



EFFECT OF ANNEALING TEMPERATURE ON THE REFRACTIVE INDEX AND DIELECTRIC PROPERTIES OF TiO₂/MnO₂ CORE/SHELL THIN FILMS

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ABSTRACT

Thin film of the form TiO₂/MnO₂ was deposited using the chemical bath method. The deposited thin films were annealed at temperatures of in order to investigate the effect of annealing temperature on the refractive index and dielectric property. To do this the films were characterized using UV-Spectrophotometer and XRD analysis was also carried out to study the structural nature of the deposited film. Our results revealed that annealing has profound effect on the index of refraction and the dielectric properties.

KEYWORDS

Core/shell; Chemical bath; annealing; temperature; refractive index; dielectric; XRD



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1. INTRODUCTION

Metal nanoparticles have been the subject of extensive research due to their unique applications in many areas such as nonlinear optical switching, immunoassay labelling and Raman spectroscopy enhancement [1,3]. Core-shell metal-semiconductor nanoparticles have attracted many interests due to their potential application in many areas and also interesting is the Physics involved in the process. In the last decades, there has been a great deal of interest in the production of inexpensive thin films, due to its high varying characteristics[10,13] Such characteristics include high resistivity, heat reflecting windows, catalytic properties, photo thermal and photovoltaic [7,8.] Practical applications of thin oxide films are in homes, electronics, recording heads, memory, and microwave devices. Most oxide thin films can also be applied in highly reproducible gas and humidity sensor materials [9,10]. Oxides thin film materials have been one of the most attractive research topics in Physics and Material Science [12,13]. 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 [5,6,15]. 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.[14,18] Manganese oxide thin films have been shown to have promising potentials due to their promising potentials for applications in various fields, such as optoelectronic devices, secondary batteries, supercapacitors and so on According to [11,9] core –shell thin films are structured films that are composed of a core of one material and a coating shell of another material. They are typically around 20 -200nm in size.[3,15] The composition of the core and the shell can be varied to a wide range of different properties. Normally, the particles of the thin film are very small with a very large geometric surface area which is easily accessible.

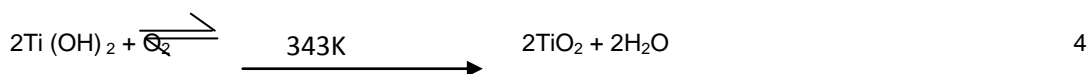
The process of synthesizing a core-shell thin film involves two steps. First, an insoluble seed (core) is synthesized using the conventional method of growing thin films. The second step involves the incubation of the seed/core with the desired shell using any method of depositing thin film of your choice. In this way, the desired (shell) grows on the substrate (core). In this communication, the effect of annealing temperatre on the refractive index and dielectric properties of $\text{TiO}_2/\text{MnO}_2$ is studied.

2.0 EXPERIMENTAL

In this work, the core-shell oxide thin films were deposited on a glass substrate. The surface of the glass slides were thoroughly cleaned and dried before dipping them into the reaction baths. To do this, the substrates were dipped in a solution of concentrated hydrochloric acid for two days to degrease them[4,6]. Thereafter, they were subjected to very good scrubbing with cold detergent solution and soft synthetic fibre sponge. This was done in order to avoid scratching of the glass substrates. They were then dried in an oven. In each core/shell oxide film to be deposited, several variations of the reaction bath constituents were used; for instance different constituents were used to deposit TiO_2 . Also to ensure standard reaction bath of the deposited films, the substrates were allowed to stay in the bath for different dip times and at different deposition temperatures. By these means, [2,3] the growth conditions were optimized and the baths standardized. The depositions of the thin films were done in two stages. However, in each of the stages, five substrates were immersed vertically into and at the centre of the desired reaction bath such that the substrate does not touch the wall of the beaker. At the end of the deposition, the substrates were removed from the bath, thoroughly rinsed with distilled water and dried in air after which four of them were annealed at different temperature while one was left un annealed to serve as the control. Pre-test runs were done at room temperature to determine the optimal values of deposition parameters like volume of complexing agent, [14,17] pH of chemical bath solution and deposition time used. This method was used to deposited core-shell oxide thin films of TiO_2/MnO , TiO_2/ZnO , $\text{TiO}_2/\text{Fe}_2\text{O}_3$ and Cu_2O on a glass substrate. First, Titanium oxide thin film (core) was deposited on five glass substrate using the empirical equations stated in equations 3.1 to 3.5 and a bath composition of 8mls of TiCl_3 , 3mls of 1M NaOH and 35mls of PVA at a temperature of 338K for 120 minutes



