IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 8, Issue 5 Ver. I (Sep - Oct. 2016), PP 10-17
www.iosrjournals.org

Some Physical Properties of ZnO/SnO2 Thin Films Prepared By Spray Pyrolysis Technique

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Abstract: *ZnO/SnO2 thin films with different percentage (1:1,1:2,2:1) were deposited on a glass substrate by Spray Pyrolysis technique using solution of zinc acetate ,tin chloride and air as the carrier gas at 400 °C temperature. The structural properties of the composite films are investigated by x-ray diffraction andAFM. The optical spectra of the films were measured in the wavelength range of 300 –1100nm by UV-VIS Spectrometer device.Optical constants such as Absorption coefficient α, refractive index n , extinction coefficient k and dielectric constant were determined from transmittance spectrum in the UV-VIS regions. The films were found to exhibit high transmittance inthe visible regions. The energy band gapof the films were evaluated as 3.85,3.70,3.70,3.85 and 3.60 eV for ZnO pure,SnO2 pure and the percentage (1:1,1:2,2:1) of ZnO:SnO2 respectively.*

Keywords: *Metal-oxides , Morphological structures,Dopant elements,spray pyrolysis ,Optical properties ,Structural properties .*

I. Introduction:

Recently transparent conducting Oxides (TCO's) have drawn much interest in the field of optoelectronics [1].Transparent conducting oxides are the material which exhibit higher optical transmittance in visible region, low sheet resistance and higher electrical conductivity. Zincstannite or zinc tin oxide (ZTO) is a class of ternary oxides that are known for theirstable properties under extreme conditions, higher electron mobility compared to itsbinary counterparts and other interesting properties. These materials is thus ideal forapplications from, gas detector, solar cells photocatalysts, light-emitting diodes, fieldeffect transistors and (heterojunction and homojunction) diodes [2-5].ZnO thin films are grown by different techniques such as pulsed laser deposition (PLD), magnetron sputtering, MOCVD, spray pyrolysis etc [6-9].Among the various TCO's such as ZnO, In_2O_3, CdO, $TiO_2$and SnO_2[10], $SnO_2$and ZnOis the most promising candidate for the development of transparent conductive material. SnO_2 is an rutile tetragonal structure with oxygen deficient n-type degenerate semiconductor with wide band gap of 3.6 eV. Its high optical transparency and electrical conductivity leads to very appealing applications in spintronics device. ZnOin view of its high transmission over a wide spectral range including the useful UV-vis region and other interesting characteristics such as low toxicity, relatively low cost, and stability in reductive chemical environments.

In the present work, ZnO:SnO_2 thin films were prepared using Spray Pyrolysis method. The influence of ZnO:SnO_2 content level on structural and optical properties in the composite had been studied.

II. Experimental procedure:

Preparation of an aqueous solution of tin Chloride $SnCl_2.2H_2O$ andzinc acetate$Zn(CH_3COO)_2.2H_2O$with purities 99.9% and concentration of 0.1M at (0,1:1,1:2,2:1,0)% ratiosby dissolving in distilled water and stirred with a magnetic stirrer for 15 minute.The spraying apparatus was manufactured locally in the department laboratories. . Figure (1) shows a typical spraying system.

