IJESRT
INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

FREQUENCY DEPENDENT ELECTRICAL PROPERTIES OF TIO2/COO CORE-SHELL THIN FILMS

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ABSTRACT

The frequency dependent electrical properties, [dielectrics] of TiO_2/CoO core-shell thin films have been studied within the ultraviolet, visible and infrared regions of the electromagnetic radiations. Orthorhombic nanocrystallites have been induced by thermal annealing for the films as confirmed by XRD analysis. The optical absorption and transmission of these thin films were studied in the wavelength range from 200-1200nm using Perkin-Elmer Lambda-2 spectrometer. The electrical properties of the films were also studied using the four points probe. However, our interest in this paper is in the dielectric properties only. TiO_2/CoO core-shell thin films are semiconducting films with high dielectric loss. The films are good materials for storage cells in dynamic random access memory and can also be used as infrared detectors. At lower frequencies [or lower photon energy values] the dielectrics of the films are not strongly dependent on the annealing temperatures. At higher frequencies,[or higher photon energy values], the dielectric loss of the film samples annealed at higher temperatures decreased faster than the dielectric loss of the film samples annealed at lower temperatures.

KEYWORDS: TiO_2/CoO, core-shell, dielectric, thermal annealing.

INTRODUCTION

In recent time, the applications of some semiconductor thin films have become extensive especially in electronic and optical devices. The wide band gap properties of semiconducting thin films like CdO are of great interest particularly for applications such as widow layers for solar cells and transport electrodes [1]. Nanocrystalline CoO thin film has attracted considerable interest in applications such as sensors and photovoltaic cells [2]. Semiconducting core-shell thin films are now novel challenges due to their potential applications in various areas like coatings, sensors for cellular imaging, biosensors and magnetic orientation of animals [3], solar cells and photocatalysis [4]

Most core-shell thin films are structured nanoparticles that comprise a core of one material and a coating shell of another material which are typically around 20-200nm in size [5,6]. The array films of ZnO/CdSe core-shell thin films were proved to be good materials for solar cell photoanodes [7]. Pt/Fe_2O_3 core-shell nanoparticles prepared using sequential synthesis have thickness which were affected by concentrations of the reactants and the reaction conditions. These Pt/Fe_2O_3 core-shell nanoparticles have potential applications in catalysis and also precursors for making property-tunable magnetic nanoparticles [8]. Various techniques such as sol-gel, electrochemical precipitation have been used in preparing oxide thin films [2,9,10]. Previous studies on core-shell thin films were mostly done on the halides. This attracted our attention and interest in the study of core-shell oxide materials where the core and the shell are different oxides of the transition metals.

In this article, we present the characterization properties of TiO_2/CoO core-shell thin films with emphasis on the dielectric [electrical] properties of the films. The frequency dependent electrical properties of a thin film include parameters such as complex dielectric constant ε^*_r [which is made up of the real part ε'_r and the imaginary part $i\varepsilon''_r$], impedance Z, electrical resistivity ρ and AC conductivity. In this study, only the dielectric constants of TiO_2/CoO core-shell thin films have been investigated in the range of $2.4x\ 10^{14}$ to $1.7\ x\ 10^{15}$ Hz [or leV to 7eV of photon energy]. This frequency range falls within the ultraviolet, visible and near infrared regions of electromagnetic waves. The dielectric constant is a measure of the polarizability of a material. Dielectric polarization is nothing but the displacement of scharged particles under the action of the electric field to which they are subjected [11,12].

MATERIALS AND METHODS

2.1 Experimental details

The chemical bath deposition [CBD] method was used in the synthesis and deposition of TiO_2/CoO core-shell thin films. The glass substrates used for the deposition of these films were first given surface pre-treatment by cleaning then with deionised water and detergent, followed by ammonia acid and finally rinsed with acetone. $TiCl_3$, NaOH and polyvinyl alcohol [PVA] were used to synthesize the core while cobaltous chloride [$CoCl_2.6H_2O$] and ammonia [NH_3] were used in synthesizing the shell, using the chemical bath deposition technique [13]. The bath temperature was 70°C and the deposition time was 3hours. Five samples of the films were obtained once from the bath in order to ensure uniformity in the bath concentration, temperature and deposition time. The deposited films were annealed in an oven from 373K to 673K range of temperature for 1 hour per sample [2,13].

2.2 Thin Film Characterization

The crystallinity of TiO_2/CoO core-shell thin films was analyzed using X-ray diffraction. Scanning electron microscope [SEM] analysis was used for studying the film's morphology. The optical absorption and transmission of TiO_2/CoO films were studied in the wavelength range from 200-1200nm using Perkin-Elmer Lambda-2 spectrometer. The electrical properties of the films were studied using the four points probe. Nevertheless, only the dielectric [part of the electrical] properties of these films are reported in this paper.