PVA [Polyvinyl alcohol] $[\text{CH}_2\text{CH}(\text{OH})]_n$ acts as a complexing agent.



The second stage involved the deposition of the oxides of manganese on the TiO_2 to form the ccore/shell thin film according to equations 5 and 6 with a reacting bath which consisted of 24mls of 1M of NH_4Cl , 24mls of 10M of NH_3 solution and 13mls of H_2O which were allowed to react for 180 minutes at a temperature of 348K. The chemical reaction involved is as shown below;



3.0 RESULTS AND DISCUSSION

Fig.1, 2 and 3 show the XRD patterns of TiO_2/MnO samples for as-deposited, thermally annealed at 373K and 673K. Peak broadening has been observed in recorded diffraction pattern of the crystalline thin films.

Comparison, among the spectrum of (1), (2), and (3) show that there is more crystallization and more orientation of the crystal growth in the case of the film annealed at 673K. The lines become stronger with slight preferential orientation at ($2\theta = 25.3398^\circ$) that corresponds to (111) plane, and at ($2\theta = 68.76^\circ$) that corresponds to (400) planes for the orthorhombic

$\text{TiO}_2/\text{MnO}_2$ which is in accordance with the value of the interplanar distance d . The XRD pattern also reveals that the sample is polycrystalline in nature with a high pressure magnetic phase of MnTiO_3 . The lattice parameters, a , and b for the orthorhombic structure is given as $a = 5.4558\text{\AA}$, and $b = 14.29\text{\AA}$. The existence of this high pressure magnetic phase shows that the film can be used as magnetic memory device.



