Optimization of Spectral and Angular Selectivity in Obliquely Deposited $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ Thin Films Prepared by Thermal Evaporation and Sputtering Methods

Haji Faki Haji^{1*} and Nuru Ramadhani Mlyuka²

1. Department of Natural Sciences, School of Natural and Social Sciences, The State University of Zanzibar (SUZA); P.O.Box 146 Zanzibar-Tanzania

2. Physics Department, Solar Energy Group, University of Dar es Salaam, P. O. Box 35063, Dar es Salaam- Tanzania

Abstract: Optical properties of obliquely deposited $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ multilayered films prepared by thermal evaporation and sputtering methods were investigated for energy efficiency of architectural and automobile windows. Investigation on the influence of layer thickness on the properties of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films yield an optimum layer thickness of 5 nm/14 nm/5 nm and 10 nm/14 nm/10 nm for optimal solar control performance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposited by sputtering and thermal evaporation methods. The optimum films were then obliquely deposited with deposition angle varying from 0° to 70° for the purpose of optimizing angular selectivity of the films. The spectral transmittances were measured by HITACHI model U-2000 double beam UV-VIS-Spectrophotometer. The optimum thickness provided a peak transmittance of 70% at a wavelength of 400 nm for near normal thermally evaporated thin films, and 72% for films deposited by sputtering unit at $\sim 320^\circ\text{C}$ for TiO_2 layers. Influence of deposition angle for obliquely deposited thin films was investigated for both sputtered and thermal evaporated thin films. The transmittance values for the films deposited by both methods gradually increased with increasing deposition angles to a peak of 80% at 400 nm wavelength. The angular transmittance measurements were taken for the optimum films with 10 nm/14 nm/10 nm thicknesses due to relatively larger overall film thickness as compared to 5 nm/14 nm/5 nm. Films deposited at 30° , 40° and 60° , with incident light angle of $\pm 10^\circ$, $\pm 30^\circ$, $\pm 50^\circ$ and $\pm 70^\circ$ were used for transmittance measurements. Best angular performance of 7% was realized at $\pm 10^\circ$ light incidence angle for films prepared at 60° deposition angle.

Key words: Spectral selectivity, angular selectivity, multilayered films, oblique deposition.

1. Introduction

The extreme use of heating systems and air conditioning in cold and hot climates respectively leads to extensive use of energy in order to sustain such systems. It is estimated that buildings are responsible for about 40% of the world's total annual energy consumption [1]. This basically leads to greater use of fossil fuels, and consequently higher emission of carbon dioxide and other pollutant gases and results in global warming, which is a major problem facing the world today. This problem is not only to the environment but also to human health [2]. Thus

alternative technologies including the use of renewable energy sources are strongly needed towards eradicating the said problem. Renewable energy sources currently supply around 15% to 20% of the world total energy demand, and of these, 20% of the global electricity is obtained from large hydropower, while around 2% is obtained from new renewable sources like wind, geothermal energy and solar energy [3].

For buildings, solar energy warms up the walls and glass windows. Walls of the buildings have an important role toward the heat transfer while glass windows are of the most concern in the controlling of heat as there can be too much energy entering or leaving the building. Through glass windows, heat transfers through conduction, convection and radiation.

*Corresponding Author: Haji Faki Haji, MSc, research field: material science for solar energy applications. E-mail: haji.faki@suza.ac.tz.

The radiation however is the most concern, because windows are used to transmit light, and the radiative properties can be conveniently modified by application of appropriate thin coatings on glass [4]. This modification of radiative properties results into energy efficient windows.

There are several techniques that energy efficiency of windows can be improvised. Such techniques include use of window coatings that exhibit spectral selectivity and those which show angular selectivity.

However, several studies on metal films have been reported due to the needs of obtaining the optimum energy performance in the buildings and motor vehicles [6-8]. Dielectric/Metal/Dielectric films have been recently studied [9-12] with the use of noble metals such as Ag, Au and Al and the dielectrics (ZnS , SiO_2 , MgF_2 , TiO_2 , CaF_2 and WO_3). These thin film materials have been designed to fabricate the spectral selective filters and energy saving devices for many applications [13].

