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Optical and Structural Properties of Nb:TiO₂ Thin Films Deposited by DC Magnetron Sputtering at Ambient Temperature

C.M. Maghanga^{1,*}, M.M. Mwamburi²¹Department of Biological & Physical Sciences, Kabarak University, P.O. Private Bag – 20157, Kabarak, Kenya.²Department of Physics, School of Science, University of Eldoret, P.O. Box 1125-30100 Eldoret, Kenya.

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ABSTRACT

This work reports on the influence of niobium on the structural and optical properties of titanium dioxide thin films made by DC Magnetron sputtering. The films were deposited on glass substrates at ambient temperature which stood at below 50 °C in the deposition chamber. Film thickness based on profilometry ranged from 432 nm to 620 nm. Parameters investigated among others include structure, optical constants, grain size and film density. The as-deposited films were found to be amorphous and turn to crystalline upon annealing in air. The film density increased with doping to a maximum estimated to be 5.77 at. % Nb, beyond which a decrease was recorded. It was also observed that the refractive index of the film increased with doping.

1. Introduction

Titanium dioxide films are extensively used in optical thin film device applications owing to their appropriate optical properties, high thermal and chemical stability in hostile environments [1-8]. These films present good durability, a high transmittance in the visible spectral range, and a high refractive index. They are suitable for applications, such as antireflection coatings, multilayer optical coatings, optical waveguides, etc. Due to their unusually high dielectric constant, titanium dioxide thin films are attractive materials for fabricating capacitors. Impurity doping induces substantial modifications in electrical and optical properties of semiconductor materials [9,10]. Several methods can be used to deposit thin films [11,12]. One of the most utilized methods for obtaining uniform and dense titanium dioxide thin films as well as for large area deposition, with well-controlled stoichiometry, is reactive sputtering [13,14]. Thin film properties are very much sensitive to the deposition environment and as such several parameters that may influence film properties can be studied. In this work, the effect of niobium doping on optical, structural and electrical properties of titanium dioxide is investigated.

2. Experimental Methods

Thin films of niobium doped titanium dioxide were deposited on unheated and heated plain glass substrates (microscope slides) by reactive D.C. Magnetron sputtering in a deposition system based on a Balzers UTT 400 unit in an argon and oxygen atmosphere with gas flow-rates set at 60.0 and 4.0 sccm respectively. Two targets were used - Nb target with purity 99.999% and Ti target with purity 99.99%. Doping by Nb was achieved by setting the target power at 20 Watts, 40 watts, 60 watts and 80 watts while the Ti target power was fixed at 350 watts. The deposition time for all the films was 21 minutes. The working pressure was maintained at 13.26 mTorr. Before deposition, the chamber was pumped down to 1.4×10^{-6} mbar (1.05×10^{-3} mTorr) and baked for 8 hours. After deposition, the films were annealed in air at 500 °C for 30 minutes. Thickness measurement was carried out using Alpha Step Profilometer while Perkin Elmer λ 900 Spectrophotometer was used to measure reflectance and transmittance in the range 300 – 2550 nm. The interference fringe method developed by Swanepoel [15] was used to

determine the optical constants and to confirm the film thickness. RBS and ERDA were used to determine film composition with films deposited on silicon substrates while crystal structure was determined using D5000 X-ray Diffractometer.

3. Results and Discussion

3.1 Film Composition

Five samples of TiO₂ with varying niobium doping were characterized and subsequently analyzed (Table 1). Film composition deduced by RBS and ERDA for two films having different niobium content is shown in Fig. 1. There is good agreement between RBS and ERDA data as demonstrated by the results of two samples containing 3.59 at. % Nb and 5.77 at. % Nb shown in Figs. 2 and 3 respectively. For instance, ERDA estimation of Nb content in T4D film is about 5.6% while RBS gives 5.77%. Further analysis of RBS and ERDA data show niobium content increased almost linearly with target power as presented in Fig. 4.

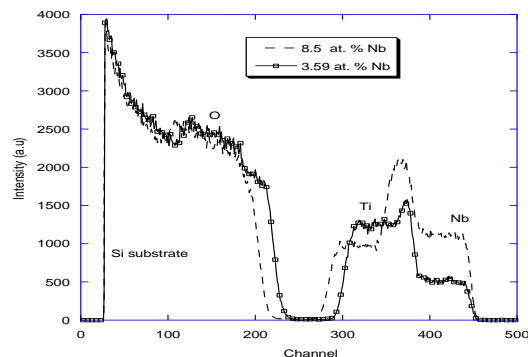


Fig. 1 RBS spectra for T4A (3.59 at. % Nb) and T4E (8.5 at. % Nb)

