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RESEARCH ARTICLE

INVESTIGATION OF THE OPTICAL PARAMETERS OF NANOCRYSTALLINE TiO_2/CoO CORE-SHELL THIN FILMS

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ABSTRACT

Investigation of the optical parameters of nanocrystalline TiO_2/CoO Core-Shell Thin Films was done within the UV, Visible and NIR regions. XRD analysis confirmed orthorhombic nanocrystralline structure for TiO_2/CoO Core-Shell Thin Films. The optical parameters of interest in this article were energy dispersion, refractive indices (n), reflectance (R) and extinction coefficients (k). The dependence of these parameters on the post deposition (annealing) temperature was particularly studied. Results showed that: refractive indices have the same maximum value of 2.25 each at a frequency of 4.83 X 10^{14}Hz in IR region. The reflectance of the as-deposited film sample and the samples annealed at 373K and 473K fluctuated in the wavelength range from 260-400nm, while the reflectance of the samples annealed at 573K and 673K respectively, increased directly with wavelengths and annealing temperatures in the visible region. Samples annealed at higher temperature have higher extinction coefficients with a peak vale of 90 each.

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INTRODUCTION

The applications of metal oxides are wide and varied due to their many properties of interest. In recent times attention has been drawn to the study of transition metal oxides (TMO) because, they exhibit two or more oxidation states usually differing by one, and iron, cobalt and nickel are three noteworthy elements in the transition metals that are known to produce a magnetic field (Hogan, 2010). More recently, semiconducting core-shell thin films have attracted special attention in the literature due to the peculiar behaviours and applications indentified in these materials. The granular Fe/Au and Co/Au core-shell thin films, synthesised using reverse micelles and traditional ball milling methods respectively have improved giant magneto-resistance (GMR) effects over conventional thin films, and could therefore be used as GMR sensors with wide applications in automobiles and computers. (O'connor *et al.,* 2004) Biocompatible magnetic nanoparticles in core-shell nanoclusters have been found to be promising in several biomedical applications for tagging, imaging, sensing and separation recently (You *et al.,* 2004). The design of interfacial reactivities of monodispersed core-shell Fe_3O_4 @Au nanoparticles was found to have magnetic, catalytic and biological applications (Lingyan *et al.,* 2005).

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Studies on core-shell oxide materials have not been extensively done (Onah *et al.,* 2012). In this paper, we therefore present the optical parameters of nanocrystalline TiO2/CoO core-shell thin films with emphasis on energy dispersion, refractive indices (n) reflectance (R) and extinction coefficient(k), and the effects of post deposition temperatures on these properties (or parameters). The variation of the refractive index with frequency constitutes the phenomenon of dispersion (Born and Wolf, 1993). Energy Dispersive spectrometer (EDS) analysis is a suitable technique in the determination of the crystalline quality and the presence of impurities in the thin films and also exciton fine structure (Deshpande *et al.,* 2008). EDS uses the spectrum of X-rays emitted by thin films bombarded with a focused beam of electrons to obtain a localized chemical analysis and hence a quantitative analysis of the films' surface compositions (Smith and King, 2000). The reflectance (R) normal to a given surface can be expressed in terms of real refractive index (n) and is give as:

$$R = \left(\frac{1-n}{1+n}\right)^2 \quad \ldots\ldots (1)$$

R is the ratio of energy reflected to incident energy. Reflectance is a directional property and hence the reflectance of thin films depends largely on their surface quality (Pillai, 2010). The optical properties of thin films (solids) are governed by the interaction between the thin films and the electric field of electromagnetic wave. A lot of information about the properties of thin films is obtained when they interact with electromagnetic radiation (Babatunde, 2005). Using equation (1) the refractive index is given as:

$$n = \frac{1-R}{2(R-1)} \quad \ldots (2)$$

Equations (1) and (2) are valid in the range of frequencies in which the films are weakly absorbing so that the square of extinction coefficient, $k^2 \ll (n-1)^2, (12-14)$. The absorption coefficient (α) expressed in terms of the extinction coefficient (k) is give by

$$\alpha = \frac{4\pi\upsilon k}{c} \quad \ldots (3)$$

where c is the velocity of light. Therefore extinction coefficient k can be calculated from equation (3) by

