Structure Characteristics of TiO_2 Thin Films Prepared by DC Reactive Magnetron Sputtering at Low Pressure

A.S. Ahmed[1*], I.H. Kadhim[2], A.A. Ramadhan[3]

Abstract

Structural properties of TiO_2 thin films play a main role in determine the characteristic of the thin films especially their stability and activity, the total pressure has a great influence in determine the crystallinity of the films and the orientation of the facets of their structure, especially the two facet (101) and (001), the enhancing the structure properties will cause to enhance the application efficiency of TiO_2 thin films such as the dissociative adsorption of water and the solar cell.

Many researcher interest to prepare the TiO_2 thin film under the low range of total pressure (less than to 10 Pa) to avoid the low degree of crystalline and the mixed of two phase anatas and rutile, so in our work tend to prepare TiO_2 thin films under a high total pressure (more than 10 Pa) with values (10, 20, 50 and 100) Pa and with (1:1) mixed ratio of Argon and Oxygen gases, the pattern of X-Ray diffraction revealed that the structure was polycrystalline and the phase was anatas. The intensity at $2\theta \approx 25.00°, 37.00°, 53.00°$ and $55.00°$ correspond to the diffraction from (101), (004), (105) and (211) planes respectively. The intensity and number of peaks decreased with increased the total pressure, the plane (101) could be considered as a prefential growth plane which take a high texture factor and this would decreased with increased the total pressure, the ratio of texture factor between 001 and 101 will increase with decrease the total pressure, The lattice constant and the interplanar distance displayed a greater deviation compared with the standard value at the lowest total pressure than the decrease observed with increased total pressure.

Key Words: Titanium Dioxide (TiO_2) Thin Films, DC Magneto-sputtering, XRD, Total Pressure, Compressive Stress, Deviation of Lattice Constant.

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Introduction

The preparation method of thin films play a main role in determining the properties of the films, the conditions for each method can be considered as an essential parameter to control the characteristic of the films (Abegunde, *et al.* 2019), one of the important methods that can be used to prepare thin films is the sputtering method, the direct current (DC) reactive magnetron sputtering have been extensively applied to produce uniform and dense thin films (Vahl, *et al.* 2019) with well-controlled stoichiometry, smooth surfaces, excellent adhesion, high hardness, and good thickness uniformity in large-area (Thaidun, *et al.* 2013).

The direct current (DC) reactive magnetron sputtering method include many conditions that can be affect on the final properties of the films such as

Corresponding author: A.S. Ahmed
Address: [1*]Physics Department, College of Science, Baghdad University, Baghdad, Iraq; [2]Ministry of Education, Baghdad, Iraq; [3]Physics Department, College of Science, Baghdad University, Baghdad, Iraq.
[1*]E-mail: asaaabi@gmail.com
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the mixed ratio of Argon and Oxygen gases, distance between the target and the substrate, bias voltage (Li, *et al.* 2016), one of these conditions which has a great influence in determine the nature of the films is the total pressure, the preparation of the TiO_2 thin films in the range less than 10 Pa take a great interest of the researcher (Dreesen, *et al.* 2009, Meng, *et al.* 1993, Jokanović, *et al.* 2016), the reason of this inters may be attributed to the fact that the probability of prepare mono morph TiO_2 with the anatas phase take a high probability, this may be beyond that the density of the plasma will decrease with decrease the total pressure (Khalaf, *et al.* 2013), which cayse to reduce the number of collision during the pathway between the target and the substrate and this will enhancement the degree of crystallinity (Asanuma, *et al.* 2004).

The TiO_2 thin films can be consider as a polymorph films (anatas, rutile and brookite), the transition boundary between these phases will depend on boundary of the temperature and the pressure that used to prepare the films, so it is very important to investigate the characteristic of the TiO_2 at low temperature (without heat substrate) and high range of pressure (> 10 Pa) to specific the effect of the high range of pressure and low temperature to determine the crystalline structure properties of TiO_2 thin films such as the crystallinity and the deviation of lattice constant from the standard value which may be then cause to high degree of strain in the films which affect on the electrical and optical properties of the films (Mergel, *et al.* 2000, L. Meng, *et al.* 2014). The present paper attempt to investigate the influence of the total pressure on the crystallographic structure properties of TiO_2 films prepared by DC reactive magnetron sputtering in the range of total pressure more than 10 Pa.