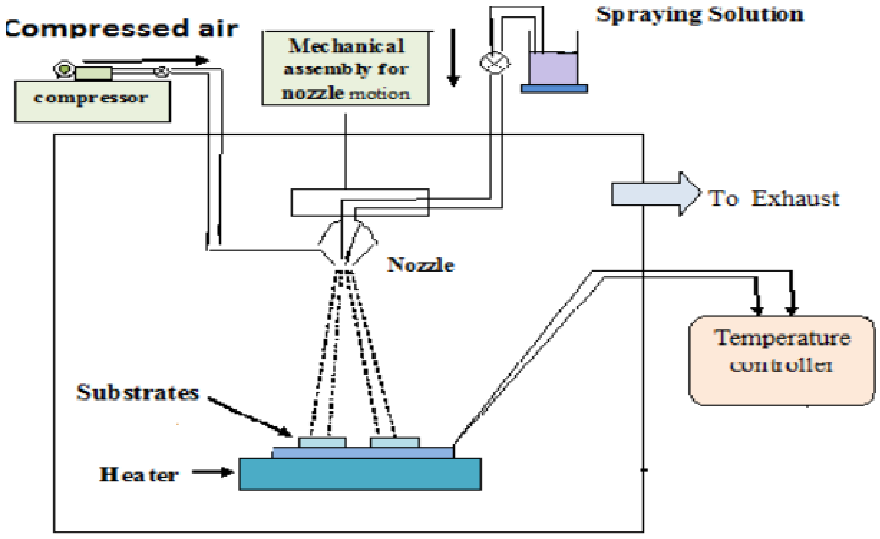


Figure (1) Schematic set-up for spray pyrolysis technique.

In this technique, the prepared aqueous solutions were atomized by aspecial nozzle glass sprayer at heated collector glass fixed at thermostatic controlled hotplate heater.Air was used as a carrier gas to atomize the spray solution with the help of anair compressor with pressure (7 Bar) air flow rate (8 cm^3/sec) at room temperature.The glass substrate were cleaned with ethanol in ultrasonically cleaner and then dried.The glass substrate(0.1 cm thickness) temperature was maintained at 400 ^oCduring spraying , coating thickness was 400 nm by tested by optical microscopy.The distancebetween the collector and spray nozzle was kept at (30 ±1 cm), number of spraying (100) and time between two spraying (10 sec).

The X-ray diffraction (XRD) data of the prepared films were taken usingCuK_α with radiation of wavelength λ =1.5406Å , current =15mA , voltage = 30 kV and scanning speed = 2 deg /min) over the diffraction angle range 2θ=20-60 at room temperature .The average crystallite size (D) was estimated using the Scherrerequation as follows[5] :

$$D=0.9\lambda/\beta \cos\theta \quad (1)$$

where λ, β, and θ are the x-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and Bragg's diffraction angle respectively.

The surface distribution of ZnO: SnO_2 thin films were measured using a scanning probe microscopy (CSPM-5000) instrument.

UV-VIS, Phoenix-2000V device was used to record the optical transmission for ZnO:SnO_2 thin films.

The values of refractive index (n) and extinction coefficient (k) can be determined from the absorption coefficient α and reflection (R) spectra. The refractive index is the written in terms of reflectance of the surface as [12]:

$$n = (4R/(R-1)^2 - k^2) - ((R+1)/(R-1))^{1/2} \quad (2)$$

While the extinction coefficientis related to the absorption coefficient α by:

$$k=\alpha \lambda /4\pi \qquad (3)$$

The forbidden energy gap of indirect transition both allowed, forbidden calculated according to the relationship [13] :

$$\alpha h\nu=\beta (h\nu - E_g)^r \quad ....(4)$$

$h\nu$: istheenergyofphoton, β:isproportionalityconstant,E_g: isenergygapofthetransition.

III. Results and Discussion

3-1-X-ray Characterization

The XRD pattern of ZnO thin film fabricated by spray pyrolysis method on glass substrate is shown in Figure 2.

