Zinc Oxide Nanofilms Prepared By Sol-Gel Method

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ABSTRACT

In the present study Nanofilms of zinc oxide have been prepared using sol-gel method using different molar ratios of zinc acetate solution (0.025M) and (0.1M). Using different experimental techniques the structural and optical properties of coated ZnO were studied. The XRD result shows different peaks corresponding the ZnO which confirms that the films were ZnO. The thickness and grain size of the films is in order of several nanometer ranges. The FTIR spectrum confirms the functional groups of the salts and the material retains the chemical structure. Optical band gap were calculated from the absorption spectra of UV-visible spectrophotometer. The polycrystalline films samples are having good transparency in visible and IR region. Wide band gap confirms that the coated nanofilms act as a semiconductor.

KEY WORDS: Nanofilm, Sol Gel, Semiconductor.

1. INTRODUCTION

Zinc oxide (ZnO) is an emerging material for an enormous number of areas. Zinc oxide has been determined as one of the most essential semiconductor materials for optoelectronics, solar cells, piezoelectricity, gas sensing, bio-applications etc. (Nagarani, 2013; Sangeetha, 2015; Vinod Kumar, 2013). ZnO has been an object of indispensable investigation, particularly in its low dimensional structures, thin layers with nanometer crystallites, nano-wires, nano-rods or nano-tubes, nano-bells and others. ZnO thin films have been made by a variety of techniques, among which there can be mentioned hydrothermal methods (Ni, 2005), electrochemical depositions (Chang, 2002), sol–gel method (Ristiac, 2005), chemical vapor deposition (Wu & Liu, 2002), thermal decomposition (Wang, 2009), and combustion method (Lamas, 1998). Recently, ZnO nanoparticles were prepared by ultrasound (Khorsand, 2013), microwave-assisted combustion method (Kooti, 2013), two-step mechanochemical - thermal synthesis (Rajesh, 2012), nanodization (Shetty, 2012) co-precipitation (Singh, 2013) and electrophoretic deposition (Vazquez, 2013; Vinod Kumar, 2013).

The sol–gel method has emerged as one of the most auspicious processing route as it is particularly efficient in producing thin, transparent, homogeneous, multi component oxide films of many compositions on various substrates at low cost and it allows the tuning of the refractive index and thickness of the film by varying synthesis parameters (Wasan, 2012). In this work, we have investigated the structural and optical properties of ZnO nanothin film sol-gel on glass substrates.

2. MATERIALS AND METHODS

The characteristics of the substrate are accompanied by the possibility of vacuum processing, availability, nature of the material surface and the price of the material. The substrate must possess high temperature stability, so that no chemical reactions can occur, or else the properties of the film will change. The nature and surface finish of the substrate material are important, because they greatly control the properties of films deposited onto them. Glass slides are the substrates chosen and cleaned with chromic acid.

Preparation of Zno Film: The ZnO films were derived by sol gel method on glass substrate by dip coating technique. The sol solution was prepared by adding Zinc Acetate is soluble in ethanol using magnetic stirrer. Organic solvent are low volume liquids hence they easily evaporated on heating. To get 0.1M concentration of solution contains, 0.5486 g of zinc acetate is accurately weighted using an electronic balance and add 25 ml of Ethanol. This beaker is placed on the magnetic stirrer to the zinc oxide is dissolve the zinc acetate completely in Ethanol. The other concentration are also prepared in the same manner, they are 0.025M, 0.1M.

Deposition of Zinc Oxide Film: Cleaned and weighted glass substrate are taken and placed into the substrate holder. Dip coating is done by immersing a substrate into a beaker containing the coating material, removing from the beaker, and allowing it to drain. The coated piece can be dried by force-drying.

Thickness and Grain Size Measurement: Thickness of the ZnO nanofilms plays an essential role in the study of properties of thin films. Different techniques are available for the measurement of thickness of the films like mechanical method, Electrical method, Magnetic method, Optical method, Gravimetric method. (Jae-Min Myoung, 2002). In the present work gravimetric method is used for thickness measurement by $T=M/\rho A$. The well cleaned glass plate is weighted. The grain size values of ZnO nanofilms are calculated adopting Scherrer's formula $t = K\lambda / B \cos \theta$.

