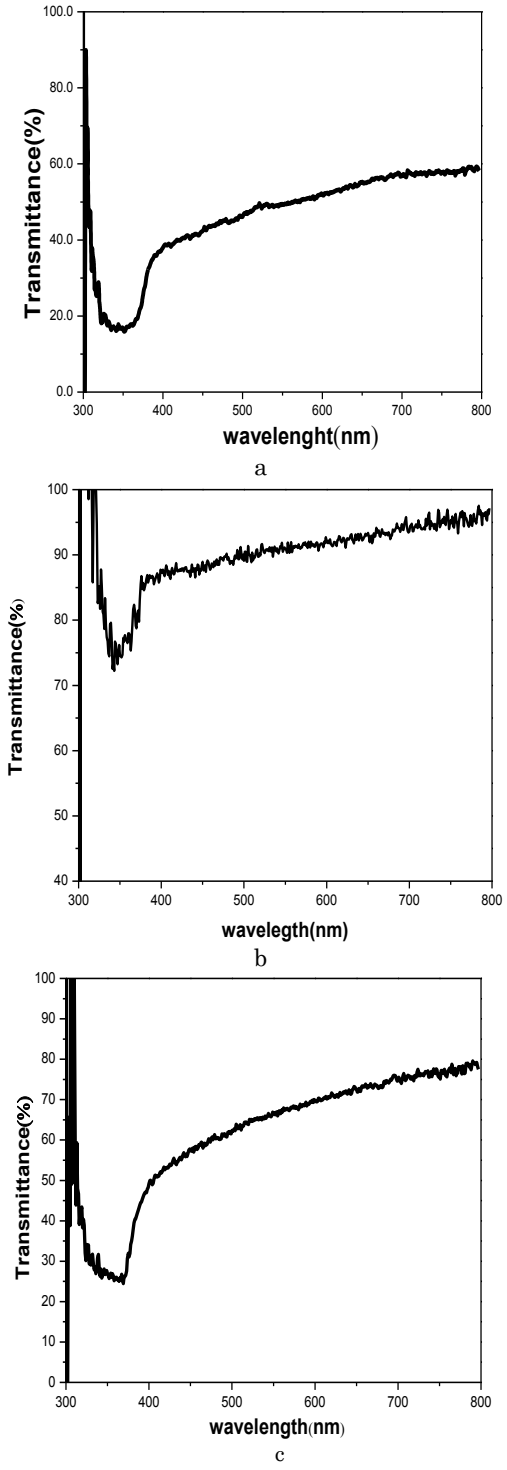


Fig. 5 – Transmittance of ZnO thin films prepared at different temperatures: 150 °C (a), 250 °C (b), 350 °C (c)

Table 2 – Different energy band gap and transmittance

№	Annealing temperature (°C)	Transmittance (%)	Band gap (eV)
1	ZnO thin film at (150 °C) pure	< 60 %	3.2 eV
2	ZnO thin film at (250 °C) 1 gm (PVA)	< 92 %	3.15 eV
3	ZnO thin film at (350 °C) 2 gm (PVA)	< 80 %	3.1 eV

