International Journal of Thin Films Science and Technology

http://dx.doi.org/10.12785/ijtfst/040104

Optical Properties of TiO_2 Based Multilayer Thin Films: Application to Optical Filters.

M. Kitui[1], *M. M Mwamburi*[2], *F. Gaitho*[1], *C. M. Maghanga*[3,*].

[1]Department of Physics, Masinde Muliro University of Science and Technology, P.O. Box 190, 50100, Kakamega, Kenya.
[2]Department of Physics, University of Eldoret, P.O. Box 1125 Eldoret, Kenya.
[3]Department of computer and Mathematics, Kabarak University, P.O. Private Bag Kabarak, Kenya.

Received: 6 Jul. 2014, Revised: 13 Oct. 2014, Accepted: 19 Oct. 2014.
Published online: 1 Jan. 2015.

Abstract: Optical filters have received much attention currently due to the increasing demand in various applications. Spectral filters block specific wavelengths or ranges of wavelengths and transmit the rest of the spectrum. This paper reports on the simulated TiO_2 – SiO_2 optical filters. The design utilizes a high refractive index TiO_2 thin films which were fabricated using spray Pyrolysis technique and low refractive index SiO_2 obtained theoretically. The refractive index and extinction coefficient of the fabricated TiO_2 thin films were extracted by simulation based on the best fit. This data was then used to design a five alternating layer stack which resulted into band pass with notch filters. The number of band passes and notches increase with the increase of individual layer thickness in the stack.

Keywords: Multilayer, Optical filter, TiO_2 and SiO_2, modeling.

1.Introduction

Thin films technology has received much attention in the recent past due to its importance in electronic, optical and optoelectronic devices. The technology is a key player in microelectronic integrated circuits, liquid crystalline displays, and planar waveguides among others.

Thin films coatings have also been used to improve both colour and energy efficiency of glass and as reflecting mirror coatings [1,2,3]. Though the application of single layer thin films have risen, there are a number of increasing applications which require multilayer films that combine attractive properties of various materials. Some of the important applications of multilayer films are in the design of computer disks, optical reflectors, antireflection coating, optical filters, and solar cells among others [1,2]. Unlike the doped semiconductors, multilayer films have a broad wavelength tunability which gives an optical response that is desired for a particular application [3]. They consist of a stack of alternating layers of non-absorbing dielectric materials having high and low refractive index respectively and operate on the basis of optical interference. Its reflectance usually depends on the constructive or destructive interference of light reflected at successive boundaries of different layers of the stack. The interface formed between the alternating layers has a great influence on the performance of the multilayer devices [4]. Therefore the appropriate sequencing of the layers of suitable dielectric materials and their thicknesses is crucial for achieving the desired spectral response and application. Thus, in designing the multilayer dielectric it is important to optimize their coating conditions [5,6].

In the designing of optical filters, the behavior of the entire multilayer system is predicted on the basis of the properties of the individual layers in the stack [7]. Therefore to achieve the optimum performance, it is important to optically characterize and accurately determine thickness of the individual layers. Previous studies focused mostly on the properties of the UV band pass filters deposited by thermal evaporation, sputtering, dip coating and sol-gel methods [7,8]. There is still limited information on the band pass with single and multinotch optical filters made from TiO_2 single layer film which is deposited by spray pyrolysis as a base material.

TiO_2 being an important dielectric material with a wide-band-gap energy and high refractive index that can be used in fabrication of multilayer thin films due to its optical properties. For example, because of its high transmittance

*Corresponding author e-mail: manassekitui2009@gmail.com

and high refractive index in the visible region (380 – 760nm) it can be employed in the production of optical filter and window glazing [9]. TiO_2 thin films can be fabricated using different technique which includes sputtering, solgel, pulse laser deposition; electrodeposition among others. Spray pyrolysis is the simplest, vacuum free technique and cost effective for large area deposition [10]. It can be pairs up well with high refractive index metals such as TiO_2, Al_2O_3, Ta_2O_3 and Nb_2O_5 among others to form optical filters [11,7].

