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Research Article

Influence of Post-deposition Heat Treatments on the Optical Properties of Chemically Deposited Nanocrystalline TiO_2 Thin Films

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Abstract: The aim of this study is to investigate the potentials of TiO_2 thin films for device applications. Nanocrystalline single phase of rutile TiO_2 thin films have been prepared by Chemical Bath Deposition (CBD) technique at bath temperature range from 75-80°C, keeping other deposition variables constant. The films were then subjected to post-deposition heat treatments with annealing temperatures in the range 373 to 673 K. The optical characterisation was done using the Elmer Lambda-2 spectrometer to investigate the transmittance and absorbance versus wavelength measurements. The data obtained from the transmittance and absorbance measurements were used to deduce the important optical constants. The results show that the energy bandgap was direct, with values in the range ≤1.8 eV for the as-deposited layers and ≥2.2 eV for the annealed layers. At lower temperatures, the band gaps of the annealed samples did not differ significantly from the energy gap (1.8 eV) of the as-deposited film. At higher thermal treatment, the energy gaps increased with the increase in annealing temperatures and a maximum of 2.2 eV for the energy gap was determined for TiO_2 film annealed at 673 K. The values of the energy bandgap obtained in study, are within the range suitable for application in photovoltaic solar cell devices and in related photonic applications.

Keywords: Energy band gap, solar cells, TiO_2, thermal annealing

INTRODUCTION

The oxides of the transition metals have gained considerable attention recently. One of such oxides is Titanium Oxide (TiO_2). Titanium Oxide (TiO_2) thin film has been widely investigated years due to its many potential applications in nanotechnology, electronic, solar-thermal and in optoelectronic applications. According to the literature, it has been reported that TiO_2 has been utilized in photo-catalysis for the purification of air and water from contaminants, photoelectrical cells or gas sensor (Bozorgtabar *et al*., 2011a; Eufinger *et al*., 2008). TiO_2 exists in different forms which include: anatase (β-TiO_2), rutile ($\alpha - TiO_2$), brokite (γ- TiO_2), pyrite (P_a), (α-PbO_2) type and baddeleyite (ZrO_2) type (Pathan *et al*., 2005). Reports by different research groups indicate that TiO_2 thin films can be deposited using different deposition techniques inculding chemical bath deposition (CBD) method (Onah *et al*., 2013), Site-Selective Deposition (SSD) (Masuda, 2010), sputtering (Dakka *et al*., 1999) and metal-organic decomposition (Fukuda *et al*., 1999) etc. TiO_2 thin films can be prepared in aqueous solutions at ordinary temperature. Deposition parameters of TiO_2 thin films such as the substrate temperature, the complexing agents, concentration of the anionic and cationic precursors and deposition time could affect the structure of these films. These parameters have been proved to change the proportion of anatase (tetragonal) while rutile phase was thermodynamically stable (Fukuda *et al*., 1999; Viana *et al*., 2006). Crystalline titanium oxide thin films have been proved to increase in crystallinity and decrease in porosity as the thermal treatment temperature increased (Natarajan and Nogami, 1996).

Titanium oxide thin film is a wide band semiconductor which is well known for its peculiar, desirable qualities or properties such as good transmission in the visible and near infrared regions, good adhesion and high stability against mechanical abrasion, chemical attack and high temperatures (Eufinger *et al*., 2008; Dakka *et al*., 1999; Ritter, 1975). It is also a candidate material for dye- sensitized solar cells and photo catalyst (Masuda, 2010). In this study the effects of thermal annealing on the optical properties of nanocrystalline TiO_2 thin films prepared by Chemical Bath Deposition (CBD) technique is reported.

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MATERIALS AND METHODS

Materials: Titanium oxide thin films were synthesized and deposited on glass substrates using 0.7mL of 1M of $TiCl_3$, 0.4 mL of 1M of NaOH and 0.36 mL of Polyvinyl Alcohol (PVA) which was used as a complexion agent.

