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ON THE EFFECT OF TEMPERATURE ON THICKNESS AND BANDGAP Tio_2/Fe_2O_3 CORE- SHELL CRYSTALLINE THIN FILM

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Core- shell crystalline thin film of the form TiO_2/Fe_2O_3 was deposited unto a glass substrate using chemical bath deposition technique. Samples of the deposited film were annealed at temperature range of 373K to 673K in step of 100K in order to ascertain the influence of post deposition annealing temperature on the thickness and optical band gap. X-ray diffraction technique was used to ascertain the structure of the films, Rutherford backscattering was used to investigate the composition of the film while Scanning electron method was employed in studying the surface morphology of the film. The optical properties were investigated using spectrophotometer analysis. The band gaps were deduced from the results of the optical analysis while the thicknesses were calculated from the optical result using the envelope method. Our results showed a reasonable trend between the annealing temperature and the film thickness and bandgap.

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1. Introduction

A hetero-junction is normally formed by joining two layers of semiconductor material with differing band – gap energies. If the layer so formed has the same conductivity, an isotype hetero-junction is formed. However if the reverse is the case, an anisotype heterojunction is formed. The requirement to get appropriate band – gap energies for device application has led to the development of binary, ternary and quaternary thin films [9]

In recent years, the development of core/shell structured materials on a manometer scale has been receiving extensive attention [5, 6].

The shell can alter the charge, functionality and reactivity of the surface, or improve the stability and dispersive ability of the core material .It is also believed that optical, catalytic or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell structured thin films has the advantage of obtaining a new composite material having synergetic or complementary characteristics of the composites. Many studies on the synthesis of composites, i.e. TiO_2, $CaCO_3$ [2], Fe_2O_3 and Ag coated with SiO_2 have been reported[8]. During the last decade, titanium dioxide (TiO_2) nanoparticles have emerged as promising photocatalysts for water purification [1,7]. TiO_2 are very versatile; they can serve both as organic inorganic pollutants. The removal of total organic carbon from waters contaminated with organic wastes was greatly enhanced by the addition of TiO_2 nanoparticles in the presence of ultraviolet light. The synthesis of visible light-activated TiO_2 nanoparticles has attracted considerable interest Bae and Choi,[3]. One of the most cited studies in the field is that published by Nitin et al [8]. They synthesized N-doped TiO_2 nanoparticles that were capable of photo-degrading methylene blue under visible light. Bae and Choi [3] have synthesized visible light-activated TiO_2 nanoparticles based on TiO_2 modified by ruthenium-complex sensitizers and Pt deposits. The Pt/ $TiO_2/RuIIL_3$ nanoparticles drastically enhanced the rate of reductive

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dehalogenation of trichloroacetate and carbon tetrachloride in aqueous solutions under visible light [3, 4].

In this paper, we report the chemical bath deposition of TiO_2/Fe_2O_3 core- shell thin films and the effect of post deposition annealing on the thickness and bandgap.

2. Materials and methods

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 12mls of 1M $TiCl_2$, 12mls of 1M $NH4Cl_4$, 12mls of 10M NH_3 and 13mls of PVA solution put in that order in 100ml cleaned and dried beaker. Five (5) 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/ Fe_2O_3 core-shell, the TiO_2 film already formed (core) was inserted in a mixture containing 13 ml of 1M KCL, 13mls of 1m $FeSO_4$, 2 drops of 1M NaOH and 50mls of water in 100ml beaker. Deposition was allowed to proceed at same temperature and time duration. Four out of the five deposited films were annealed in an oven for 373K, 473K, 573K and 673K respectively for 1hr. One of the samples was left unannaeled to serve as the control. The surface morphology of the films was observed by scanning electron microscopy (SEM) with JEOL 35C instrument, the energy used was 10 kV. The X-ray diffraction (XRD) studies were carried out in a Rigaku D/max-2100 diffractometer (CuK_α radiation, 1.5408Å) in the 2θ range of 200 - 750 with a thin film attachment. The chemical composition of the thin film was determined using Rutherford scattering equipment.

