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**Research article**

# Influence of Films Thickness on Optical Properties of Nb-Doped $TiO_2$ (NTO) Thin Films Deposited by DC Reactive Magnetron Sputtering

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## Abstract

Transparent conducting oxide (TCO) thin films, particularly sputter-deposited Sn-doped $In_2O_3$ (ITO) have a wide application in optical coatings and optoelectronics. However, due to the scarcity and increasing cost of indium, efforts have been done to search for indium-free materials. Sputter-deposited Nb-doped $TiO_2$ (NTO) is among recent materials which have shown great potential for TCO applications. In this study we report and discuss on the influence of films' thickness on the optical properties of Nb-doped $TiO_2$ (NTO) films deposited on glass substrate from an alloy target of $Ti_{0.99}$ $Nb_{0.01}$ (purity 99.9%). It was observed that luminous transmittance ($T_{lum}$), solar transmittance ($T_{sol}$) and the band gap energy ($E_g$) increased with increased films thickness while optical constant ($n$,$k$) decreased with films thickness. An average $T_{lum}$ and $T_{sol}$ of above 60% and a relative increase of IR reflectance were achieved. The results implied a possibility for achieving low-emissivity (low-E) material upon improving the IR reflectance by raising the Nb-doping level.
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**Keywords** Magnetron sputtering, Optical properties of semiconductors

## 1. Introduction

Transparent conducting oxide (TCO) thin films have a wide application on optical coatings and transparent electrodes in devices such as flat-panel displays, light-emitting diodes, touch panels, defrosters, and solar cells [1]. In particular, sputter-deposited Sn doped $In_2O_3$ (ITO) has been established as a practical TCO material because of its excellent low resistivity ρ (~2×10−4 Ωcm) and visible transmittance (~80–90%) and simple preparation process [2]. However, efforts have been made to find materials that can replace indium because of

its [3]. Therefore, the replacing materials must be abundant and non-toxic materials such as zinc, titanium and tin [4].

In search for varieties of materials alternative to ITO, Furubayashi *et al*. (2005) discovered Nb-doped $TiO_2$ (NTO) as TCO materials [5]. However, to make NTO as a practical TCO, there should be sputtering procedures to fabricate the films. Normally, practical TCO films, including ITO, have been mostly manufactured by sputtering technique, which is characterized by low-cost production on a large-area uniform coating [6]. The general objective of the present work was to establish the sputtering procedures to fabricate NTO thin films for practical low-E on a window glasses. Toward achieving the objective, here we report sputtering procedures of NTO films on a glass slide and on the influence of films thickness on optical properties of the films.

## 2. Experimental Details

Nb-doped $TiO_2$ films were deposited on glass slide (76 mm x 26 mm x1 mm) by Dc magnetron sputtering in the argon-oxygen environment. A $Ti_{0.99}$ $Nb_{0.01}$ (purity 99.9 %) alloy disk 2" diameter x 0.250" thick, (supplied by Plasmaterials Inc.) was used as the target. Oxygen (purity 99.999 %) was used as reactive gas and argon (purity 99.999 %) was used as sputtering gas. BALZERS BAE 250 coating unit, was used to deposit the films. The unit chamber of the unit was evacuated in two stages; by rotary pump (DUO 016B) down to 5.0 $x10^{-2}$ mbar then picked up by air-cooled turbo-molecular pump (TPH33O) to a base pressure of 1.7 $x10^{-6}$ mbar. Then, heating of the chamber was carried out by means of a radiant heater, whose temperature controlled by a.c. variac transformer with output 0-260 V. The substrate temperature was recorded from digital Multi-meter (FLUKE 87 V) connected to the substrate through locally constructed and calibrated, heat resistant chromel-alumel thermocouple. Figure 1 represents a calibration of a constructed chromel-alumel thermocouple against a standard thermocouple. The constructed chromel-alumel was used to establish equilibrium substrate temperatures for several set points of the transformer with 75.4 mil/min argon. Figure 2 is a plot of equilibrium temperatures of the chamber as a function of several variac set points. The plot enabled to estimate substrate temperature during sputtering, thus replacing a need for using thermocouple in the actual sputtering process. Sputtering power was controlled by W. MDX 1.5 Magnetron drive (750 V/2 A/1.5 KW). The glass slides were ultrasonically cleaned in an Ultrasonic (Decon FS300) frequency sweep for 25 minutes and then suspended in ethanol vapor before kept into desiccators ready for use. The target was clean-sputtered for 5 min in order to remove surface oxide layers and contamination and then pre-sputtering for 10 min under the same condition as the film deposition. Films in interval of 50 nm from 200 to 350 nm were fabricated at about 300 $^oC$ substrate temperature ($T_s$), 6.0 x $10^{-3}$ mbar working pressure and 200 W sputtering power and 0.04 $O_2$/Ar flow ratio.