In this work, high refractive index TiO_2 and a low index BaF_2 (Refractive Index ≈ 1.42) were used to model five layer optical filter.

2. Modeling of optical properties of optical filters

The characteristics matrix formalism for multilayer thin films was used to model the optical properties of the optical filters [12,13]. For light of wavelength λ incident on a multilayer of N layers, the characteristic matrix is the product of individual matrices for each interface $I_{m-1,m}$, and for each layer, L_m, expressed as:

$$\begin{bmatrix} E^+(0^-) \\ E^+(0^-) \end{bmatrix} = \left\{ \left[\prod_{m=1}^{N} I_{m-1,m} I_m \right] I_{N,N=1} \right\} \begin{bmatrix} E^+(z^+) \\ 0 \end{bmatrix} = \begin{Bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{Bmatrix} \begin{bmatrix} E^+(z^+) \\ 0 \end{bmatrix} \quad (1)$$

Here E^+ and E^- are the complex amplitudes of forward and backward travelling plane waves. The front interface towards air of the assembly is denoted 0^- and the back interface towards the substrate is denoted z^+. The interface matrix components can be obtained from the Fresnel relations as shown in [12]. The layer matrix is obtained from the phase factor

$$\delta_m = (2\pi/\lambda) d N_m \cos\theta_m \quad (2)$$

where θ_m represents the direction of propagation in the m^{th} layer and can be obtained from the incident angle using Snell's law, $N_m = n_m + ik_m$ is the complex refractive index, and d denotes the layer thickness. The reflectivity amplitude of this assembly may then be found from

$$r(\theta, \lambda) = E^-(0^-)/E^+(0^-) \quad (3)$$

A dielectric optical filter consists of alternating layers of high (n_H) amd low (n_L) refractive indices as shown in Figure. 1. n_1 and n_2 represent left and right semi-infinite media refractive indices.

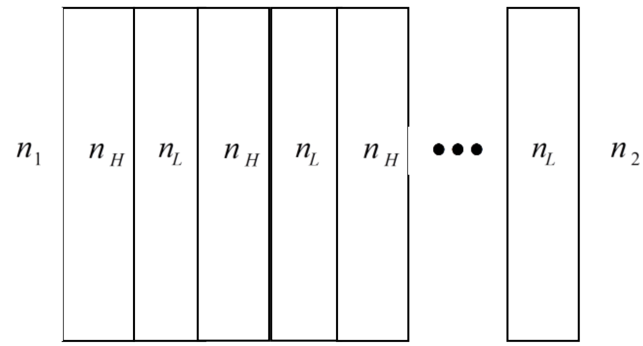

Figure 1: A dielectric layer model

The reflectivity amplitude at some operating wavelength for such a structure has been shown to take the form

$$r(\theta, \lambda) = \frac{1 - \left(\frac{n_H}{n_L}\right)^{2n} \frac{n_H^2}{n_1 n_2}}{1 + \left(\frac{n_H}{n_L}\right)^{2n} \frac{n_H^2}{n_1 n_2}} \quad (4)$$

Where n is the number of identical bilayers of low and high refractive index.

If n is large, $r(\theta, \lambda)$ will tend to −1, meaning 100 % reflection.

3. Experimental details

3.1 TiO2 Thin Film Deposition conditions

The samples of TiO_2 thin films were prepared with all other factors held constant while varying the deposition time. The nozzle-substrate distance was 2cm. The sample deposition temperature was 500^o c ± 15^o. The initial volume of the solution at every loading was 100ml. the deposition time was varied from 5 minutes to 30 minutes. A spray pyrolysis system using an air-atomizing nozzle and nitrogen carrier gas was used (Figure. 2).

