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Influence of Process Parameters on the Growth of Pure-Phase Anatase and Rutile TiO_2 Thin Films Deposited by Low Temperature Reactive Magnetron Sputtering

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In this work is investigated the optimal conditions for deposition of pure-phase anatase and rutile thin films prepared at low temperatures (less than 150°C) by reactive dc magnetron sputtering onto well-cleaned p-type Si substrates. For this, the variation of deposition plasma parameters as substrate-to-target distance, total gas pressure, oxygen concentration, and substrate bias were studied and correlated with the characteristics of the deposited films. The XRD analysis indicates the formation of pure rutile phase when the substrate is biased at voltages between -200 and -300 V. Pure anatase phase is only attained when the total pressure is higher than 0.7 Pa. Moreover, it's noticeable a strong dependence of surface roughness with parameters studied.

Keywords: Keywords: titanium dioxide; magnetron sputtering; X-ray diffraction; Atomic force microscopy.

1. INTRODUCTION

A variety of semiconductor materials can be found in the II-VI compounds with metal oxides and nitrides amongst. Of these materials, the titanium dioxide (TiO_2) is very intensively investigated because its outstanding optical, electrical and chemical properties which make it suitable for a variety of thin film applications [1]. For example, anatase TiO_2 phase of film has better photocatalytic activity allowing its use in many applications as photochemical solar cell and gas sensor, e.g. for the detection of NO_2 [2]. On the other hand, rutile TiO_2 phase has high dielectric constant and high resistivity ($\rho \approx 10^{13} \Omega \cdot \text{cm}$), which make it very attractive for use in fabricating capacitors in microelectronic devices [3,4]. Also, because its high refractive index ($n \approx 2.5$) and optical transparency in the visible range, the rutile phase was applied as dielectric interference filters, antireflective coating, optical wave guides, etc. However, the performance of thin film electronic devices depend substantially on crystalline quality and orientation of the films employed [5]. Thus, numerous efforts have been done to improve the film quality by means of several kinds of growth techniques.

Recently, amongst the several TiO_2 growth techniques has been distinguished those that make possible the growth of crystalline films in unheated substrates, because enable advantages as low substrate deterioration, low defect formation, easy handling and operation, and a relatively low cost [6]. Between existing techniques, the reactive magnetron sputtering has demonstrated interesting results [7,8] in the control of film properties as crystallinity, orientation and morphology. However, it is worth to note that, until now there is no general consensus about the exact role of the deposition parameters on low temperature films properties as the crystallographic orientation change and surface morphology.

In this work is investigated the optimal conditions for deposition of single-phase anatase and rutile thin films on unheated Si substrates by reactive direct current (dc) magnetron sputtering technique. For this, the influence of deposition parameters namely substrate-to-target distance (d_{s-t}), total gas pressure (P_t), O_2 concentration in $Ar + O_2$ gas mixture

($O_2\%$) and substrate bias (V_{bias}) were studied and correlated with the characteristics of the deposited films as microstructure and surface morphology.

2. EXPERIMENTAL

TiO_2 films were growth onto well-cleaned p-type Si substrates by the reactive dc magnetron sputtering technique where pure titanium was used as the sputtering target. Details about the reactor can be seen in references [9,10]. A base pressure of 10^{-3} Pa was routinely achieved by a two-pump-system comprising a rotary pump and a diffusion pump. Then high-purity argon and oxygen were introduced into vacuum chamber as working ambience by a mass flow control system. Prior to deposition, the target was sputter-cleaned by 10 min at a pressure of 0.7 Pa. In this investigation, a fixed dc power of 150 W was used for all depositions. During depositions no intentional substrate heating was applied, being the only heating source proceeding from the plasma. A thermocouple fixed into substrate holder monitored the substrate temperature (T_s) that reaches temperatures up to 150°C . The experimental apparatus allows the variation of d_{s-t} in up to 200 mm, however in our experiments d_{s-t} was varied only between 15 to 40 mm. For investigate the effect of P_t , this was varied in the range 0.4 to 7.0 Pa. Another considered effect is the reactive gas concentration, here the oxygen flow ratio [$O_2/(O_2 + Ar)$] was varied between $0-100\%$ for a fixed $P_t = 0.7$ Pa. Finally, it was observed the dc substrate bias for values up to -300 V. Table 1 gives a summary of the sputtering parameters.

