

Refractive Index and Dielectric Properties of TiO_2/CuO Core – Shell Thin Films

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Abstract
Core-shell metal oxide thin film of the form TiO_2/CuO was deposited on a glass substrate using the chemical bath technique. The deposited thin films were subjected to various annealing temperature in order to investigate the effect of thermal annealing on the properties of interest. The films were characterized to study the effect of thermal annealing on refractive index and the dielectric behaviour. 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 structure, the index of refraction and the dielectric constant. 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 results showed a reasonable trend between the annealing temperature and the film refractive index and dielectric constant.
Keywords: XRD,refractive index, SEM, dielectric constant, photon energy, core-shell

1. Introduction

Progress in technology had lead to the search of new advanced materials to meet the challenges of the contemporary industries. Thus thin films of various metal oxides are frequently utilized for fabricating a wide variety of electronic devices in modern industry. They are used in electronic devices as fundamental components with various functionality,such as insulators, diffusion barriers, dielectric capacitors, sometimes even as conducting electrodes and piezoelectric components, etc. These components are especially important for construction of integrated circuits that is a core technology for versatile LSI and semiconductive memories (flash, DRAM, SRAM, etc.)

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. (Bhosale et al, 2005). Many studies have been reported on electrical and thermal properties of some core shell thin films (Sqan et al, 2004). 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 (Borges, 2009).

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. (Habib et al, 2005). Zinc oxide is a semiconductor piezoelectric material which has been widely investigated for its numerous applications (Kadi et al, 2007). Also 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 (Asogwa, 2010 and Chikodize,2008). Cuprous oxide (CuO) is a low cost and non-toxic semi conducting material with potential in solar energy converting devices. The band gap of CuO is 2.0eV which is acceptable range of window material for photovoltaic applications (Siripala et al, 1996).

The index of refraction of a material is a physical parameter that shows the effect of the electric field component of light wave on the distribution around each of the atom in the crystal structure. Materials/ atoms with high polarisable electron give rise to a high value of the index of refraction and vice versa. On the other hand, the dielectric constant (real) characterizes the energy storage of the material and depends on frequency. The imaginary part of the dielectric constant characterizes the energy dissipation in the material due to relaxation dipole and space charge polarization and due to resonance of ionic and electronic polarization. In general, the ac conductivity of a material is a function of the dielectric constant. Studies have also showed temperature dependence of refractive index and dielectric constant.

In this communication, the effect of thermal annealing on the refractive index and dielectric property of TiO_2/CuO thin film deposited by chemical bath technique is studied. The chemical bath technique was used because of its simplicity and relative cost.

2. 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/ CuO core-shell, the TiO_2 film already formed (core) was inserted in a mixture containing 13 ml of 1M KCL, 13mls of 1m $CuSO_4$, 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 and b show the XRD pattern of the as-deposited and TiO_2/CuO film annealed at 673K respectively. 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 CuO (JC PD Card No.41-1432) and assigned to the diffraction line produced by (200) and (111) planes of the CuO – 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:

$D = 0.89 \lambda/\beta \cos \theta$, (Engin et al, 2009) 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/CuO 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 of evaporation of absorbed water and reorganization of the grain.