Experimental Work

The vacuum chamber of the custom-made reactive magneto-sputtering system was cleaned using the glow discharge for five minutes with 10 mA discharge current to remove contamination in the electrodes and chamber. The chamber was evacuated to a base pressure of about 0.5 Pa, and then the chamber was filled with Argon and Oxygen gases (99.99% purity) with mixed ratio (1:1) to about desired pressure. The target was a solid Titanium (99.99%). A glow discharge was generated to prepare the TiO_2 thin films by applying the current about 50mA for 90 minutes between the two electrodes.

Results and Discussions

Polymorph Phase and the Total Pressure

The structure of TiO_2 films recognized by study the pattern of X-Ray diffraction (XRD) as shown in the figure 1. Peaks at $2\theta \approx 25.00°$, $37.00°$, $53.00°$ and $55.00°$ corresponding to the diffraction from (101), (004), (105) and (211) planes respectively, which belong to the tetragonal structure and the phase was anatase according to American Society for Testing and Materials (ASTM) card no. 96-900-9087 as shown in table 1.

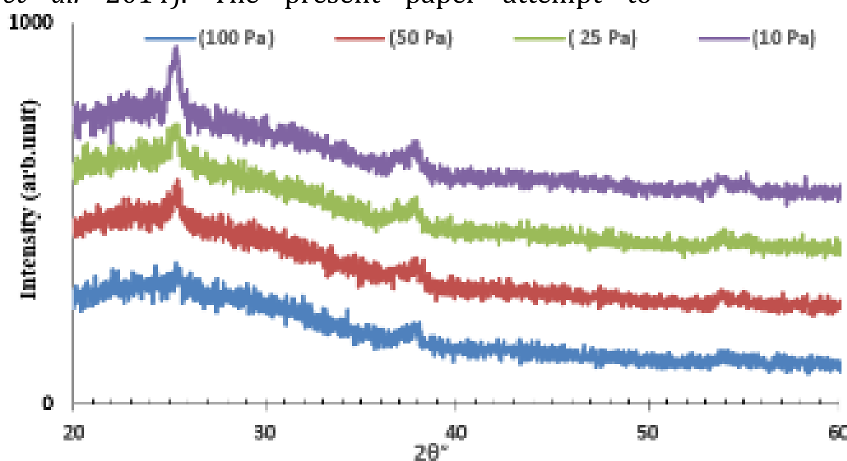

Figure 1. XRD pattern of TiO_2 thin films with different total pressure

The three most widely known polymorphs of TiO_2 are rutile, anatase, and brookite [12], the result obtain that the phase of crystalline structure was anatase, the appearance of this phase and disappear the two other phases may be refer that this phase has a properties that give it more probability to dominate in the morphology phase such a highest cohesive energy (24.46 $\frac{eV}{TiO_2}$) and lower surface energy (0.44 $\frac{J}{m^2}$) (Navrotsky 2003,. Lazzeri, *et al.* 2001), and the method of preparation offer an optimum condition for these properties to take

place to play a role in dominate the anatas phase in the identity of morphology.

The pressure – temperature (P-T) diagram illustrate that the anatas is regular phase, it is [low pressure – low temperature] phase and the anatas / rutile phase boundary is given by the relation [P =0.009T+5.44] while [P: Pressure in GPa and T: Temperature in Celsius] (Nie, *et al.* 2009), and in addition the anatas has a lowest bulk modelus that is 179 GPa (Lazzeri, *et al.* 2001), so at low range of temperature and pressure one can expected that the anatas phase will dominate and the probability of this dominate will increase with decrease the total pressure and this satisfy in the experimental result.

Table 1. Relative intensity peak and $TC\ h\ k\ l$ for TiO_2 thin films prepared by DC sputtering

P_T (Pa)	2θ°	hkl	$\frac{I}{I_0}$	$\frac{I_{101}}{I_{004}}$	TC_{hkl}	
10	25.3036	(101)	100	0.431	2.02	Card No.(ASTM) : 96-900-9087 Phase : Anatase
	37.7937	(004)	43.1		0.87	
	53.8840	(105)	28.5		0.58	
	55.0614	(211)	26.3		0.53	
25	25.3146	(101)	100	0.483	1.92	
	37.8047	(004)	48.3		0.93	
	53.8950	(105)	31.7		0.61	
	55.0724	(211)	27.8		0.54	
50	25.3241	(101)	100	0.471	1.69	
	37.8157	(004)	47.1		0.79	
	53.9060	(105)	29.9		0.51	
100	25.3350	(101)	100	0.527	1.31	
	37.8267	(004)	52.7		0.69	

Orientation of the Growth and the Total Pressure

It can be observed from figure 1 that for each total pressure (P_T), the highest intensity of the peaks at diffraction angle [2θ≈ 25.00°], this indicate that the films have a preferential orientation along 101 direction. The preferred growth is mainly depends on the method of interaction between the deposited atoms and the substrate which condense over it, and this affected by the surface energy, which at lowest value of the surface energy the probability of growth take a highest value and the plane can be consider as a preferred growth plane (E. Alfonso, *et al.* 2012).

