Titanium oxide thin film deposition by pulsed arc vacuum plasma

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Abstract. The experimental study of effects of deposition conditions and plasma parameters on the structure of titanium oxide films is presented. The films are deposited by reactive deposition from a plasma generated by a pulsed cathodic vacuum arc source. The effects of deposition time and substrate bias voltage are studied, the films being deposited at different substrate temperatures. Bragg-Brentano X-ray diffraction and electron microscopy were used to investigate the structure of deposited films. Correlation between plasma parameters, deposition conditions and structure of synthesized films are established.

1. Introduction

Titanium oxides show a great variety of forms and compositions, such as rutile, anatase or brookite [1]. All these forms present the same empirical formula (TiO₂), but their physical and chemical properties are different, due to their crystalline structure. Non-stoichiometric compounds can also be formed in case of an incomplete oxidation of titanium: some of these structures are known as Magnéli phases [2]. For these titanium oxides, the relative amount of titanium and oxygen is expressed by the empirical formula TiₓO₂₋₁ₓ. Magnéli phases find applications in tribology and mechanics as economical and effective coatings, since they are solid lubricants [3]. Titanium dioxides show relevant photocatalytic activities, both in the crystalline form and in the amorphous one. This property is useful for purification of water [4], disinfection [5] or for self cleaning coatings [6]. Nevertheless, titanium dioxide, especially in rutile form, is also widely used as oxygen gas sensors [7], in pigments [8], in cosmetic products [9] or optical interference coatings [10].

The growing interest for titanium dioxide and its application as thin films is accompanied by the availability of efficient, versatile and relatively simple deposition techniques, such as pulsed filtered cathodic vacuum arc (FCA, [11]). This method provides many advantages, such as a very high deposition rate [12], a good control of the deposition parameters, and an excellent quality of the coating (very low concentration of defects). In addition, the adhesion [13] of FCA TiO₂ films is good, due to the nearly fully ionized plasma [14]. The structure of titanium dioxide films depends strongly on the deposition conditions: for example, when deposited at room temperature, it can be amorphous [15-17], or crystalline [18-20]. The aim of this work is to understand the relationship between deposition conditions and titanium dioxide film properties; this investigation is in fact needed to achieve a complete control of the film features through a correct tuning of the process parameters.
2. Experimental details
The effect of the substrate temperature ($T_{\text{dep}}$), substrate bias ($U_{\text{bias}}$), deposition time ($t_{\text{dep}}$), arc current ($I_{\text{arc}}$) and working pressure ($p_{\text{dep}}$) were taken into account in this work. The study of the effect of each experimental parameter on the deposited films was considered separately, except for arc current and deposition pressure, whose simultaneous contribution to coating formation was investigated in the same set of samples. The vacuum chamber setup is schematically represented in figure 1. The vacuum arc plasma source and the power supply are described in details elsewhere [21, 22]. Table 1 summarizes the deposition parameters used for the experiments. The grounded cathode is made of pure titanium (99.5% wt). The ion source is operating in the DC-pulsed mode with a maximum arc current of $I_{\text{arc}} = 400$ A, a pulse repetition rate of 3 pps, and a pulse length of 1.5 ms.

![Figure 1. Schematic representation of the deposition chamber: (1) vacuum chamber; (2) cryopump; (3) vacuum arc ion source; (4) magnetic duct; (5) substrate; (6) substrate holder; (7) plasma plume; (8) screens.]

The residual pressure in the chamber was $5 \times 10^{-6}$ mbar. The deposition conditions that were kept constant for all samples are reported in table 1. Pure oxygen gas ($O_2$ 99.5% pure) was introduced at different flow rates in the chamber, to reach, during the experiments, the working pressures reported in table 2. No other gases except oxygen are present, since the deposition is achieved without the use of any sputtering gas (argon, etc.). In the experimental setup used for the deposition, the intake flow of the gas feeding system could be regulated very accurately, to achieve different deposition pressures. On the contrary, the suction line of the vacuum system was not provided with valves, and the pumping rate can only be roughly regulated for pressures less than $\sim 10^{-3}$ mbar. Changing the flow rate to achieve different deposition pressures is an approach used by other authors in literature, such as Rosén and coworkers [23].

