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Advances in Applied Science Research, 2011, 2 (6):393-399

ISSN: 0976-8610
CODEN (USA): AASRFC

Effect of Thermal Annealing on Optical and Band gap of chemically deposited Tio_2/Fe_2o_3 Core/shell Oxide Thin Films

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ABSTRACT

Titanium oxide (TiO_2) thin film was first deposited on the glass substrate to serve as the core. Then ferrous oxide (Fe_2o_3) was deposited on the core to form novel core/shell oxide thin film of the form Tio_2/Fe_2o_3 using the simple and easily reproducible chemically deposition method. The deposited films were annealed at 373K and 673K in an oven in order to investigate the effect of thermal annealing on the optical properties and band gap. Optical properties such as the absorption coefficient α, extinction coefficient k, and refractive index n, were determined using the absorbance and transmission measurement from Unico UV-2102 PC Spectrophometer at normal incidence of light in the wavelength range of 200-1200nm. The films displayed transmittance in the VIS-FIR region that range between 5% -45%. From absorbance and transmittance spectra, the band gap energy determined lie in the range of 1.92eV-3.19eV. The structural properties, the optical properties and the wide gap exhibited by the thin films made them good candidate for wide range of applications.

Keywords: As-deposited, Thin films, Thermal annealing, optical properties, XRD, Optical spectrum.

INTRODUCTION

The development of new materials, blends, composites and advanced materials is a necessity for modification of mechanical, electrical, optical and thermal properties of thin films to fulfil the demand for improved materials in industries. The development runs parallel with the intense series of studies aiming at describing the structure-property relationship of the modified materials. Many studies have been reported on electrical and thermal properties of some core shell thin films [12]

The study of semi conducting thin film are being pursued with increasing interest on the account of their proven and potential applications in many semiconductor devices such as solar energy converters, optoelectronics devices etc.[2,12] In the last decades, there has been a great deal of interest in the production of inexpensive thin files, due to its high varying characteristics. Such characteristics include high resistivity, heat reflecting windows, catalytic properties, photo thermal and photovoltaic[3]. Practical applications of thin oxide films are in house hold, electronics, recording heads, memory and microwave devices. Most oxide thin films can also be applied in highly reproducible gas and humidity sensor materials ([4] Oxides thin film materials have been one of the most attractive research topics in physics and material science. Materials like Fe_3O_4, CrO_2, manganese pervoskites, double and layered pervoskites, $BiFeO_3$ and more recently transition metal doped semiconductors thin films such as TiO_2, ZnO, MnO to mention but a few have been reported and have received new and exciting attentions [5]

For instance, Titanium oxide thin film has been one of the most extremely studied oxides because of its role in various applications namely photo-induced water splitting, dye synthesized solar cells, environmental purifications gas sensors display devices, batteries etc.[6]

This study reports the synthesis of novel Tio_2/Fe_2o_3 thin film in a PVA matrix via simple and inexpensive chemical both deposition technique. The effect of post deposition annealing on the optical and electrical properties were also reported.

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 298K. To obtain the deposition of TiO_2, the chemical bath was composed of 12 ml of 1M $MnCl_4$, 12ml of 1M $NH4Cl_4$, 12ml of 10M NH_3 and 13 ml of PVA solution put in that order in 100ml cleaned and dried beaker. Four clean glass slides were then inserted vertically into the solution. The deposition was allowed to proceed at 338K for 3hr in an oven after which the coated substrate were removed, washed with distilled water and allowed to dry. To obtain the TiO_2/MnO core-shell, the TiO_2 already formed (core) was inserted in a mixture containing 12ml of 1M $MnCl_4$, 12ml of IM NH_4Cl, 12ml of 10M NH_4OH and 40ml of PVA in 100ml beaker. Deposition was allowed to take place at a temperature of 338K for a period of three hours. Two of the deposited films were annealed in an oven at 373K and 673K respectively for one hour. One of the samples (as-deposited) was left unannaeled to serve as the control.

CHARACTERIZATION

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 surface morphology was examined using Scanning Electron Microscopy. The optical properties of the CBD deposited films were measured at a temperature of 298K 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 Scherer formula $D=0.89\lambda/\beta\cos\theta$ [1,8,12].

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.