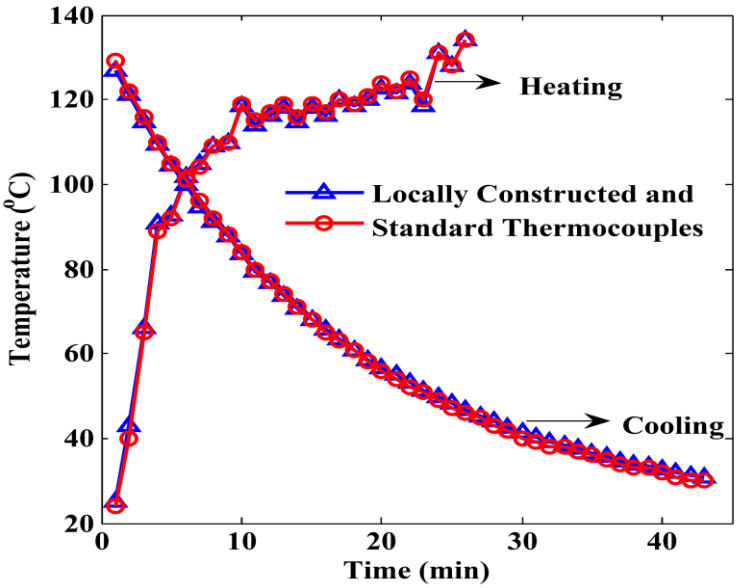



**Figure 1:** Heating and cooling curves for both locally constructed and a standard FLUKE 87 V cable chromel-alumel thermocouples.

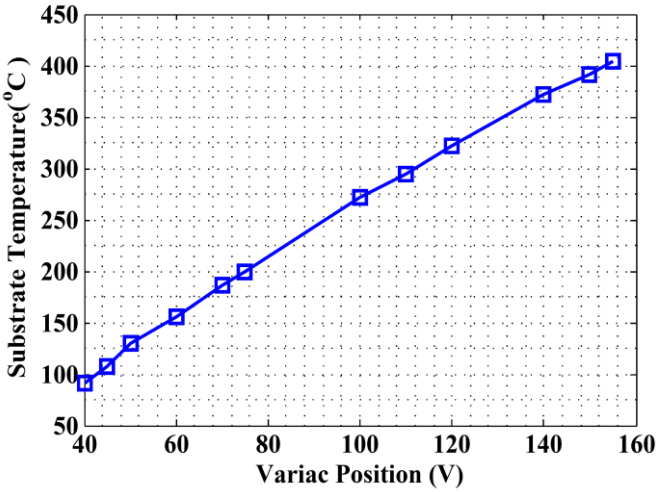



**Figure 2:** Substrate equilibrium temperatures as a function of a.c. variac transformer set points.

Films' thickness was determined using Alfa step IQ based on mechanical stylus. Films' UV/VIS/NIS transmittance was determined using SHIMADZU SolidSpec-3700 DUV spectrophotometer (250-2500 nm) and IR reflectance using PERKIN ELMER spectrum BX FT-IR spectrophotometer in the range (2500-50,000 nm). Surface morphology was determined using Atomic Force Microscope (AFM) and films' band gap energy (Eg) was estimated from Tauc plots developed from MATLAB 7.1. The optical constants (n,k) were worked out from commercial software SCOUT2.