Table 1 Sample composition and density as deduced from RBS spectra

Sample	Nb composition (at. %)	Stoichiometry with reference to O	Thickness nm	Density g/cm ³
T4C (undoped)	0	Ti _{0.86} O ₂	432	2.26
T4B (20 W Nb target)	0.45	Ti _{0.87} Nb _{0.013} O ₂	420	2.59
T4A (40 W Nb target)	3.59	Ti _{0.89} Nb _{0.11} O ₂	494	3.3
T4D (60 W Nb target)	5.77	Ti _{0.697} Nb _{0.176} O ₂	550	3.36
T4E (80 W Nb target)	8.5	Ti _{0.682} Nb _{0.263} O ₂	620	3.31

*Corresponding Author: cmaghanga@kabarak.ac.ke (Christopher Maghanga)

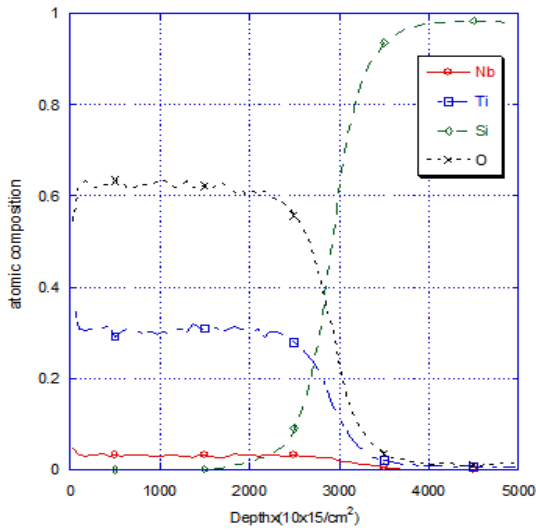


Fig. 2 Elemental composition of the film obtained by ERDA for the sample containing 3.59 at. % Nb

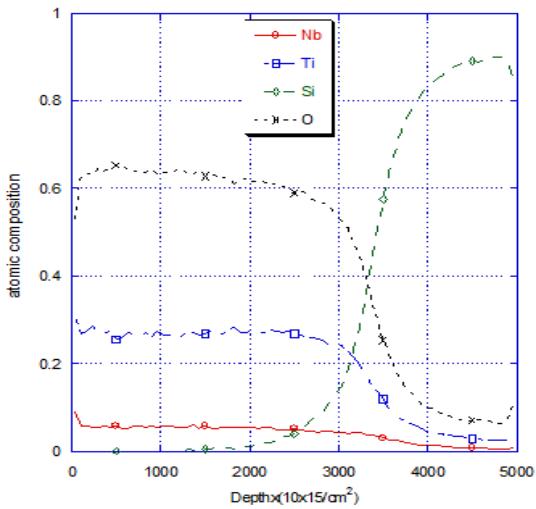


Fig. 3 Elemental composition of the film obtained by ERDA for the sample containing 5.77 at. % Nb concentration

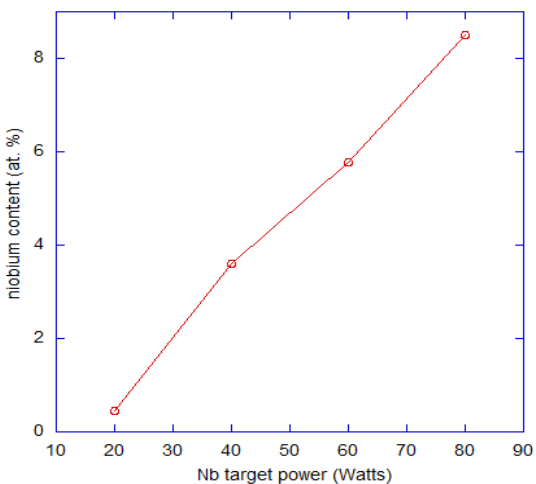


Fig. 4 Variation in niobium content in the film with power applied on the niobium target

3.2 Film Structure

As revealed by the XRD pattern in Fig. 5, the as-deposited films were amorphous and this was true for all samples before annealing. Upon annealing in air, all samples adopted a crystalline structure as shown in Fig. 6. Undoped TiO₂ film showed a preferential orientation along the (004) plane at 2θ = 37.8°. The inter-plane spacing (*d*) values were compared with the standard JCPDS data card (00-021-1272) which corresponds to the anatase phase. As niobium concentration increased in the film, the intensity of the peak corresponding to the plane (004) decreased and that of (101) increased.