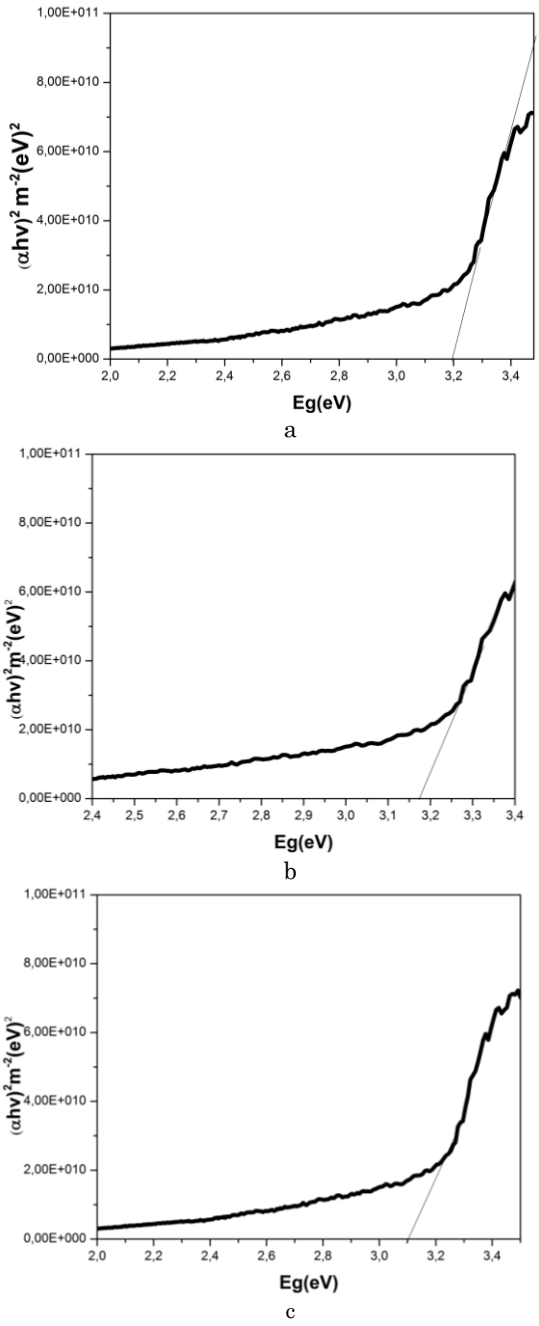


Fig. 6 – Band gap of ZnO thin films prepared at different temperatures: 150 °C (a), 250 °C (b), 350 °C (c)

Table 2 shows different values of energy band gap and transmittance.

This experiment calculates the exact value of band gap energy with lower energies. ZnO thin film annealed at different temperatures shows transparency in the visible range. The band gap variation of ZnO thin film annealed at different temperatures is shown in Fig. 6. The optical band gap was obtained by Tauc's method, which is intercepted along x-axis. The band gap for ZnO thin film grown at 150 °C was (3.2 eV). As the temperature increased from 250 °C to 350 °C, then optical band gap shifted from 3.15 eV to 3.1 eV. It was found that the band gap increases at high temperatures. It decreases from its actual band gap that is 3.37 eV. The small variation of band gap shows that band gap energy might originate

from the defects in ZnO thin films.

These investigations suggest that capping appears to control the structural defects and hence modify the optical properties of ZnO thin films. Further studies in light of variation of capping agent concentration need to be done for band gap engineering.

4. CONCLUSIONS

We used the low-cost method to prepare the thin films and nanopowder. ZnO nanopowder is prepared by sol gel process and analyzed by X ray diffraction, which shows that ZnO nanopowder has crystalline structure. Also in XRD graph, some impurities were found. The size of particles was near about 58.93 nm. In addition, the ZnO thin films were successfully prepared by the sol-gel dip coating method. All the pure and capped thin film samples were calcined at different temperatures that are 150 ˚C, 250 ˚C and 350 ˚C. SEM gave the morphological structure of thin films at different temperatures (150 ˚C, 250 ˚C and 350 ˚C) which show nanorods and polycrystalline structure. Moreover, ZnO thin films show small optical band gap of 3.2 eV for pure ZnO sample, band gap of 3.15 eV for 1 gm PVA capped ZnO thin film, and 3.1 eV for 2 gm PVA capped ZnO thin film. Therefore, band gap decreases and shows less transmittance in thin films in the visible region. All films exhibit good transmittance (approximately from 70 % to 80 %) in the range from 300 nm to 800 nm, and the films show a direct transition in the range from 3.1 eV to 3.2 eV, thus making the films suitable for optoelectronic devices such as window layers in SCs.

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Нанопорошок та тонкі плівки ZnO, отримані методом золь-гелю

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У роботі вивчено структурні та оптичні властивості тонких плівок ZnO. Чисті тонкі плівки ZnO готували на скляній підкладці методом золь-гелю із зануренням та відпалювали при температурі 150 ºC. Аналогічно, тонку плівку ZnO, леговану 1 гм PVA, готували і відпалювали при температурі 250 °C, а останній зразок – тонку плівку ZnO, леговану 2 гм PVA, готували і відпалювали при температурі 350 °C. Збільшення часу старіння золю призвело до поступового поліпшення кристалічності гексагональної фази для усіх дифракційних піків. Вплив старіння золю на оптичну прозорість цілком очевидний через посилене пропускання із збільшенням часу старіння золю. Цікаво, що 24-годинний час старіння золю виявився оптимальним для досягнення гладкої морфології поверхні, гарної кристалічності та високого оптичного пропускання, які були пов'язані з ідеальною стабільністю розчину. Тонкі плівки ZnO характеризувалися морфологічними, структурними та оптичними властивостями за допомогою скануючої електронної мікроскопії та ультрафіолетової та видимої спектроскопії (UV–Vis). Спектр пропускання ультрафіолетового випромінювання синтезованого зразка дає значення оптичної забороненої зони 3.2 еВ, 3.15 еВ і 3.1 еВ. Так само як і тонкі плівки, нанопорошок синтезується методом золь-гелю, характеризується XRD і може бути потенційно використаний у косметичній промисловості. Метод золь-гелю із зануренням створює чисті і леговані плівки ZnO з можливістю застосування як прозорі провідні електроди в оптоелектронних пристроях, таких як сонячні елементи і світлодіоди.

Ключові слова: ТСО, Нанесення покриття зануренням, Структурні властивості, Заборонена зона.