## 3. Results and Discussion

### 3.1 Luminous and Solar Transmittance

Luminous transmittance ($T_{lum}$) and solar transmittance ($T_{sol}$) as functions of films thickness is represented in Figure 3. The $T_{lum}$ (400 - 760 nm) and $T_{sol}$ (300 - 2500) nm were computed based on the following respective formula [7]:

$$T_{lum} = \frac{\int_{0.4\mu m}^{0.76\mu m} Q(\lambda)T(\lambda)d\lambda}{\int_{0.4\mu m}^{0.76\mu m} Q(\lambda)d\lambda} \qquad (1)$$

and

$$T_{sol} = \frac{\int_{0.3\mu m}^{2.5\mu m} G(\lambda)T(\lambda)d\lambda}{\int_{0.3\mu m}^{2.5\mu m} G(\lambda)d\lambda} \qquad (2)$$

where $T(\lambda)$ is transmittance in a given wavelength range, $G(\lambda)$ is Air Mass 1.5 solar irradiance ISO 9845 and $Q(\lambda)$ ) is Air Mass 1.5 illuminant ISO/CIE 10526 [8]. The Integrated $T_{sol}$ and $T_{lum}$ are the calculated area under the curve and normalized using standard data that is ISO 9845 and ISO/CIE 10526 respectively.

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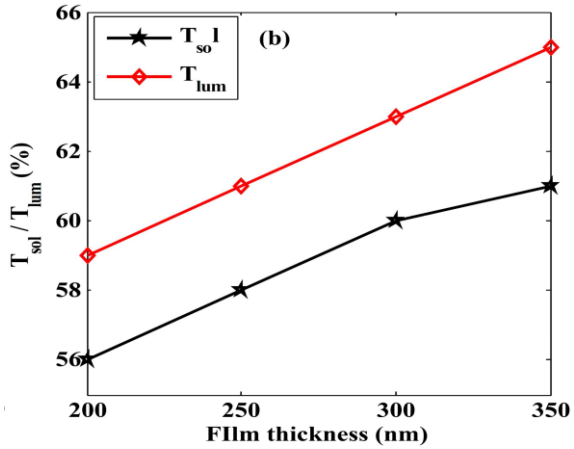
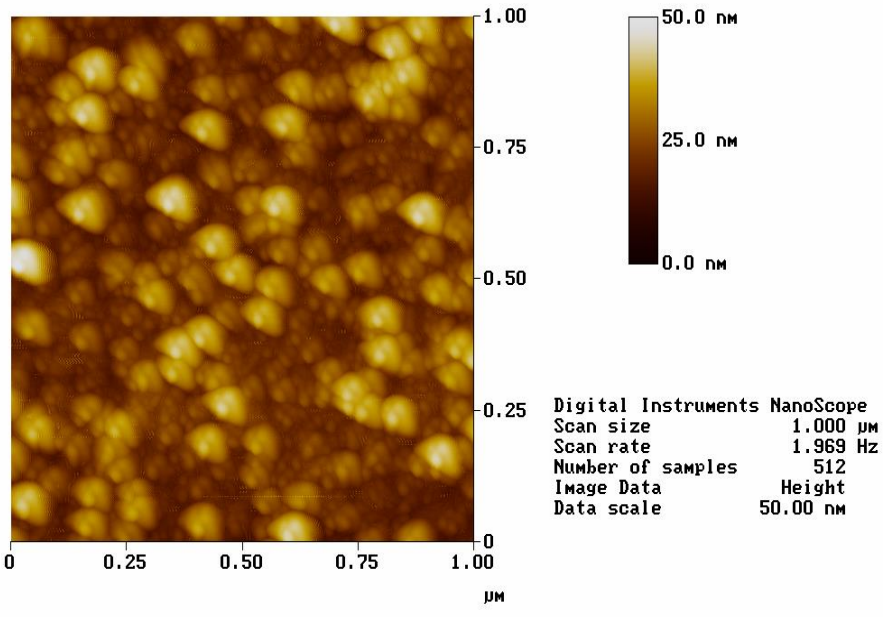