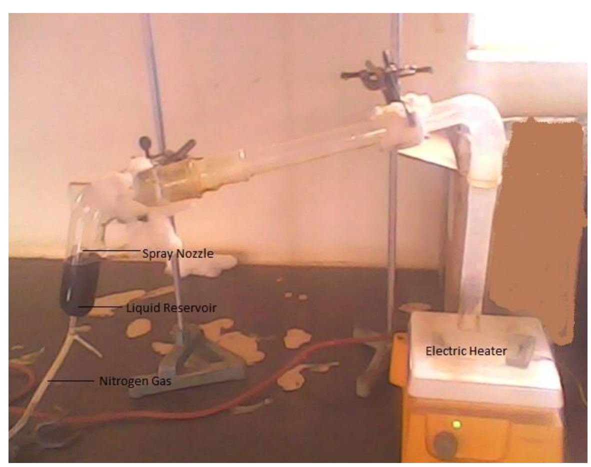

Figure 2: A photograph of set up that was used in the film deposition.

3.2 Preparation of Solutions for Spray Pyrolysis

The solutions were prepared according to the Andreas Kay procedure [14]. The TiO_2 films were produced from a precursor solution consisting of titanium (iv) isopropoxide (TPT) (97% Alfa Aesar) was prepared by mixing 34.7g of TPT with 54ml of 2,4-pentanedione (acetylacetone) (99% Alfa Aesar).

The beaker containing this mixture became hot because this reaction was exothermic. The beaker was left to cool. After cooling, 810 ml of pure ethanol was added to the solution in the beaker then stirred for 1 hour at room temperature and left for 24 hours for proper mixing. During this stirring step, plastic wrap was used to cover the top of the beaker to prevent reaction with humidity.

3.3 Characterization of TiO_2 Film

The thickness of the TiO_2 single layer film was determined directly from using commercial software the Scout while optical characterization of TiO_2 was done using a solidspec – 3700/3700DUV spectrophotometer.

The maximum sample dimension for this machine was 30mm square by 3mm thickness. Both experimental and theoretical were analyzed using computer software; Kaleidagraph version 4.02, scout 3 and Matlab programme version 7.60 (R2008a).

4. Results and Discussion

4.1 Transmittance and Reflectance

The optical transparency and reflectance of various TiO_2 thin films deposited for time ranging from 5 minutes to 30 minutes are shown in the figure 4.1. The T(λ) and R(λ) were measured in the range 300 to 2500nm using the solidspec – 3700/3700DUV spectrophotometer. The spectrophotometer was equipped with an integrating sphere coated with barium sulphate. The barium sulphate plate was used as reference.

The films exhibited varying transmittance and reflectance at different wavelength. The transmittance was 70%, 56.12% and 80% at 375nm, 617nm and 2500nm respectively. The reflectance was 34.9%, 9.8%, 30.3% and 9.8% at 325nm, 375nm, 617nm and 2500nm respectively. The highest transmittance of 80% and lowest reflectance of 9.8% was realized at 2500nm.

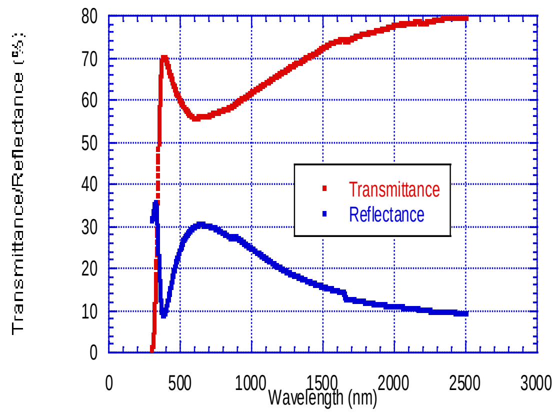

Figure 3: Transmittance and Reflectance of TiO_2 for different deposition time against wavelength.

4.2 Analysis of Optical Properties

The optical constants n(λ) and k(λ) are reported in the figures 3. Dispersion analysis using a model of dielectric susceptibility of the films consisting Kim oscillator, Campi-Coriasso and Tauc-Lorentz models were used to simulate the measured transmittance and reflectance. Model parameters were obtained from the best fit between the computer simulated and experimental using the computer software known as scout [15].

