Effect of Substrate Temperature and Target-Substrate Distance on Growth of TiO_2 Thin Films by Using DC- Reactive Sputtering Technique

Laith Rabih[1,2], **Sudjatmoko**[3], **Kuwat Triyana**[1], **Pekik Nurwantoro**[1]
[1]Department of Physics, Gadjah Mada University, Sekip Utara BLS.21 Yogyakarta 55281, Indonesia
[2]Mosul University, AL-majmoaa St., Mosul, Iraq
[3]Centre for Accelerator and Material Process Technology, BATAN, Jl. Babarsari Kotak Pos 6101 YKBB Yogyakarta 55281, Indonesia

[*)] e-mail: triyana@ugm.ac.id

Abstract - *Titanium oxide (TiO_2) thin films have been deposited by a DC sputtering technique onto microscope glass slides. The effect of substrate temperature (Ts) and target-substrate distance (Dts) on some optical and electrical properties have been studied each individually. The structure of TiO_2 thin films has been improved and became more crystalline when Ts has been increased (from 150 ºC to 250 ºC). The conductivity (σ), deposition rate (D_R) and average values of grain size (G.S) have been increased with increasing Ts while the values of band gap (Eg) and weight percentage of the anatase phase (W_A) have been decreased. The thickness of TiO_2 film has been increased from 920 nm to 960 nm with increase Ts while it has been decreased from 960 nm to 680 nm with increase Dts (from 25mm to 35mm). As Dts has been increased, the conductivity σ, thickness (d) and average values of grain size have been decreased. The decreasing of conductivity at Dts=35 maybe attributes to increase the weight percentage of the rutile phase (W_R). The XRD results show that the TiO_2 structure phase has been varied. The results show that the optical and electrical properties of TiO_2 film affected by changes the condition parameters especially Ts and Dts as well as the density and energy of the impinging atoms. The surface morphology and component of TiO_2 thin films, resistance, optical transmittance and structure of film were characterized by SEM (EDX), I-V meter, UV-VIS spectrophotometer and XRD respectively.*

Keywords: *substrate temperature, TiO2 thin films, DC-reactive sputtering, conductivity, transparency, target-substrate distance*

I. INTRODUCTION

Titanium dioxide TiO_2 is one of the metal oxide semiconductors. TiO2 has been considerably investigated and utilized in a wide range of applications because of their useful electrical and optical properties, such as high dielectric constant [1], high electrical resistivity, high refractive index, excellent optical transmittance in the visible range [2], non-toxicity, low cost and large band gap [3]. There are many deposition methods used to prepare TiO2 thin films, reactive sputtering is one of those methods and it is very useful technique because of the possibility to produce thin film with high optical quality, dense and good homogeneity [1]. TiO_2 has three main crystalline structures: anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). Rutile is usually stable at high temperatures. Different structures lead to different physical properties which, in turn, lead to different applications. [4]

Conductivity and transparency of TiO_2 thin films are important in many applications especially for solar cells. TiO2 thin films are using as transparent electrodes in solar cells [3]. The conductivity, transparency and structure can be influenced by many parameters of sputtering conditions such as energy, angle of incidence, etc. of the impinging atoms [4], temperature of substrate Ts [6-8], target–substrate distance Dts and the geometrical configuration of the system.

The energy loss of sputtered flux (ions, atoms, etc.) affected by many parameters such as their collisions and scattering as well as geometric angle between substrate and target. The impinging atoms moving have been affected by Knudsen's cosine law. [9] That, in turn, means that the deposition by plasma sputtering is also characterized by the Knudsen's cosine law. [10]

The last maybe effect on sputtering flux by making many atoms of sputtered flux will escape out of perpendicular direction of axis of targets. This phenomenon has been making the density decreasing in the vicinity of substrate surface [4].