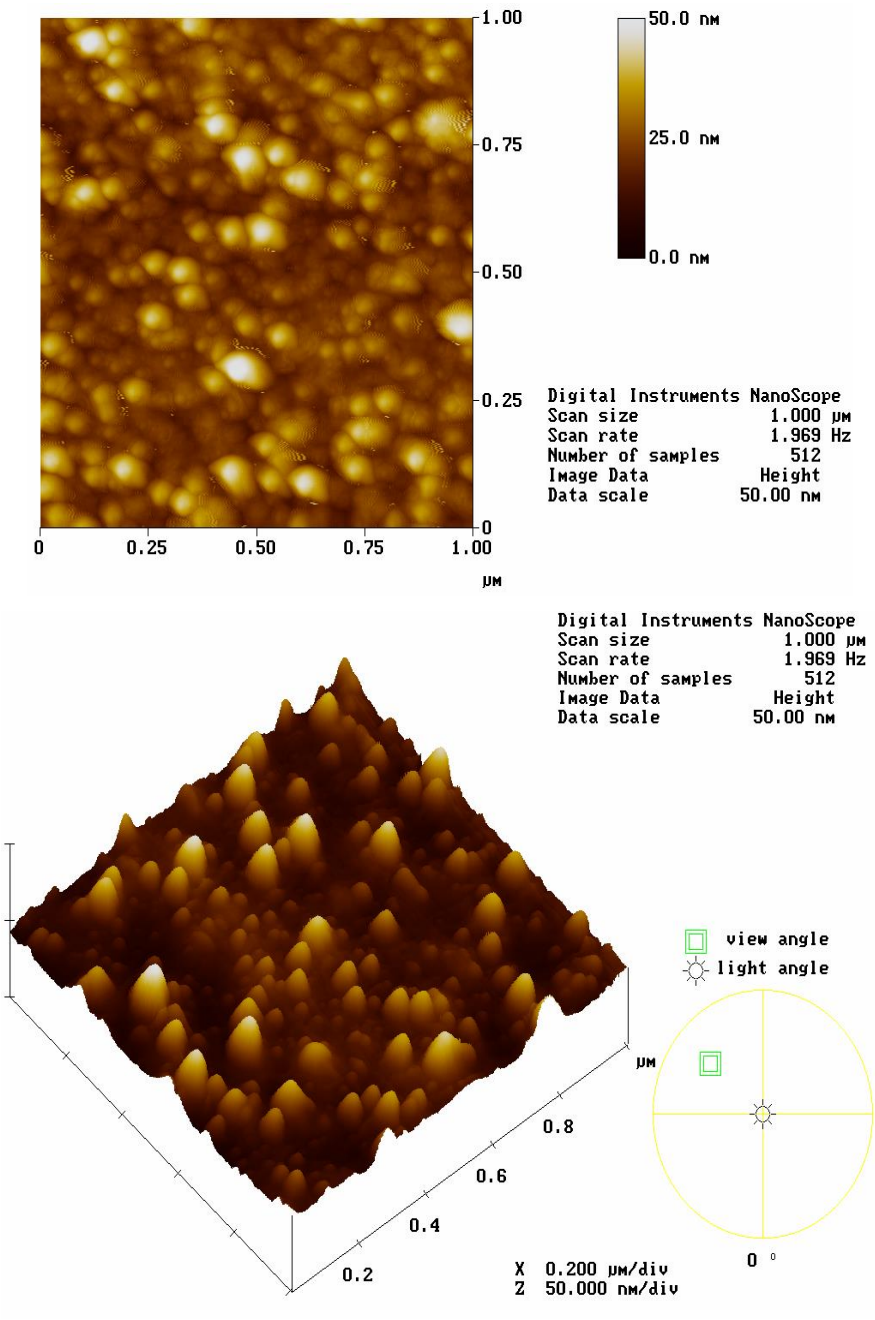

**Figure 3:** $T_{sol}$ and $T_{lum}$ on films thickness for 200, 250, 300 and 350 nm TNO films deposited at 300 oC and 0.04 O2/Ar flow ratio.