The Kim oscillator has four adjustable parameters which include: resonance frequency, oscillator strength, damping constant, and the so called Gauss–Lorentz-switch constant. The Kim oscillator models the weak broad interband absorption in the measured wavelength range [16]. The Tauc-Lorentz model is an interband transition model with four adjustable parameters which include: resonance frequency, strength, damping constant and gap constant. This model determines the imaginary part of the dielectric function [15,17]. The Campi-Coriasso model is an interband transition model. It has four adjustable parameters which include: resonance frequency, oscillator strength, damping constant, and gap constant [15,18].

Figure 3 shows refractive index n (λ) and extinction coefficient $k(\lambda)$ for TiO_2. The refractive index shown by the films are in the range of 2.23 to 2.4. At 300nm is 2.4 and reduces to 2.23 at 500nm to 2500nm. This almost agrees with the refractive index of TiO_2 which about 2.488 for anatase state. From the graphs it can be noted that *k* is close to zero. These shows a clear –cut dielectric properties for the undoped films.

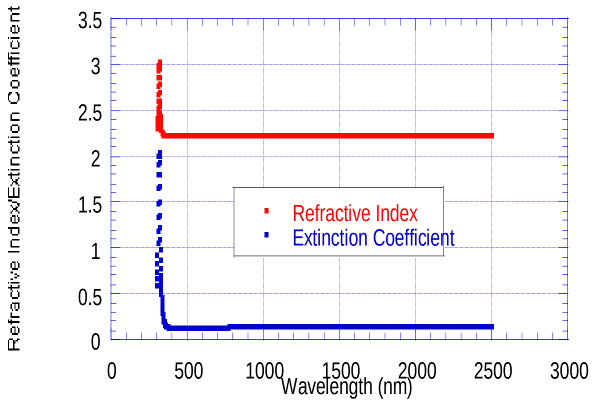

Figure 4: Refractive index and Extinction coefficient of TiO_2 for different deposition time against wavelength.

The data for silicon dioxide that was used in this study was acquired theoretically by use of commercial software known as GetData Graph Digitizer version 2.24 programme [19].

4.3 Modeled optical filters of TiO_2 based SiO_2

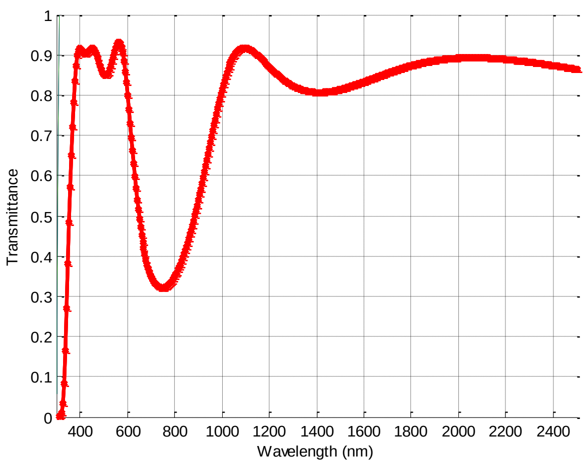

Figure 5: Simulation of the transmittance versus wavelength of a single band pass a notch optical filter (composed of TiO_2 and SiO_2 only).

Figure 5 shows a single band pass with a notch optical filter. The alternating layers of dielectric materials TiO_2 having high refractive index (H) and SiO_2 having low refractive index (L) with the following thicknesses (nm) H1 = 100, L1= 115, H2= 100, L2=115, H3=100 used in the simulation were five.

The single band pass has response wavelength in the spectral range of 325 – 755nm with a transmittance of 88.24%. This optical filter operates well in the UV with the highest transmittance being 91.53% at 400nm and 93.21% at 565 for the VIS range of the spectrum.