Fig.1: XRD for as-deposited TiO_2/MnO Thin Film

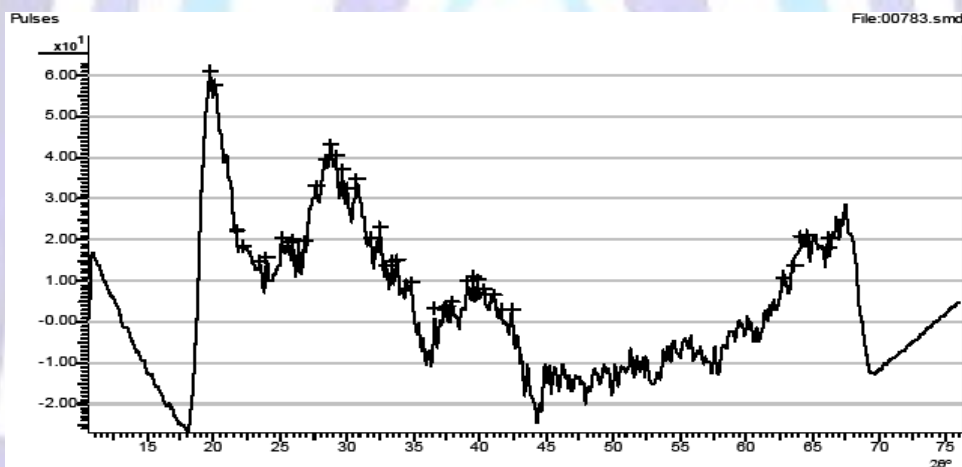


Fig.2: XRD for TiO_2/MnO Thin Film Annealed at 373K

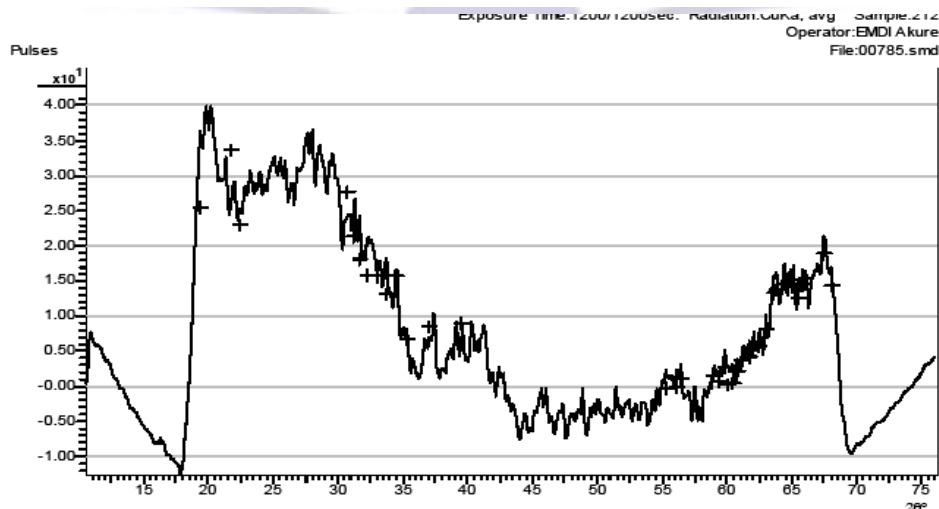


Fig.3: XRD of TiO_2 Thin Film

The variation of the refractive index, n for TiO_2/MnO is displayed in Fig.4. The index of refraction, n , observed a peak around 2.45 and decreases with increasing wavelength at low energies. The minimum value of n is around 1.1 within the UV region. The film annealed at 673K has a maximum value of 2.2 within the UV range. For as-deposited and samples annealed between 373K and 573K, n increased, reached a peak and start to fall uniformly. The sample annealed at 673K displayed a different trend. Here n decreased from the maximum to almost zero with increasing photon energy. This behaviour suggests that these transparent films seem to behave like a transparent insulator. Transparent insulators are expected to prevent high UV while allowing only visible light.[13] However this does not agree with the films grown. A transparent insulator in our case admits UV-Vis-NIR radiations hence it can be used as thermal control coatings.

The annealing process has been noted to be helpful in improving the elect-optical properties of films. These enhancements have been attributed to a better crystalline quality and oxygen deficiency after the annealing [19]. Transparent films like TiO_2/MnO are good candidate for optical filters, polarizer, narrow pass band etc.