Experimental procedure: The experiment was carried out at the Solid State Physics and Materials Science Laboratory, University of Nigeria, Nsukka, Nigeria. Chemical bath deposition method was used in the preparation of TiO_2 thin films in this study. Before deposition, the glass substrates were first cleaned with detergent, followed by deionised water, ammonia acid and then rinsed with acetone. This pre-treatment of the substrates was done in order to break the bond between substrates and any contaminants without damage to the substrates. The bath containing the materials was put in an electro-thermal thermostatic drying box. The whole arrangement was maintained at a temperature range from 75 to 80°C. All the samples of TiO_2 thin films were deposited once in the same bath solution to ensure uniformity in bath parameters such as temperature and concentration etc. Four samples were annealed at 373, 473, 573 and 673K, respectively, in order to improve the crystallinity of the films and also determine the effects of thermal annealing on their optical band gaps.

Thin Films characterization: The characterisation was done at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile Ife, Nigeria. The synthesized films were characterized for their structural, optical, surface morphology, compositional analysis and electrical properties using: Rigaku D/max 2100 diffractometer equipped with a Cukα (λ = 5406Å), Elmer lambda-2 spectrometer for spectrophotometric analysis, Scanning Electron Microscopy (SEM) analysis, Rutherford Backscattering Spectrometry (RBS) analysis and Quardpro301- Auto calculating four points probe, respectively. X-ray diffraction analysis indicated that the thin films were nanocrystalline with tetragonal structure and were also single phase rutile TiO_2 (Onah *et al*., 2013). However, only the effects of thermal annealing on the optical band gaps of TiO_2 thin films are discussed in this study. For the sake of clarity, the films were carefully labeled as; 1T for as-deposited and $1T_1$ to $1T_4$ for films annealed at 373, 473, 573 and 673K, respectively.

RESULTS AND DISCUSSION

Figure 1 show the variation of the absorbance against wavelength for the as-deposited and annealed films. The optical absorption studies of TiO_2 thin films were carried out in the wavelength range from 200-1200 nm. In Fig. 1, a zero absorbance at about 198 nm and very high absorbance in 200-320 nm wavelength in the NIR region, for both the as- deposited and annealed film samples were observed. The absorbance decreased sharply for all the film samples in about 325 nm. Between 350-1100 nm the absorbance became low and also has slight variations with the annealing temperatures. The absorbance of the sample annealed at 473K decreased fastest reaching the lowest value of 0.2 in 450-800 nm wavelength range, while both the as-deposited sample and the sample annealed at 373K have a little higher absorbance in same range in wavelength as can be observed in Fig. 1. The further decrease in absorbance after annealing might be due to decrease, in the hydroxide accumulation along grain boundaries thereby increasing the transmittance (Deshpande *et al*., 2008; Mordi *et al*., 2009; Ubale *et al*., 2006).

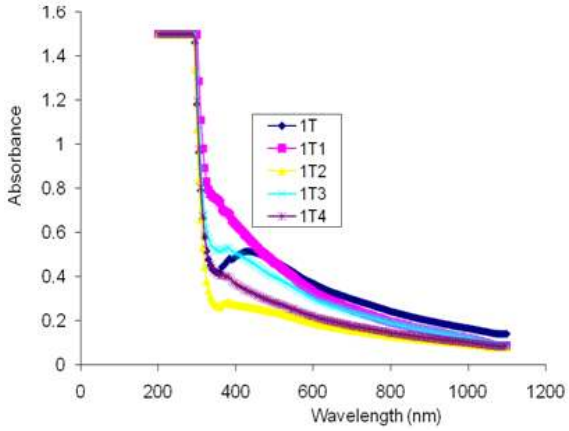

Fig. 1: Absorbance vs. wavelength for TiO_2 thin films

Figure 2 gives the graphs of $(\alpha h\upsilon)^2$ versus photon energy (hv). According to the literature, the theory of optical absorption is given by equation (Pankove, 1985; Nwofe *et al*., 2013a, 2013b):

