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CORE-SHELL TiO_2/ZnO THIN FILM: PREPARATION, CHARACTERIZATION AND EFFECT OF TEMPERATURE ON SOME SELECTED PROPERTIES

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Novel TiO_2/ZnO core-shell thin film have been synthesized in a PVA matrix via simple, inexpensive and highly reproducible chemical bath deposition technique and were thermally treated under various annealing temperatures up to 673K in order to determine the effects of thermal annealing on the structural and optical properties of the film. Our results showed that there is more crystallization and more orientation of the crystal growth with increase in temperature. The results also revealed that the films show very high transmittance (60-95%) in the visible/near infrared regions of the electromagnetic spectrum thereby making the film a very good material for warming applications. Both the absorbance and the reflectance are generally low (<20%), dwindling with wavelength. The band gap of the thin films is in the range of 3.8 - 4.2eV. The values showing considerably variation with annealing temperatures. The wide range of band gap expands the possibilities of using the thin films for solar photo voltaic application. The maximum index of refraction within the temperature range is 2.2.

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1. Introduction

The need to harness the abundant solar energy resources cannot be overemphasized. Energy conversion in solar modules consists of electron-hole pairs creation in semiconductors by the absorption of light and separation of electrons and holes by an internally generated electric field [1]. When two terminals of such semiconductor is connected externally, charge carries are collected by electrodes giving rise to a photocurrent [1,2]. The spectrum of solar light energy spreads from the ultra violet region (300nm) to the infra red region (3000nm). When a photon of energy, hυ, smaller than the band gap of a semiconductor material is impinged on such material, the light is transmitted through the material. On the other hand, when the photon energy is larger than the band gap, electrons in the valance band are excited to the conduction band thereby creating an electron- hole pair. This process is called band – to – band conduction [2,3]. The cut off wavelength is very important when deciding for a solar cell material because light with wavelength longer than the cut off wavelength cannot be used for solar energy conversion [4,6].The use of heterojunction (HJ) with large band gap window material and a small band-gap absorber material is a means to reduce the surface recombination loss that might otherwise dominate in direct band gap materials. Thus the use of heterojunctions expands the semiconductor material possibilities for solar photo voltaic application. Thin films of TiO_2 and ZnO oxide film are some of the metal oxide semiconductors which have been found to be very useful as a UV detector [5]. As important group II-IV semiconductor thin films with versatile characters, these films possess wide applications in various field: such as gas sensors, transducers, catalysis, secondary batteries and super capacitors [6]. In recent years, the development of core/shell structured materials on a nanometer scale has been receiving extensive attention [7,8]. The shell can alter the charge, functionality, and reactivity of surface, or improve the stability and dispersive

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ability. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material having synergetic or complementary behaviours between the core and shell materials. Many studies on the synthesis of composites, i.e. TiO_2 [9], $CaCO_3$ [10], Fe_2O_3 [11] and Ag coated with SiO_2 shells have been reported.

In this study, we report the synthesis of novel TiO_2/ZnO thin film in a PVA matrix via simple and inexpensive chemical both deposition technique. We also present the effect of post deposition annealing on the as-deposited film at temperature of 373K and 673K.

2. Theory

The uses of films in optical applications require accurate knowledge of the optical constants over a wide wavelength range [12]. The relationship between reflectivity (R) of materials of refractive index (n) and the extinction coefficient (k) is given by [11]

$$R = \frac{(n-1)^2 + k^{\ 2}}{(n+1)^2 + k^2} \tag{1}$$

While optical transmittance (T) is related to the absorption coefficient (α) and the refractive index (n) by the relation [12]

$$T= \frac{(1-R)^2 \exp(-\alpha d)}{(1-R^2)\exp(-2\alpha d)} \tag{2}$$

Also the absorption coefficient (k) and the extinction coefficient (α) are related to each other by the relation [5, 12]

$$K = \frac{\alpha\lambda}{4n} \tag{3}$$

From equation (1), k and n can be defined from the measurement of R and T.
The real part of the dielectric constant is related to n and k by the relations [10]

$$\varepsilon_r = n^2 - k^2 \tag{4}$$

While the imaginary part of the dielectric constant is related to n and k by the relation [5]

$$\varepsilon_I = 2nk \tag{5}$$

The absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors are employed in the determination of the energy gap E_g. The E_g was calculated ΔE_g using the relation,

$$\alpha = \frac{A\left(\lambda\upsilon - E_g\right)^n}{h\upsilon} \tag{11}$$

Where A is a constant, hυ is the photon energy and α is the absorption coefficient, n depends on the nature of transition. For direct transition n = $\frac{1}{2}$ or $\frac{2}{3}$ while for indirect, n=2 or 3 depending on whether they are allowed or forbidden respectively. However, the usual difficulty in applying this concept to polycrystalline thin films with nanometre scale crystalline grain is the size distribution of grains and consistent change in the band gap due to quantum confinement effect