3. Results and discussion

Fig.1a shows the XRD pattern of the TiO_2/Fe_2O_3 film deposited in this work. The samples were annealed from 373K to 673K for 1 hour. This was done to improve upon the intensities of the peaks crystallinty of the films and to investigate the effect of post annealing on the deposited films. The peak at 2θ value of 19.78 and are attributed to orthorhombic TiO_2 (JCPD cardNo.350088) having lattice parameters a = 9.7965 Å, b= 9.980 Å and c=3.7301 Å. These were assigned to the diffraction lines produced (200) and (111) planes. However the additional peaks at an angle of 19.36 and 22.15 are identified to be Fe_2O_3 (JC PD Card No.41-1432) and assigned to the diffraction line produced by (200) and (111) planes of the Fe_2O_3 – plane. These results suggest that the thin film deposited in this work is a mixture of the two oxides. The XRD pattern also revealed that the annealed film has better crystallinty as is evident in Fig. 1b. The average crystallite size of the film was calculated from the recorded XRD patterns using the Scherer formula:

$D = 0.89\ \lambda/\beta \cos\theta$, [5] where D is the average crystallite size, θ 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. Fig.2 shows the RBS of the deposited film. The average crystallite size of the deposited film was found to be 2.65Å. Fig.3a, b, c, d, and e show the SEM of TiO_2/Fe_2O_3 for as-deposited, thermally annealed at 373K, 473K, 573K and 673K respectively. The SEM show an increase in grain size at higher annealing temperature due to effects of evaporation of absorbed water and reorganization of the grain.