However, Silver was found to perform best as the middle metal layer while TiO_2 selected to be the dielectric materials in D/M/D systems. This is because the optical properties can be adjusted to achieve various transmittances with a peak in the spectra by suitably varying Ag and TiO_2 thicknesses [14]. Both Ag and TiO_2 have been subjected to broad academic and technological research for many years due to their remarkable optical properties that normally depends on particular deposition conditions. It has been noted that TiO_2 is useful resources for optical coatings for the

reason that its exhibit high visible transmittance with high refractive index of about 2.31, but its applications has been limited because of its low evaporation rate. Ag was found to have excellent optical properties that can be altered using different dielectrics including TiO_2 ; These might be the reasons of choosing both Ag and TiO_2 materials through suitable deposition condition that might provide good results for solar control coatings [15].

2. Experimental Procedures

Fabrication of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ thin films was done using Edwards E306A thermal evaporation unit and BALZER BAE 250 Coating System sputtering unit. The Edwards E306A coating unit was used to thermally evaporate $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ thin films. During evaporation process the pressure was monitored by the Pirani and Penning gauges. The TiO_2 (99.9% purity) pellets approximately 10 mm tall were first grinded to tiny granules before being placed into the tungsten boat source in the vacuum to be evaporated on to a glass slide. Silver layer was deposited on top of TiO_2 layer by evaporation of 3-6 mm random size granules of Ag (99.99% purity). And finally TiO_2 (99.9%) layer evaporated on top of Ag film forming $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ thin films (Fig. 2).

The deposition chamber was initially evacuated to less than 3×10^{-5} mbar before starting of evaporation process. This pressure rose to 7×10^{-5} mbar after deposition of TiO_2 layers. After TiO_2 deposition the deposition chamber was then pumped down to 6×10^{-5} mbar for Ag layer deposition. The deposition rates (r) were $0.02 < r < 1.53$ nm/s for TiO_2 and $0.4 < r < 1.25$ nm/s for Ag films respectively. Deposition was done by

Fig. 1 Schematic model for light incident onto a columnar microstructure, the orientation of the light beam is specified by the angles θ and ϕ [5].

TiO_2
Ag
TiO_2
Glass substrate

Fig. 2 Schematic diagram for sandwich of multilayer of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposition.

applying current to the tungsten boat containing TiO_2 or Ag granules. The current was slowly increased to 40 A and to 70 A during Ag and TiO_2 deposition respectively. However, the temperature of cell was not monitored during evaporation and the chamber gained heat thorough resistive current applied to the evaporation sources. Constant thicknesses of 5 nm and 10 nm of TiO_2 with variable thicknesses of Ag films ranging from 5 to 18 nm were deposited. The choice of these thicknesses was based on the fact that Ag films with thickness equal to 5 nm yield an impressive luminous transmittance value of about 85% [2] and for films thicker than 20 nm it is very difficult to achieve higher transmittance values in experiments [14]. Thickness of the TiO_2 and Ag films were monitored by FTM7 quartz crystal thickness monitor in a vacuum deposition chamber. The TiO_2 and Ag layers were first deposited at near normal angle of incidence for the purpose of obtaining optimum thickness values. The optimized film thickness values were then used when depositing multilayer films with varying incident angles of evaporated species. The depositing angles were 10° , 20° , 30° , 40° , 50° , 60° and 70° . These angles were determined by the geometry of the experimental set up as shown in Fig. 3.

The multilayer $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ thin films with the same thickness combinations and geometry as those prepared by thermal evaporation were also prepared by sputtering method using Ti (99.99%) and Ag (99.99%)

targets. The TiO_2 layers were grown by reactive sputtering in a mixture of Ar (99.99%) and O_2 (99.99%). During TiO_2 deposition the argon (Ar) and oxygen (O_2) flow rates were kept at a constant values of 75 ml/min and 30 ml/min respectively. The vacuum pressure was initially pumped to 4×10^{-6} mbar. This pressure was the increased to 2×10^{-5} mbar after heating the chamber. The working pressure was about 3×10^{-3} mbar. Substrate temperature was at a constant value of 320°C . The sputtering power was set at 150 W, giving deposition rate of about 12 nm/min.