The texture coefficient (T_C) represent the texture growth of a plane, and this can be calculated using the following equation (Boukhachem, *et al.* 2017):

$$T_{C(hkl)} = \frac{\frac{I_{(hkl)}}{I_{0\,(hkl)}}}{\frac{1}{N}\sum_n \frac{I_{(hkl)}}{I_{0(hkl)}}} \qquad (1)$$

Where N is the number of reflections, $I_{o\ (hkl)}$ is the standard intensity of the plane *(hkl)* taken from the (ASTM) data, and $I_{(hkl)}$ is the measured relative intensity of the plane (*hkl*).

From Table 1 one can note that the first peak which correspond to the (101) orientation has a high texture coefficient for each value of the total pressure, this indicate that this plane has a preferential growth, and this will dominate in growing regardless of the value of the total pressure. On the other hand one can observed that the texture factor decrease with increase the total pressure and some of the plane disappear at a higher total pressure, this decreases in the texture factor suggest that there is a degradation in the crystalline quality and this can be related to degradation in the mobility of adatoms (Ahmed, *et al.* 2017).

The probability of the particles that cannot reach the substrate is very sensitive to the degree of the total pressure, these particles when bombarded the surface of the film will transfer their energy to the adatoms and then will affect on the mobility of them. This probability P(d) is given as the following equation (Mitin, *et al.* 2017):

$$P\,(d) = 1 - e^{-\frac{d}{\lambda}} \qquad (2)$$

Where d is the distance between the target and substrate and λ is the mean free path. The mean free path take the following relation (Mitin, *et al.* 2017):

$$\lambda = \frac{K_B \times T}{P_T \times \sigma} \qquad (3)$$

Where K_B is the Boltzmann constant, T the temperature, P_T the total pressure, and σ the cross section of the collision.

From equations (2) and (3), the [P (d) → 0 at λ→∞] and this satisfy when [P_T → 0], so the decreasing of the total pressure will give more probability for the particles to reach the substrate and this mean more

and more energy that transfer to the substrate which then increase the energy of adatom and their ability to move and this will led to enhancement the structure and then the texture factor will increase with decrease the total pressure as shown in Table 1.

In other hand the number of the particles that reach the film can be given as (Mitin*, et al.* 2017):

$$N_F = N_0 e^{-\frac{d}{\lambda}}, \quad (4)$$

Where N_0 is the initial number of the particles at the target, N_F is the final number of the particles at the substrate, so when [d→ 0 and λ→∞ or P_T →0] → [N_F =N_0], this mean when decreasing the pressure the probability of the particles that reach the surface of the film will increase and the loss of the energy during the pathway between the substrate and the film will be in the minimum level, this will led to a high energy that delivered to the film and then will increase the energy of adatom and their mobility which cause to enhancement the crystallinity or increase in the texture factor with decrease the total pressure and this satisfy in the experimental result as shown in Table 1.

In addition of the mobility of adatoms, the main other factors that play a main role in determine the probability of the growth are the surface energies of the substrate (γ_s) and thin films (γ_f) and the interfacial energy (γ_i), these factors can be related to each other through the following relation (Bauer*, et al.* 1986):

$$\Delta\gamma = \gamma_f + \gamma_i - \gamma_s \leq 0 \quad (5)$$

This relation give us the threshold condition for the start the growing and tendency to encourage this growing, which at least need to satisfy $\gamma_f+\gamma_i = \gamma_s$, to start the growing, and when $\gamma_f+\gamma_i < \gamma_s$ this give more encourage to growing, so one can re-write equation (5) to estimate the mismatch between the surface energies as a function to estimate the probability for the growing, as shown in equation (6):

$$\text{Mismatch surface energies} = \frac{\Delta\gamma}{\gamma_s} = \frac{\gamma_f+\gamma_i}{\gamma_s} \leq 1 \quad (6)$$

The factor ($\frac{\Delta\gamma}{\gamma_s}$) play a main role to determine the growing of the films and when use the same substrate this main the same probability of (γ_s) and for homo growth (layer A above layer A) the γ_i consider equal zero (Bauer*, et al.* 1986), so the condition for the growing can be depend only on (γ_f) if one compare between different films and same substrate, and from this one can deduce that the films with lower γ_f has a higher probability to grow.