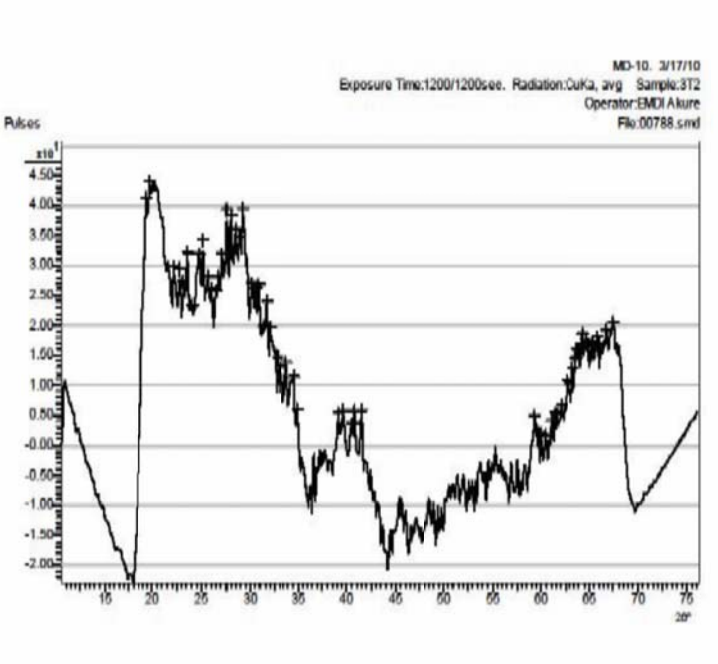

Fig.1a: XRD Pattern of as-deposited TiO_2/Fe_2O_3 Thin Film

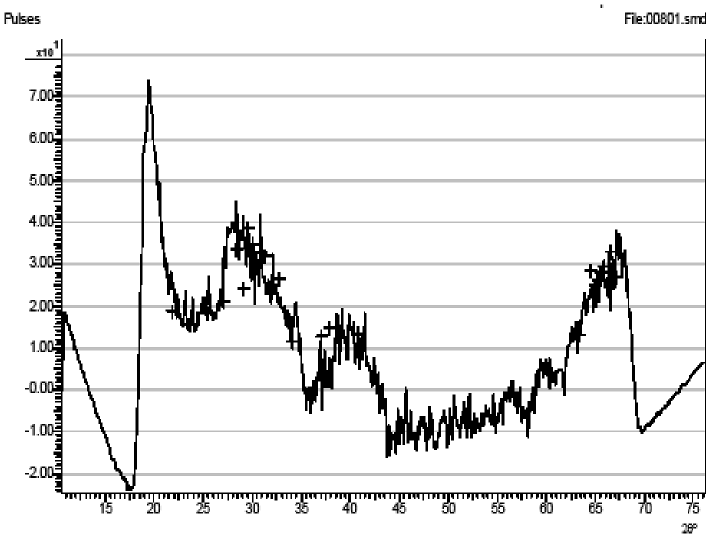

Fig.1b: XRD of TiO_2/Fe_2O_3 Thin Film Annealed at 673K

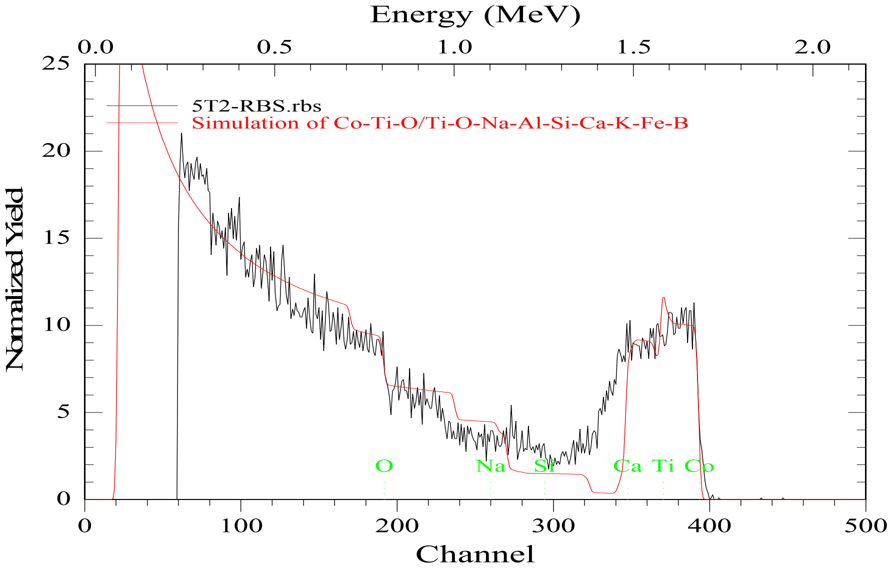

Fig. 2: RBS of TiO_2/Fe_2O_3 Thin Film

Table 1: Variation of Thickness and Bandgap for various samples of TiO_2/Fe_2O_3

Samples TiO_2/Fe_2O_3	Thickness (nm)	Bandgap (eV)
As-deposited	32.08	3.81
373K	36.03	4.00
473K	66.38	3.73
573K	70.08	3.90
673K	88.04	1.92