After the depositions, the film thickness was measured by a TENCOR Alpha-Step 500 profilometer. The crystalline structure and orientation of the films were investigated by Philips X'Pert MRD diffractometer using $CuK\alpha$ radiation. The grazing incidence spectra were recorded with a 2θ scan and an incidence angle $\omega = 3^{\circ}$. Moreover, the morphology of the surface and its root mean square (RMS) roughness were studied using a Shimadzu Atomic Force Microscope (AFM) SPM-9500 J3 operating in tapping mode.

TABLE 1: Deposition parameters for the reactive magnetron sputtering of TiO_2 films

Parameter	Value
Target material	Ti (purity: 99.6%)
Target diameter	34 mm
Sputtering gas	Ar (purity: 99.999%)
Reactive gas	O_2 (purity: 99.99%)
Base pressure	$< 10^{-3}$ Pa
Total gas pressure (P_t)	0.4-7.0 Pa
Sputtering power	150 W
Substrate temperature (T_s)	$< 150^\circ C$
Substrate material	p-type silicon (100)
Substrate-to-target distance (d_{s-t})	15-40 mm

3. RESULTS AND DISCUSSION

A. Dependence of substrate-to-target distance and oxygen concentration on properties of TiO_2 films

In depositions without intentional substrate heating a parameter to be initially evaluated is the d_{s-t} in order to adjust the best condition for deposition of well-crystallized films. Fig. 1a shows the XRD patterns of TiO_2 films deposited at three d_{s-t} values for 60% O_2 and $P_t = 0.7$ Pa. As observed in the XRD spectra, the films deposited at $d_{s-t} = 15$ mm tends to grow with a well-crystallized anatase phase (characterized by A(101) reflection), changing to an anatase + rutile phase mixture (characterized by A(101) + R(110) reflections) for $d_{s-t} = 20$ mm and to a low crystalline/amorphous phase for $d_{s-t} = 25$ mm. This reduction in the film crystallinity comes of the fact of the substrate to be less exposed to the plasma, consequently lowering T_s , preponderant factor for the film crystallization process [11]. Therefore, a high crystallinity is attained for condition $d_{s-t} = 15$ mm. From this value we carry through the other analyses as follow.

Fig. 1b shows the structure development of the TiO_2 films as a function of $O_2\%$ for $P_t = 0.7$ Pa. Exactly the same trend in development of the film structure is observed when the $O_2\%$ is increased from 30 to 100%. This is an indicative that both d_{s-t} and $O_2\%$ parameters affect in similar manner the structural characteristics of the deposited TiO_2 films. The low film crystallinity at 20% O_2 can be attributed to the low $O_2\%$ in the gas mixture, making it difficult the formation of the TiO_2 compound. The relationship of d_{s-t} and $O_2\%$ parameters on the RMS roughness of the TiO_2 films is illustrated in Fig. 2. The AFM analysis indicates a linear decrease of the surface roughness with increase of d_{s-t} for films deposited at 60% and 100% O_2 . In that conditions, the surface morphology features uniform, free of defects, tending to have smoothly topography. On the other hand, this linear behavior is broken when the $O_2\%$ is decreased for values lower than 60%. Here, for the case of 20% O_2 , a reduction of up to 10 nm is observed when d_{s-t} is decreased in 10 mm. This different roughness is related with the Ar amount and the energy with that the particles reach the substrate surface. For small d_{s-t} , the substrate is more exposed by energetic particles as Ar^+ ions, energetic neutrals, etc., causing as result a degradation of film surface and consequently a high rough-

ness. With the reduction of d_{s-t} the particles lose its energy by collisions, diminishing the energy with that bombs the substrate. For this case, the surface was noticeably flat with surface roughness around 3 nm.