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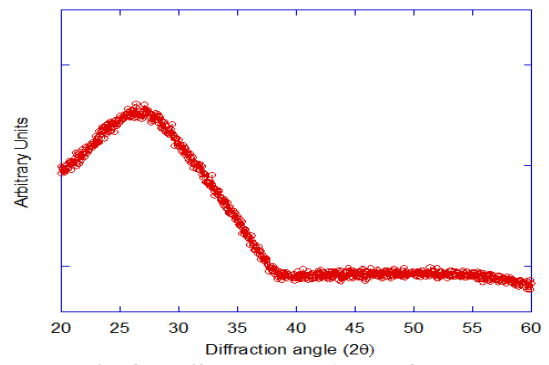


Fig. 5 XRD spectra for Nb:TiO₂ film containing 8.5 at. % niobium

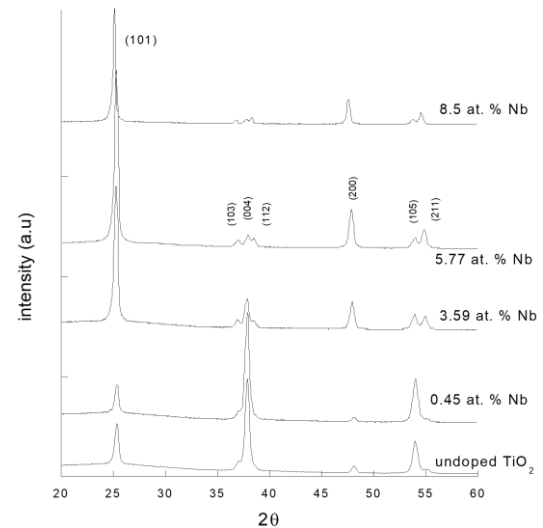


Fig. 6 XRD spectra of the samples after annealing in air at 500° for 30 minutes. The spectra was compared with PDF card 00-021-1272

The grain size of the films was estimated using the Debye-Scherrer formula, $D = (0.9\lambda)/(\beta\cos\theta)$, where *D* is the diameter of the crystallites forming the film, λ is the wavelength of CuK α line, β is FWHM in radians and θ is the Bragg angle.

The grain size was found to remain almost constant then increase drastically at higher dopant level (8.5 at. %) as shown in Fig. 7. The XRD spectra for T4E show a systematic shift to low angles which we attribute to strain induced by the dopant atoms. When the XRD peak intensities for T4E and T4D are compared (Fig. 4), it is found that the former yields peaks of lower intensity indicating lower degree of crystallinity as compared to T4D.

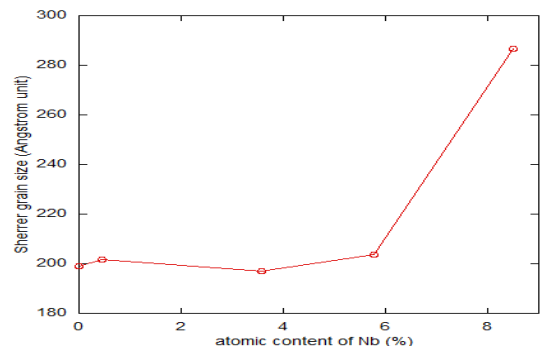


Fig. 7 Variation of grain size with niobium content in the films

The film density was estimated from RBS spectra using the relation [16]

$$\rho = \sum_i \frac{(\rho_{areal})_i (MW)_i}{N_A (t_f)} \quad (1)$$

where ρ_{areal} is the areal density in atoms/cm² obtained from the fit of RBS spectra using SIMNRA program [17], *MW* is the molecular weight of the elements in grams/mole, *N_A* is Avogadro's number, and *t_f* is the thickness of the film in Å. The density is plotted in Fig. 8. The film density increases with doping but at higher dopant concentration, it starts to decline. The decline could be attributed to the larger grain size which might reduce the packing fraction of the film.

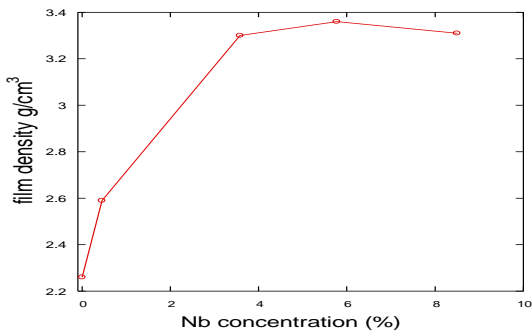


Fig. 8 Variation of density with niobium concentration

All the films have a high transmittance in the measured range as shown in Fig. 9. Upon annealing in air, the spectra shift to the shorter-wavelength region due to reduced thickness of the film [18]. The transmittance is also slightly higher indicating reduced absorption especially in the wavelength below 1000 nm.