$$k = \frac{\alpha\lambda}{4\pi} \quad \ldots (4)$$

MATERIALS AND METHODS

Experiment Details

Titanium trichloride ($TiCl_3$) solution, Ammonia (NH_3), distilled water (H_2O), Cobaltous chloride ($CoCl_2.6H_2O$) and (Sail brand) microscopic glass slides (Cat. No.7102) with dimensions of $76.2 \times 25.4 \times 1.1$mm each, were the main materials used in the synthesis and deposition of TiO_2/CoO core-shell thin films. The chemical bath deposition (CBD) technique was used. Four out of the five samples of the films deposited (4T1, 4T2, 4T3 and 4T4), were annealed in an electrothermal thermostatic drying box, NO BKYY31-2000 model GZX-DH30 X 31, from 373-673K range of temperature per an hour. Other experimental details have already been reported (Onah *et al.,* 2016).

Thin Film Characterization

The structure and crystallinity of the thin films were analyzed and studied using X-ray diffractometer with Cukα radiation, and the analysis confirmed orthorhombic nanocrystalline structure. The optical parameters of interest in this paper were studied within the UV, Visible and NIR regions with Perkin-Elmer Lambda-2 spectrometer and energy dispersive spectrometer (Onah *et al.,* 2013).

RESULTS AND DISCUSSIONS

Energy Dispersive Spectrometer (EDS) Analysis

Figure 1,a-c show the EDS for the as deposited TiO_2/CoO core-shell thin film sample and the samples annealed at 373K and 573K respectively. Strong and sharp emission peaks can be observed at 0.50KeV and 1.75KeV for the as- deposited and annealed thin film samples. These indicate absence of crystalline defects induced during films' growth (Nishad *et al.,* 2008). The concentration of the elements contained in film samples are represented by the peak intensities in EDS. ''Absence'' of noisy background is a typical of crystalline films.

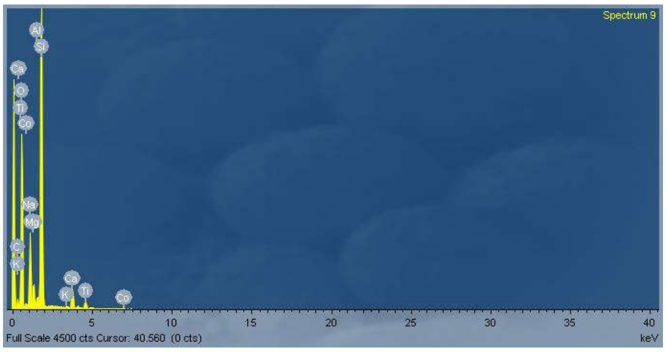

Figure 1a. EDS for as-deposited TiO2/CoO core-shell thin film

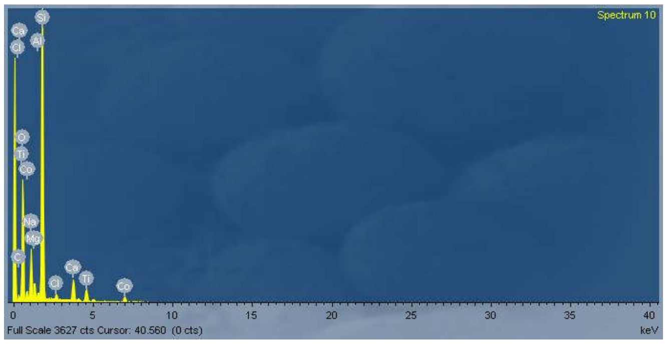

Figure 1b. EDS for TiO2/CoO core-shell thin film annealed at 373K

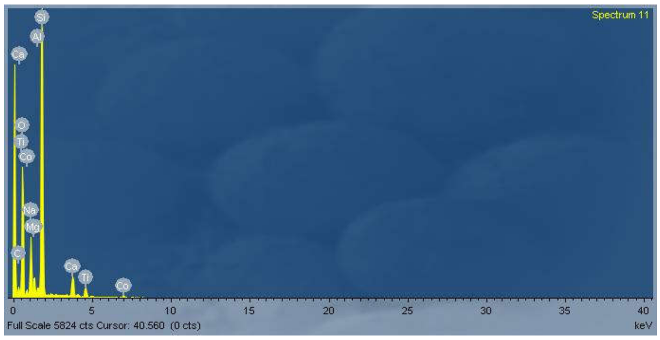

Figure 1c. EDS for TiO2/CoO core-shell thin film annealed at 573K

Refractive Index (n)