The silver films were grown at room temperature with a base pressure of 1.8×10^{-5} mbar. The argon flow rate was 55 ml/min which lead to 5×10^{-3} mbar working pressure. The DC sputtering power was kept constant at 50 W. Deposition angles in this particular case were varied in equal intervals of 10° from normal to approximately 70° from the direction of impinging particles.

3. Experimental Results

3.1 Effect of Ag Film Thickness on Spectral Transmittance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ Films

The transmission of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films structures strongly depends on the Ag layer thickness. As can be observed in Fig. 4, the spectral transmittance in the visible range decreases with increasing film thickness, for Ag layer greater than 14 nm in thickness implying

Fig. 3 Substrate holder for variable oblique angle film deposition used in this work.

Fig. 4 Spectral transmittance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films for different Ag film thickness with 5 nm of TiO_2 layers.

that reflectance increases with increasing Ag layer thickness. Spectral transmittance was initially measured to find out the optimum thickness of Ag films from 5 nm to 18 nm with a constant layer of 5 nm of TiO_2 . Layer thickness of 14 nm for Ag proved to be the optimum as shown from Fig. 4. This is in agreement with an observation that when Ag layer is thinner than 20 nm, it will be very simple to archive higher transmittance in the visible spectrum range and lower infrared transmittance [12, 14].

The optimized thickness of Ag in the $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure with 5 nm thickness for TiO_2 layer resulted into a maximum transmittance of about 70% at 400 nm. Ag film thickness higher than or below the optimum value lead to decrease in transmittance as shown in Fig. 4. The integrated luminous transmittance for the optimized thickness of Ag (5 nm/14 nm/5 nm) for normally deposited films, was found to be about 48%, this value was higher than that of (5 nm/12 nm/5 nm) and (5 nm/18 nm/15 nm) having integrated luminous

Transmittances of 22% and 34% respectively. It was then observed that integrated solar transmittance for the optimum $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure was 42% while 25% and 31% solar transmittance values was obtained for 5 nm/12 nm/5 nm and 5 nm/18 nm/5 nm film structures respectively. An average luminous transmittance (48%) for the optimum thickness (5 nm/14 nm/5 nm) being much larger compared to its solar transmittance (42%), which was calculated to the wavelength range of 300 to 1,100 nm shows that the $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure is a promising candidate for solar control coatings.

Optimization of Ag layer thickness was also done for 10 nm thick layer of TiO_2 as was done for $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure with 5 nm of TiO_2 . The trial and error method was used to obtain 5 nm and 10 nm thicknesses for TiO_2 layer. The transmittance peaks were found to decrease with increasing TiO_2 layer thickness. It can be seen from Fig. 5 that 14 nm thickness of Ag layer produced best visible

transmittance; and in this case it was 63% at 400 nm. However this value is lower than that found for the corresponding structure with 5 nm thick TiO_2 layers (Fig. 6). The average luminous transmittance for 14 nm of Ag with 10 nm of TiO_2 was 37%, which is much larger as compared to 12 nm and 18 nm of Ag that yielded 34% and 22% respectively. The solar transmittance for 14 nm of Ag in the $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure was 32% while those for 12 nm and 18 nm of Ag layers, were 30% and 21% respectively. Despite the increase in the dielectric layer thickness from 5 nm to 10 nm with constant layer of (14 nm) Ag, the luminous Transmittance (37%) for structure remains higher as compared to its solar transmittance (32%). This is a property desired for solar heat rejection application, and can ensure that if used in architectural windows the inside of the buildings and automobiles remains cool.

The optimum layer thicknesses values of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure obtained from thermal

evaporation unit were also used to fabricate the same film structure using sputtering method. The dielectric layers were deposited at substrate temperature of $\sim 320^\circ\text{C}$ while Ag layers were deposited at room temperature. It was observed that luminous transmittance and solar transmittance at 55% and 45% respectively, for the multilayer structure $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ with thickness 5 nm/14 nm/5 nm were greater than that of 10 nm/14 nm/10 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ structure at 42% and 38% respectively. It is clearly observed from Fig. 6 that films with 14 nm of Ag sandwiched between two 5 nm TiO_2 layers provided best solar control performance; that is high luminous transmittance in the visible region together with low infrared transmittance. The multilayer structure with 5 nm/14 nm/5 nm thickness arrangements produced visible transmittance of 72% at 400 nm. The transmittance decreased with increasing wavelength to less than 20% in the NIR (Near infrared region). The maximum transmittance for 10 nm/14 nm/10 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structure was 60% at 380 nm.