RESULTS AND DISCUSSION

Fig. 1 shows the RBS analysis of the core/shell film under review. The analysis of the RBS shows that the film contains 16.5% of iron, 9.1% of titanium, 72.7% of oxygen and 1.8% of calcium. The incorporation of calcium in the sample must have resulted from the experimental conditions.

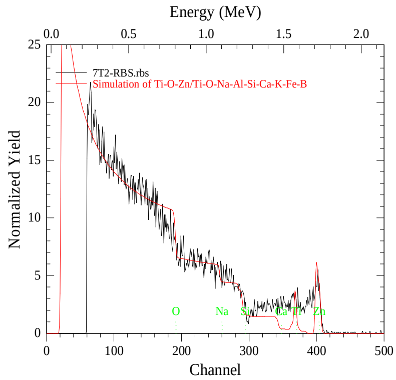

Fig. 1 RBS analysis for TiO_2/Fe_2O_3 core/shell thin film

Fig.2 (a-c) show the XRD pattern of the TiO_2/Fe_2O_3 samples reported in this work, for the as deposited, thermally annealed at 373K, and 673K respectively.

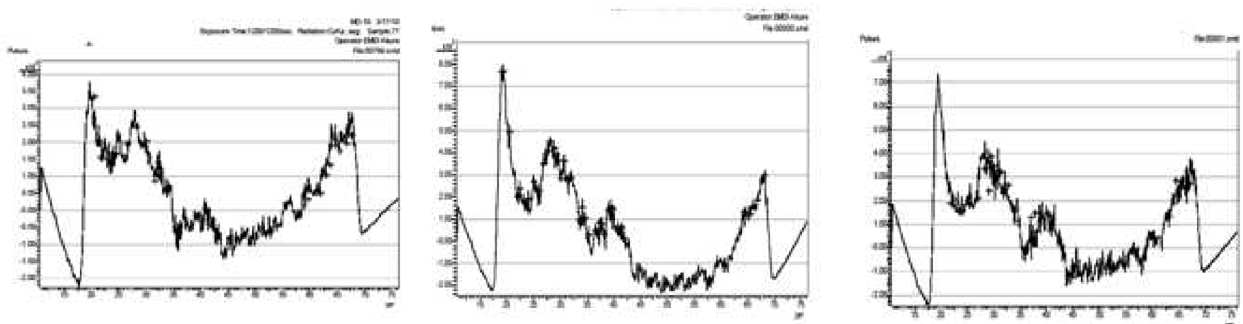

Fig.3: XRD for $Ti0_2/MnO$ (a) as-deposited (b) annealed at 373K (c) annealed at 673K

The peak at 20^o value of 19.69^o are attributed to orthorhombic TiO_2 (JCPD card #35-0088) having lattice parameters a= 9.7965 Å b=9.980Å and c=3.7301Å.

These were assigned to diffraction lines produced by (200) and (111) planes. However, the additional peaks at an angle of 19.36^o, 22.15^o are identified to be Fe_2O_3 (JCPD card# 41-1432) and assigned to the diffraction line produced by (200) and (111) planes of Fe_2O_3 planes. 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 TiO_2/Fe_2O_3 film is amorphous and polycrystalline in nature. The average crystallite size of the samples as calculated using the Scherer's formula are 5.234, 5.987 and 7.110nm for as-deposited, thermally annealed at 373K and 673K respectively.

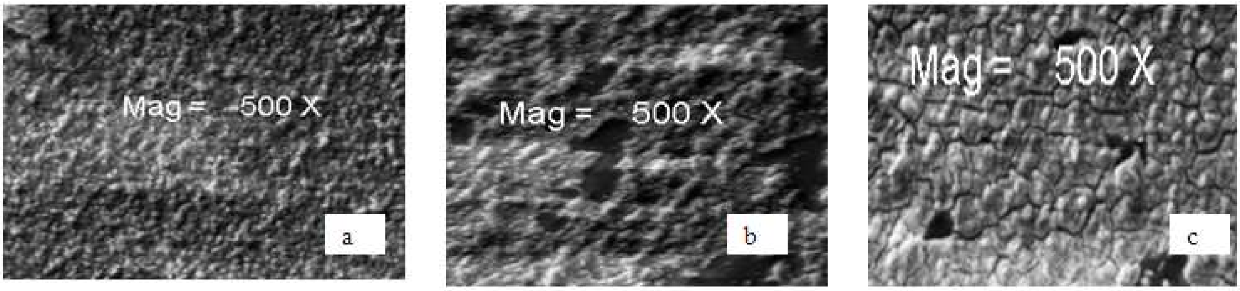

Fig.4 SEM result for samples of TiO_2/Fe_2O_3 thin film (a) as-deposited (b) annealed at 373K (c) annealed at 673K