The single notch has transmittance maxima of 93.21% at 565nm and 91.66% at 1105nm resulting in a notch width of 540nm and notch reference at 750nm. The average transmittance in the passband specified between 400 – 560nm and 1090 – 2500nm is 87.75%.

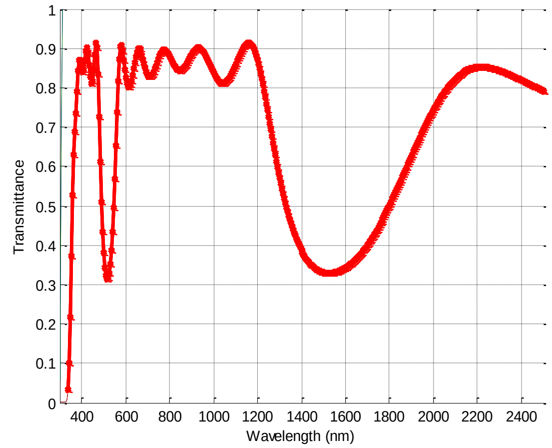

Figure 6: Simulation of the transmittance versus wavelength of a two band pass with two notch optical filter (composed of TiO_2 and SiO_2 only).

Figure 6 exhibited a two band pass with two notch optical filter. Alternating layers of dielectric materials TiO_2 having high refractive index (H) and SiO_2 having low refractive index (L) with the following thicknesses (nm) H1 = 192, L1= 263, H2= 192, L2=263, H3=192 used in the simulation were five.

The two band passes have response wavelength in the spectral range of 355 – 515nm with a transmittance of 88.81% and 515 – 1515nm with a transmittance of 84.57%. This optical filter operates well in the UV with the highest transmittance being 87.04% at 390nm, 91.29% at 465 for the VIS and 91.36% at 1160nm for the NIR range of the spectrum.

The first notch has a transmittance maxima of 91.12% at 465nm and 90.81% at 515nm resulting in a notch width of 115nm and notch reference at 515nm. The average transmittance in the passband specified between 390 – 465nm and 580 – 1160nm is 86.69%. The second notch has transmittance maxima of 91.36% at 1160nm and 85.25% at 2220nm resulting in a notch width of 1060nm and notch reference at 1540nm. The average transmittance in the passband specified between 580 –1160nm and 2220 – 2500nm was 83.78%.

Figure 7 shows a three band pass with two notch optical filter. Five alternating layers of dielectric materials TiO_2 having high refractive index (H) and SiO_2 having low refractive index (L) with the following thicknesses (nm) H1 = 302, L1= 420, H2= 302, L2=420, H3=302 were used in the simulation. The three band passes have response wavelength in the spectral range of 360 – 490nm with a transmittance of 82.78%, 490 – 815nm with a transmittance of 84.15% and 815nm – 2385nm with a transmittance of 79.84%. This optical filter operates well in the UV with the highest transmittance being 84.07% at 390nm, 89.46% at 525 for the VIS and 89.79% at 735nm for the NIR range of the spectrum.

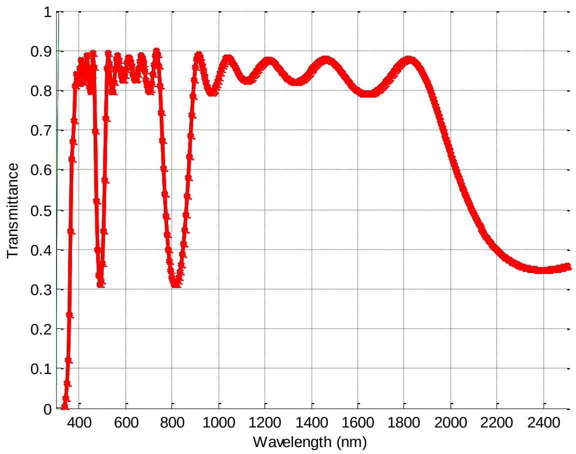

Figure 7: Simulation of the transmittance versus wavelength of a three band pass with two notch optical filter (composed of TiO_2 and SiO_2 only).