[12, 14]. Thus the straight line portion may not extend beyond a few tenths of an electron volt and hence value of the band gap could turn out to be very subjective [13]. The details of the mathematical determination of absorption coefficient can be found in literature [14, 16]

3. Experimental

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following order. First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA and stirred at 363K for 60mins. The solution was aged until the temperature dropped to room temperature. To obtain the deposition of TiO_2, the chemical bath was composed of 12 mls of 1M $ZnCl_2$, 12mls of 1M $NH4Cl_4$, 12mls of 10M NH_3 and 13 mls of PVA solution put in that order in 100ml cleaned and dried beaker. Four (4) clean glass slides were then inserted vertically into the solution. The deposition was allowed to proceed at a temperature of 338K for 3hrs in an oven after which the coated substrate were removed, washed with distilled water and allowed to dry. To obtain the TiO_2/ZnO core-shell, the TiO_2 already formed (core) was inserted in a mixture containing 12mls of 1M $ZnCl_2$, 12mls of IM NH_4Cl, 12mls of 10M NH_4OH and 40mls of PVA in 100ml beaker. Deposition was allowed to proceed at same temperature and duration. Two of the deposited films were annealed in an oven at 473K and 673K respectively for 1hr. One of the samples was left unannaeled to serve as the control.

4. Results and discussion

Structural analysis of the films was carried out using X-ray diffraction (XRD) method within the range of 15- 75^0 on a computer controlled Phillips pin 1500 X-ray diffractometer of CU-Kα wavelength (1.5408Å). The composition of the films was determined using Rutherford back scattering (RBS) ,while the optical properties of the CBD deposited films were measured at room temperature from Unico-UV-2102PC Spectrophotometer at normal incident of light in the wavelength range of 200-1200nm. From the absorption spectra, optical band gaps of the samples were determined. The crystalline grain size was calculated using the Scherrer formula

$$D=0.89\lambda/\beta\cos\theta \tag{15}$$

Where D is the average crystalline size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The crystallite size for the annealed film at 373K and 673K are 18.31nm and18.03nm respectively.

The chemical status and the elemental composition of the film analysed by using RBS method are presented in fig.1 and table 1 respectively. We can deduce that the thin film of TiO_2/ ZnO deposited has no impurity and that the thickness is 950nm.

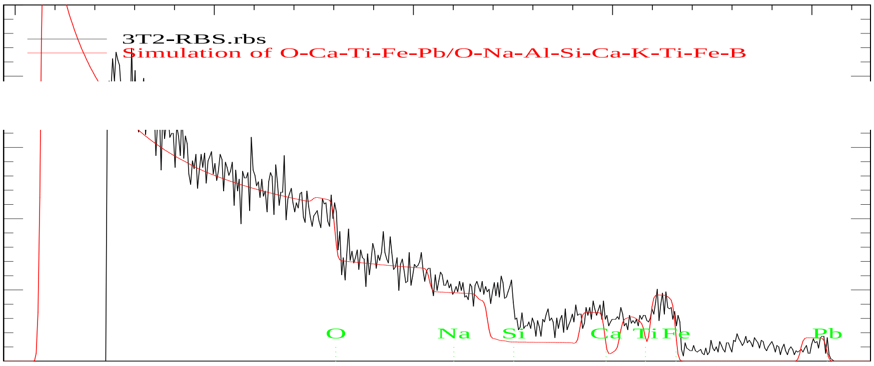
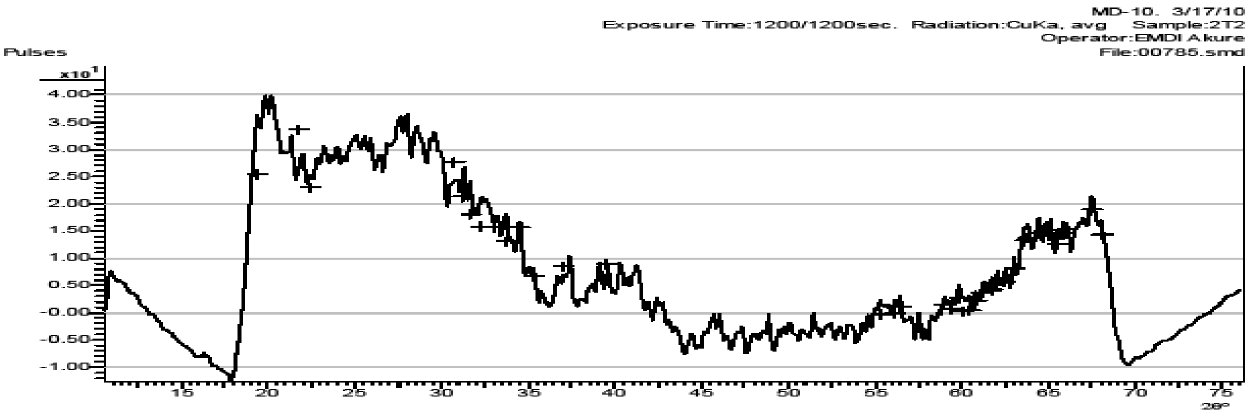