3. RESULT AND DISCUSSION

ZnO nanofilms are prepared by Dip coating technique. The structural and optical characteristics are studied using XRD, FTIR and UV-visible spectrometer and the interpretations are discussed in detail.

XRD Analysis: The structural properties of ZnO are studied for different concentration 0.025M and 0.1 M. The deposition parameters are concentration (0.025M, 0.1M), solvent (Ethanol), dipping Time (15 min), No of times (30) constant.

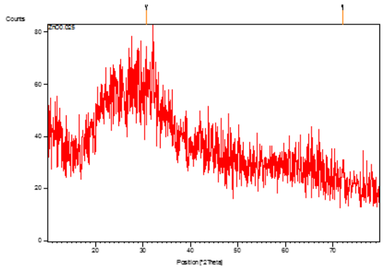


Figure.1. XRD Pattarn Of Zno Film (0.025M)

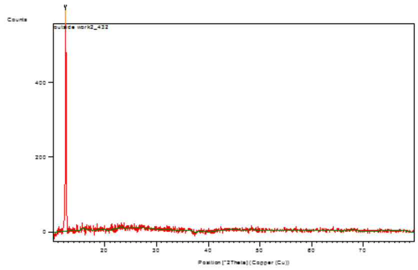


Figure.2. XRD pattern of zno film (0.1M)

Table.1a. XRD pattern of 0.025M

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
12.4328	558.06	0.1632	7.11370	100.00

Table.1b. XRD pattern of 0.1M

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
30.7604	25.64	4.0000	2.90435	100.00
72.0364	13.18	1.1769	1.30994	51.38

Fig.1 and 2, shows the XRD pattern of 0.025M & 0.1 M ZnO films respectively. The XRD result shows different peaks corresponding to ZnO which aggress with JCPDS values. Table.1, shows the grain size values calculated using Scherrer's formula. It confirms the formation of Nano ZnO film.

Table.1c. The grain size values calculated using Scherrer's formula

concentration (M)	2θ	FWHM	Grain size (10^{-9}m)
0.025	72.0364	1.1769	8.719099
0.1	12.4328	0.1632	50.8676

FTIR Analysis: The FTIR transmittance spectrum reveals the information about the phase composition as well as the way in which oxygen is bound to the metal ion structures. Fourier transform IR spectra were recorded for all the ZnO films prepared for different precursor in the range 400-4000 cm^{-1}. Figs.3 and 4, shows the FTIR spectrum of 0.025M & 0.1M respectively.

Table.2. (0.025M) (0.1 M)

Absorption band region cm^{-1}	Assignment	Experimental absorption cm^{-1}
3600-3200	OH stretching, H bond	3540.88
1660-1500	N-O asymmetric stretching	1581.12
675-1000	C-O stretching	1184.99
400-700	Oxide group	656, 539.99
Absorption band region cm^{-1}	**Assignment**	**Experimental absorption cm^{-1}**
3200-3600	OH stretching, H bond	3546.03
1500-1660	N-O asymmetric stretching	1593.99
1000-1320	C-O stretching	1184.99
400-700	Oxide group	656

The spectrum pertaining to ZnO film shows that the band approximately 3456 cm^{-1} for deposited film which reveals the presence of weakly hydrogen bonded hydroxide .The appearance of the string bands at 631cm^{-1} in the FTIR spectra is a clear evidence for the presence of the crystalline ZnO (Guru Prasad, 2013). These absorption are the figure print for the confirmation of oxide films. Thus it is evidenced from the above observations that the film consists mostly of ZnO with a small concentration of hydration.