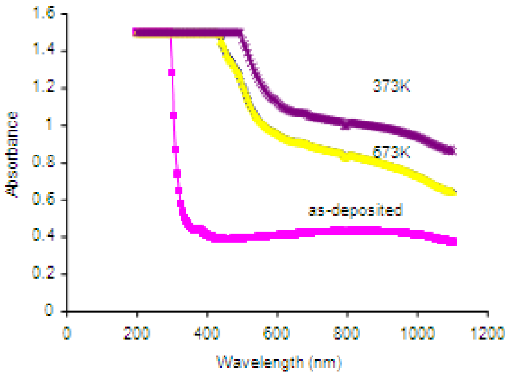

Fig.5. Absorbance for TiO_2/Fe_2O_3 thin film

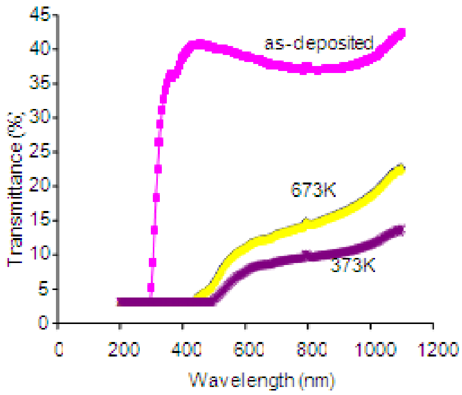

Fig.6. Transmittance for TiO_2/Fe_2O_3 for thin film

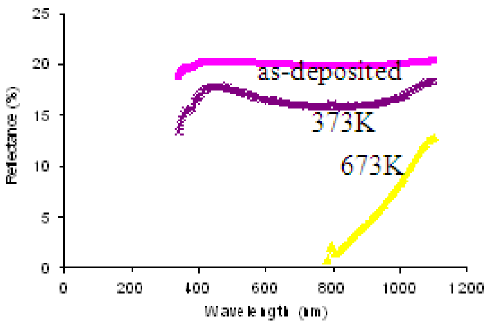

Fig. 7. Reflectance for TiO_2/Fe_2O_3 thin film

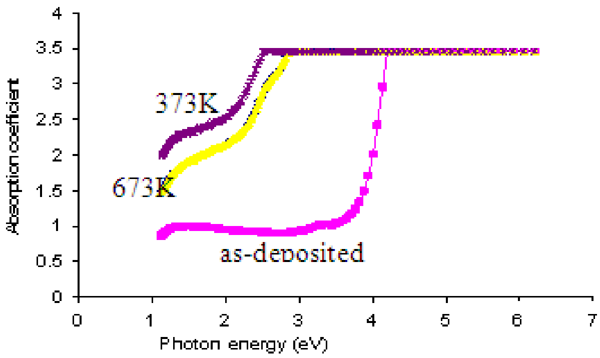

Fig.8. Absorption coefficient TiO_2/Fe_2O_3 thin film

The scanning electron microscopy (SEM) of the as-deposited, thermally annealed at 373K and 673K are displayed in figures 4 (a-c) respectively. The SEM shows an increase in grain size as annealing temperature increases. This could be attributed to the effects of evaporation of absorbed water and reorganization of the grain. Uniform distribution of the grain is also observable.