Sputter deposition is a complex process and it is known that the properties of thin-film materials deeply depend on sputtering conditions therefore; we have tried to find optimal sputtering conditions by preparing many samples under same conditions. Ts and Dts have been varied to study the structure and conductivity as well as optical properties of TiO_2 thin films by using low cost DC-reactive sputtering technique.

II. EXPERIMENTAL

The microscope glass slides type (7101) have been used as substrates of TiO_2 thin films which deposited by using a homemade reactive DC sputtering system. (Ti) metal disc of 99.99 purity and 50 mm diameter has been used as a target. Ar and O_2 gases have been used as sputtering and reactive gases respectively. Rotary pump (Type: H8L2B / Edward) and diffusion pump (Type: Du 05 M / Pfeiffer/Vacuum) have been used. Prior to the film deposition, substrates were sequentially cleaned for 15 min in an ultrasonic bath with

water and acetone and dried in air. The sputtering conditions: sputtering voltage, sputtering current, ratio of (Ar/O_2) and deposition time (Dt) have been set at 4 KV, 15 mA, (90/10) and 3:30 hours, respectively. Our work has been divided into two parts. In the first part, Ts has been varied between (150 – 250) ºC while Dts was set at 25mm. in the second part, Ts has been fixed at Ts=250 ºC while Dts varied between (25-35) mm. I-V Meter [11] has been used at room temperature to measure the resistant (R) of TiO_2 thin films. Transparency of the films was measured by using UV-vis spectrophotometer (Type: Perkin Elmer /Lambada 25 series). Thickness and components of TiO_2 have been estimated by using SEM (EDX) (Type: ISPEX S50-FEI). The crystallinity of TiO_2 thin films has been examined by using XRD (Type: Shimada).

III. RESULTS AND DISCUSSION

A. Effect of substrate temperature on structure and optical properties of TiO_2

Fig (1) shows the structure of TiO_2 thin films with the temperature of substrate Ts. The structure phase has been varied with changing of Ts. The structure has been improved and became more crystalline. We can show the peaks as a flowing:

At Ts= 150 ºC, there is a random growth structure because of some deposited atoms (or molecules) that do deposited on the substrate haven't obtain sufficient kinetic energy to diffuse on the substrate and coalesce with other nuclei therefor, they create "clusters" on the substrate. The clusters maybe caused a heterogeneous surface especially on upper layer of TiO_2 film. The clusters have been caused the resistant R increasing as a result of decrease the mobility (μ). The crystal structure contained anatase A(101) structure phase and beginning growth of the rutile R(110) structure phase. The relation between the conductivity, carrier concentration and mobility is shown in Eq. (1).

$$\sigma = en\mu \qquad (1)$$

where σ, μ and n are conductivity, mobility and carrier concentration, respectively.

At Ts= 200 ºC, the crystal structure became more crystalline and it contained structure phase of the following sequence: A(101), R(110) and A(004) peaks. There are no clusters on this sample because the deposited atoms have obtained sufficient kinetic energy to diffusion on the substrate and coalesce with other nuclei. As a result of increase Ts, the carrier concentration has been increased. [12] That means that the resistant became less than (Ts=150ºC) sample. The relation between the carrier concentration and temperature is shown in Eq. (2).[13]

$$n_c = n\, e^{-\frac{E_g}{2k_B T}} \qquad (2)$$

Where n_c, k_B, Eg and T are number of charger carriers in conduction band, Boltzmann constant, band gap and temperature, respectively.

At Ts= 250 ºC, the crystal structure has been improved and it contained structure phase of the following sequence: A(101), R(110), A(004), A(200) and A(211) peaks. The increased Ts played an important role in aggregation the small grain sizes of nuclei during deposition processes and merged them to create the large sizes of grain and finally obtain homogenous thin film. In this case the resistant became lower than before due to increase the carrier concentration.