The plasma plume passed through an electromagnetic filter, for removing the macroparticles ejected from the cathode during the discharge. The distance between the macroparticle filter outlet and the substrate is about 40 mm. The total distance between the cathode and the substrate is about 250 mm. P-doped Si(100) wafers (15×15 mm², 0.6 mm thickness) were used as substrates. A heated substrate holder and a water-cooled one built of copper were used. The heated substrate holder could achieve deposition temperature higher than 773 K, while the other one was used to dissipate as well as possible the heat during deposition at “room temperature” (RT, corresponding at a temperature of about 288 K).

The plasma ionized fraction composition was measured with a RGS 200 (Stanford Research System) gas analyzer, used as a quadrupole-mass spectrometer. The analyzer can identify species with a kinetic energy lower than 12 eV. In the case of a vacuum filtered cathodic arc ion source, the extracted ions can easily reach energy higher than 100 eV, so the energy spectra obtained with this method have to be considered as qualitative. Plasma diagnostic results obtained for different deposition conditions are in accordance with the literature [6, 24 - 26]; Ti$^{2+}$ amount is much higher than Ti$^+$ or Ti$^{3+}$ ones. Other species present in small amounts are TiO$^+$, O$^+$ and O$_2^+$, and the presence of a small quantity of Fe$^{3+}$...
can be attributed to contaminants. The presence of Ti$^{3+}$ and O$^{+}$ ions could be detected, but the contribution of each species cannot be resolved, because of the same mass-to-charge ratio of these ions.

Table 2 gives the sample names and deposition conditions for each set of experiments.

**Table 1.** Fixed deposition conditions for all samples investigated in this work.

| Base pressure | ~ $5 \cdot 10^{-6}$ mbar |
|---------------|--------------------------|
| Working gas   | O$_2$, 99.5% pure        |
| Ti comm. pure |                          |
| Target features | Ti = 99.5% wt.      |
| Ø = 13 mm     |                          |
| Pulse duration| 1.5 ms                   |
| P pulses per second | 3                   |
| Duty cycle    | 4.5‰                    |
| Cathode-substrate distance | ~ 25 cm   |
| Substrate    | P-doped Si(100)         |

**Table 2.** Deposition conditions specifically set for each sample.

| Set | Sample name | Substrate temperature | Applied bias | Deposition time | Arc current | Working pressure $\cdot 10^{-5}$ mbar | Flow rate sccm |
|-----|-------------|-----------------------|--------------|-----------------|-------------|----------------------------------------|---------------|
| A   | A01         | 773                   | 0            | 60              | 400         | $\sim 60$                              | 30            |
|     | A02         | 773                   | 0            | 120             | 400         | $\sim 60$                              | 30            |
|     | A03         | 773                   | 0            | 240             | 400         | $\sim 60$                              | 30            |
|     | A04         | 773                   | 0            | 90              | 400         | $\sim 60$                              | 30            |
| B   | B01         | 573                   | 0            | 60              | 400         | $\sim 60$                              | 30            |
|     | B02         | 573                   | 0            | 120             | 400         | $\sim 60$                              | 30            |
|     | B03         | 573                   | 0            | 240             | 400         | $\sim 60$                              | 30            |
| C   | C01         | 423                   | 0            | 90              | 400         | $\sim 60$                              | 30            |
|     | C02         | 423                   | -10          | 90              | 400         | $\sim 60$                              | 30            |
|     | C03         | 423                   | -50          | 90              | 400         | $\sim 60$                              | 30            |
|     | C04         | 423                   | -70          | 90              | 400         | $\sim 60$                              | 30            |
| D   | D01         | 473                   | 0            | 240             | 100         | $\sim 60$                              | 30            |
|     | D02         | 473                   | 0            | 240             | 100         | $\sim 10$                              | 5.3           |
|     | D03         | 473                   | 0            | 240             | 100         | $\sim 6$                               | 2.3           |
|     | D04         | 288                   | 0            | 240             | 100         | $\sim 6$                               | 2.3           |
|     | D05         | 473                   | 0            | 180             | 200         | $\sim 60$                              | 30            |
|     | D06         | 473                   | 0            | 180             | 200         | $\sim 10$                              | 5.3           |
|     | D07         | 473                   | 0            | 180             | 200         | $\sim 6$                               | 2.3           |
|     | D08         | 288                   | 0            | 180             | 200         | $\sim 6$                               | 2.3           |