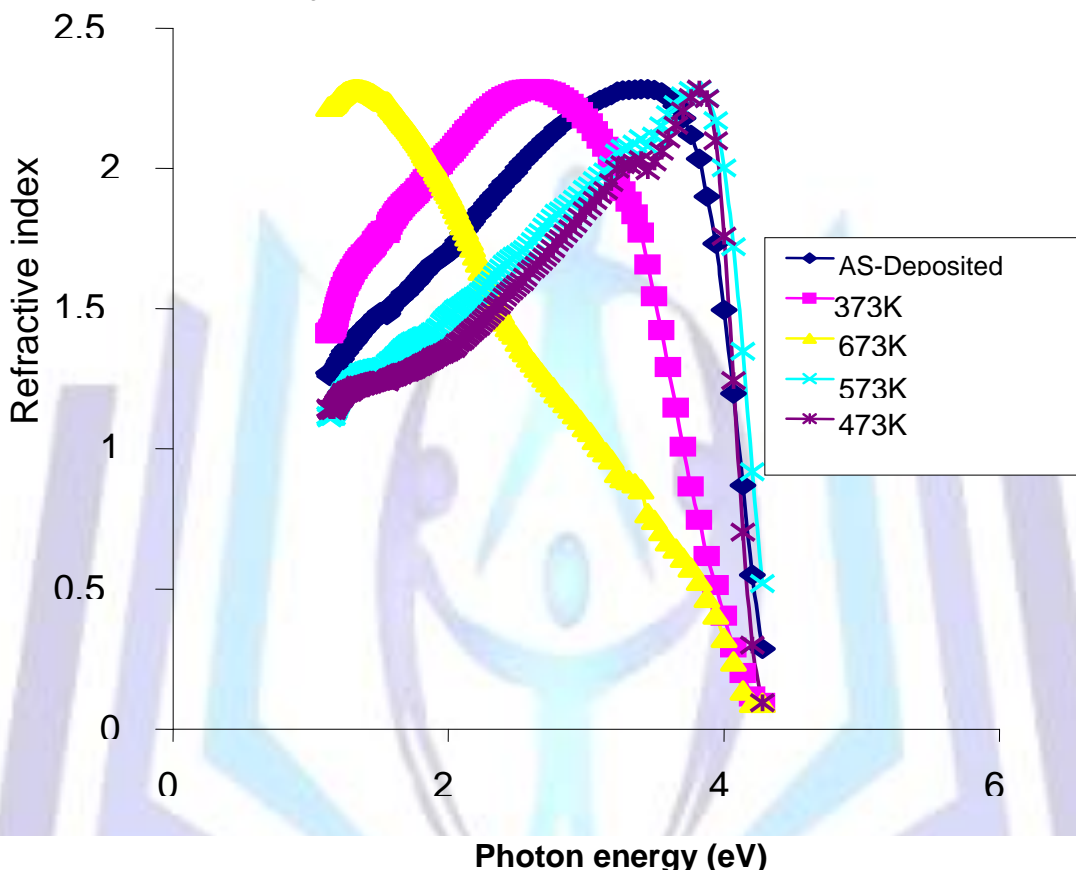


Fig.4: Refractive index Vs Photon energy for TiO_2/MnO Thin Films

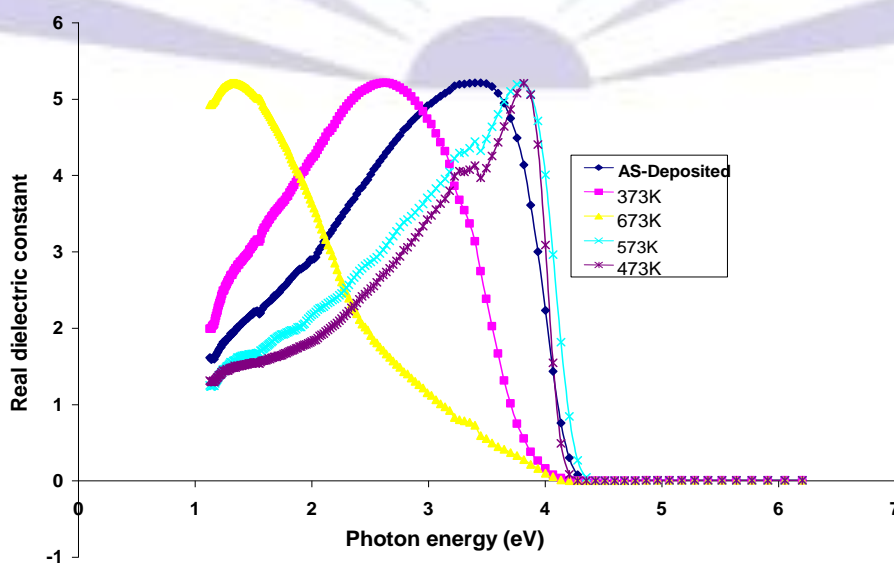


Fig.5: Real dielectric constant vs $h\nu$ for TiO_2/MnO Thin Films

Figures 5 and 6 show the plot of real and imaginary dielectric constant against photon energy for TiO_2/MnO core/shell thin film samples deposited. The samples showed an increase in real dielectric constant with photon energy up to 2.5eV and suddenly fall to zero.