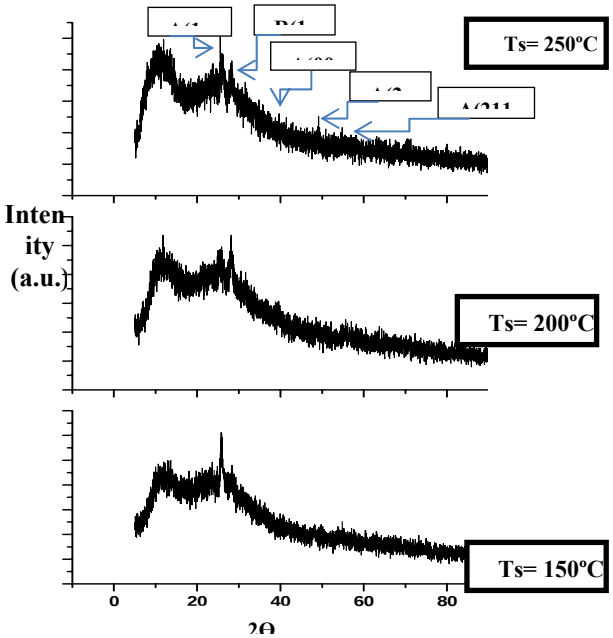

Fig. 1. XRD patterns of TiO_2 films deposited at different substrate temperature.

The weight percentage of the anatase phase (W_A) was determined by using the Eq. (3) [3].

$$W_A = \frac{1}{1 + 1.265\, I_R / I_A} \qquad (3)$$

where I_A and I_R are the intensities of anatase peak and of rutile peak, respectively.

The grain size value (G.S) of thin films has been calculated by using the Debye –Scherrer formula (Eq. (4)) [14].

$$G.S = \frac{0.9\,\lambda}{\beta \sin\theta} \qquad (4)$$

where λ is the wavelength of the X-ray (λ=1.5406 nm) , β is the broadening of the diffraction line measured at half of its maximum intensity in radians FWHM, and θ is the diffraction angle.

Table 1. Summary of characteristics of TiO_2 thin films: d is thickness, D_R is deposition rate, R is resistant of thin films, σ is

Ts (ºC)	d (nm)	D_R (nm/h)	R(Ω)	σ=1/ρ $(\Omega.cm)^{-1}$	G.S (A) (nm)	G.S (R) (nm)	W(A) %	Eg (eV)
150	920	262	5.08E+09	1.08E-06	94.26	90.3	59	3.46
200	957	273	3.6 E+09	1.45E-06	97.08	99.3	58	3.40
250	960	275	2.68E+09	2.33E-06	106	102	52	3.36

conductivity, G.S(A) is anatase grain size, G.S(R) is rutile grain size, W_A weight percentage of the anatase phase and Eg is band gap.

Table (1) shows that the thickness (d) of TiO_2 films has been increased with increase Ts because of the deposition rate D_R was increasing too. Sticking coefficient played a significant role in affecting on increasing the D_R [15]. The σ of TiO_2 thin film has been increase with increasing Ts due to improve the crystal structure and the grain size became bigger. Fig (2) shows the effect of Ts on σ and d.

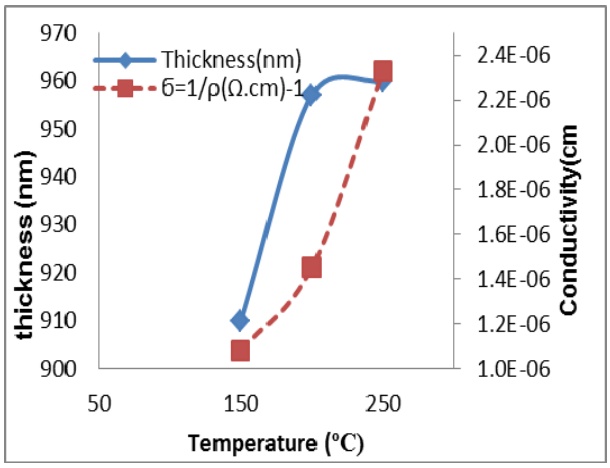

Fig 2. change the conductivity and thickness of TiO_2 films deposited at different substrate temperature

Fig. (3) presents SEM images of TiO_2 thin films surface. The morphology of films varied with Ts. The average value of grain size was increased with the increasing Ts because of improved crystal. At Ts= 150 ºC, the morphology of film was different with other samples because of it has the clusters. Every cluster has contained about (3-6) molecules. The grain became bigger with increase Ts = 200 ºC Ts = 250 ºC.