Fig. 5 Spectral transmittance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films as a function of wavelength for different Ag film thickness with 10 nm of TiO_2 , deposited at room temperature prepared by thermal evaporation.

Fig. 6 Spectral transmittance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposited by sputtering method at a substrate temperature of 320°C for TiO_2 layer.

3.2 Influence of Deposition Angle on Transmittance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ Films

The influence of deposition angles on spectral transmittance of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films was first done for film structures deposited by thermal evaporation at room temperature and then compared with those deposited by sputtering method at substrate temperature of 320°C . This temperature was used so as to produce anatase form of TiO_2 films as has been documented [16, 17]. The transmittance values of 5 nm/14 nm/5 nm and 10 nm/14 nm/10 nm film structures for various deposition angles ranging from 0° to 70° are plotted in Figs. 7 and 8 respectively. As can be seen in Fig. 7, only a slight change in peak transmittance for all deposition angles. All of the films displayed peak transmittance above 70% at 360 nm. The highest peak transmittance (74%) for 5 nm/14 nm/5 nm multilayer structure is observed with 20° deposition angle at 360 nm wavelength while that of 10

nm/14 nm/10 nm structures produced peak value at the same wavelength with 60° deposition angle.

Off peak spectral transmittance values however, were observed to increase as deposition angles increased. Very large increases were noticed for NIR transmittances of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ multilayer films with increasing deposition angles. In the NIR least transmittance was observed for 10° deposition angle, while 70° deposition angle displayed largest transmittance. Therefore near normal angles of deposition is best for solar control $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films for applications where the incident light is near normal as they provide high transmittance in the visible range coupled with high reflectance in the NIR region.

The behavior of spectral transmittances at different film deposition angles ranging from 0° to 70° inclusively was also observed with a sandwich of 5 nm/14 nm/5 nm and 10 nm/14 nm/5 nm deposited at a substrate temperature of 320°C by sputtering method using Balzers BAE 250 coating unit. It was observed

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Fig. 7 Spectral transmittance of 5 nm/14 nm/5 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structures thermally evaporated at different deposition angles in room temperature.

Fig. 8 Spectral transmittance of 10 nm/14 nm/10 nm thermally evaporated $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structure at different deposition angles in room temperature.

that both 5 nm/14 nm/5 nm and 10 nm/14 nm/10 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structures showed spectral transmittance peaks and near infrared transmittance increases with increasing deposition angles. $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structures with thickness 5 nm/14 nm/5 nm displayed peak transmittances at wavelengths ranging from 360 nm to 460 nm, while films with 10 nm/14 nm/10 nm thickness produced peak transmittances in wavelength range of 360 nm to 420 nm. Multilayered films of 5 nm/14 nm/5 nm thickness arrangements deposited at 60° produced maximum transmittance of 83% at 360 nm of wavelengths and 81% transmittance value was observed for 10 nm/14 nm/5 nm multilayered films at the same wavelength (Figs. 9 and 10, respectively).

3.3 Integrated Luminous and Solar Transmittance for $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ Multilayered Films

Integrated solar and luminous transmittance values have been calculated for $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films prepared at different deposition angles. Both solar and luminous

transmittance values increases with increasing values of the deposition angles, the maximum luminous transmittance of 45% observed at 40° deposition angle, with solar transmittance at the same deposition angle being 42%. The peak vale for solar transmittance was observed to be 49% at 60° deposition angle with the corresponding luminous transmittance of 44% as shown in Fig. 11.

However, it was noticed that smaller deposition angles of 0° , 10° , 20° , and 30° with respect to normal produced average luminous transmittances of (48%, 29%, 42%, and 41%) respectively. These values which were higher compared to integrated solar transmittances calculated to be 42%, 24%, 35% and 36% respectively. The noticeable behaviors proved by these small angles of deposition deduce the solar control behavior for the multilayer films of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$. The integrated transmittances stated above are for 5 nm/14 nm/5 nm film structures. Similar observations were made for $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films with thickness arrangements of 10 nm / 14 nm / 10 nm as shown

Fig. 9 Spectral transmittance of sputtered deposited 5 nm/14 nm/5 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structure prepared at different deposition angles.