Fig.1 RBS of TiO_2/ ZnO thin film

Table 1. Composition of TiO_2/MnO film from RBS analysis

sample	Na	Ca	K	Al	Ti	Zn	B	Fe	O	Si
Glass slide	0.136	0.002	0.003	0.027	0.003	-	0.026	0.006	0.629	0.050
TiO_{2-} /ZnO_2	-	-	-	-	0.060	0.061	-	-	0.888	

Fig.2 and fig.3 show the XRD patterns of TiO_2/ZnO thin films deposited. A close look at the two diffractograms show several peaks. Prominent among them are peaks at 2θ values of around 20.87^0, 32.11^0, 69.54^0 corresponding to diffraction lines produced by (101), (104) and (119) plane (JCPDS 35-0D88) respectively. A close look at figures 2-3 shows an improvement in the crystallinity of the films. A comparison between the spectra of the two films in (2) and (3) show that there is more crystallization and more orientation of the crystal growth in the case of film annealed at 673K. The peaks at 2θ values of 25.68^0 and 59.99^0 are attributed to orthorhombic TiO_2 (JCPD -29-1360) with lattice parameter a=b=c=4.120 Å. These were assigned to the diffraction line produced by (111) and (123) planes. However the additional peaks at an angle of 34.89 and 48.01 are identified to be ZnO (JCPD –29-0902) and are assigned diffraction line produced by (110) and (024) planes of the $ZnTiO_3$ (pyrophanite) phase. These results suggest that the thin films deposited in this work are a mixture of zinc and titanium. The existence of this high pressure magnetic phase implies that the film can be used as magnetic resonance element.



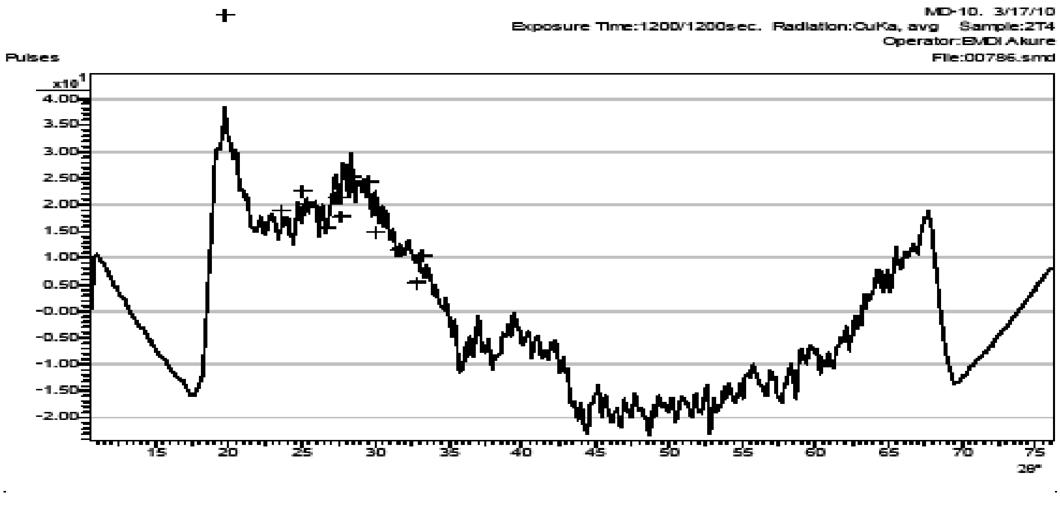
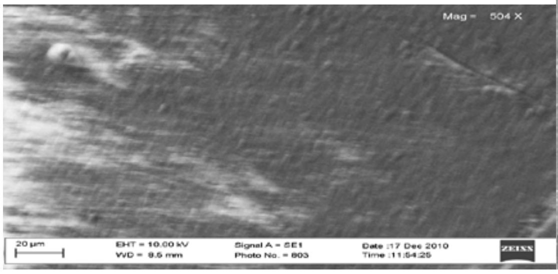