Table (2) shows results of Energy-dispersive X-ray spectroscopy (EDX) for TiO_2 thin films. We observed there are low weight percentages of impurity elements.

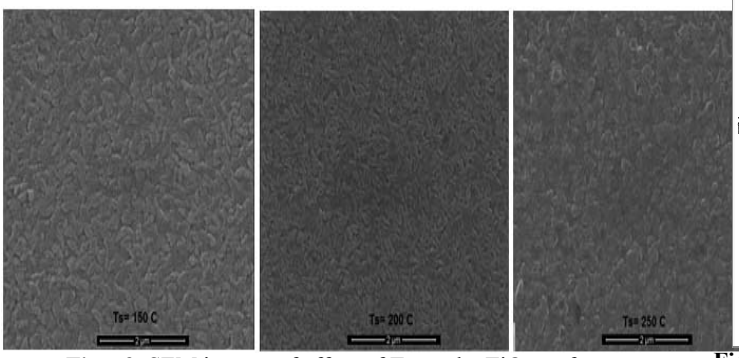

Fig 3. SEM images of effect of Ts on the TiO_2 surface morphology.

Table 2. Summary of element content for all TiO_2 films measured by using EDAX

Element	Ts= 150 ºC		Ts= 200 ºC		Ts= 250 ºC	
	Wt%	At%	Wt%	At%	Wt%	At%
CK	02.88	06.67	05.04	11.79	05.25	11.77
OK	32.88	57.26	29.98	52.63	30.09	50.69
NaK	-	-	-	-	03.19	03.74
SiK	01.99	01.97	01.92	01.92	02.40	02.30
AuM	05.00	00.71	05.50	00.78	04.34	00.59
CaK	00.84	00.58	00.73	00.51	00.94	00.63
TiK	56.41	32.81	53.89	31.60	54.13	30.61

The absorption coefficient (α) has been calculated by using Eq. (5) [16].

$$\alpha = \frac{-\ln(T)}{d} \quad (5)$$

where d and T are the thickness and the transparency of the films, respectively. The optical band gap E_g can be derived from Eq. (6) [17].

$$\alpha h\nu = A(h\nu - E_g)^r \quad (6)$$

where $h\upsilon$ is the photon energy, and r is numeric that has four numeric values (1/2, 2, 3, 3/2) depend on direct or indirect and allowed or forbidden transitions).

The transmittance spectra of TiO_2 films deposited at different Ts have been presented in Fig. (4). TiO_2 films were transparent in the visible region and its transparency exhibits a sharp decrease in the UV region. The average transmittance exceeds 85% in visible and infrared ranges for all samples except Ts=150 ° C sample because of there are the clusters on film. The clusters have been caused an increase in the scattering of incident light (less transmittance). The absorption edge shifted to longer wavelength with increase the Ts.

The plot of $(\alpha h\nu)^2$ versus photon energy E(eV) at different Ts is shown in Figure 4. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ on the y-axis versus photon energy E(eV) on the x-axis gives the value of the optical band gap Eg. The variation of band gap with substrate temperature is given in Table 1. Typically band gap decreases from 3.46 to 3.36 eV due to improve the crystalline structure.

