Effect of Thermal Annealing on Optical and Band gap of chemically deposited TiO$_2$/Fe$_2$O$_3$ 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$_2$O$_3$) was deposited on the core to form novel core/shell oxide thin film of the form TiO$_2$/Fe$_2$O$_3$ 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 $\alpha$, 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 household, 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$_3$O$_4$, 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$_2$O$_3$ 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 NH$_4$Cl, 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 1M NH$_4$Cl, 12ml of 10M NH$_3$OH 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 unannealed 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-Ka 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 $D=\frac{0.89\lambda}{\beta \cos \theta}$ [1,8,12].

Where D is the average crystalline size, $\lambda$ is the wavelength of the incident X-ray, $\beta$ is the full width at half maximum of X-ray diffraction and $\theta$ 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$_2$O$_3$ core/shell thin film

Fig. 2 (a-c) show the XRD pattern of the TiO$_2$/Fe$_2$O$_3$ samples reported in this work, for the as deposited, thermally annealed at 373K, and 673K respectively.

Fig. 3: XRD for TiO$_2$/MnO (a) as-deposited (b) annealed at 373K (c) annealed at 673K

The peak at 20° value of 19.69° 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 °, 22.15 ° are identified to be Fe$_2$O$_3$ (JCPD card# 41-1432) and assigned to the diffraction line produced by (200) and (111) planes of Fe$_2$O$_3$ 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$_2$O$_3$ 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.

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.

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for the film under review was observed. However, the as-deposited film recorded higher values of $E_g$ 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

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

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. $\Delta E_g$ 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 $\Delta E_g$ will decrease.

The variation of the refractive index $n$, with $\upsilon_0$ for samples of TiO$_2$/Fe$_2$O$_3$ 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.

**CONCLUSION**

Novel TiO$_2$/Fe$_2$O$_3$ 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$_2$O$_3$ 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.

**REFERENCES**