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Fig. 10 Spectral transmittance of 10 nm/14 nm/10 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structures prepared by sputtering method at different deposition angles.

Fig. 11 Variation of integrated Transmittances with deposition angles for thermal evaporated $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films at room temperature.

in Fig. 8. The integrated luminous transmittances for the same deposition angles are 37%, 56%, 56% and

40%, while that of solar transmittances are 32%, 46%, 46%, and 36% respectively. However the integrated

luminous transmittances for multilayer structures of 5 nm/14 nm/5 nm deposited at larger angles such as 50° and 60° are 39% and 45%, while solar transmittances for these deposition angles are 41% and 49% respectively. For 10 nm/14 nm/10 nm $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film structure the integrated luminous transmittance values were 40% and 45% while the integrated solar transmittance values were 39% and 51% for the deposition angles of 50° and 60° respectively (Fig. 11). The results are in an agreement with the study conducted by [6].

Contrary to the films deposited by sputtering method, the integrated solar and luminous transmittances in this case was found to gradually increase with increasing deposition angle as can be seen in Fig. 12 below. Thus larger deposition angles might be useful to produce good visibility for solar control coatings.

3.4 Influence of Deposition Angle to Angular Transmittances of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ Films

Angular selectivity of obliquely deposited

$\text{TiO}_2/\text{Ag}/\text{TiO}_2$ thin films was investigated for both thermal evaporated and sputtered film structures. The angular transmittance measurement of multilayer films of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ with thickness arrangement of 10 nm/14 nm/10 nm was determined at four different positions for positive and negative directions of columnar microstructures of the formed multilayer films. The selected films with 30° , 40° and 60° deposition angles were used to determine these transmittances; and hence angular performances (ΔT) in percentage were then determined using a relation

$$\Delta T = T(\theta) - T(0^\circ) \quad (1)$$

where, $T(\theta)$ is the luminous transmittance at 10° , 30° , 50° and 70° to both directions and $T(0^\circ)$ is luminous transmittance at $\theta = 0^\circ$.

The promising feature observed when 10 nm/14 nm/10 nm was deposited at 60° , these films was found to transmit more at this angle than at horizontal, which is a useful property for car wind screens and glass louvers used in most buildings in the tropic countries like Tanzania. The multilayer films deposited at 60°

Fig. 12 Variation of integrated luminous (Tlum) and solar (Tsol) Transmittances with deposition angles for $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposited at substrate temperature of 320°C by sputtering method.

produce high transmittance of 97% and 95% at the wavelength of 340 nm when incident light is from $+10^\circ$ and -10° respectively, these values decreases with increasing incidence angle; for $+30^\circ$ the peak transmittance observed is 89% at a wavelength 360 nm and 93% at 340 nm is shown from -30° incident light, approximately the same transmittance (88%) observed at 340 nm for $+50^\circ$ and -50° incident light, it is further observed that at the wavelength of 340 nm peak transmittances of 75% and 81% corresponds to incident light angle of $+70^\circ$ and -70° (Fig. 13).

Visible peak transmittances were found to increases with increasing deposition angles; thus at 60° deposited multilayer films with 10 nm/14 nm/10 nm thickness arrangement shows (Fig. 14) transmittances of 98 % at a wavelength of 340 nm when light is incident at $+10^\circ$ and -10° respectively, it is further shown that at -30° and $+30^\circ$ of incident light; transmittance decreased to 96% and 97% at a wavelength of 340 nm. The 85% and 81% transmittances occurred at wavelengths 340 nm and 360 nm when light is incident from -50° and $+50^\circ$ respectively. At 70° incident angle the peak transmittance decreased to 68% and 67% at

340 nm when light comes from -70° and $+70^\circ$ correspondingly.

3.4 Influence of Film Structure on the Optical Properties of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ Films

SEM (Scanning electron microscope) images in Figs. 15-17 show the influence of deposition methods and film thickness on structure of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ multilayered films. Fig. 15 is SEM surface micrographs for the multilayered structure of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ with 5 nm/14 nm/5 nm thickness arrangements deposited by thermal evaporation and sputtering method respectively. For thermal evaporation (Fig. 15a), films were deposited at room temperature, the structures of these films consists of some larger grains found on the surface of the films. Films deposited from sputtering unit (Fig. 15b) produced smaller grains and are almost uniformly distributed over the films as compared to those prepared by thermal evaporation. Both Fig. 15, is taken with the same magnification of 5.00 KX and SEM energy of 5.00 kV with a size of $23.47 \mu\text{m}$ in width.