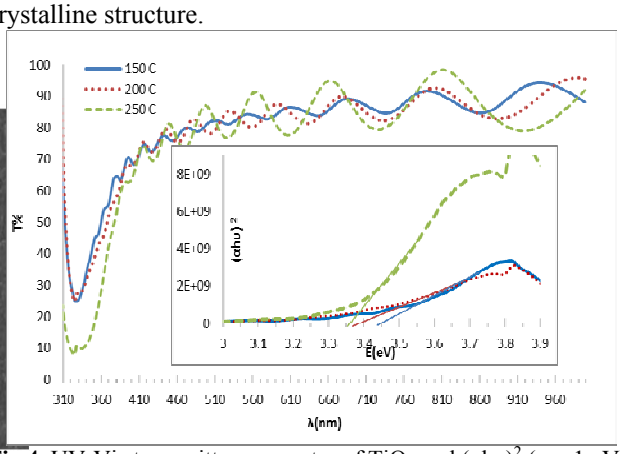

Fig 4. UV-Vis transmittance spectra of TiO_2 and $(\alpha h\upsilon)^2$ (cm-1.eV)^2 versus Photon Energy E(eV) to found band gap energy

B. Effect of the distance between target and substrate on structure and optical properties of TiO_2.

Fig (5) shows XRD patterns obtained from TiO_2 films grown with different distance between target and substrate Dts. At Dts=25mm the structure crystalline contained A(101), R(110), A(004), A(200) and A(211) peaks. At Dts=30mm the structure has become amorphous (non-crystalline) and couldn't recognized distinctive peak. On the other hand, the structure of film at Dts=35mm has been contained A(101), R(110), R(101), A(004) and R(200). The difference between the crystallization of (D=25mm) and (D=35mm) samples and the amorphous (non-crystalline) of (D=30mm) sample may be attributing to the energy of deposited atoms (or molecules) on the substrate or geometric angle between target and substrate. The moving of impinging atoms is followed Knudsen cosine law. [10]

At Dts=25mm, the density of plasma flux has been higher than other distances which caused increased collisions between plasma components; therefor the average energy of impinging atoms has been reduced. The impinging atoms have been deposited on the substrate.

At Dts=30mm, the free path of the sputtered atoms is comparable to the physical dimensions of the geometric angle between substrate and target therefore; it is possible that the majority of the sputtered flux escape from the vicinity of the substrate surface. The density of sputtered atoms numbers have been decreasing in vicinity of the substrate surface which led to decrease the collisions between impinging atoms. The reducing of collisions means that the impinging atoms had enough energy to bombarded the substrate strongly comparing with D=25mm and D=35mm distances. With the continuation of substrate bombarded, the thin film became damaged (non-crystalline).

At Dts=35mm, the collisions have been decreased because of the density of plasma flux was low. It is possibility that there are multiple collisions of the impinging atoms between substrate and plasma flux in the vicinity of the substrate or/and another possibility the film was located within range of rebound impinging atoms which rebounding from the walls of the chamber and deposited on the substrate with a suitable energy. The energy of impinging atoms has been reduced and deposited on the substrate under condition: ($E_{25} < E_{35} < E_{30}$) where E_{25}, E_{30}, E_{35} are energy of impinging atoms at distances 25, 30, 35 mm, respectively. Therefore; there is no damage on the film comparison with the previous case. A new rutile phase R(200) has been appeared. The thickness, conductivity, grain size, weight percentage of the anatase phase and deposition time D_R of TiO_2 thin films have been calculated (see table.3).

Table 3. Summary of characteristics of TiO_2 thin films: Dts is the target-substrate distance, d is thickness, D_R is deposition rate, σ is conductivity, G.S(A) is anatase grain size, G.S(R) is rutile grain size, W_A weight percentage of the anatase phase and Eg is band gap.