Fig.3 Diffractogram of TiO_2 / ZnO thin films at 673K

The SEM of the as-deposited, thermally annealed at 373K and 673K are displayed in figures 4, 5 and 6 respectively. The SEM show a decrease in grain size as annealing temperature increases due to effects of evaporation of absorbed water and reorganization of the grain. Uniform distribution of the grain is also observable with the gradual fading in colour from grey to yellowish brown.



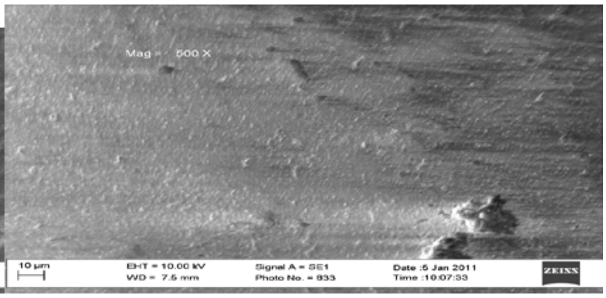


Fig.4. SEM of film as deposited film

Fig.5 SEM of film annealed at 373K

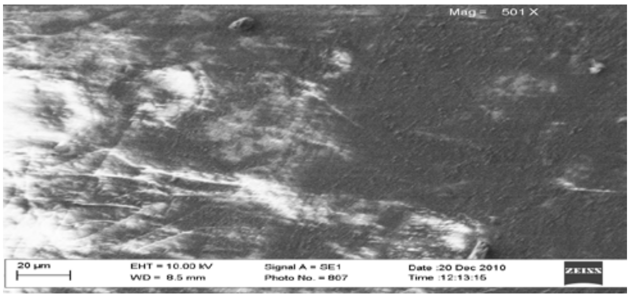
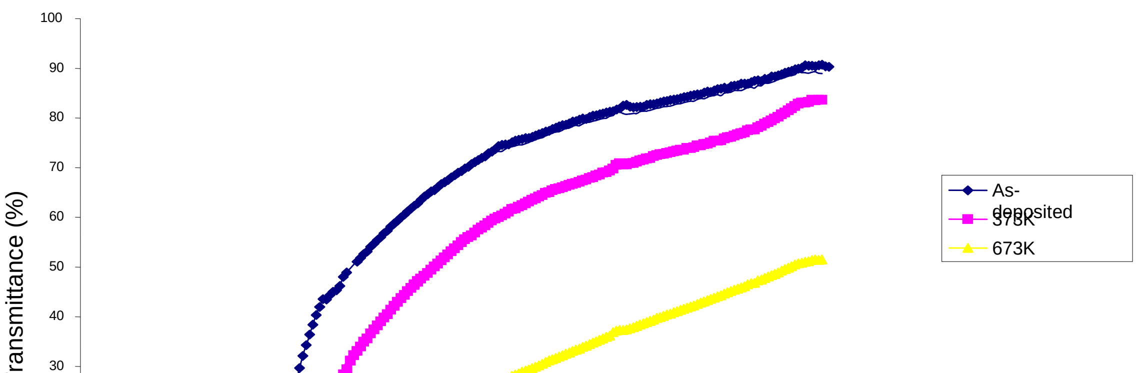


Fig.6 SEM of film annealed at 673K.