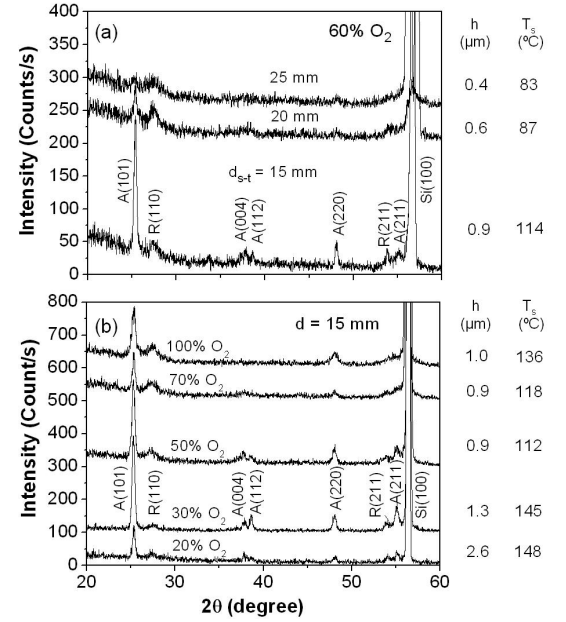


FIG. 1: Structure development of the TiO_2 films deposited on unheated Si substrate with increasing of (a) d_{s-t} and (b) $O_2\%$. Where h: film thickness, T_s : maximum substrate temperature reached, A: anatase phase and R: rutile phase.

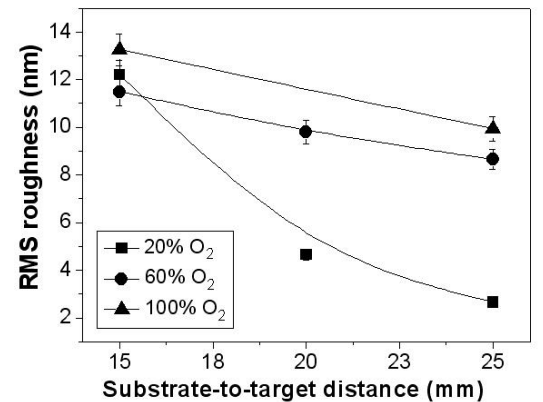


FIG. 2: Surface roughness (RMS) of deposited TiO_2 films as a function of d_{s-t} for different O_2 concentrations and fixed $P_t = 0.7$ Pa. The AFM scan area was $2.5 \times 2.5 \mu m$.

B. Dependence of substrate bias and total gas pressure on properties of TiO_2 films

The XRD spectra of the TiO_2 films deposited at different negative biases for a fixed $P_t = 0.7$ Pa are shown in Fig. 3a.

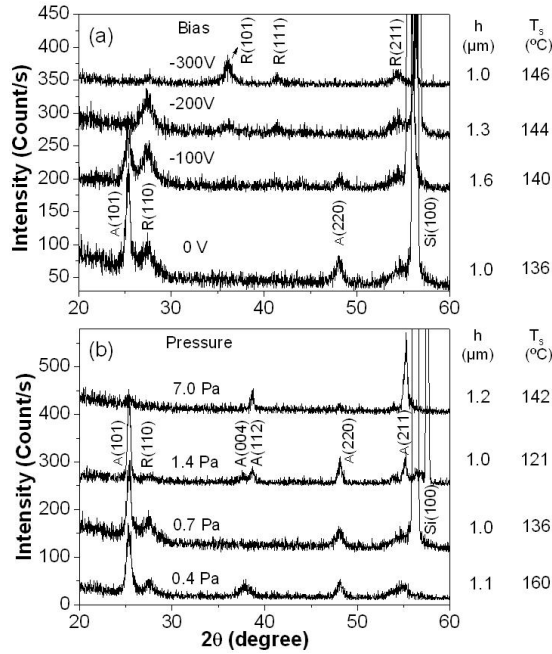


FIG. 3: Structure development of the TiO_2 films deposited on unheated Si substrate with increasing of (a) V_{bias} and (b) P_t . The O_2 concentration was fixed in 100%.