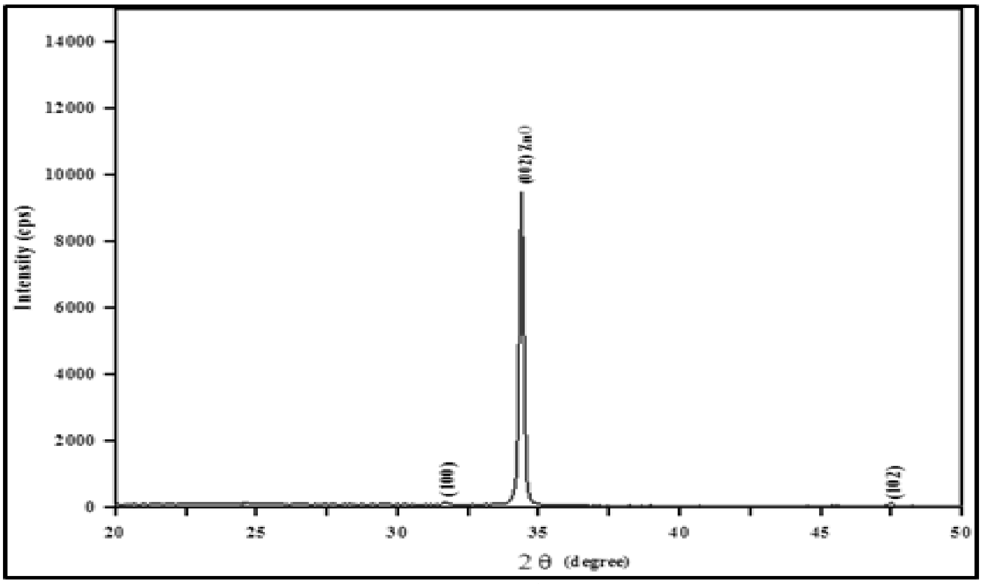


Fig. 2XRD patterns for pureZnO

All the peaks of the ZnO thin films correspond to the peaks of standard ZnO (JCPDS S6-314). ZnO have wurtzite type polycrystalline thin film with a hexagonal system revealing that the highly dominant to c-axis oriented(The appearance of the preferentialdiffraction peak, assigned to the plane (002), indicates that the film growth is achievedalong the axis c of the hexagonal structure normal to the substrate surface). The film was grown, no characteristic peaks for any otherimpurities were observed, suggesting sample have high purity.This result is agree withZiaulRaza Khanetal[14]

The three peaks indexed to the (110), (101) and (200) diffraction planes of the tetragonal lattice of SnO_2[15]show that SnO_2 has beensuccessfully deposited throughspray pyrolysis technique(as shown in figure 3).