For the anatase, rutile, and brookite phases, one can report the following sequence for the surface energies: anatase (101) < anatase (100) < anatase (001) < anatase (110) (Esch*, et al.* 2014).

From previous sequence one can note that anatase in the phase (101) has a lowest surface energy and this give this phase of morph a high probability to grow and this satisfy for all experimental result.

The effect of the total pressure on the surface energy can be illustrated from the Laplace–Young equation which describe the relation between the applied (or total) pressure and surface energy, the Laplace–Young equation can be written as $\Delta P=\frac{2\gamma}{r}$ (Kaptay 2012), where $\Delta P=P_0-P_i$, P_0 external pressure which prevent the atoms in droplet to escape or the films to expanded and P_i internal pressure which push the atoms to escape or the films to expanded, γ surface energy which represent the ability of the film to increase it is area and r radius of the droplet (Kaptay 2012), one can note the direct relation between the total pressure and the surface energy, so to increase the nucleation one need to decrease the total pressure to get a lower surface energy and this will enhancement the texture factor and this satisfy in the experimental result.

Crystallization Degree and the Total Pressure

The behavior of the XRD pattern revels us a sufficient insight about the degree of crystallization through the number and intensity of the peaks, when the number and intensity of the peaks increase this assign that the degree of crystallization increase.

Figure (1) obtained that the total pressure has an affect on the shape of the XRD pattern where the number and intensity of the peak increase with decease the total pressure, this indicate that the degree of crystallization increase with decrease the total pressure and the films tend to enhancement the transition from weak crystallization to higher crystallization degree.

It is well known that the site in the lattice of the crystalline has a highest thermal relaxation [$Enthalpy_{cryst.} < Enthalpy_{amorph.}$] (Einfalt*, et al.* 2013), this deviation in the enthalpy occur when the particles on the substrate may be do not have enough diffuse energy to reach the position where the thermal energy of the particles is in the minimum level.

One of the important parameter that play a main role in determine the crystallization process is the surface mobility of the sputtered particles on the substrate (Meng *et al* 1993) which when increases, the particles may be have enough energy to diffuse

and then the probability of nucleation and growth increase, which cause to increase in the degree of the crystallization (Meng, *et al.* 1993), Two process can be affected on the diffuse energy the first one is the heating of the substrate (increasing the substrate temperature Ts) and the second one is increase the energy of the bombarding particles that hit the substrate (increase in the bombarding ions energy E_{bi}) (Musil, *et al.* 2007).

For the first parameter that is the heating of the substrate, one can note that the conventional heating between the substrate and the condensed material play a main role to increase the ability of the particle to reach the optimum thermal relaxation and the probability of this increase when the temperature of the substrate and condensed material become more and more closer to each other and the thermal misfit between them tend to reach the unity as shown in the following equation (Alfonso, *et al.* 2012):

Thermal misfit = $\frac{Substarte\ temperature}{condenced\ temperature} = \frac{T_S}{T_m} \approx 1$ (7)

Note that the strain in the films depend on differences between the temperature of the substrate and condensed material which is given as the following equation (Thornton, *et al.* 1989):

Thermal strain = $\Delta\alpha \times \Delta T = (\alpha_s - \alpha_f) \times (T_S - T_f)$ (8)

Where (α_s, α_f) are the thermal expansion coefficient for the substrate and films respectively, (T_S, T_f are the temperature of the substrate and film respectively.

So the thermal strain decrease with decrease the differences between the temperature of the substrate and the films (ΔT≈0), in this work the deposition done without the external source of heating that is ($T_S << T_m$) and ($\frac{T_S}{T_m} << 1$), but depending on the Clausius – Clapeyron equation that is (Reinhardt 2019):

$$\ln\frac{P_2}{P_1} = \frac{-\Delta H_{vap.}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad (9)$$

where P_1 and T_1 can be consider the vapor pressure and melting point at the standard condition at the level of the sea and P_2, T_2 the vapor pressure and melting point in the chamber, from previous relation one can deduce the exponential relation between the pressure and melting point, so when the pressure decrease this will causes to decrease in melting point and ($T_m \rightarrow T_S$) then the ratio ($\frac{T_S}{T_m}$) tends to reach the unity or (ΔT →0), which mean that the strain tends to decreases (strain → 0) and this will enhancement the crystallization in the structure, this enhancement can be deduce from Thornton structural zone model (SZM) (Musil 1998) which obtain the behavior of the structure as a function of ($\frac{T_S}{T_m}$) and the effect of the total pressure, from this model the boundary between the zones affected with the ratio ($\frac{T_S}{T_m}$) and this boundary decreases with decrease the total pressure which mean even at $T_S < T_m$ there is a probability to the films to obtain the crystallinity and this can be seen obviously in the experimental result which the crystallinity increase with decrease the pressure.