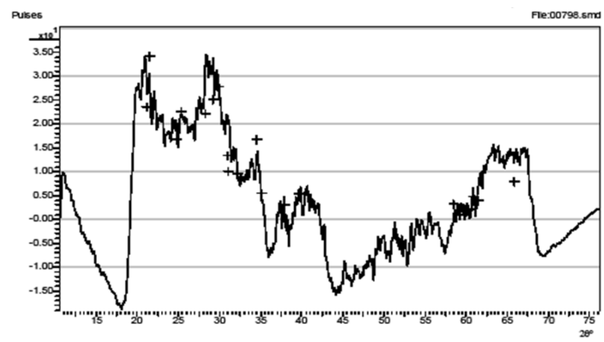

Fig.1a: XRD of as-deposited TiO_2/CuO Thin Film

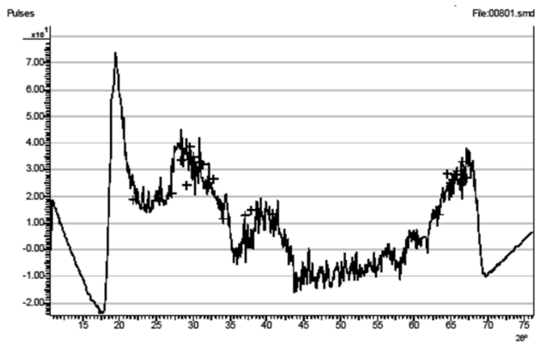

Fig1b: XRD of TiO/CUO Thin Film Annealed at 673K

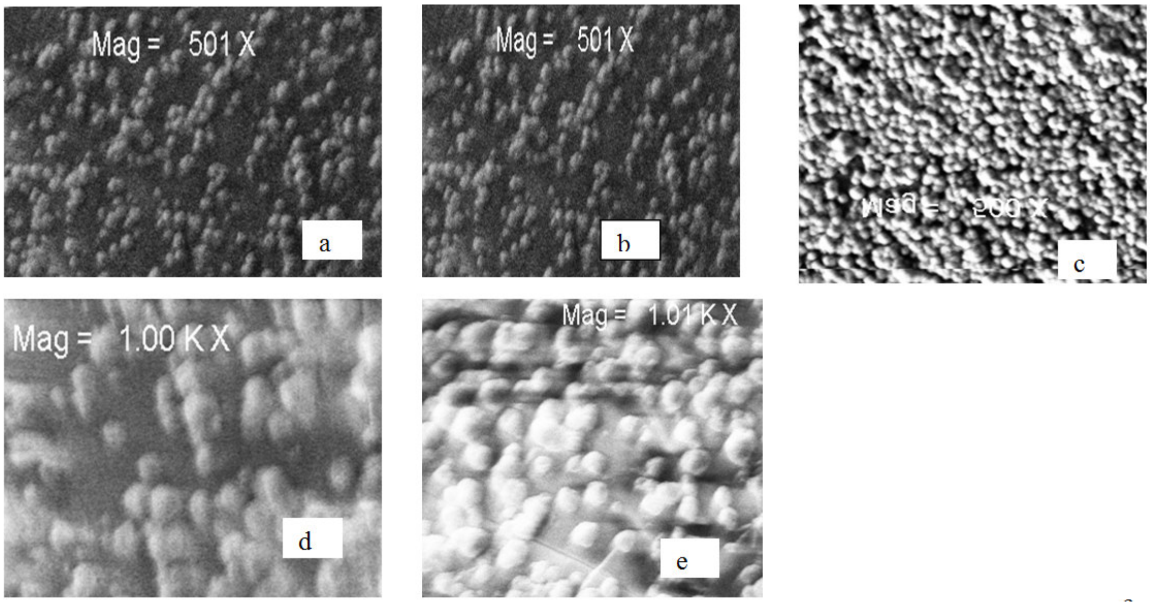

Fig.3: SEM results for TiO_2/ CuO Thin Films Annealed at (a) as-deposited (b) 373K (c) 473K (d) 573K (e) 673K