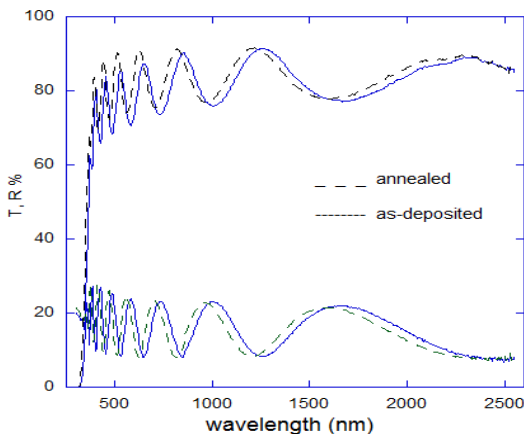


Fig. 9 Reflectance and transmittance of T4E film (8.5 at. % Nb)

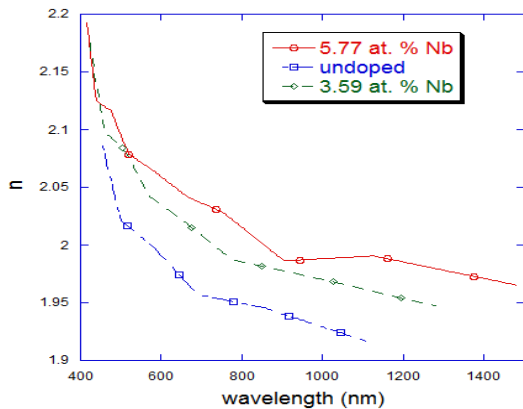


Fig. 10 Variation of refractive index as a function of wavelength

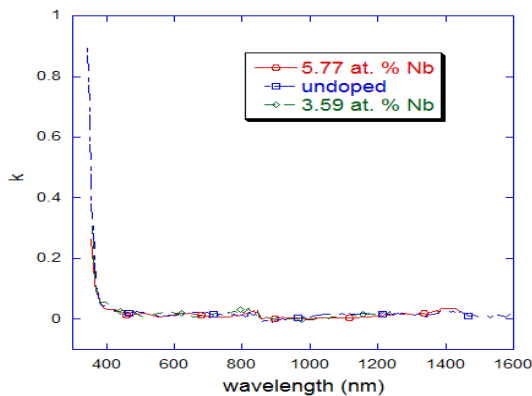


Fig. 11 Variation of extinction coefficient as a function of wavelength

3.3 Optical Properties

In order to determine the optical constants, a method developed by Swanepoel [15] was used. The graph in Fig. 10 shows that refractive index <https://doi.org/10.30799/jtfr.019.19030101>

increases with doping but absorption (Fig. 11) does not change much. Mardare et al. also observed an increase in refractive index when they doped titanium dioxide with chromium [19]. This is related to the density of the film which increases with doping for the samples presented on the graph.

We have also estimated the band gap of the films from the relationship between absorption coefficient α and photon energy expressed as

$$\alpha h\nu \propto (h\nu - E_g)^m \quad (2)$$

where $m=2$ for indirect allowed transition which dominates in titanium dioxide [20,21]. By plotting $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$ and with straight part extrapolated to $(\alpha h\nu)^{1/2} = 0$, the value of the band gap can be estimated (Fig. 12). The band gap was found to be 3.22 eV for the doped film (T4E) and 3.29 eV for the undoped film (T4C).

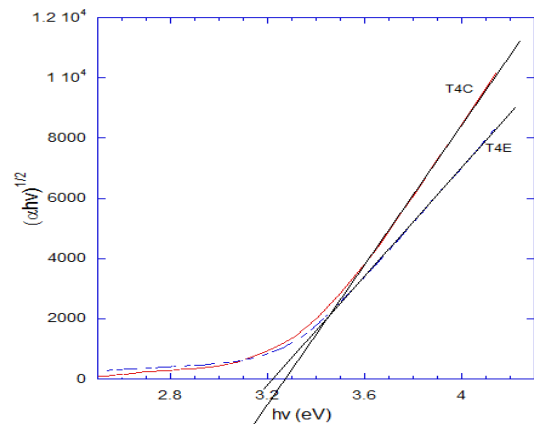


Fig. 12 A plot of $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) used to determine the band gap

4. Conclusion

This work has shown that films deposited under the conditions used produce films which are amorphous which turn to crystalline upon annealing in air. The refractive index of the films increases with the dopant concentration. It has also been noted that the niobium doping increases almost linearly with power applied on its target. There was also a shift in bandgap to lower energies with doping.

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