Dts (mm)	d (nm)	D_R (nm/h)	σ=1/ρ $(\Omega.cm)^{-1}$	G.S(A) (nm)	G.S(R) (nm)	W(A) %	Eg (eV)
25	960	275	2.33E-06	106.89	102.96	52	3.36
30	800	228	2.32E-06	-	-	-	3.375
35	680	194	2.29E-06	99.70	98.75	23	3.365

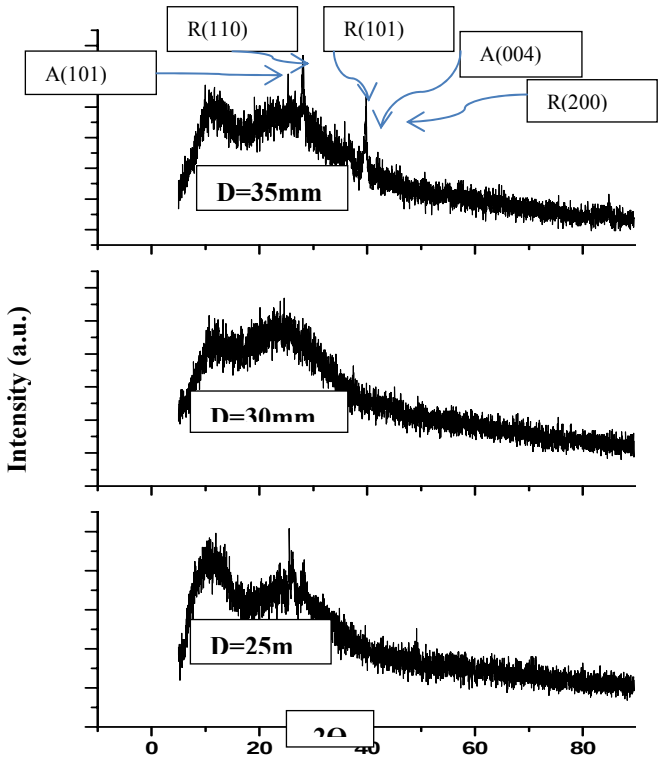

Fig 5. XRD patterns of TiO_2 films deposited at different Dts.

The thickness of films has been decreased because of the deposition rate D_R has been reduced where most of the impinging atoms moved away from the vertical axis on the substrate surface. The average values of grain size of (Dts=35mm) sample has been decreased. It is maybe attributed to transform the TiO_2 structure to rutile phase where it denser and smaller than anatase. [15] The conductivity has been reduced at (Dts=35mm) sample because of the mobility of charge carrier has been decreased due to decreased the grain size. The weight percentage of anatase phase (W_A) has been reduced rapidly because of transform the TiO_2 structure to rutile phase.

Fig (6) shows the effect of Dts on the TiO_2 surface morphology for Dts=30mm and Dts=35mm.

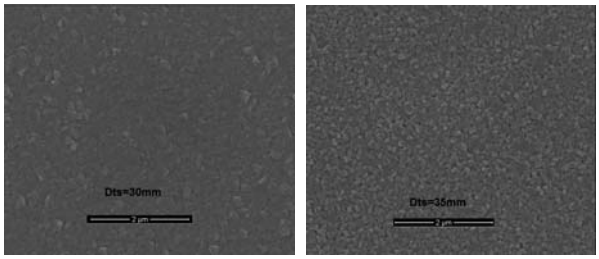

Fig 6. SEM images of effect of Dts on the TiO_2 surface morphology.

Fig (7) shows the transmittance spectra of TiO_2 films deposited at different Dts. the average transmittance at the D=25mm and D=35mm were exceeds 85% in visible and infrared ranges. The transmittance at the D=30mm were decreased because of this sample was a non-crystalline phase. The increasing in light scattering caused the reducing of transmittance at the D=30mm. The band gap Eg has been varied slightly with increasing the Dts. As Eg has been increased, the number of charger carriers in conduction band have been decreased which means that the conductivity decreased according to Eq. (2). [13] The band gap of (Dts=30mm) sample was higher than other samples because of the film was non-crystalline. At Dts=35mm, the band gap has been reduced and closed to band gap of (Dts=25mm) sample due to transform the structure to rutile phase where rutile phase has a band gap less than anatase phase.[18,19]