The second factor that can affect on the surface mobility is the energy of the bombarding ions (E_{bi}), The final energy of bombarding ions when reach the substrate can be written as the following equation (Poláková, *et al.* 2003):

$$E_{bi}\left(\frac{J}{Cm^3}\right) \approx \frac{(U_s\, i_s)}{a_D} . e^{\frac{-L}{\lambda_i}} \quad (10)$$

Where U_s is the substrate bias, i_s is the substrate ion current density, a_D is the film deposition rate, L is the sheath thickness and λ_i is the ion mean free path for collisions leading to losses of the ion energy in the sheath. equation (10) explain that the maximum bombarding energy (E_{bi}) can be occur when [$e^{\frac{-L}{\lambda_i}} \rightarrow$ 1] and this satisfy when [L → 0, $\lambda_i \rightarrow \infty$] which mean that this staify when the mean free path (λ_i) take the highest value.

The mean free path λ_i can be calculate from the Dalton relation as shown in equation (11) (Vlček, *et al.* 1999):

$$\lambda_{mfp}\ (\text{cm}) \approx \frac{0.4}{P_T}\ [\text{Pa}]^{-1} \quad (11)$$

From equation (11) one can observed the inverse relation between the mean free path and the total pressure, so at lowest total pressure one can get a highest value of the mean free path [(PT → 0), (λ_{mfp} → ∞) and then reach the higher value of the ion bombarding energy.

From equation (10) one can note that if the ions bombarding energy (Ebi) increase and this can be achieve as shown previously by decreases the total pressure, the deposition rate [a_D] will be decrease, this mean the interval time separated between two growing layers will increase [$a_D = \frac{thickness}{time}$], [$a_D \rightarrow 0$, $time \rightarrow \infty$] this will increase the exposure time by the flux of the particles that hit the surface of the film and this will increase the energy that delivered to the top monolayer and neighboring subsurface layers which causes to give a sufficient defuse energy to the adatoms and then enhancement the crystallization in the film (Musil, *et al.* 2005).

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From Kevin Mayer equation, one can estimated the final energy of sputtering atom as shown in equation (9) (Meyer, *et al.* 1981):

$$E_F = (E_0 - K_B T_G)\, e^{N \ln\left(\frac{E_1}{E_2}\right) + K_B T_G} \qquad (12)$$

Where E_0 and E_F are the initial and final energies of sputtered particles respectively, K_B is the Boltzmann constant, T_G is the temperature of the sputtering gas, N is the frequency of the collision (number of the collision), and $\frac{E_1}{E_2}$ is the ratio of energy before and after a collision, $\frac{E_1}{E_2} = 1 - \frac{2y}{(1+y)^2}$ and $y = \frac{m_{sg}}{m_{sp}}$ is the atomic mass ratio of collision particles. Where m_{sp} mass of particle, m_{sg} mass of molecule gas.

And the number of collision can be given as in the equation (13) (Meyer, *et al.* 1981):

$$N = \frac{d\, P_{tot} \sigma'}{K_B T_G} \qquad (13)$$

Where d is the distance between the target and the substrate, Ptot is the total pressure and σ' is the collision cross-section.

From equation (12 and 13), one can consider that the total pressure can affect on the final energy of the sputtered particle at the surface of substrate, equation (13) explain that the number of collision during the travelling between the target and substrate has a direct correlation with total pressure and this led to increase in the probability of the scattering with gas molecules and this may be change the direction of the sputtered particles which decrease the flux of particles reach the substrate and in other hand there is some of the energy of the particles will loss during the collision and this will increase with increase the number of collision, so when decreases the number of collision by decreasing the total pressure this mean decreases in the loss of energy and this will cause to increase in kinetic energy of the particles which increase the exponential term in equation (12) and then at last increase the final energy of the particles that arrive the substrate which causes to increase the diffuse energy of adatoms on the substrate and this will enhancement the crystallization in the films.