Figs. 7 and 8 are plots of transmittance against wavelength and absorbance against wavelength respectively for TiO_2/ZnO core shell oxide films deposited in this work. From fig.7, we deduce that the transmittance increases with wavelength for all the samples. This is due to the increase in crystalline size associated with higher densifications of the film. The figure also shows high transmittance of the film in the NIR region of the solar spectrum. The plots also show that in the UV region, samples exhibit low transmittance. Thin films of TiO_2/ ZnO of displays high absorbance values in the IR region and virtually non-absorbing in the UV-VIS at all temperatures.
The spectral absorbance and transmittance displayed in figures 7 and 8 shows that TiO_2/ ZnO thin films could be used as spectrally selective window coatings in cold climate to facilitate transmission of VIS and NIR while suppressing the UV portion of the solar radiation. The thin film can be used for coating eyeglasses for protection from sunburn caused by UV radiations.



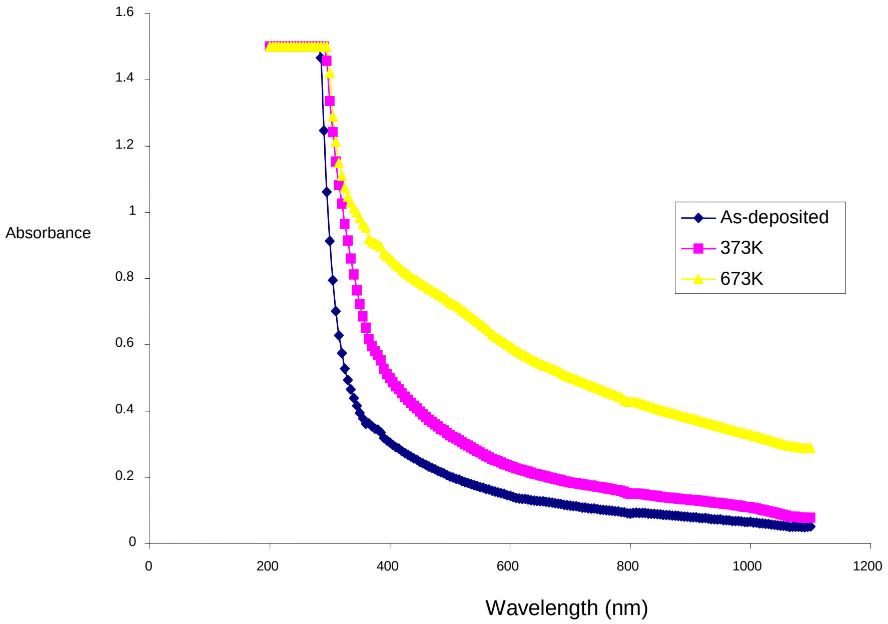
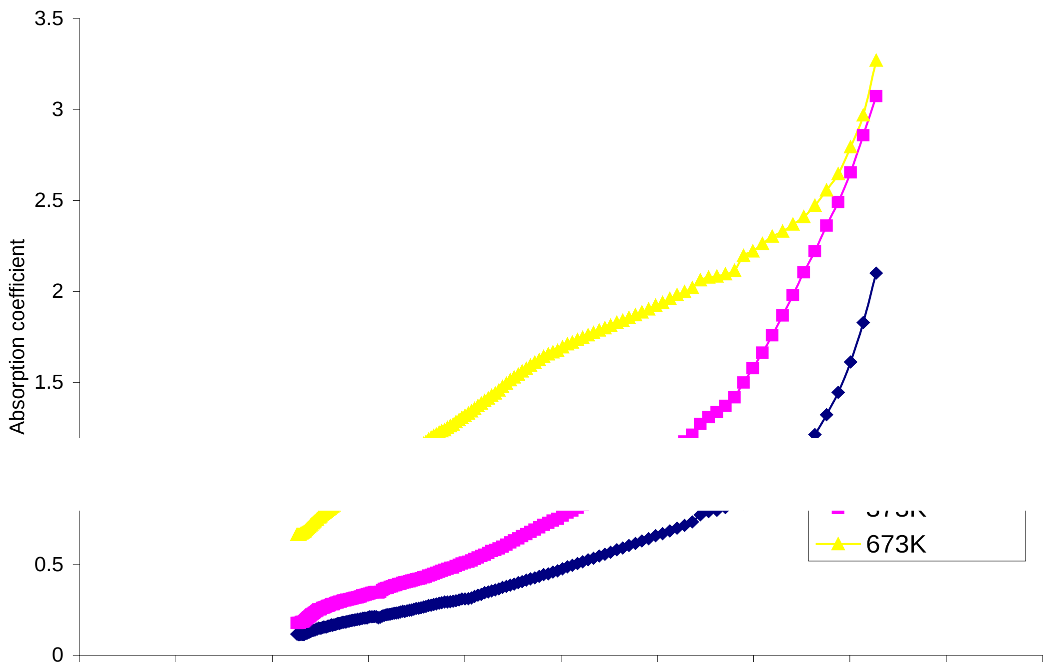