IV. CONCLUSION

Substrate temperature Ts is one of the most important factors affecting on the films structure during the deposition process. We have successfully deposited TiO_2 thin films by using low-cost homemade DC-reactive sputtering machine. We observed improving in the films structure with increasing Ts. As Ts increasing, there are new peaks appear that is indicates to improve crystalline film. At Ts=150 ° C, we observed existence clusters because of some deposited atoms (or molecules) haven't obtain sufficient kinetic energy to diffuse on the substrate and coalesce with other nuclei. The clusters caused increasing the TiO_2 thin film resistant. These clusters have been disappeared at Ts=200 and 250 ° C and the film structure has been become more crystalline. The conductivity has been increase with Ts increasing because of increase the charge carrier's numbers. The thickness of TiO_2 films has been increased with increase Ts because of the deposition rate D_R was increasing. As a result of Ts increasing, the average values of grain size has been increasing and the band gap values have been decreasing (varied from 3.46 - 3.36 eV). The band gap values have been affected by increasing the carrier concentration and the improving of the film structure.

The (D=25mm) and (D=35mm) samples have been more crystalline films while the (D=30mm) sample has been non-crystalline film. The density of (D=25mm) sample has been higher than other samples, so the sputtering flux has a lot of collisions which caused reduced the average energy of impinging atoms.

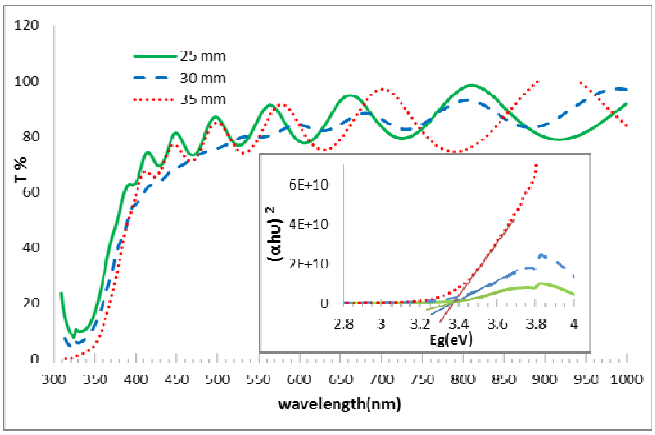

Fig 7. UV-Vis transmittance spectra and band gap of TiO_2 with the different Dts.

The free path of the sputtered atoms of (Dts=30mm) sample has been comparable to the physical dimensions of the geometric angle between substrate and target therefore; it is possible that the many atoms of the sputtered flux escape from the vicinity of the substrate surface which caused reduced the collisions of sputtering flux. That means, the impinging atoms had enough energy to bombard the substrate and damaging the film.

The collisions at Dts=35mm have been decreased because of the density of sputtering atoms has been lowed nevertheless the energy of impinging atoms has been reduced maybe because of their multiple collisions between substrate and plasma flux in the vicinity of the substrate or/and there are many atoms hit the wall of chamber and bounce from the walls toward the substrate and deposited on it.

The transmittance spectra at the D=25mm and D=35m samples have been exceeds 85% in visible and infrared ranges. The transmittance at the D=30mm has been decreased because of this sample was a non-crystalline phase. The increasing in light scattering caused the reducing of transmittance at the D=30mm. the band gap Eg has been varied slightly with increasing the Dts. The conductivity has been decreased with increased the distance.