In other hand when the total pressure increase, this mean the partial pressure of the Argon gas will be increase ($P_T = P_{Ar} + P_O$) and the relation between sputtering pressure and mean free path (λ) as shown in equation (14) (Kavitha, *et al.* 2017):

$$\lambda = 2.33 \times 10{-18} \frac{T}{P \delta_m^2} \qquad (14)$$

Where T is the room temperature in [K], P is Argon sputtering pressure in [Pa] and δ_m is the molecular diameter in [cm]. equation (14) indicate that there is an inverse relation between the sputtering pressure and mean free path of the particles, this mean at higher pressure the mean free path is shorter, and the distance between the target and the substrate may not sufficient enough for sputtered particle to reach the substrate with enough energy to achieve the diffuse energy for adatom to nucleation and growth all of obvious indicate that the crystallinity increase with decreases the total pressure.

Deviation of the Inter Planner Distance and the Total Pressure

From the closely matching of the calculated and standard inter planer distance (d), one can confirms the successful lattice sites in matrix and deduce that the deposited films belong to pure TiO_2 (Sivaraman, *et al.* 2015). It can be observed from the experimental result as shown in table 2 that the inter planer distance has a dependence on miler indices hkl. For the tetragonal structure the relation between the inter planer distance and the miler indices can be given as the following equation (Wiatrowski, *et al.* 2018):

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (15)$$

From this equation one can note that there is an inverse relation between the $[(h^2 + k^2)\, c^2 + l^2\, a^2]$ and d^2, the value of the inter planer distance decrease with increase $[(h^2 + k^2)\, c^2 + l^2\, a^2]$ value and this satisfy for all standard and experimental result as shown in table 2.

Table 2. The deviation of the inter planer distance and strain of TiO_2 prepared under different total pressure

hkl	P_T (Pa)	$d_{(exp.)}$ (Å)	$d_{(Std.)}$ (Å)	Δd_1 (Å)	S1	Δd_2 (Å)	S_2
101	10	3.5187	3.5169	0.0	0.0	+18	+511.8
	25	3.5172	3.5169	-15	-4.2	+3	+85.3
	50	3.5159	3.5169	-28	-7.9	-10	-284.3
	100	3.5144	3.5169	-43	-12.2	-25	-710.8
004	10	2.3796	2.3785	0.0	0.0	+9	+378.4
	25	2.3790	2.3785	-6	1.7	+5	+210.2
	50	2.3783	2.3785	-13	3.7	-2	-84.1
	100	2.3776	2.3785	-20	5.7	-9	-378.4
105	10	1.7009	1.7001	0.0	0.0	+8	+470.5
	25	1.7006	1.7001	-3	0.85	+5	+294.1
	50	1.7003	1.7001	-6	1.7	+2	+117.6
211	10	1.6673	1.6665	0.0	0.0	+8	+480.0
	25	1.6670	1.6665	-3	0.85	+5	+3.00

$\Delta d_1 = (d_{H.P} - d_{L.P}) \times 10^{-4}$, $\Delta d2 = (d_{exp.} - d_{Std.}) \times 10^{-4}$, $S_1\% = \frac{\Delta d_1}{d_{L.P}} \times 100\%$, $S_2\% = \frac{\Delta d_2}{d_{std.}} \times 100\%$

From table (2) one can note , for each hkl plane the inter planer distance decrease with increase the total pressure, this decreasing in the inter planer distance indicate that the deviation of inter planer distance as compare the inter planer distance with

inter planer distance at lowest total pressure [$\Delta d_1 = d_{H.P} - d_{L.P}$] it will take a negative value which refer that [$d_{L.P} > d_{H.P}$] for each hkl, this mean the film at lowest total pressure has more tendency to expanded resulting from the highest flux and energy of the particle that bombarded the surface of the films which give more energy to the adatoms to move away from their position which causes the stretching in the distance that separated between the planes and this stretching may be decrease with increase the total pressure (Pulker 1999). The increasing in the deviation [Δd_1] with decreasing the total pressure indicate that there is a development in the compressive stress with decreasing the total pressure and this may refer that there is an increasing in the size (D_1) for each hkl with decreasing the total pressure or increasing in the average size (D_2) for each total pressure with decreasing the total pressure as shown in table (3), this mean that with decreasing the total pressure the atoms at the boundaries of the grains have enough energy to pass these barriers for growing and dissolve the boundaries then the grain will incorporate with each to other causing to increase in the size of crystals and decrease in the dislocation densities as shown in table (4).