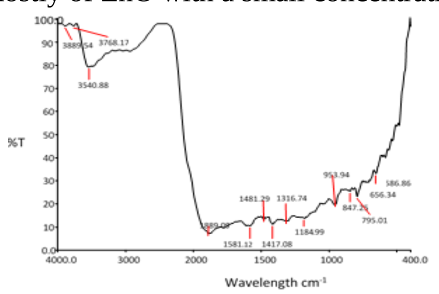


Figure.3. FTIR spectrum of ZnO film (0.1M)

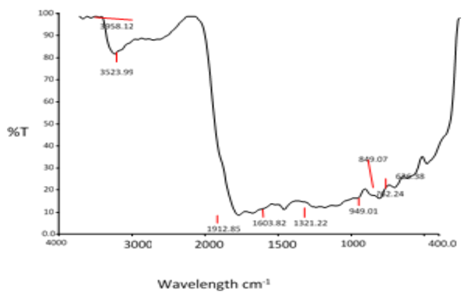
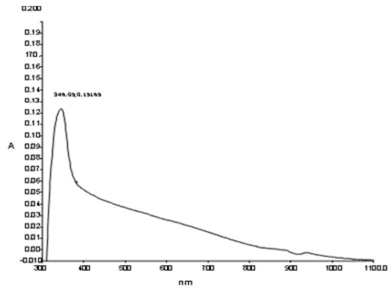


Figure.4. FTIR spectrum of ZnO film (0.025M)

Optical Studies:

Absorbance Studies For Zno Films: The absorption spectra of the ZnO films for different molar ratios are studies. From the studies graph are plotted between absorbance 'a' and the wavelength 'λ' in the range 300-1100 nm. The absorbance value enabled us to calculate the absorption co-efficient and band gap energies for the corresponding wavelength. The absorption edge occurs in the UV range. This is an important for applications such as transparent conductive devise and solar cell.



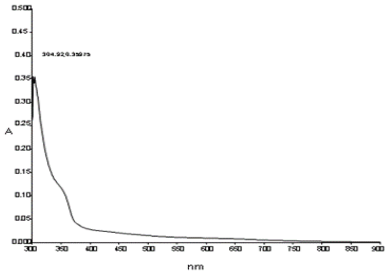
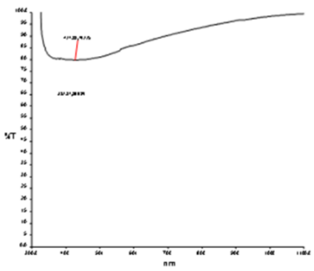


Figure.5. Absorbance Studies For ZnO FILM (0.025 M) **Absorbance Studies For ZnO film (0.1 M)**

Transmittance Studies For ZnO Film: From the studies graph were plotted between percentage of transmittance and wavelength.



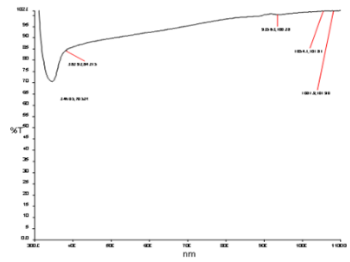
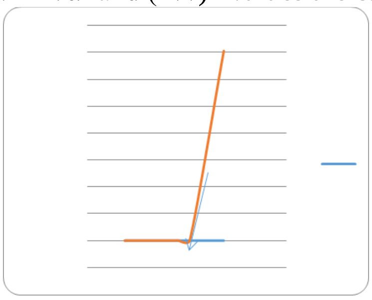


Figure.6. Transmittance Spectrum of ZnO (0.025 M) **Transmittance Spectrum Of ZnO (0.1M)**

The transmittance values for all the film have been tabulated in tables (3 & 4) and the corresponding graph are plotted in fig.7. From the graphs is clear that the transmittance increases with increase in wavelength and reaches the maximum value at (≈95%) and also there is constancy occurs in the visible region (850-1000 nm) for all molar ratio films (Mathammal, 2015).

Band Gap Studies for Zno Film: The band gap was obtained from the absorbance studies. From the absorbance values 'α' 'hν' 'hνα' and $(h\nu\nu)^2$ values are calculated and the values are tabulated.



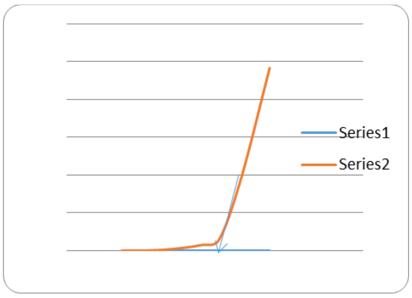


Figure.7. Band Gap Studies For ZnO film (0.025M & 0.1M)

The band gap value for all samples are obtained by plotting the corresponding graphs between hν along x-axis and $(h\nu\alpha)^2$ along y-axis as shown in fig.7. The band gap value is Eg≈3.1 eV.