Increased films thicknesses in interval of 50 nm from 200 to 350 nm improved $T_{sol}$ and $T_{lum}$ from 56 to 61 % and $T_{lum}$ from 59 to 65 % respectively as shown in Figure 3. The increased $T_{sol}$ and $T_{lum}$ were attributed to improved films formation with increased films thickness as suggested by the AFM surface morphology images in Figure 4. The images reveled that, the films developed from deprived grains shape for films of 200 nm (Figure 4.a) to a fairly developed grains with existing islands for films of 250 nm (Figure 4.b) into a more defined mix of small and large grain shape for films of 300 nm (Figure 4.c). The morphological improvement of the films with increased films thickness likely reduced films absorption as a result improved both $T_{sol}$ and $T_{lum}$.

(a)



(b)


1.00
0.75
0.50
0.25
0
0
0.25
0.50
0.75
1.00
µm
50.0 nm
25.0 nm
0.0 nm
Digital Instruments NanoScope
Scan size 1.000 µm
Scan rate 1.969 Hz
Number of samples 512
Image Data Height
Data scale 50.00 nm
Digital Instruments NanoScope
Scan size 1.000 µm
Scan rate 1.969 Hz
Number of samples 512
Image Data Height
Data scale 50.00 nm
view angle
light angle
µm
0.2
0.4
0.6
0.8
0 °
X 0.200 µm/div
Z 50.000 nm/div

(c)