Table 3. Size and the dislocation density of TeO2 prepared under different total pressure $D1 = \frac{0.9\,\lambda}{\beta\, Cos\,\theta}$, $D2 = \frac{\sum D_{hkl}}{\sum T_{C_{hkl}}}$

P_T (Pa)	hkl	$\beta_0 \times 10^{-4}$	D_1 (nm)	D_2 (nm)
10	(101)	5600	29.40	15.04
	(004)	5800	12.62	
	(105)	6549	7.84	
	(211)	7140	10.31	
25	(101)	5992	26.15	14.05
	(004)	6206	12.59	
	(105)	7008	7.76	
	(211)	7640	9.71	
50	(101)	6411	21.52	12.55
	(004)	6640	10.10	
	(105)	0.7498	6.02	
100	(101)	0.6860	15.55	11.85
	(004)	0.7105	8.15	
$D1 = \frac{0.9\,\lambda}{\beta\, Cos\,\theta}$, $D2 = \frac{\sum D_{hkl}}{\sum T_{C_{hkl}}}$				

In other hand the deviation [Δd_2] when compare the experimental value of inter planer distance [$d_{exp.}$] for each hkl at different value of total pressure with standard value [$d_{Std.}$] that is [$\Delta d_2 = d_{exp.} - d_{Std.}$], one can note that this deviation take a highest positive value at lowest total pressure for each hkl plane, than the deviation began to decrease with increase the total pressure, but for the plane which has a highest texture factor that is [101 and 004] one can note that this decreasing continuous with decreasing the total pressure tell it change it is sign to negative and began to increase in the negativity with increasing the total pressure tell reach the highest negative value at highest total pressure. This alter in sign refer that the stress change from compressive to the tensile, this mean the strain tend to stretch the distance and this may attributed that when the total pressure decrease the adatoms do not have enough energy to reach the standard distance, so the strain applied force in the opposite direction for the reason of this unfitting distance and try to stretch the distance (tensile strain) to reach the position which has an optimism thermal equilibrium.

Table 4. Lattice constant and the total pressure for TiO2 Thin films

P_T (Pa)	C_{Exp} (Å)	$C_{Std.}$ (Å)	ΔC_1 (Å)	ΔC_2 (Å)	$a_{Exp.}$ (Å)	$a_{Std.}$ (Å)	Δa_1 (Å)	Δa_2 (Å)
10	9.518	9.514	0.004	0.000	3.7870	3.785	0.0022	0.0000
25	9.516	9.514	0.002	-0.002	3.7852	3.785	0.0004	-0.0017
50	9.513	9.514	-0.001	-0.005	3.7838	3.785	-0.0010	-0.0032
100	9.510	9.514	-0.004	-0.008	3.7821	3.785	-0.0027	-0.0048

Deviation of the Lattice Constant and the Total Pressure

In sputtering deposition the particles bombardment the substrate and they will passes the energy to the deposition film, this pass energy cause to increase the kinetic energy of the atoms in the film and these will incorporated to each other into spaces in the growing film which are smaller than the usual atomic volume this will led to an expansion of the film outwards from the substrate but the film is not free to expanded and the entrapped atoms causes a compressive stress (Pulker 1999).

The implantation rate (n_i) per unit area which represent the atom that transition from there equilibrium position due to the energy that transfer to the surface of the film by bombarded particles is approximately related to the particles flux and there energy by ($n_i \ \alpha \ j \ \sqrt{E}$)(Davis 1993), this relation indicate that when the energy of bombarded particles increase the rate of implantation will

increase and then the stress will increase, and it is well known obviously the invers relation between the total pressure and the energy of the particles that arrive the substrate, so one can expected that the compressive stress will increase when the total pressure decrease and then the lattice constant will change depending on that variation of this stress.

The stress and the strain can be related to each other using the Hook's law through the Young modulus [stress α strain →Y=$\frac{Stress}{Strain}$ = $\frac{\sigma}{\varepsilon_{\parallel}}$], where Y is the Young modulus, and the sign (‖) represent that the strain is in the same direction of applied force, note that the stress applied force on the surface of the film against the expansion along the axis which perpendicular to the plane of the film which mean the c-axis , so one can consider the stress and the strain obtain the similar behavior as a function of the variation of the total pressure (Lukyanov*, et al.* 2016).