Table.3. (0.025M)

Thickness=0.03708*10^{-6} m

Wavelength (λ) nm	Absorption	Transmittance (T)	α=2.303A/t μm	E=1234/λ	(hυα)	$(h\upsilon\alpha)^2$
300	0.1982	63.365	12.30833	4.11333	50.62828	2563.223
350	0.1138	76.940	7.067046	3.52571	24.91638	620.8262
400	0.0422	90.742	2.620644	3.085	8.084688	65.36218
450	0.0339	92.484	2.10521	2.7422	5.772953	33.32698
500	0.0266	94.062	1.651875	2.468	4.076829	16.62053
550	0.0217	95.134	1.347583	2.2436	3.023485	9.101463
600	0.0187	95.780	1.161281	2.05667	2.388368	5.7043
650	0.0164	96.285	1.01845	1.89846	1.933487	3.738373
700	0.039	96.858	0.863198	1.76285	1.521695	2.315855

750	0.0122	97.235	0.757627	1.64533	1.246549	1.553885
800	0.0108	97.555	0.670686	1.5425	1.04534	1.01026
850	0.0097	97.786	0.602376	1.45176	0.874508	0.764760s
900	0.0086	98.030	0.534065	1.37111	0.732262	0.532608
950	0.0078	98.216	0.484385	1.2989	0.62919	0.39588
1000	0.0073	98.328	0.453334	1.234	0.559414	0.312945
1050	0.0065	98.517	0.403654	1.17523	0.474389	0.225045
1100	0.0062	98.584	0.385324	1.12181	0.431926	0.18656

Table.4. (0.1M)

Thickness=0.024396*10^{-6} m

Wavelength (λ) nm	**Absorption**	**Transmittance (T)**	**α=2.303A/t μm**	**E=1234/λ**	**(hυα)**	**(hυα)2**
300	-0.204	274.88	-0.37767	4.11333	-1.55349	2.41336
350	0.1481	96.085	0.274184	3.52571	0.96669	0.93449
400	0.0658	94.485	0.121819	3.085	0.37581	0.14123
450	0.0542	94.861	0.100343	2.7422	0.27515	0.07570
500	0.0468	95.247	0.08664	2.468	0.21382	0.04572
550	0.0406	95.780	0.07516	2.2436	0.16863	0.02843
600	0.0338	96.517	0.06257	2.05667	0.12869	0.01656
650	0.0277	97.437	0.051282	1.89846	0.09735	0.00947
700	0.0209	98.631	0.038693	1.76285	0.06821	0.00465
750	0.0135	99.834	0.025081	1.64533	0.041266	0.00170
800	-0.0071	100.96	0.013144	1.5425	0.020275	0.000411
850	-0.0032	101.92	0.005924	1.45176	0.00860	0.000073
900	-0.001	102.60	-0.00185	1.37111	-0.00253	0.0000064
950	-0.002	103.11	-0.00370	1.2989	-0.00480	0.000023
1000	-0.005	103.60	-0.00925	1.234	-0.01142	0.00030
1050	-0.007	103.86	-0.01295	1.17523	-0.01522	0.00023
1100	-0.009	104.05	-0.01666	1.12181	-0.01869	0.000349

4. CONCLUSION

A zinc oxide nanofilm was prepared using dip coating method in different ratio 0.025M, 0.05M and 0.1M. Using different experimental techniques the structural and optical properties of coated ZnO was studied. The XRD result shows different peaks corresponding the ZnO which confirms that the film was ZnO. XRD peaks agreeing with the standard JCPDS values. The thickness of the films is in order of several nanometer ranges. The FTIR spectrum confirms the functional groups of the salts and the material retains the chemical structure. Optical band gap were calculated from the absorption spectra of UV-visible spectrophotometer. The polycrystalline films samples are having good transparency in visible and IR region. Wide band gap confirms that the coated nanofilms act as a semiconductor.

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