The first notch has a transmittance maxima of 89.4% at 460nm and 89.48% at 525nm resulting in a notch width of 65nm and notch reference at 490nm. The average transmittance in the passband specified between 390 – 460nm and 525 – 735nm is 83.38%. The second notch has transmittance maxima of 89.79% at 735nm and 89% at 915nm resulting in a notch width of 180nm and notch reference at 815nm. The average transmittance in the passband specified between 525 –735nm and 915 – 1825nm was 81.99%.

Acknowledgments

This work was carried out at the PV laboratories of University of Eldoret and University of Nairobi hence their assistance is appreciated. The support of the IPPS of Uppsala University in Sweden is highly appreciated.

References

[1] S. D. Bhamare, Determination of Optimal Material Combination for Multilayer Thin Films to Improve Performance against Surface Crack Probagation. Unpublished Msc Thesis, University of Cincinnati (2009).

[2] S. Mathew. *C*haracterization of CdS Based Multilayer Thin Films Useful for Photovoltaic Device Fabrication Using Different Techniques with Emphasis on Ellipsometry. Unpublished Ph.D Thesis, Cochin University of Science and Technology (2012).

[3] M. A. Angadi and K. Nallamshetty, *Solar Energy Materials*, **17,** 137-142 (1988).

[4] A. F. Khan, Effect of annealing on structural optical and electrical properties and SnO_2, TiO_2, Ge and multilayer TiO_2-Ge thin films prepared by physical deposition technique. Unpublished Ph.D Thesis, Pakistan Institute of Engineering and Applied Sciences. (2010).

[5] V. A. Kheraj, C. J. Panchal, M. S. Desai, and V. Potbhare, *Pramana-Journal of Physics*, **72**, 1011-1022 (2009).

[6] F. Richter, H. Kupfer, P. Schlott, T. Gessner, and C. Kaufmann, *Thin Solid Films.* **389**, 278-283 (2001).

[7] D.S. Hinczeweski, M. Hinczeweski, F.Z. Tepehen and G.G. Tepehen (2005), *Solar Energy Materials and Solar Cells*, **87**, 181-196 (2005).

[8] A. Chandran, Self-Assembled Multilayer Dielectric Spectral Filters. Unpublished Msc Thesis, State University (2001).

[9] M. M. Hasan, A. B. M. Malek, A. S. M. A. Haseeb and H. H. Masjuki. (2010). *ARPN Journals of Engineering and Applied Sciences.* **5**, 22-28 (2010).

[10] C. Manoharan and R. Srindhari, *International journal of recent scientific research*, **3**, 775-777 (2012).

[11] S. I. Jun, T. E. McKnight, A. V. Malechko, M. L. Simpson and P. D. Rack, *Characterization Electronic Letters.* **41**, 14-16 (2005).

[12] R. M. A. Azzam and N. M. Bashara. Ellipsometry and Polarized Light, North-Holland, Amsterdam, (1987).

[13] Z. Knittel, Optics of Thin Films, Wiley, London. (1976).

[14] K. Andreas, Solar Cells Based on Dye-Sensitized Nanocrystalline TiO_2 Electrodes. Unpublished Ph.D Thesis, Uppsala University, (1994).

[15] W. Theiss, Scout Thin Film Analysis Software Handbook, Hard and Software, Aachen: Germany, (2002).

[16] C.C. Kim, J.W. Garland, H. Abad and P.M. Raccah, *Physical Review B*, **45**, 11749 (1992).

[17] G. E. Jellison, L. A. Boatner, J. D. Budai, B. S. Jeong and D. P. Norton. Spectroscopic ellipsometry of thin film and bulk anatase(TiO_2), *Journal of Applied Physics*, **93,** 9537 (2003).

[18] D. Campi and C. Coriasso, *Journal of Applied Physics* **64 (8)**, 4128-4134 (1988).

[19] http://getdata-graph-digitizer.com