Fig.8 Absorbance vs. wavelength for TiO_2/ ZnO heterojunction thin films



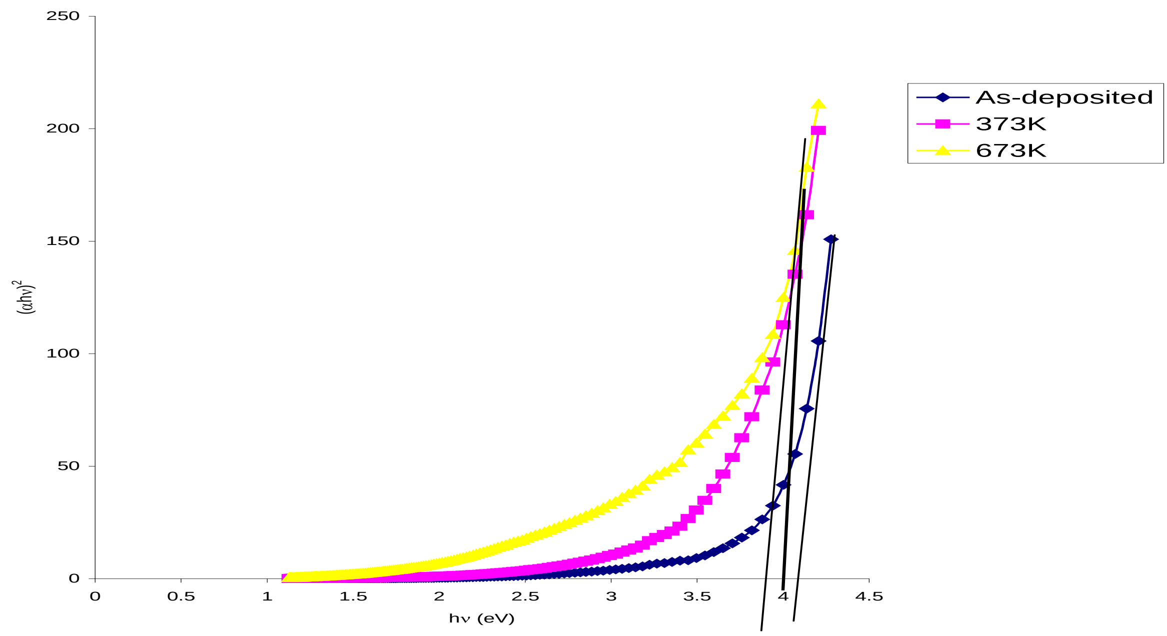
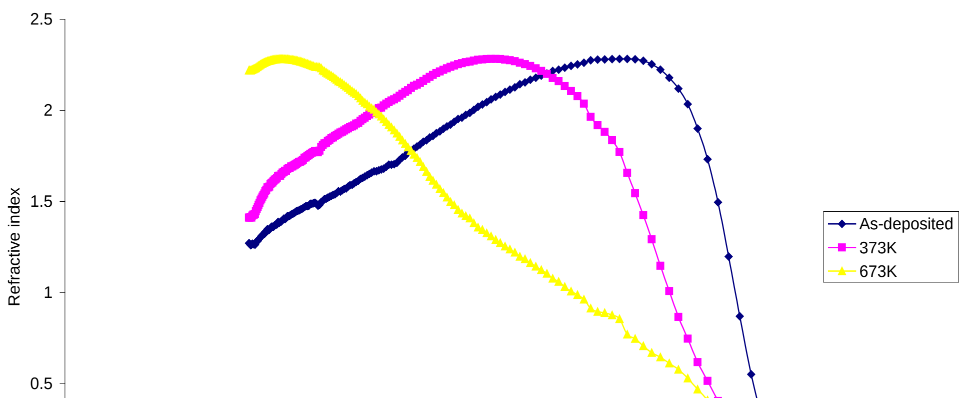


Fig. 10 Direct band gap energy for TiO_2/ ZnO heterojunction thin films

The plot of absorption coefficient against photon energy is shown in fig.9. From fig. 10 one can observe that the direct band gaps are 4.2eV, 3.85eV and 3.40eV for the as deposited, thermally annealed at 373K and 673K respectively. The above suggests that annealing the sample in oven lowers the values of the band gap. This may be a consequence of the increase in crystalline size associated with high temperature [16].