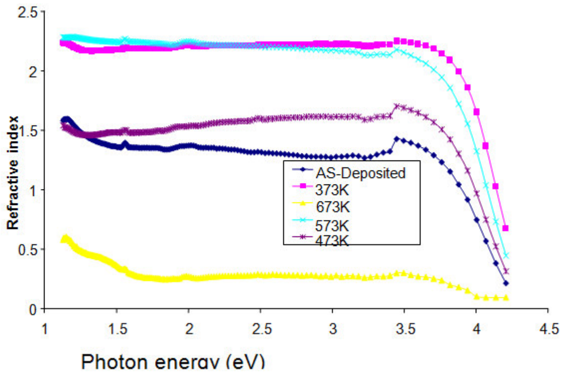

Fig.4: Refractive index Vs hυ for TiO_2 / CuO Thin Films

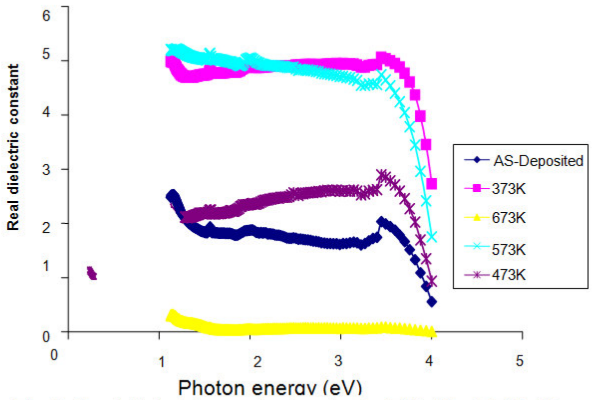

Fig.5: Real dielectric constant vs hυ for TiO_2/ CuO Thin films

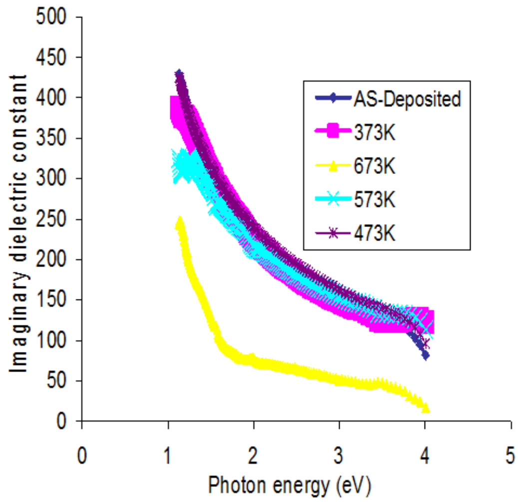

Fig.6 Imaginary dielectric constant vs hυ for TiO_2/ CuO Thin film

Fig. 5 shows the plot of index of refraction vs photon energy for the thin film under review. The plot showed that the index of refraction n was almost constant with photon energy for all the samples up to 1.3eV. However the index of refraction increased sharply from 1.3 to 1.4 as photon energy increases from 3.4eV-3.5eV and falls with increasing photon energy for as- deposited film. For the film annealed at 673K, the sharp fall and rise in n was very negligible. Similarly for film annealed at 373K, peak value of n was recorded at 3.47eV before it began to fall. Similar behaviour was displayed for other samples annealed at different temperatures indicating the semi conducting nature of the film. The plot of Real dielectric constant and the imaginary dielectric constant for TiO_2/CuO core/shell thin film is shown in Fig.5 and Fig.6. The figures show that the film annealed at 673K, showed the least dependence of real dielectric constant with photon energy while other samples shows a fall and rise in real dielectric constant with photon energy with a sharp fall and rise recorded at around 3.49eV for all the samples. The display of the imaginary dielectric constant for all the samples annealed shows high value of ε_r between 1.0eV and 1.7eV. However, for all the samples, the dielectric constant decreases with increase in photon energy.

CONCULSION

Thin film of the form TiO_2/CuO was deposited on a glass substrate. The deposited films were annealed between 373k to 673K in step of 273K in order to ascertain the influence of annealing temperature on the refractive index and the dielectric constant. XRD analysis revealed better crystallization of the grains as annealing temperature increased. The result also revealed the dependence of index of refraction on annealing temperature confirming the result of the XRD and SEM analysis on the sample. Several authors had attributed (Cai and Muth 2003) the trend to the effect of reorganization of the grains due to the evaporation of water during post deposition annealing. The result showed a decrease in the dielectric constant as photon energy increases irrespective of the annealing temperature.

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