Figure 2, shows the graphs of refractive indices (n) against photon energy $(h\upsilon)$ for the five thin film samples. It can be observed that the refractive index is an increasingly function of photon energy or frequency within the NIR region and each film sample has a maximum value of refractive index as 2.25 at the energy of 2.0eV (or frequency of 4.83×10^{14}Hz). Post deposition temperature has no significant effect on the refractive index (n) in NIR. At higher values of photon energy, (ranging from 2.2-4eV), refractive index decreased faster with increasing annealing temperatures (4T3 and 4T4 in Fig 2). This trend disagreed with the result obtained with aluminium doped Zinc Oxide (ZnO: Al) thin films (Baydogan *et al.,* 2013)

Reflectance(R)

The graphs of reflectance versus wavelengths for the as deposited under EDS analysis TiO_2/CoO core-shell thin films are shown in Figure 3. It can be observed from Fig. 3, that the as-deposited film sample (4T) and annealed samples have low values of reflectance ranging from a minimum value of 2.5% to a maximum value of 20.0%.

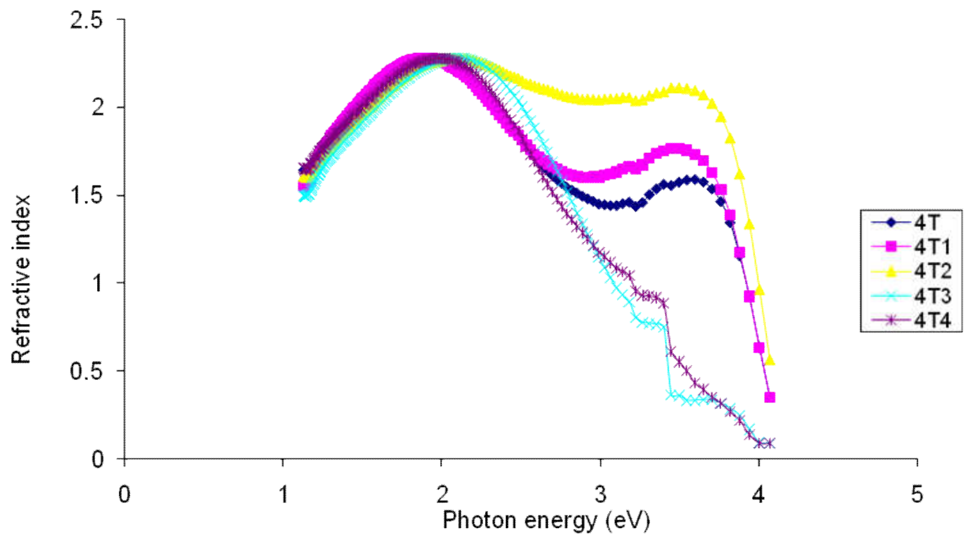

Fig. 2. Refractive index vs. photon energy for TiO_2/CoO core-shell thin films

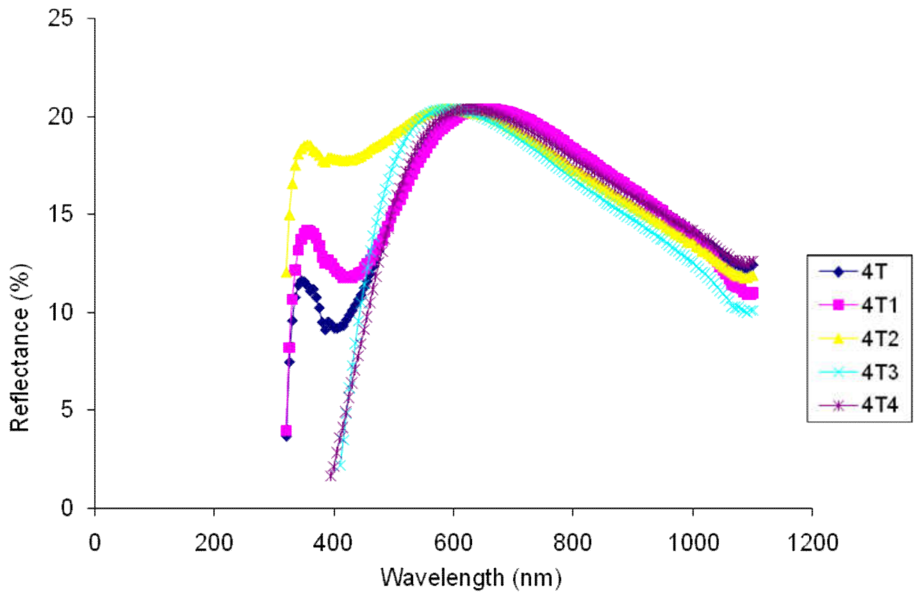

Fig. 3. Refectance vs. wave length for TiO_2/CoO core-shell thin films

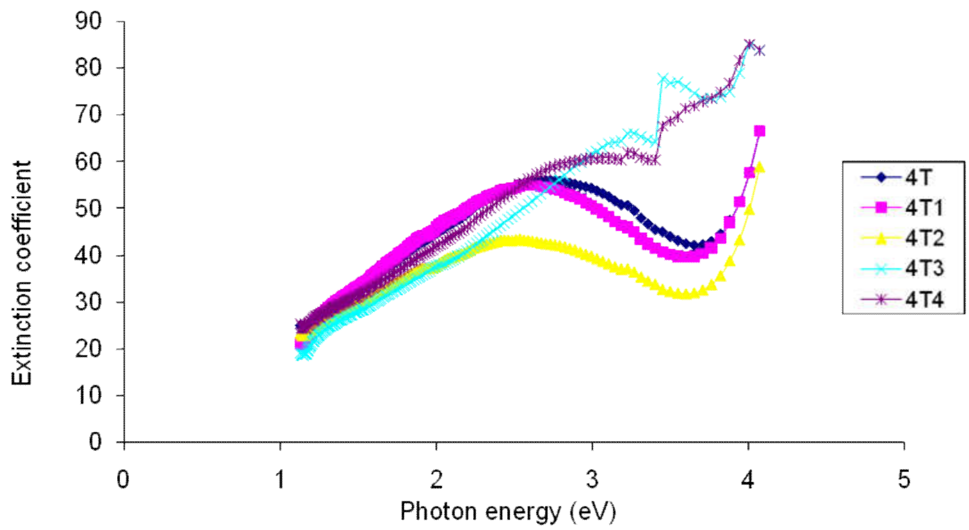

Fig. 4. Extinction coeffient vs. photon energy for TiO_2/CoO core-shell thin films