RESULTS AND DISCUSSION

3.1 Real dielectric constant [ε'_r]

Figure 1, shows the graphs of real dielectric constants [ε'_r] against frequencies [or photon energy [hf] for the film samples.

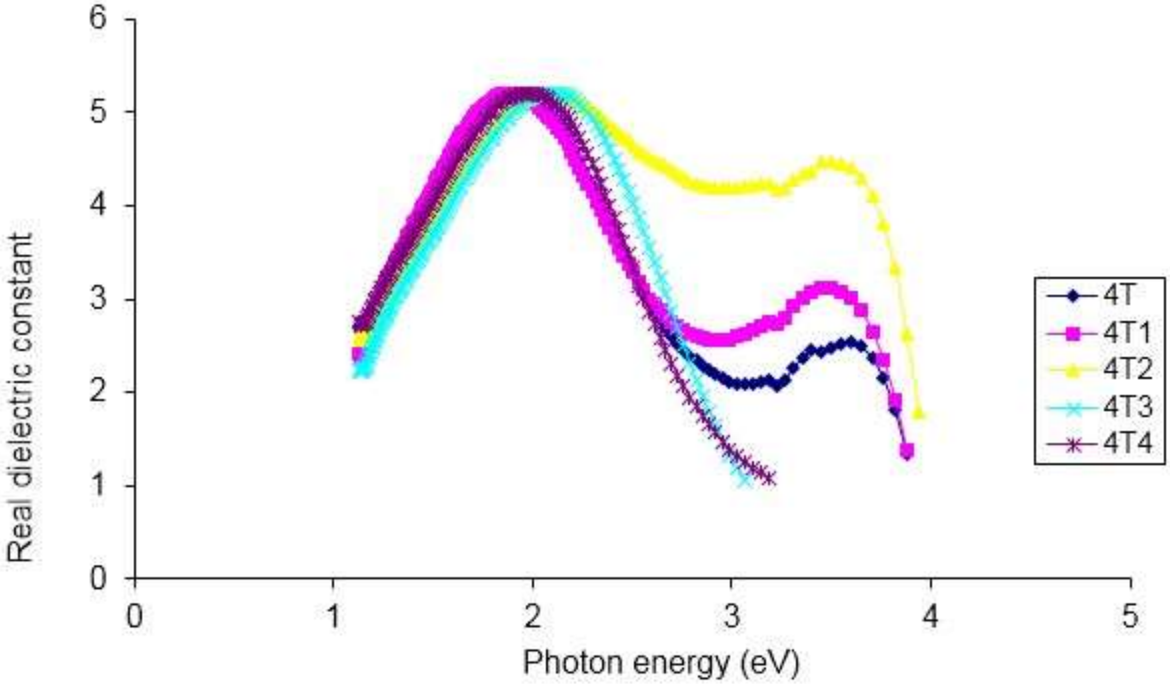

Fig. 1: Real dielectric constant vs. photon energy for TiO2/CoO core-shell thin films

It can be observed, in Fig.1 that the values of ε'_r increased as the frequency increased and reached peak values 5.2 for each sample. This trend occurred at lower frequency range from 2.4 x 10^{14} to 4.8×10^{14} Hz. The trend can be explained in terms of the behaviour of the dipole movement and the permittivity related to free dipoles oscillating in the presence of alternating electric field. At very low frequencies the dipoles follow the electric field provided that the frequencies are less than 1/ τ where τ is the relaxation time. This accounted for the observed increase in the values of ε'_r within

2.4x 10^{14}- 4.8x10^{14} Hz [1eV-2eV]. Relaxation occurred in ε'_r when f= 1/τ and ε'_r reached its peak value [12,14]. At low frequencies, [low photon energy], the values of the dielectric constant were high due to the accumulations of charges at grain boundaries known as space charge polarization [15].

As the frequencies [or photon energy] increased, dipole lagged behind the electric field and thereby leading to a decrease in $\varepsilon'_{r.}$ At very high values of the frequencies [or photon energy], when f > 1/τ , the dipoles could no more follow the electric field [16] hence ε'_r decreased sharply. This can be observed in Fig. 1 within the frequency range from 4.8x 10^{14} – 7.7x10^{14}Hz [2eV to 3.2eV]. However, the as-deposited TiO_2/CoO core-shell thin film sample and samples annealed at 373K and 473K respectively, the dipoles followed the electric field further within the frequency range from 7.2x10^{14} – 9.2x10^{14}Hz [3eV–3.8eV] The dielectric loss was therefore not fast within the same frequency [or energy] range as seen in Fig. 2. These samples have more dielectric properties than those annealed at higher temperatures, and are therefore good materials as storage cells along with capacitors in dynamic random access memory. Irradiation by light is one of the factors that can excite electrons in semiconducting thin films. Mostly materials [and thin films] with increasingly wider band gaps are used as semiconductors [17].