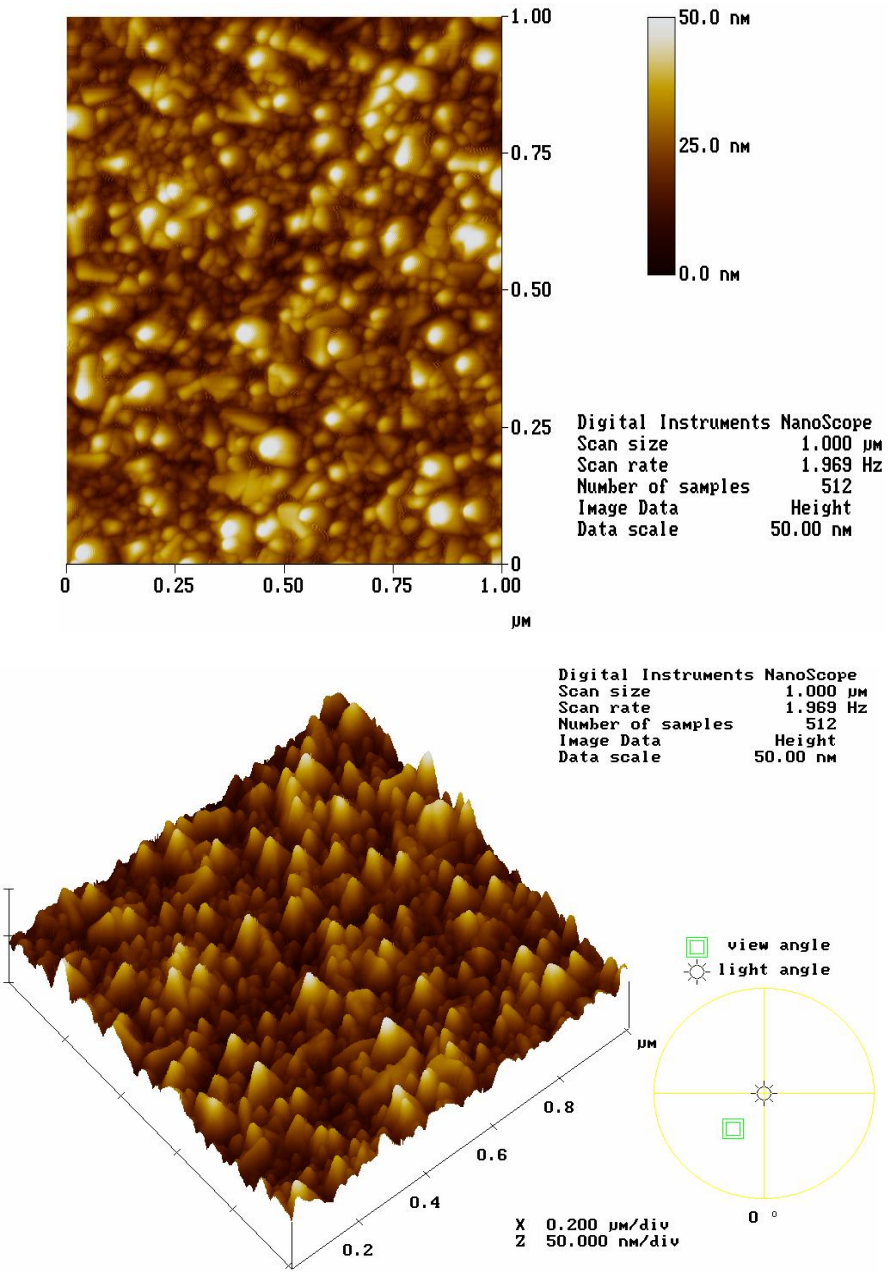



**Figure 4:** AFM images for (a) 250 nm (b) 300 nm and (c) 350 nm TNO films deposited at 300 oC and 0.04 $O_2$/Ar flow ratio.

## 3.2 Optical Band Gap Energy

Figure 5 represents dependence of optical band gap energy ($E_g$) films thickness. The $E_g$ was computed using MATLAB m-file program based on the Tauc plot governed by the equation [9];

$$\alpha h\nu = A(E_g - h\nu)^m \qquad (3)$$

where $\alpha = 2\pi k/\lambda$ is the absorption coefficient, $h\nu$ is the photon energy, $m = 2$ account for indirect allowed transition across the allowed band gap and A depends on transition probability which can be taken as constant within the optical frequency range. Increased films thickness in interval of 50 nm from 200 to 350 nm

increased band gap energy ($E_g$) from 3.35 to 3.40 eV. The increase ($E_g$ ) was associated with improved films' structure with increased films thickness.

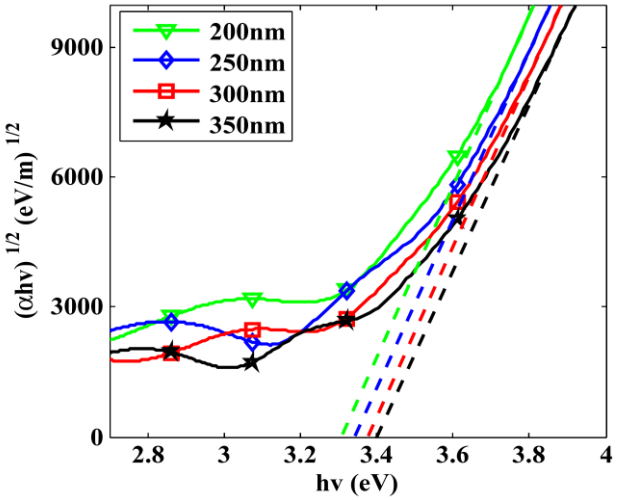



**Figure 5:** Dependence of $(\alpha hv)^{1/2}$ on photon energy $hv$ for 200, 250, 300 and 350 nm TNO thin films deposited at 300 oC and 0.04 $O_2$/Ar flow ratio.

## 3.3 Optical Constants

The optical constants ($n$,$k$) of the films were obtained after a model parameter fit of the simulated transmittance spectrum to the measured transmittance spectrums using commercial software SCOUT2. From the fit the complex dielectric permittivity $\varepsilon(\omega)$ hence, the complex refractive index $n(\omega)+ik(\omega)$ extracted. Based on the software $\varepsilon(\omega)$ was defined as [10]:

$$\varepsilon(\omega)=\varepsilon_0+\chi_B+\chi_D \qquad (4)$$

Where $\chi_B$ is the inter-band dielectric susceptibility defined as;

$$\chi_B=\frac{1}{\sqrt{2\pi\sigma}}\int_{-\infty}^{\infty}\exp-\left(\frac{(x-\Omega_o)^2}{2\sigma^2}\right)\frac{\Omega_f^2}{x^2-\omega^2-i\omega\Omega_\Gamma}dx \qquad (5)$$

where $\Omega_o$ is the resonance frequency, $\Omega_f$ is the oscillator strength parameter and $\Omega_\Gamma$ is the damping and $\sigma$ is the width of distribution