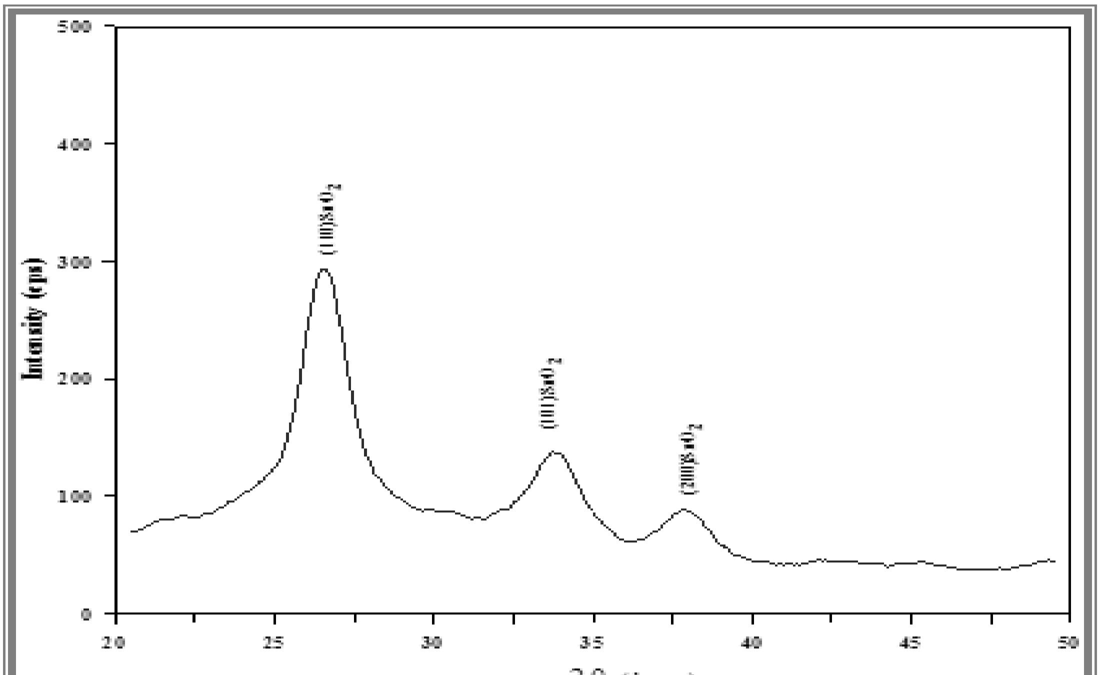


Fig. 3XRD patterns for pureSnO_2

The result of X-ray diffraction which represent all mixing ratiofor precipitation thin films on glass substrates are shows in Figure4.The XRD patternsresult shows match with standard value in (JCPDS card No. 36-1451). Howeverpeaks of SnO_2 (110) and (101) planes can be clearly seen for the film with 1:2 for ZnO:SnO_2, and the peak intensity of SnO_2 increases with the decreasing SnO_2 content in the composite. It is also seen that as the content of SnO_2 increases, the peak of ZnO can be clearly detected.

However peak of ZnO (002) plane can be clearly seen for the film with 1:1 and 2:1 for ZnO:SnO_2, and the peak intensity of ZnO increases with the decreasing ZnO content in the composite. This indicates that the addition of SnO_2 modifies the growth orientation of ZnO layers, as the crystal structure of SnO_2 tetragonal structure is quite different from that hexagonal structure of ZnO. During the deposition process, ZnO and SnO_2 were alternately deposited on each other, different crystal structures and different surface energy would induce lattice distortion and some preferred orientation growth.

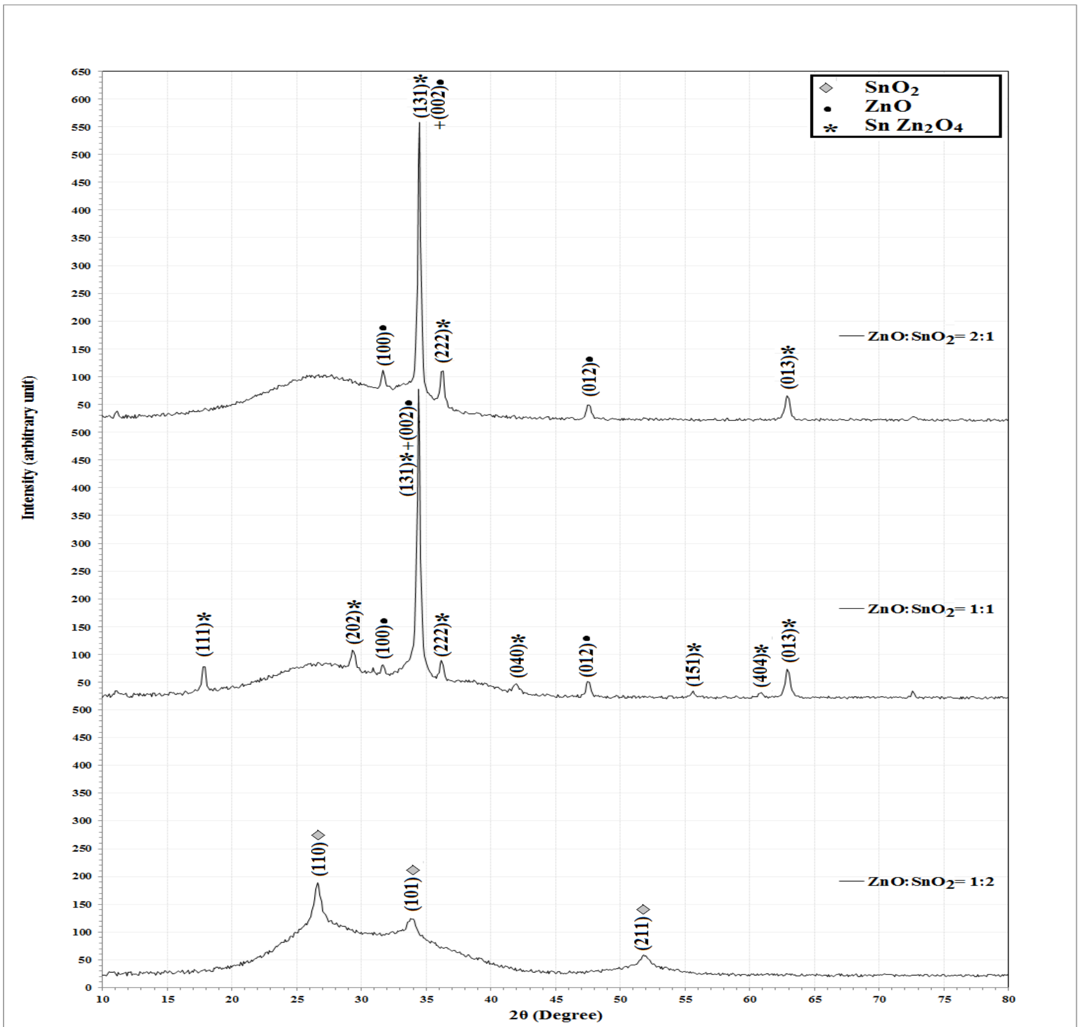
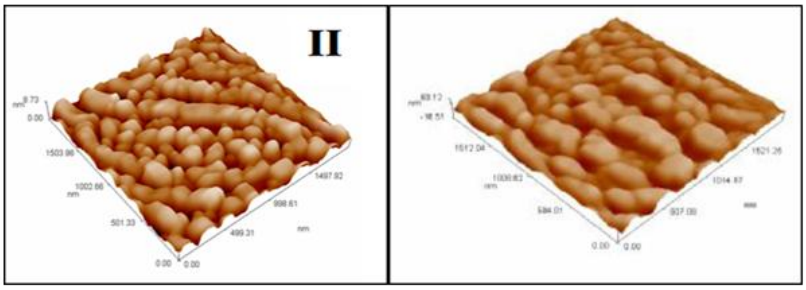