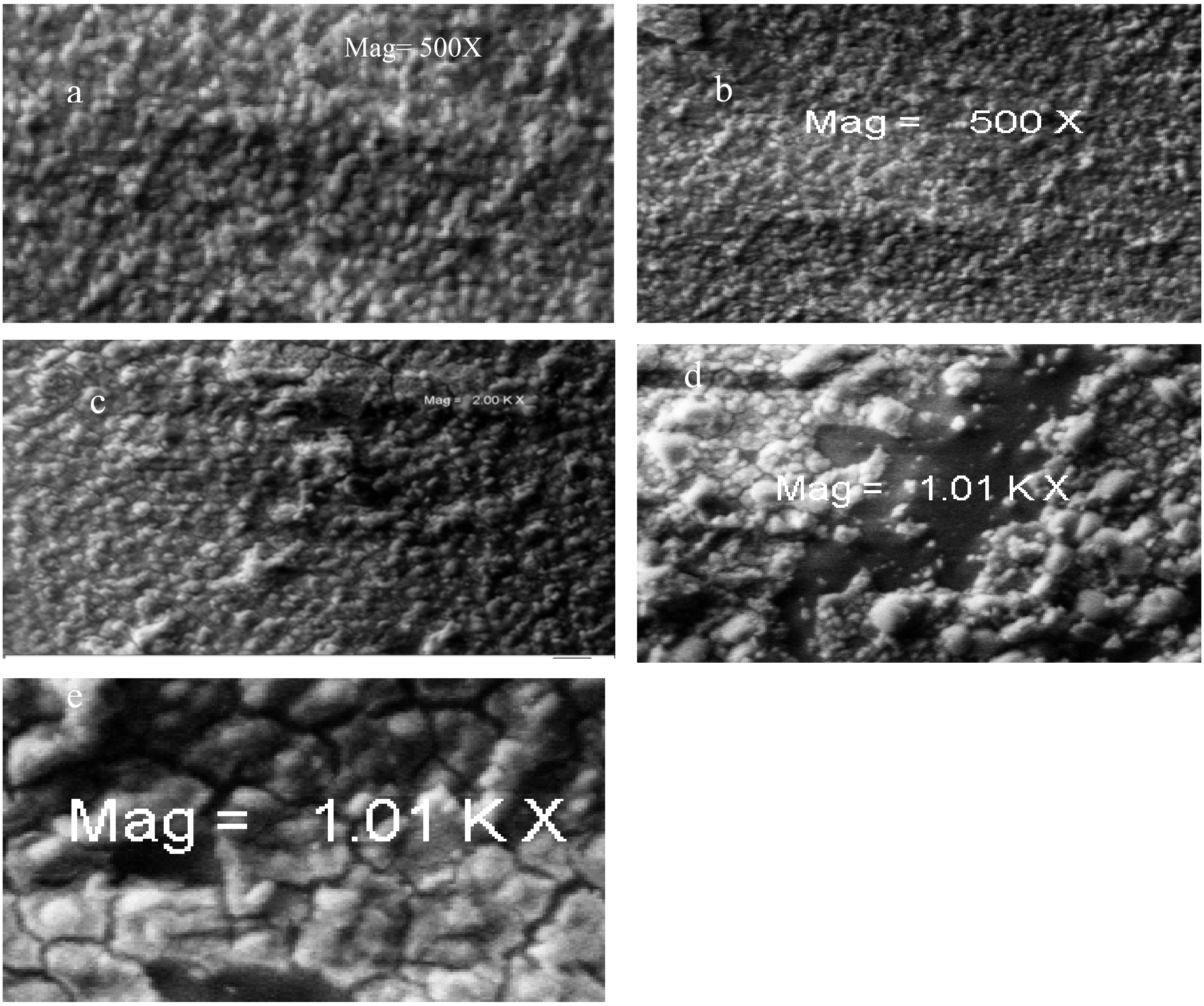

Fig.3: SEM results for (a) As-deposited (b) Annealed at 373K (c) Annealed at 473K (d) Annealed at 573K (e) Annealed at 673K

The optical absorption spectra of the film were studied in the range of wavelength 200nm – 1200 nm. The variation of absorbance (A) and percentage transmittance (%T) with wavelength for all the samples of the film under study are shown in fig.4 and 5 respectively. Thin film of TiO_2/Fe_2O_3 show better absorbance in the visible region and a lower absorption in the IR of the solar spectrum with a peak absorbance of 1.5. The absorbance decreases exponentially with wavelength for the entire sample annealed at different temperature. A sharp decrease in absorbance was noticed for the entire sample at a wavelength of 800 nm. The optical spectrum of the transmittance of TiO_2/Fe_2O_3 in Fig.5 shows that the film transmits well in the NIR and IR and tends to be constant in the UV portion of the solar spectrum. The sample annealed at 473K showed lowest transmittance. There is no clear trend in relation between transmittance and annealed temperature as can be seen in the plot. The sample annealed at 373K has peak transmittance of

38.15% at 360nm. Peak % transmittance of 42.36 at 110nm wavelength was recorded for the film annealed at 373K. Between 0-380nm all the samples showed low transmittance which is consistent with the spectrum of absorbance. Low transmittance in the UV and high transmittance in the NIR and IR make the film good material for thermal control coatings inside buildings. The shape of absorption spectrum and dispersion near the fundamental absorption edge are caused by electron transition from upper part of the valence band to the lower part of the conduction band. This electron transition can be direct or indirect. It is direct when there is no phonon participation and without change in crystal momentum of an electron. In other words it is indirect when the interaction with a phonon produces a considerable change in the crystal momentum. The various types of transition give rise to different frequency dependencies of the absorption coefficient near the fundamental absorption edge. The coefficient for direct transition is given by

$$A = \alpha \left(hv - E_g\right)^n \qquad 2.20$$

where n = ½, if the transition between the upper part of the valence band to the lower part of the conduction band are allowed by the selection rules and n=3/2, if the transition are forbidden. Hence for allowed transitions the relation is given by

$$\alpha hv = A(hv - E_g) \qquad 2.21$$

In most cases, indirect transition is weaker than direct ones by 3 or 2 orders of magnitude. This is because they result only by second order perturbation and can be observed in energy regions which are free of direct transition. The dependence of the absorption coefficient on the energy of light quanta near the fundamental edge is given by

$$\begin{aligned} &\alpha = (hv - E_g)^{1/2} \\ &\text{or} \qquad\qquad\qquad 2.22 \\ &\alpha^2 = hv - E_g \end{aligned}$$

The estimated values of the direct band gap for samples TiO_2/Fe_2O_3 thin films are displayed in table1 .In Fig.5. no trend between the band gap and the annealing process for the film under review was observed as the as-deposited film recorded lower values of bandgap than the annealed ones. Using the optical data, the thickness of the thin films can be calculated using the relation [4].

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$$t = \frac{\lambda_1 \lambda_2}{2\left(n_1 \lambda_2 - n_2 \lambda_1\right)} \qquad 2.23$$

where n_1 and n_2 represent the refractive indices of the film at wavelengths λ_1 and λ_2 respectively [6].