The low values of reflectance make TiO_2/CoO core-shell thin films good photovoltaic materials, since it has been proved that "reflectance (reduced reflection) enhances both the short-circuit current and open-circuit voltage, which in turn improves cell efficiency,, (Sze, 1981).There is fluctuation in reflectance of the as-deposited film sample and the samples annealed at a temperature range from 373-473K while a more direct proportional relationship exists between reflectance.

Extinction coefficient (k)

Figure 4, shows the graphs of extinction coefficients (k) versus photon energy ($h\upsilon$) for the as – deposited and annealed TiO_2/CoO core-shell thin films. From Fig. 4 it is clear that increase in annealing temperature leads to increase in the extinction coefficients (4T3 and 4T4). This agrees with the results obtain by another scalar (Baydogan *et al.,* 2013).

Conclusion

Investigation of the optical parameters of nanocrystalline TiO_2/CoO Core-Shell Thin Films has been concluded, within the UV, Visible and NIR regions. The optical parameters of interest in this article were energy dispersion, refractive indices (n), reflectance (R) and extinction coefficients (k). Reflectance has low values in a range of 2.5-20%, and increased with increase in annealing temperatures. Other results showed that: refractive indices have the same maximum value of 2.25 each at a frequency of 4.83 X 10^{14} Hz in IR region for all the film samples. The reflectance of the as-deposited film sample and the samples annealed at 373K and 473K fluctuated in the wavelength range from 260-400nm, while the reflectance of the samples annealed at 573K and 673K respectively, increased directly with wavelengths in the visible region. Samples annealed at higher temperature have higher extinction coefficients with a peak vale of 90 each.

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