According to [17], a change in energy band gap is given by

$$\Delta E_g = \frac{\hbar^2 \upsilon^2}{2R^2}\left(\frac{1}{Me} + \frac{1}{Mh}\right) - \frac{(1.76e^2)}{ER}$$

where M_e, M_h are the effective masses of electrons in the conduction band and holes in the valence band respectively and E is the static dielectric constant of the material ΔE_g is the change in the band gap. The first term represents the particle in a-box quantum localization energy and has an inverse square relation $\frac{1}{R^2}$ dependence where R is the particle radius, while the second term represents the Coulomb energy with $\frac{1}{R}$ dependence. Therefore as R increases due to the increase in the crystalline size associated with temperature annealing the value of ΔE_g will decrease.

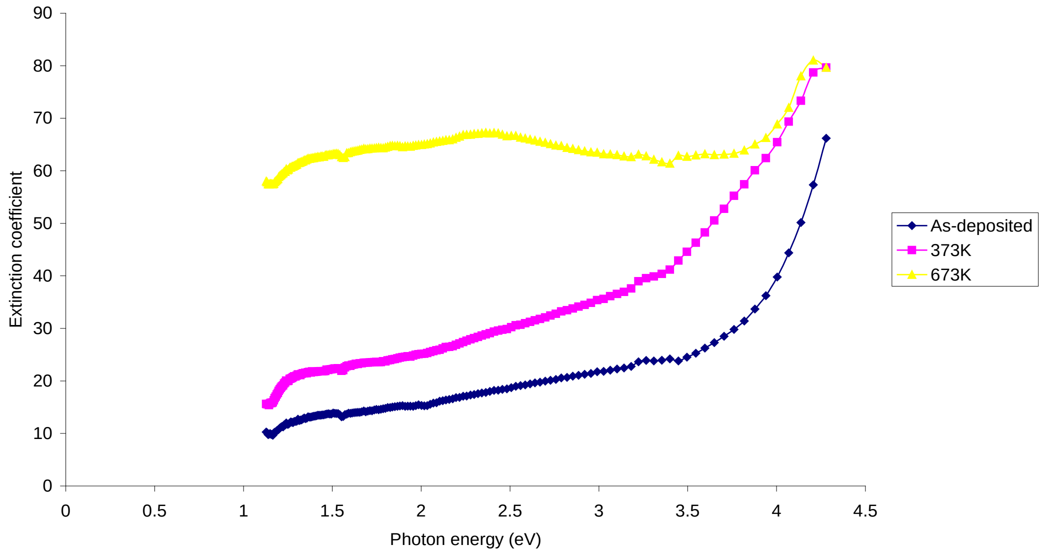


Fig. 12 Plot of extinction coefficient against photon energy for TiO_2/ ZnO heterojunction thin films