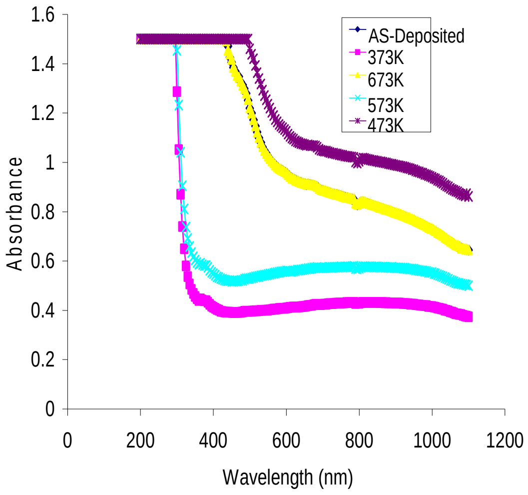

Fig.4: Absorbance against wavelength TiO_2/Fe_2O_3 Thin Film

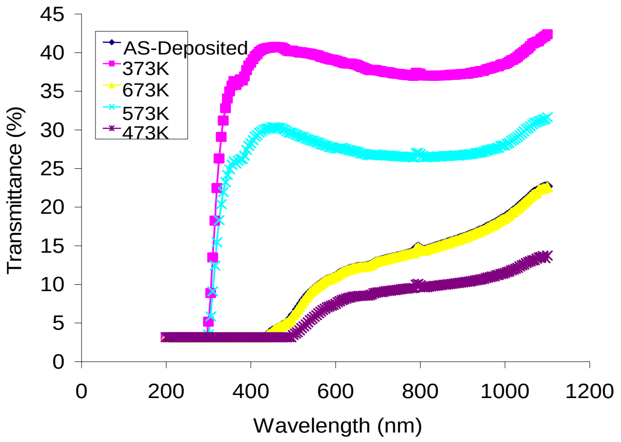

Fig.5 :Transmittance vs Wavelength for TiO_2/Fe_2O_3 Thin Film

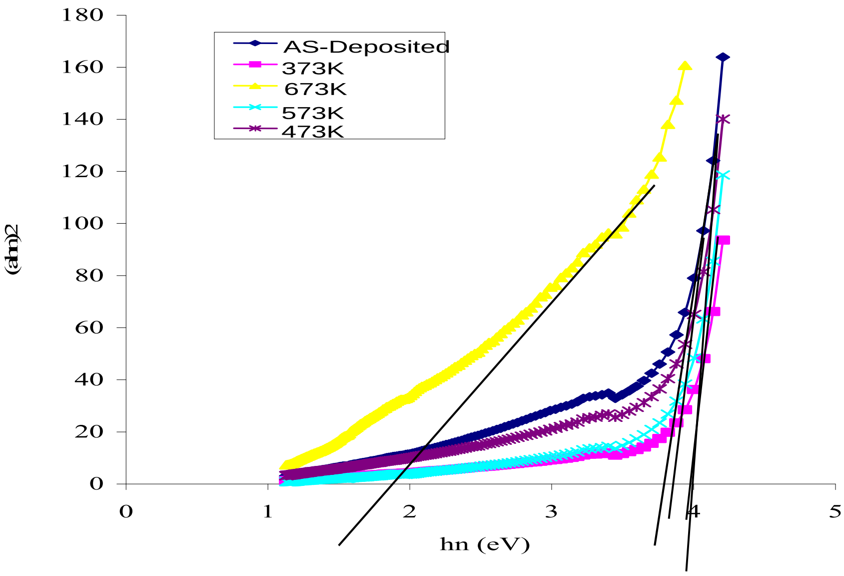

Fig.6: $(\alpha h\nu)^2$ vs $h\nu$ (ev) for TiO_2/Fe_2O_3 Thin Films

4. Conclusion

In summary, we demonstrated the possibility of depositing core/shell oxide thin film of the form TiO_2/Fe_2O_3 using solution growth technique. Our results have shown that the shell can alter the structure, charge functionality, reactivity or improve the stability and dispersive nature of the core. As can be observed from our results, some properties of the core is modified by the incorporation of the shell. The spectral behaviour, the band gap, the thickness was affected by thermal annealing. Thermal annealing from our analyses improves the stability and orientation of the crystals thereby affecting the properties of the thin films.

The energy band gap lies between 1.92eV to 4.00eV. The values of E_g shows that the film can be applied in the formation of p-n junction solar cell in conjunction with other suitable materials for photo voltaic applications, antireflection and photosynthetic applications.

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