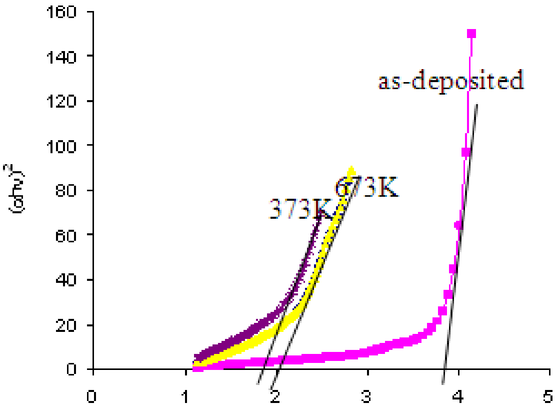

Fig.9. Plot of determination of band gap for TiO_2/Fe_2O_3 thin film

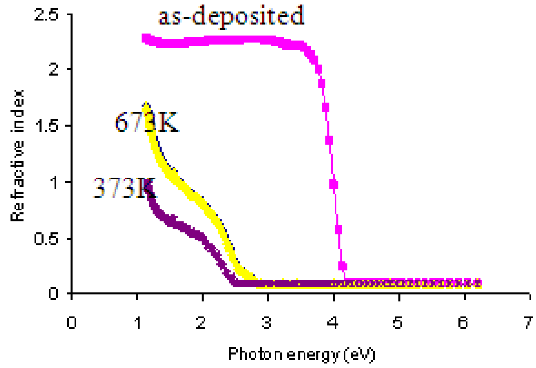

Fig.10. Refractive index Vs photon energy for TiO_2/Fe_2O_3 for thin film

The plot of absorbance, for the $Ti0_2/Fe_2O_3$ film for as-deposited and thermally annealed films at 373K and 673K is displayed in fig.5. Core/shell thin film of TiO_2/Fe_2O_3 show better absorbance in the visible region of the spectrum and lower absorbance in the IR of the solar spectrum with a peak absorbance value of 1.5 at 205nm for all the samples. The spectral distribution of absorbance also showed lack of trend between the absorbance and annealing temperatures. A sharp decrease in absorbance was noticed for the entire samples at a wavelength of 800nm. High absorbance in the UV region as depicted by TiO_2/Fe_2O_3 makes the material useful in formation of p-n junction solar cells with other suitable materials for photovoltaic applications[12]. The optical spectrum of the transmittance of TiO_2/Fe_2O_3 as displayed in fig.5 (a-c) 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 200-505nm all the samples showed low transmittance which is consistent with the spectrum of absorbance. These properties of low transmittance in the UV and high transmittance in the NIR and IR make the film good material for thermal control coatings inside buildings. Fig.6 shows the spectra of reflectance for TiO_2/Fe_2O_3. The plot displayed almost flat response for samples annealed at 373K, while the sample annealed at 673K and as-deposited sample indicates an increase in reflectance with wavelength from 760nm in the infra red portion of the spectrum. The lack of trend could not be discerned. The variation of absorption cofficient at various annealing temperature for TiO_2/Fe_2O_3 core/shell as displayed in fig.8 indicates an increase of the absorption coefficient with photon energy for all the samples up to 4.0eV. Between 1-3.54eV the coefficient of absorption were almost flat for all the samples however, from 3.54eV, the absorption coefficient increased with increase in photon energy with a peak value of 3.45 at 4.20eV for the sample annealed at 673K.

The estimated values of the direct band gap E_g for samples of TiO_2/Fe_2O_3 core-shell oxide thin film are 3.910eV for as-deposited, 1.92eV for sample annealed at 373K, and 2.00eV for sample annealed at 673K as shown in fig.9. No trend between the band gap and the annealing process for the film under review was observed. However, the as-deposited film recorded higher values of Eg, than the annealed ones.

The annealing process has been noted to be helpful in improving the electro-optical properties of thin film. This is attributed to better crystalline quality and oxygen deficiency after annealing, however, the effect of these processes is still not well known [12]. According to [9,11], 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.

The variation of the refractive index n, with hυ for samples of TiO_2/Fe_2O_3 is shown in fig.10. The plot shows that from photon energy of 4.20eV upwards, the refractive index for all the samples were the same and almost zero. The maximum index of refraction recorded is 2.42 at photon energy of 1.50eV.These results suggest that by varying the annealing temperature one can vary the refractive index of the film.

The thickness of the thin film at different annealing temperature were calculated using the relation, $t = \frac{\lambda_1 \lambda_2}{2(n_1\lambda_2 - n_2\lambda_1)}$ [10]. The calculated thicknesses are 32.08, 36.03 and 88.04 for as-deposited, annealed at 373K and 673K respectively. The calculated film thickness shows that the thin films grown are nano sized. This implies that they can be used in biomedical applications.

CONCULSION

Novel TiO_2/Fe_2O_3 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/Fe_2O_3 heterojunction considerably modified the optical properties and band gap of the independent films. Analysis of the thickness shows that the deposited film is nanocrystalline in nature

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