The compressive stress will take the negative sign but the strain along the axis which is perpendicular on the plane of the film that is c-axis will take a positive value, the dimension tend to increase but the stress tend to act against this increasing , both of them in opposite direction (stress negative → strain positive), note that [$\sigma = -\frac{Y}{\nu}\varepsilon = -\frac{Y}{\nu}(\frac{\Delta C}{C_0})$], and when [$\varepsilon_{\perp} > 0$] or [$\Delta C > 0$] → [$C > C_0$], the sign (⊥) represent the strain is in the direction of axis that is perpendicular to the plane of the film that is c-axis (Maniv*, et al.* 1982), so one can expected at the compressive stress there is an expanded on the c-axis value and at the tensile stress which take a positive sign there is a shrink in c-axis value.

So when put the c-axis at lowest total pressure as a reference to investigated the effect of the total pressure on the c-axis one can note that the deviation [$\Delta C_2 = C_{H.P} - C_{L.P}$] take a negative value and this negativity increase with increase the total pressure, the negative value of [$\Delta C_2 = C_{H.P} - C_{L.P}$] for all value of total pressure indicate that [$C_{L.P} > C_{H.P}$] and this refer that the c-axis expanded with decreasing the total pressure till it take a highest expanded at lowest total pressure, and in other hand the increasing the negativity of deviation [ΔC_2] with increasing the total pressure indicate that the c-axis shrinking as a compare with c-axis at lowest total pressure, the negative sign of strain mean a positive sign of stress which mean there is a tensile stress tend to stretch the dimension with increase the total pressure, or if one take the c-axis at highest total pressure this mean a compressive stress develop with deceasing the total pressure, this develop in compressive stress with decreasing the total pressure refer that the rate of implantation of atoms increase due to increase in the energy of bombarded particles with decreasing the total pressure and this will increase of tendency to expanded which cause to increase in c-axis value with decrease the total pressure and this satisfy in the experimental result as shown in table (4).

In other hand when compare the experimental c-axis value with the standard value one can note the similar behavior that the deviation [$\Delta C_1 = C_{Exp.} - C_{Std}$] increase with decreasing the total pressure which indicate that the c-axis increase with decrease the total pressure but here the sign of deviation ΔC_1 alter from positive at low pressure to negative at high pressure which mean that the stress alter from compressive to tensile stress, this may be indicate that at high total pressure the bombarded particles not possess enough energy to replacement the atoms away from it position which causes the tendency to shrink the axis and then tensile stress attempt to stretch it to fit with dimension of the substrate (Davis 1993) as shown in table (4).

From the inter planer distance calculation equation [$\frac{1}{d^2_{h\,k\,l}} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$], one can deduce that if (d and c) increase, the a-axis value will increase surly as shown in table (4), and the a-axis will show the similar behavior with variation the value of total pressure, so when compare the a-axis value at higher pressure with that at lower pressure, the deviation [$\Delta a_2 = a_{H.P} - a_{L.P.}$] will take a negative value which indicate the shrinking in a-axis value as the total pressure increasing, so the [$a_{H.P} < a_{L.P}$] and this refer that the atoms will have more and more energy when decreasing the total pressure which give there more probability to expanded , and when compare the experimental value of a-axis with standard value for each total pressure the deviation [$\Delta a_1 = a_{Exp.} - a_{Std.}$] will decrease as the total pressure increase and the sign will alter from positive at low pressure to the negative at higher pressure which indicate that the stress will change from compressive to tensile.

So to illustrated this behavior, the sputtering deposition causes a process which can named the peening shot, this peening shot causes to implant the atoms under the surface of the films, the number of implant atoms which causes the stress have a direct correlation with the energy of bombarded particles that is ($n_i \; \alpha \; J\sqrt{E}$) (J: Flux of bombarded particles, E energy of bombarded particles), so when the energy of the bombarded particles increase, one can

expected that the stress will increase and this is satisfy the experimental result.

Conclusion

The total pressure has a significant effect on the structural properties of the film deposited using sputtering method, the intensity and number of number of XRD peaks increase with decreasing total pressure likely due the high diffusion energy of adatome in the substrate when decreasing the total pressure, and the morphology will take the anatast phase and the probability of appear this morphology will increase with decreasing total pressure, the intensity ratio between the low index facet (004) and high index facet (101) will increase with decreasing the total pressure, this result has important due to the high activity of 004 facet, the inter planer distance and the lattices constant, there deviation from the standard and as compare with value at lowest total pressure was increase with decrease the total pressure which indicate that the increase in the strain, and this may be refer that the atoms has more ability to move away from their position by atomic peening shot process and this will causing increase in the strain.

Conflicts of Interest

None.

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