Fig. 13 Angular Transmittances for thermally evaporated $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposited at an oblique angle of 60° .

Fig. 14 Angular Transmittances for sputtered $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposited at an oblique angle of 60° .

Fig. 16a shows a SEM image of 10 nm/14 nm/10 nm thickness arrangement of multilayered structure of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ deposited at 320°C (for TiO_2 layers) with sputtering method. SEM image for the same thickness arrangement of deposited by thermal evaporation method at room temperature is shown in Fig. 16b. The SEM micrographs $\sim 5.1\ \mu\text{m}$ in size taken to the same magnification of 20.00 KX with SEM energy of 5 kV, the micrographs show different morphology of grains and different grain sizes. Fig. 16b displays non uniform grain sizes randomly distributed on the films, as compared to Fig. 16a, with film uniformity and almost the same grain sizes with even distribution.

The SEM micrographs in Fig. 17a is a top surface of multilayered film of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ with thickness arrangement of 10 nm/14 nm/10 nm deposited at 60° from sputtering method from this work. While the micrographs shown in Fig. 17b display a top view of SEM image of glancing angle deposition TiO_2 at 60° where Fig. 17c shows its columnar microstructure (Xia et al. 2007) inserted here for comparison. The topography of the SEM micrographs (Fig. 15a) from this work resemble to SEM image of TiO_2 from the work of Xia et al. 2007 (Fig. 15b), and hence it might

be used to suggest presence of columnar microstructures in our samples. The columnar microstructures played important role on angular performances of the multilayered films. The growth of columnar microstructures to such kind of films depends on films deposition angle; thus inclination of the films columns was found to increase with increasing deposition angles and consequently improves angular performance of the films.

4. Conclusions

A study on obliquely deposited $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ multilayer films exhibiting spectral and angular transmittance measurements was conducted. Solar control performance was best observed for the $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ multilayered films with 5 nm/14 nm/5 nm and 10 nm/14 nm/10 nm thickness arrangements. The film structures produce higher transmittance on the visible range and low transmittance in the NIR region.

The current study employed two deposition methods; thermal evaporation and DC magnetron sputtering method. Both methods produced multilayered films that exhibit solar control properties, but sputtering method displayed best transmittance values in the visible region.

(a)

(b)

Fig. 15 SEM imaged of multilayered structure of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ with 5 nm/14 nm/5 nm thickness arrangements deposited by (a) thermal evaporation method and (b) sputtering method.

(a)

(b)

Fig. 16 SEM images of 10 nm/14 nm/10 nm thickness arrangement of multilayered structure of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films deposited by (a) sputtering method and (b) thermal evaporation.

Fig. 17 (a) SEM image from multilayered structure of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ film with 10 nm/14 nm/10 nm thickness arrangement deposited at 60° from sputtering methods; (b) top view SEM micrographs of 60° TiO_2 films; (c) cross section SEM image of TiO_2 film prepared at an angle of 60° (from Xia et al. 2007).

The multilayered $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ films were also obliquely deposited from 0° to 70° deposition angles. Films deposited at lower angles were observed to be more transparent in the visible region than the near infrared region of the spectrum. However the angular transmittances for multilayered films with 30° , 40° , and 60° deposition angles were measured with light incident angles of $\pm 10^\circ$, $\pm 30^\circ$, $\pm 50^\circ$, and $\pm 70^\circ$, and

among these $\pm 10^\circ$ light incident angles proved to produce good angular performance for samples prepared at the deposition angle of 60° . It should be noted that multilayer films fabricated using sputtering unit showed better transmittance values as compared to that from thermal evaporating unit.

The multilayered film structures of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ were investigated using SEM, only top surfaces of the

films were scanned and the arrangements of grain sizes were observed. Larger grains were observed for the films deposited from thermal evaporation methods while sputtering images showed closely packed smaller grains, evenly distributed on top surface. The columnar microstructures were achieved and found to depend on film deposition angles. Significant angular selectivity was observed for films prepared at 60° deposition angle.