In Fig.5 and 6, it is observed that ϵ_r increases with increasing photon energy for all the samples with a sharp drop which arises suddenly around 3.495eV. High values of ϵ_r and ϵ_i are requirement for application as insulators in electronic devices.

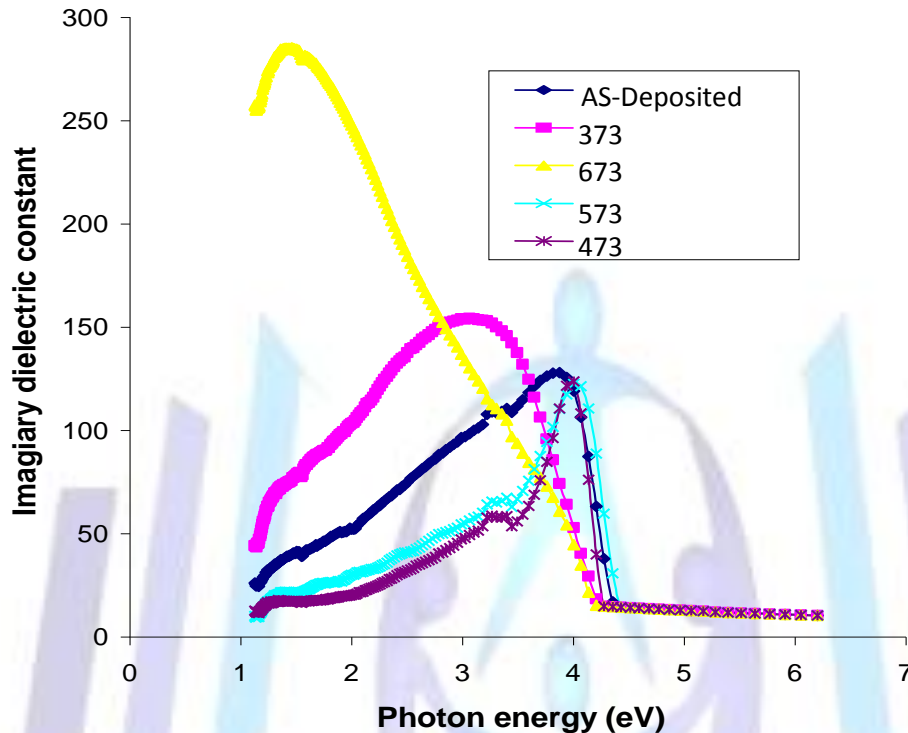


Fig.6: Imaginary dielectric constant vs $h\nu$ for TiO_2/MnO Thin Films

4.0 CONCLUSION

We have successfully grown, optimized and characterized thin film of TiO_2 and shell of MnO onto TiO_2 as the core to form novel core/shell oxide thin films of the form; TiO_2/MnO by the cheap, simple and easily reproducible solution growth technique.

The deposited films were characterized using X-ray diffraction and Spectrophotometer techniques.

The films grown were annealed between the temperature range of 373K to 673K in order to find out the effect of post deposition annealing on the properties of deposited thin films. The structural analysis reveals the formation of high pressure magnetic phase for core shell oxide thin films of TiO_2/MnO . The analysis also showed increase in grain size and better crystallization as the annealing temperature increases.

Our results also showed that thermal annealing has profound effect on the properties of the deposited film. Thermal annealing from our analyses improves the stability and orientation of the crystals thereby affecting the properties of the thin films. These core/shell oxide films thin films deposited in this research have not been reported using any technique of depositing thin films.

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