Figure4 show the x-ray diffraction (XRD) patterns of the ZnO/SnO_2 composite films with different contents

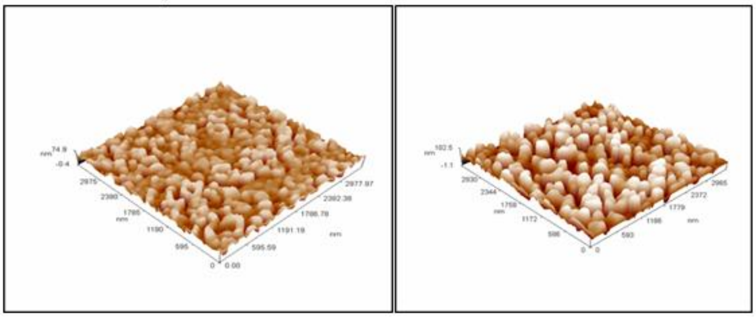
3-2-Atomic force microscopy:

The surface morphology of ZnO/SnO_2 thin films were prepared at different concentration deposited on glass substrate at substrate temperature (400^{O}C) has been examined by atomic force microscopy .

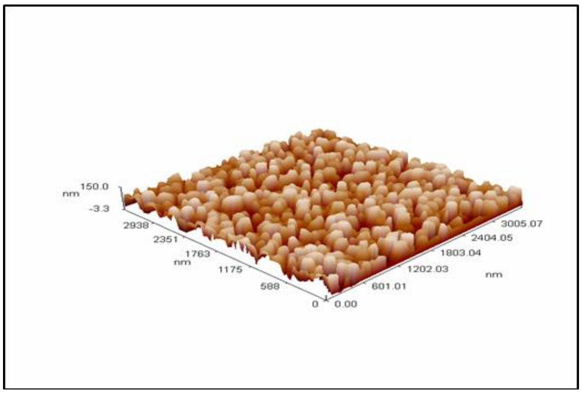
The three-dimensional (3D) topographic views of AFM images for films are shown in figure (5). The AFM images reveal that the concentration rate has a strong effect on the surface morphology. The films reveal homogenous surface and consists of well-shaped pyramidal grains with sharp edges and tip. The roughness of the pure ZnO film is measured to be 8.73 nm, for pure SnO_2 films is measured to be 53.12 .the roughness of the samples decreases with increase SnO_2 concentration. The roughness of 1:1, 1:2, and 2:1 for ZnO:SnO_2 measured is 102.5,150 and 74.9nm respectively. The grain size of thin films were evaluated at (50.9, 64.5 and 75.5) nm respectively .



pure ZnO　　　　Pure SnO_2



1:2 for SnO_2:ZnO composition1:1 for SnO_2:ZnO composition



1:2 for ZnO:SnO_2 composition

Fig-5: AFM of ZnO/SnO_2 composite thin films deposited with different content

3-3-Optical properties:

The Uu-Vis spectra of the ZnO/SnO_2 composite films with different contents in the wavelength range of 300 –1100nm are shown in Fig. 6.