Figure 5 and 6 represent dependence of optical constants $(n,k)$ on the films thickness. Increased films thickness in interval of 50 nm from 200 nm to 350 nm decreased from 2.1 to 1.8 and 0.058 to 0.027 respectively. The decrease was related to improved compactness and uniformity of the films with increasing films thickness

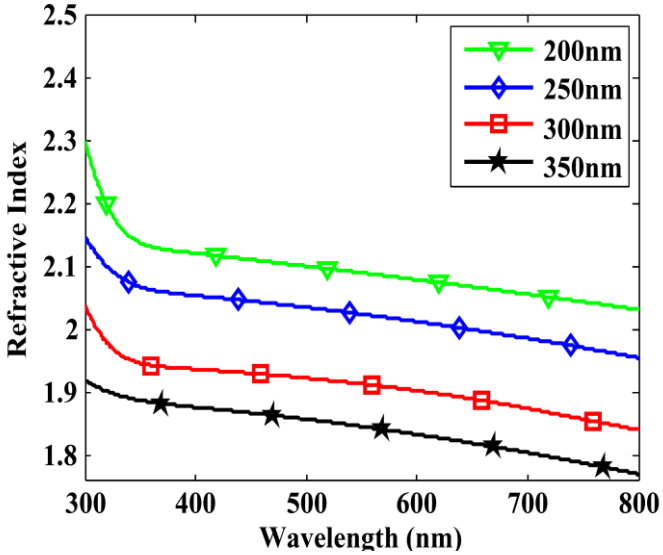



**Figure 6:** Dependence of refractive index $(n)$ on film's thickness for 200, 250, 300 and 350 nm TNO films deposited at 300 $^{o}$C and 0.04 $O_2$/Ar flow ratio.

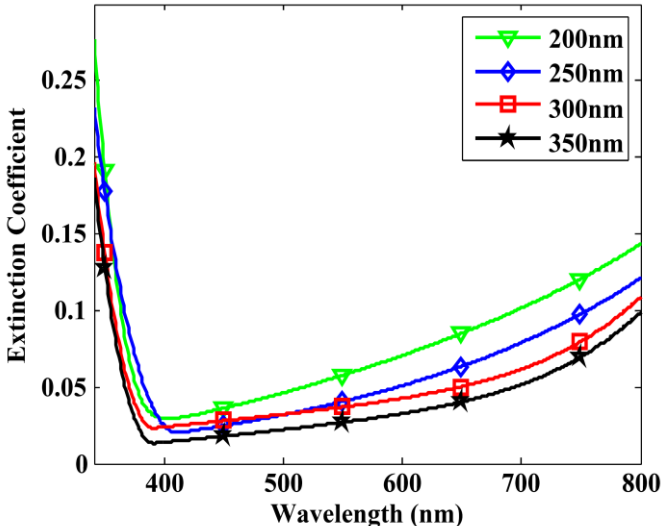



**Figure 7:** Dependence of extinction coefficient $(k)$ on films thickness for 200, 250, 300 and 350 nm TNO films deposited at 300 $^{o}$C and 0.04 $O_2$/Ar ratio

## 3.4 IR reflectance

Figure 8 depict the IR reflectance of the films as a function of films thickness. The IR reflectance of the TNO thin films was characterized by valleys at around 8 $\mu m$ and 12 $\mu m$ and a peak at around 10 $\mu m$. According to Tonooka *et al.*, 2009 and Martin-Palma *et al.*, (1998), the peak belongs to radiations of Si – O stretching from the glass. Increased films' thickness indicated a relative increase of IR reflectance of the films. The observation implied a possibility for achieving low-e material upon improving the IR reflectance by raising the Nb-doping level.