As we can observe, for $V_{bias} = -100$ V the resultant structure is a mixture of anatase and rutile phases. On the other hand, when $V_{bias} > -100$ V occurs the formation of a single rutile phase, however with lower intensity compared with the anatase phase. It is known of the literature [12] that the rutile phase needs more energy for its formation. This fact can be observed in the Fig. 3a, with the increase of V_{bias} a larger potential drop is generated giving to incident particles enough energy for formation of a pure rutile phase. Furthermore, an interesting fact is observed for $V_{bias} > -200$ V, here the R(101) reflection starts to be the main rutile peak.

Together with V_{bias} , the P_t exerts great influence on crystalline orientation of the low temperature TiO_2 films. As seen in Fig. 3b, it is possible to get a change of main anatase orientation from A(101) to A(211) with the increase of P_t . Also it is observed that for P_t higher than 0.7 Pa the rutile phase practically disappears, being possible the growth of a pure anatase phase.

Besides influencing the film structure, the variation of V_{bias} and P_t strongly modify the film morphology (see Fig. 4). This figure shows the dependence of surface roughness of as-deposited TiO_2 films on V_{bias} and P_t . It is observed in Fig. 4a that the surface roughness increases up to approx. -100 V where it returns to decrease for high V_{bias} values. This behavior tends to be smaller when d_{s-t} is increased. One explanation for the reduction in surface roughness for $V_{bias} > -100$ V is that high V_{bias} induce additional effects in ion bombardment at substrate surface such re-sputtering, consequently initiating combined processes of deposition and etching during film growth. This fact promotes a decrease of film thickness (see h values in Fig. 3a) and consequently

a smoothing of surface roughness.

Different behavior of surface roughness is observed when P_t is changed (see Fig. 4b). In this case a continuous increase of surface roughness is observed when P_t is increased. At low P_t values the mean free path of particles are large, consequently increasing the energy with that they collide in the substrate, thus limiting the final surface roughness. On the other hand, for high pressures the mean free path of particles is short, causing them to suffer several collisions before reaching the substrate surface. This causes a decrease in collision energy and formation of large clusters of particles during film formation.

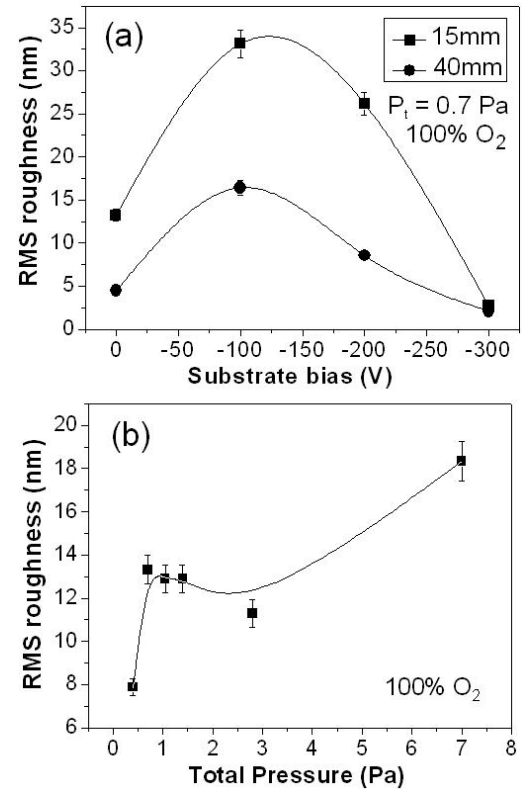


FIG. 4: Dependence of surface roughness (RMS) of deposited TiO_2 films on (a) V_{bias} and (b) P_t . The AFM scan area was $2.5 \times 2.5 \mu m$.

4. CONCLUSIONS

Pure anatase and rutile phases of TiO_2 films have been successfully synthesized at low temperatures ($< 150^\circ C$) using the reactive dc magnetron sputtering. The XRD studies reveal that the TiO_2 films tend to form in amorphous or anatase phase for majority of the studied conditions. The pure rutile phase was only attained when the substrate was biased at voltages above of -100 V. Pure anatase phase is only attained when the total pressure is higher than 0.7 Pa. Moreover, AFM measurements pointed out that the formation of films with roughness of the order of several nm (form-

ing several tips on the film surface) when the substrate was biased at voltages between -50 and -200 V. This is an interesting fact when is desired the application of this material as electron field emitter.

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