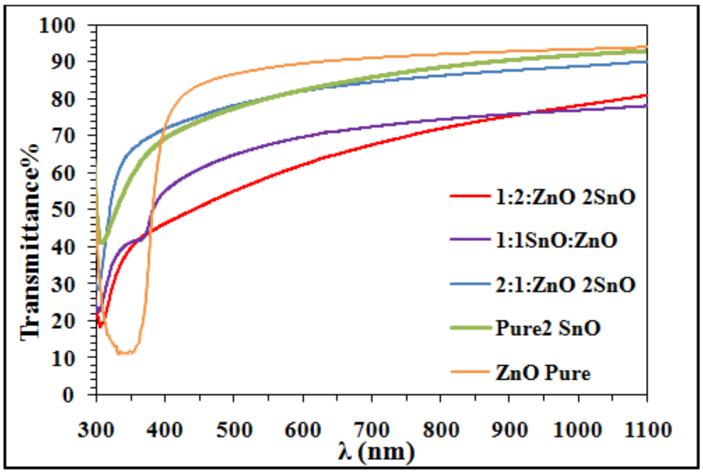


Fig.6. Optical transmission spectra of ZnO/SnO_2 pure and their compostion thin films deposited with different percentage.

All the pure ZnO and SnO_2films show highly transparent in the visibleregion and some oscillations due to thin film interference effects. It can also be observed that thereis a slight shift in the absorption edge towards longer wavelengths, as well as a loss in the absorption edge sharpness, as the content of ZnO in the composite film increases.The sharp rise in transmission is an identification of good crystallinity of films [16]. It is observed that the films obtained at mixed film shows slightly less transmittance in visible region as compared to the pure films. These results slightly increase in optical band-gap of ZnO films and it may be due to the small grain size of the polycrystalline ZnO films.
The optical absorbance in R.T were from 400 to 1100 nm is shown in fig.7.

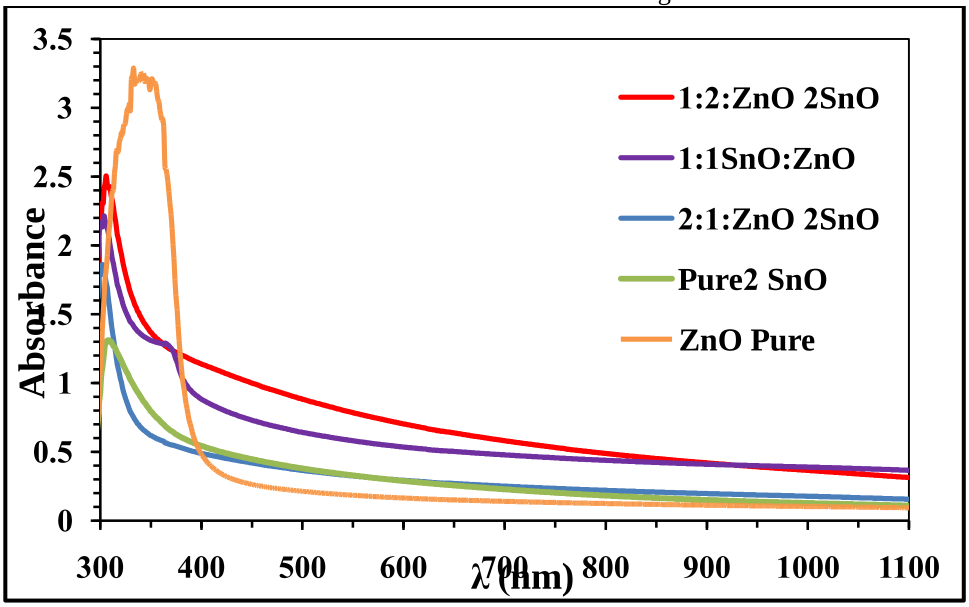


Fig.7: Absorptionspectra forof ZnO/SnO_2 pure and their compostion thin films deposited with different percentage.