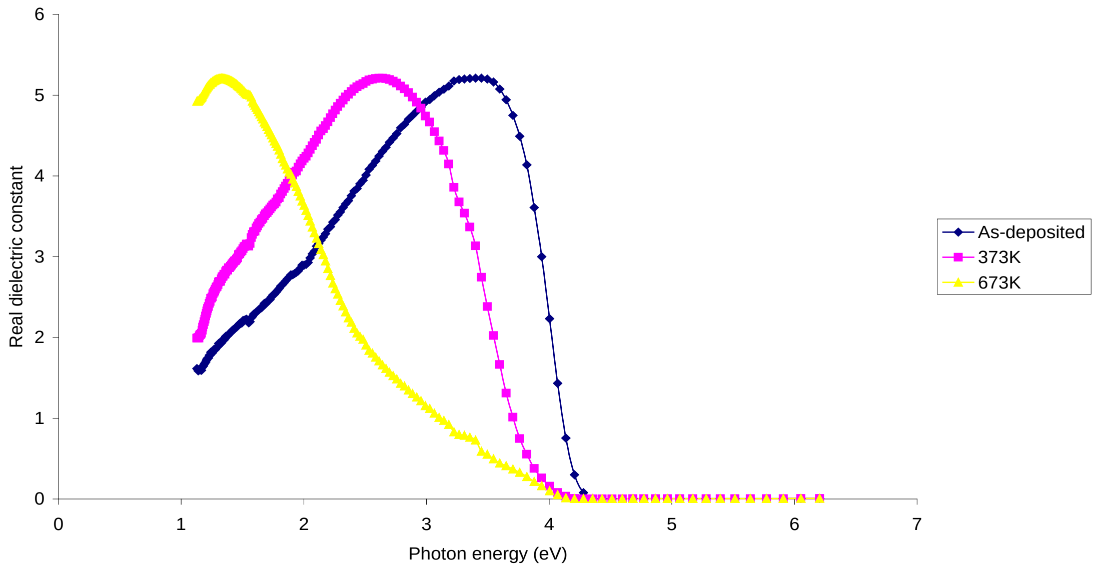


Fig.13 Plot of real dielectric constant against photon energy for TiO_2/MnO heterojunction thin films

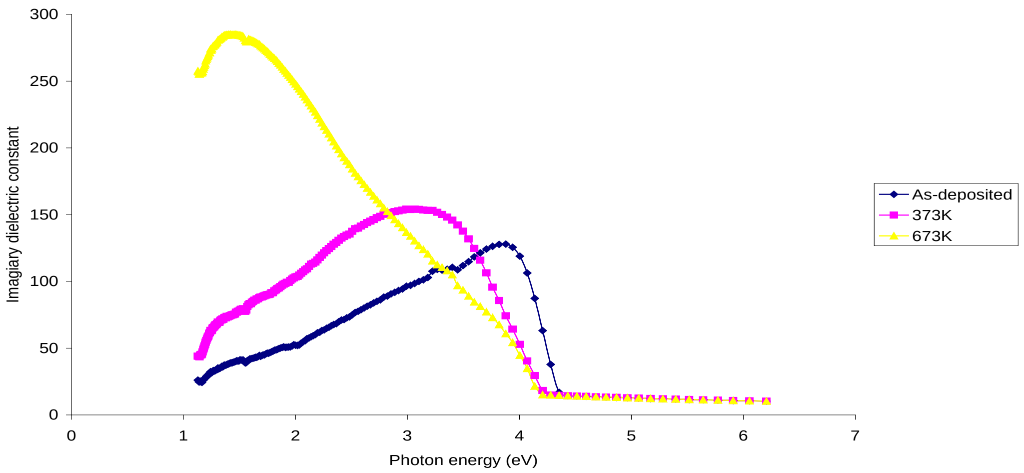


Fig.14 Imaginary dielectric constant Vs photon energy for TiO_2/ ZnO heterojunction thin films

The variation of the plot of extinction coefficient, real and imaginary dielectric constant ε, with photon energy for the films under study are displayed in figs.12, 14 and 13 respectively. From the plots, we can see that the extinction coefficient increases with wavelength for all the films with a maximum at photon energy of about 4.1eV. The imaginary part of the dielectric constant increases with photon energy in the range of 1eV to about 4.1eV. The film annealed at 673K has the greatest peak of imaginary dielectric constant. However at photon energy above 4.3eV, the imaginary dielectric constants are the same for all the films. The dependence of the refractive index on photon energy is shown in figure 11. It can be seen that from the plots that the index of refraction and real part of the dielectric constant increase with increasing photon energy up to a maximum 4.1eV and4.4eV of and then decays exponentially. The plot also shows that the index of refraction exhibits a significant dispersion in the short wavelength region below wavelength=386nm (3.85eV) where absorption is strong. It decreases with the increase of energy of the incident light, becoming flat in the higher region. It is observed also that n reached a peak value at 2.2eV, 2.3eV and 2.45eV for the as deposited, film annealed at 373K and film annealed at 673K respectively suggesting that annealing enhances the dependence of n on photon energy.

4. Conclusion

Novel TiO_2/ZnO films have been successfully deposited onto a glass slide using the CDB technique. XRD study reveals better crystallization of the films and band gap analysis show that high temperature annealing has pronounced effect on these properties. The formation of TiO_2/ZnO heterojunction considerably modified the optical properties and band gap of the independent film.

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