V. REFERENCE

[1] Sang-Hun Jeong,_ Bong-Soo Kim, Byung-Teak Lee, Hyuk Ryul Park and Jae-Keun Kim: "Structural and Optical Properties of TiO2 Films Prepared Using Reactive RF Magnetron Sputtering".Journal of the Korean Physical Society, Vol. 41, No. 1, July 2002, pp. 67_72

[2] A.A. Akl, H. Kamal and K. Abdel-Hady. "Fabrication and characterization of sputtered titanium dioxide films". Applied Surface Science 252 (2006) 8651–8656

[3] Laith Rabih, Sudjatmoko, Kuwat Triyana, Pekik Nurwantoro."Structural evolution and optical properties of TiO_2 thin films prepared by DC-reactive sputtering technique. "accepted as a regular paper in MSCE 2013 and to publish by Advanced Materials Research (http://www.ttp.net/1022-6680.html)

[4] W. Li , C. Ni, H. Lin , C. P. Huang, S. Ismat Shah: "Size dependence of thermal stability of TiO_2 nanoparticles" Journal of Applied Physics, Vol 96, No 11, 2004, pp.6663-6668
[5] A. Settaouti, L. Settaouti. "Simulation of the transport of sputtered atoms and effects of processing conditions". Applied Surface Science 254 (2008) 5750–5756
[6] A. Yildiz, S. B. Lisesivdin, M. Kasap and Diana Mardare. "The substrate temperature dependent electrical properties of titanium dioxide thin films".J Mater Sci: Mater Electron (2010) 21:692–697
[7] A. Yildiz, S.B. Lisesivdin, M. Kasap, D. Mardare. "Electrical properties of TiO2 thin films". Journal of Non-Crystalline Solids 354 (2008) 4944–4947
[8] Diana Mardare , G.I. Rusu." Electrical conduction mechanism in polycrystalline titanium oxide thin films". Journal of Non-Crystalline Solids 356 (2010) 1395–1399
[9] R. Feres and G. Yablonsky: "Knudsen's Cosine Law and Random Billiards". Dept. of Mathematics, Washington University, St. Louis, MO 63130, USA. Dept. of Chemical Engineering, Washington University, St. Louis, MO 63130, USA.
[http://www.math.wustl.edu/~feres/knudsen_paper.pdf]
[10] Zheng Cui, "Nanofabrication: Principles, Capabilities and Limits", Edition:1, springer (2008).
[11] Khairurrijal, M. Abdullah, A. Suhendi, M. M. Munir and A. Surachman: "A simple microcontroller-based current electrometer made from LOG112 and C8051F006 for measuring current in metal–oxide–semiconductor devices "Sci. Technol. Vol. 18 (2007), p. 3019–3024.
[12] S. S. Alrawee, Sh.J. Shakir and Y.M. Hasan:"Solid State Physics", Mosul university press, (1999).
[13] Y. N. Aljammal: "Solid State Physics", 2nd edition, Mosul university press,(2000).
[14] Takao Ishida, Masahisa Okada, Tetsuo Tsuchiya, Takashi Murakami and Miki Nakano. "Structural and surface property study of sputter deposited transparent conductive Nb-doped titanium oxide films. Thin Solid Films. Vol 519, Issue 6, 3 January (2011). 1934–1942
[15] Ludmila Eckertova. "physics of thin films"-Second revised edition- Plenum press-new york and London 1990
[16] D. Mardare, G.I. Rusu. "The influence of heat treatment on the optical properties of titanium oxide thin films". Materials Letters 56 (2002) 210–214
[17] M. Manssor."Studying the Structural and Optical Properties of ZnO:Cu Prepared by APCVD". Technique Jordanian Journal of Physics (JJP) Vol. 5 Issue. 2 (2012), p.89-103.
[18] Wan-Jian Yin, Shiyou Chen, Ji-Hui Yang, Xin-Gao Gong, Yanfa Yan and Su-Huai Wei: "Effective band gap narrowing of anatase TiO_2 by strain along a soft crystal direction". APPLIED PHYSICS LETTERS 96, (2010). 221901-221903.
[19] Rong Tu and Takashi Goto: "High Temperature Stability of Anatase Films Prepared by MOCVD". Materials Transactions, Vol. 49, No. 9 (2008) pp. 2040 to 2046