The absorbance decrease with increase of wavelength and composition.The exciton absorption at 360 nm is observed in the absorption spectrum for pure ZnO. When photons of higher energy are larger than band gap of the semiconductor, an electron is transferred from the valence band to the conduction band where there occurs an abrupt increase in the absorbency of the material to the wavelength corresponding to the band gap energy. The refractive index of coated ZnO/SnO_2 thin film as a function of wavelength is given in Fig. 8.

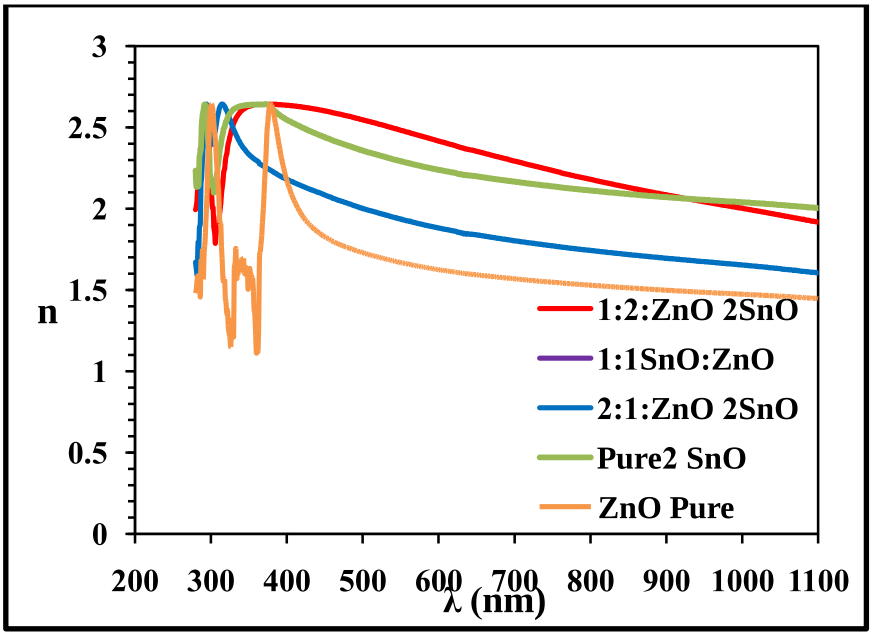


Fig.8. Reflective index spectra of ZnO/SnO_2 pure and their composition thin films deposited with different percentage.

The refractive index decreases with the increase of wavelength according to the Sellmeier formula[17].

$$n(\lambda) = \{ A_n + B_n\lambda^2/(\lambda^2 - C^2_n)\}^{-0.5}$$

where A_n, B_n and C_n, are the fitting parameters.

Figure 9 represents the extinction coefficient of the ZnO/SnO_2 thin film with respect to wavelength. The extinction coefficient shows dispersion behavior according to the Sellmeier relationship of extinction coefficient.

$$k(\lambda) = [n(\lambda)(B_1\lambda) + B_2/\lambda + B_3/\lambda 3]^{-1}$$

whereB_1, B_2, and B_3 are the fitting parameters.