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References

- [1] Omer, A. M. 2008. "Energy, Environment and Sustainable Development." *Renew. Sustain. Energy Rev.* 12: 2265.
- [2] Grangvist, C. G. 2007. "Transparent Conductors as Solar Energy Materials." *Panoramic Review, Solar Cells* 91:1529.
- [3] Herzog, A. V., Lipman, T. E., Edwards, J. L. and Kammen, D. M. 2001 "Renewable Energy: A Viable Choice." *Environment* 43: 8-20.
- [4] Mlyuka, N. R. 2003. *Structural Stability of Vanadium Dioxide Films Under Different Ambient Condition*. Dissertation submitted for a master's of science (Physics). University of Dar es Salaam.
- [5] Mbise, G. W. 1995. *Optical and Structural Properties of Obliquely Evaporated Thin Films*. PhD. Thesis, University of Dar-es-Salaam, Dar es Salaam-Tanzania.
- [6] Kivaisi, R. T. and Mbise, G. W. 1993. "Angular Dependent Transmittance in Multilayer Coating." *Solar Energy Material and Solar Cells* 30: 1-11.
- [7] Mbise, G. W., Niklasson, G. A. and Granqvist, C. G. 1996. "Angular Selective Optical Transmittance through Obliquely Evaporated Cr Films: Experiments and Theory." *J. Appl. Phys.* 80: 5361.
- [8] Mbise, G. W. 1998. "Spectral and Angular Selective Surfaces." *Proc. Fifth Collage on Thin Film Technology* 5.7, Dar es Salaam- Tanzania.
- [9] Dima, I., Popescu, B., Lova, F. and Popescu, G. 1991. "Influence of Silver Layer on the Optical Properties of the TiO₂/Ag/TiO₂ Multilayer." *Thin solid Films* 200: 11-8.
- [10] Leftheriotis, G., Yianoulis, P. and Patrikeos, D. 1997. "Deposition and Optical Properties of Optimized ZnS/Ag/ZnS Thin Films for Energy Saving Applications." *Thin Solid Film* 306: 92-9.
- [11] Zhou, J., Wu, Z. and Liu, Z. 2008. "Optical and Electrical Properties of TiO₂/Ag/TiO₂ Multilayer Coatings in Large Area Deposition at Room Temperature." *Rare Metals* 27: 457-62.
- [12] Behforooz, M. R. and Kangarlou, H. 2012. "Structural and Optical Properties of TiO₂/Ag/TiO₂ Multilayers." *Journal of Basic and Applied Scientific Research* 2 (10): 10234-40.
- [13] Marti-Palma, R. J. 2009. "Spectrally Selective Coatings on Glass: Solar Control and Low-Emissivity Coatings." *J. Nanophotonic* 3: 030305.
- [14] Chen, L. Y., Li, J., You, H.Y., Xie, H., Zhou, P. and Jia, J. H. 2004. "Study of Optical and Electrical Properties of TiO₂/Ag/TiO₂ Multilayers." *Journal of the Korean Physical Society* 44: 717-21.
- [15] Kanu, S. S., Binions, R. 2010. "Thin Films for Solar Control Applications." *Proc. R. A* 466: 19-44.
- [16] Shankar, S. S., Rautaray, D., Pasricha, R., Pavaskar, N. R., Mandale, A. B. and Slasty, M. 2003. "Growth of TiO₂ Nanoparticles in Thermally Evaporated Fatty Amine Thin Films by a Method of Ion Entrapment." *Journal of Material Chemistry* 13: 1108-11.
- [17] Chiodo, L., Sazar, M., Romero, A. H., Laricchia, S., Sala, F. D. and Rubio, A. 2011. "Structural, Electrical and Optical Properties of TiO₂ Atomic Clusters: An Abinitio Study." *J. Chem. Phys.* 135: 244-704.
- [18] Xia, G., Wang, S., He, H., Yi, K., Shao, J. and Fan, Z. 2007. "Structural and Optical Properties of Nanostructured TiO₂ Thin Films Fabricated by Glancing Angle Deposition." *Journal of Alloys and Compounds* 431: 287-91.