Any given dielectric material can also be characterized by a complex dielectric constant given by,

$$\varepsilon^*_r = \varepsilon'_r - i\varepsilon''_r \qquad 1$$

where ε'_r and $i\varepsilon''_r$ are the real and imaginary parts respectively. The imaginary part gives rise to energy absorption by the material from the alternating electric field [18]. Figure 2 shows the frequency [ors photon energy] dependent of dielectric loss $i\varepsilon''_r$ for the film samples at room temperature.

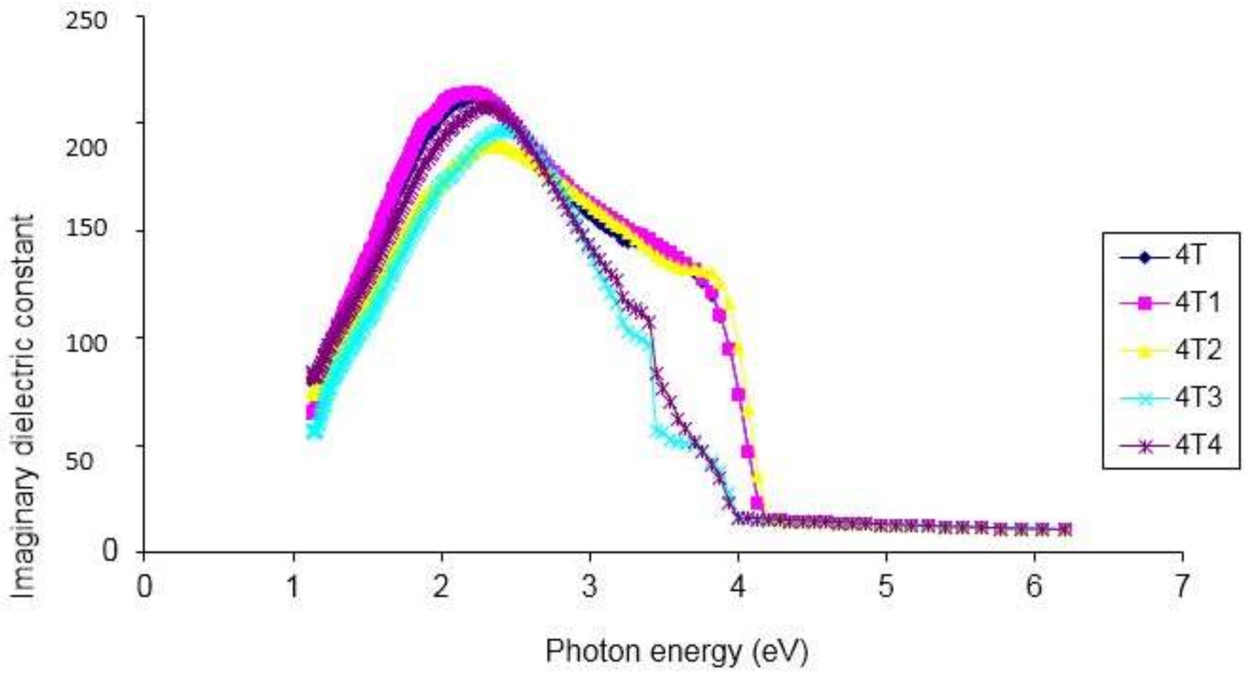

Fig. 2: Imaginary dielectric constant vs. photon energy for TiO2/CoO core-shell thin films

Similar feature for real dielectric constant ε'_r is observed for dielectric loss $i\varepsilon''_r$ in the lower frequency range. However, the observed peak in $i\varepsilon''_r$ occurred at a frequency of 5.3x 10^{14} Hz [or 2.2eV]. The dielectrics absorbed energy at high frequencies [high photon energy] with an alternating electric field. This can be observed in Fig. 2, in the frequency range from 9.7x 10^{14}- 1.5x 10^{15} Hz [4.0eV- 6.2eV]. Since the values of the real dielectric constants [ε'_r] for the films are not high as observed in Fig. 1 and high dielectric loss $i\varepsilon''_r$ is observed in Fig.2, TiO_2/CoO core-shell thin film are semiconducting films [17] and are not only suitable materials for dynamic random access memory but they can also be used as infrared detectors [14,19].

CONCLUSION

Investigation of the dielectric properties of thin film is essential because it provides information on the dielectric loss of the films. Studies of the frequency dependent electrical properties [dielectric constants] of nanocrystalline TiO_2/CoO core-shell thin films have been concluded within the UV, Visible and NIR regions of the electromagnetic waves. TiO_2/CoO core-shell thin films are semiconducting films with high dielectric loss. These films are good materials for dynamic random access memory and also for infrared detectors. Increased temperature of the thermal annealing decreased the dielectric loss of these films at higher frequencies [or higher photon energy values]

ACKNOWLEDGMENT

The authors are grateful to Nanoscience Research Group, University of Nigeria Nsukka.

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