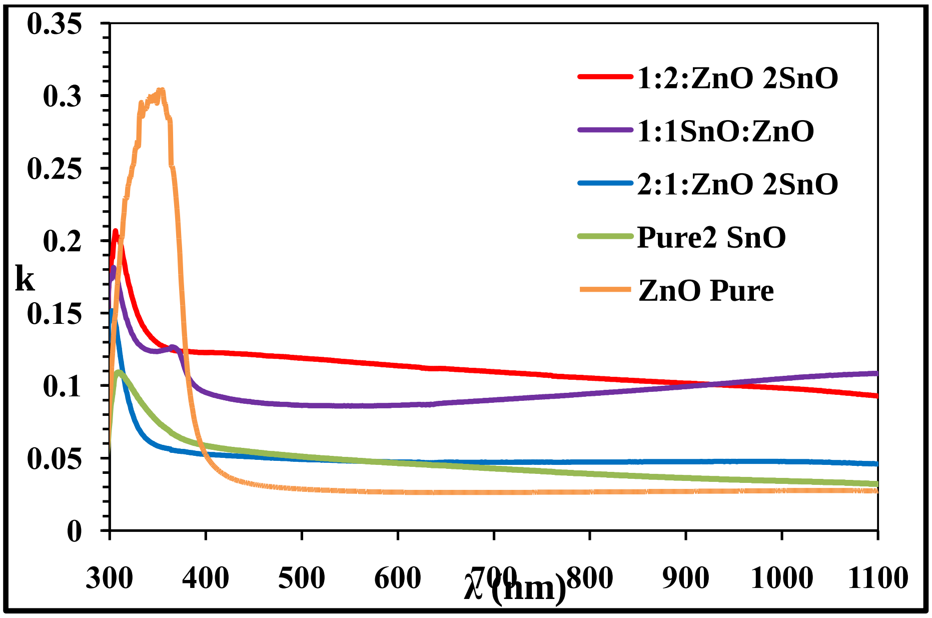


Fig.9. extinction coefficient spectra of ZnO/SnO_2 pure and their composition thin films deposited with different percentage.

The value of the optical band gap calculated using the standard fundament absorption[18]. Optical band gap of these thin films deposited on glass substrate, was calculated from the intercept on energy axis obtained by extrapolating the linear portion of the Tauc plot of $(\alpha h\nu)^2$ vs photon energy (hν) as shown in Fig. 10.

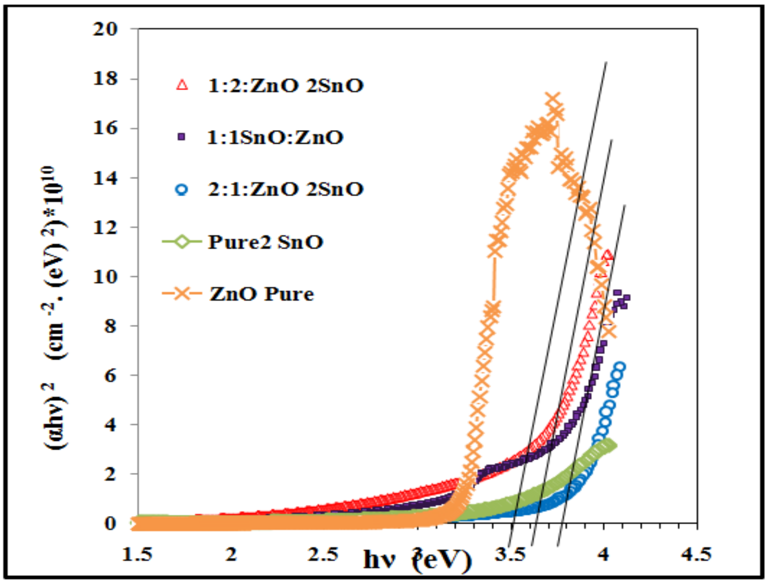


Fig.10: Optical band gap for ZnO/SnO_2pure and their composition thin films deposited with different percentage.

Band gap for as-grown SnO_2 thin film is found to be 3.70 eV .For band gap for as-grown ZnO thin film is found to be 3.85 eV and the band gaps for ZnO:SnO_2 is 3.60,3.70and 3.85 for2:1,1:1and 1:2 showing a slightly increasing with the increasing ZnO percentage.As the size of semiconductor particles decreases to the nanoscale, the band gap of the semiconductor increases, causing a blue shift in the UV–Vis absorption spectra due to quantum confinement [18].

IV. Conclusion

ZnO/SnO_2 composite films have been obtained on glass substrates by Spray Pyrolysis under a substrate temperature of 400∘C. The physical properties of these films have been studied in detail as a function of diffrent content. The films consist of two phases of ZnO and SnO_2 nano crystalline grains, and the grain size of the film decreases significantly with the increasing ZnO content. All the ZnO/SnO_2 composite films show high transmittance in the visible region.

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