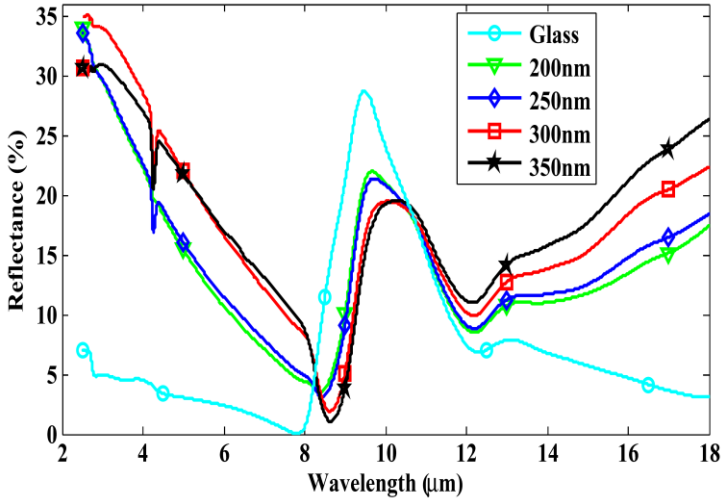



**Figure 8:** Influence of films thickness on IR reflectance for 200, 250, 300 and 350 nm TNO films deposited at 300 $^{o}$C and 0.04 $O_2$/Ar ratio

## 4. Conclusion

Thin films of thickness in interval of 50 nm from 200 nm to 350 nm were prepared from alloy target of $Ti_{0.99}$ $Nb_{0.01}$ by DC reactive magnetron sputtering at at 300 $^{o}$C and 0.04 $O_2$/Ar ratio. The influence of films thickness on the optical and IR reflectance was investigated. Analysis indicated an increase of both $T_{lum}$ and $T_{sol}$ and band gap energy ($E_g$), and a decrease of refractive index ($n$) with an increased films thickness. An average of above 60 % $T_{lum}$ about 70% and E of 87 % were achieved. The results implied a possibility for Low-E with the material upon lowering the emissivity by raising the Nb-doping level

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## REFERENCES

[1] K.L. Chopra, S. Major, D.K. Pandya, “Transparent conductors- a status review,” Thin Solid Films 102 (1983) 1.

[2] I. Hamberg, C. Granqvist, “Evaporated Sn-doped In2O3 films: Basic optical properties and applications to energy-efficient windows,” J. Appl. Phys. 60 (1986) R123.

[3] Y.Sato, H.Akizuki, T. Kamiyama, Y.Shigesato, “Transparent conductive Nb-doped TiO2 films deposited by direct-current magnetron sputtering using a TiO2 − x target,” Thin Solid Films, 516 (2008) 5758–5762.

[4] K. Tonooka, T. Chiu and N. Kikuchi, “Preparation of transparent conductive TiO2: Nb thin films by pulsed laser deposition” Applied Surface Science, 255 (2009), 9695–9698.

[5] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, K. Inaba, G. Kinoda, Y. Hirose, T.Shimada and T. Hasegawa,” A transparent metal: Nb-doped anatase TiO2,” APPL. PHY. LETTERS 86, (2005) 252101.

[6] N. Yamada, T. Hitosugi, N. L.H. Hoang, Y. Furubayashi, Y.Hirose, S. Konuma, T. Shimada, and T. Hasegawa, "Structural, electrical and optical properties of sputter-deposited Nb-doped TiO2 (TNO) polycrystalline films"Thin Solid Films, 516 (2008), 5754–5757

[7] C.M. Maghanga, J.Jensen, G.A.Niklasson , C.G.Granqvist, M.Mwamburi, "Optical modeling of spectrally selective reflectors based on TiO2:Nb transparent conducting oxide films for silicon solar cell applications," Sol.Energy Mater. Sol. Cells (2009), doi:10.1016/j.solmat.2009.02.023

[8] American Society for Testing and Materials (1992), Reference Solar Spectral Irradiance: Air Mass 1.5 (online) available: http://rredc.nrel.gov/solar/spectra/am1.5S

[9] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, The Netherlands, 1995, pp. 265–275.

[10] C.M. Maghanga, J. Jensen, G.A. Niklasson, C.G. Granqvist, and M. Mwamburi, Sol. Energy Mater. Sol. Cells, 94(2009), 1.

[11] C.G. Granqvist, "Transparent conductors as solar energy materials: A panoramic review" Solar Energy Materials & Solar Cells 91 (2007) 1529–1598

[12] http://www.wtheiss.com/docs/sc2_tu1/index.