$$\alpha h\upsilon = A\left(h\nu - E_g\right)^n \quad (1)$$

In Eq. 1, h = Planck's constant, ν = frequency, E_g = energy gap, A is an energy independent constant and the value of n determines the nature of the transitions (direct or indirect). N = $^1/_2$ for allowed direct transitions and n = 1.5 for allowed indirect transitions. The optical or energy gaps (E_g) of the films were determined from the extrapolations of the straight line portions of the graphs of $(\alpha h\upsilon)^2$ versus photon energy (hv). From the graphs of $(\alpha h\upsilon)^2$ against photon energy (hv) for the (as-deposited and annealed) TiO_2 thin films, in accordance with Eq. (1) in Fig. 2, the plots are more or less straight line graphs indicating that the electron transition or optical transmittance is direct in the k-space, where k is the crystal momentum. Extrapolations of the straight portions of the graphs in Fig. 2, intercept the energy (hv) axis and these points of intersections provide the

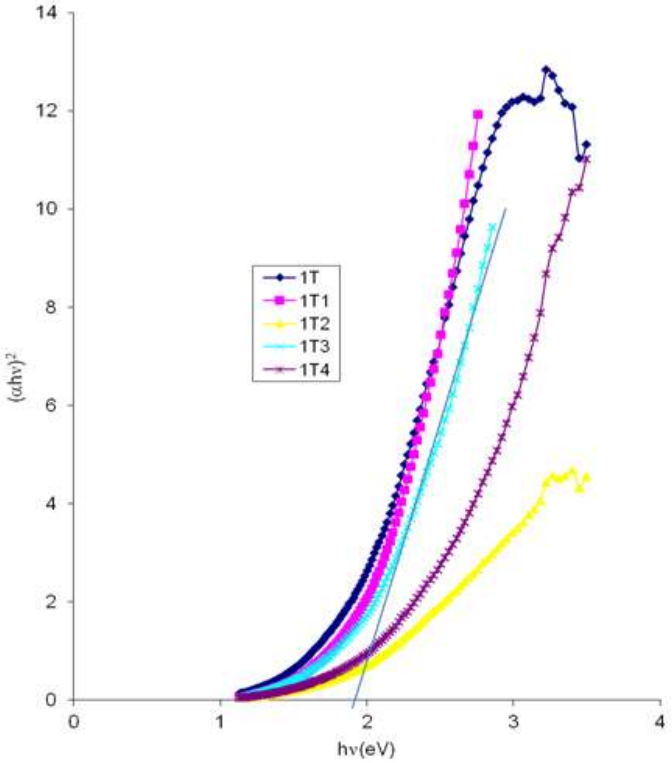

Fig. 2: Direct band gap plot for TiO_2 thin films

values of energy (or optical) band gaps of the thin film samples. The band gaps were determined to be 1.8eV, 1.9eV, 1.8eV, 2.0eV and 2.2eV for as-deposited sample and the samples annealed at 373, 473, 573 and 673K, respectively. The band gaps increased with thermal annealing. These mean that the optical qualities of TiO_2 thin films were significantly affected by annealing. Nevertheless, the range in the band gaps from 1.8eV-2.2eV makes these films suitable materials for photovoltaic applications. The increase in the energy bandgap as observed in this study was attributed to the effect of oxidation during the annealing process. The values of the energy bandgap observed in the present investigation is within the range reported by other research groups in the literature (Bozorgtabar *et al*., 2011b; Pathan *et al*., 2005).

CONCLUSION

Nanocrystalline and single phase of rutile TiO_2 thin films have been deposited on glass substrates using the Chemical Bath Deposition (CBD) method. The films have direct transitions in the k-space. At lower temperatures, the band gaps of the annealed films did not differ significantly from the energy gap (1.8eV) of the as- deposited film. At higher thermal treatment, the energy gaps increased with the increase in annealing temperatures. A maximum value of 2.2eV was determined for the sample annealed at 673K. These values are within the range suitable for application of the films in photonic devices.

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