To determine the structure of the films, XRD measurements were carried out with a D500 Siemens® diffractometer, equipped with a Cu $K_a$ source ($\lambda_{K_a} = 0.154059$ nm). The diffractometer, in the Bragg-Brentano configuration, was operated at 30 mA and 40 kV; data acquisition was set to a stepsize of 0.04° for an acquisition time of 4 sec. for step. The range scan spans from 24° to 64° (2θ angle). Transmission electron micrographies were obtained with a Philips® CM 20 TEM operating at 200 kV, with a tungsten filament. Scanning electron microscopies were taken with a FEI® Quanta 200 3D, equipped with a tungsten filament; the sample thickness was evaluated from the micrographies.
3. Results

X-rays diffractometry

Set A

The temperature dependence of the TiO$_2$ films structure has been analyzed, and relevant reflections detected are indexed in the diagram (figure 2 (a)). The reflections at \( \sim 33^\circ \) (2\( \theta \)) and \( \sim 62^\circ \) (2\( \theta \)) correspond to the Si(100) substrate [21]. For both \( T_{\text{dep}} = 773 \) K and \( T_{\text{dep}} = 573 \) K, the reflections present in the patterns can be attributed entirely to the rutile phase. In particular, for the samples of the examined set, peaks at \( \sim 27.4^\circ \) (110), \( \sim 36.1^\circ \) (101), \( \sim 41.2^\circ \) (111) and \( \sim 54.3^\circ \) (211) are present for the patterns corresponding to all deposition times. The integrated intensity ratios \( I_{(101)}/I_{(110)} \), \( I_{(111)}/I_{(110)} \) and \( I_{(211)}/I_{(110)} \) does not have the same values of the ones of the reference pattern (PDF 021-1276): this is the case of a film growth along preferential directions [21]. The (111) orientation is often the most relevant, independently of the deposition time. New orientations appear after a deposition time of 120 min., at \( \sim 44.1^\circ \) (210) and \( \sim 56.6^\circ \) (220), and they cannot be any more distinguished after a deposition of 240 min., due to the superposition with the peaks corresponding to (111) and (211) planes. No peaks related to other phases have been found for higher deposition temperatures.

Figure 2, (a) and (b), right. XRD diffraction patterns for samples of set A (a) (from bottom to top: A01, A02 and A03) and set B (b) (from bottom to top:B01, B02 and B03)

Figure 3, below. XRD diffraction patterns for samples of set C from bottom to top: samples C01, C02, C03 and C04).

Set B
Several reflections appears in the diffraction patterns of set B samples, but this set shows different preferential growth orientations with respect to the ones already seen for the samples of set A. In this case, in fact, the most relevant peaks are at \( \sim 27.4^\circ \) (101), \( \sim 41.2^\circ \) (111), \( \sim 54.3^\circ \) (211) and \( \sim 62.7^\circ \) (002). The reflection corresponding to the (002) planes appears only for longer deposition times, that is 120 and 240 min.. For all the deposition times, the reflection corresponding to (110), which is the most relevant peak in the PDF reference pattern, is present in the diffractogram only as a broad and weak
peak. On the contrary, the peaks corresponding to (111) and (211) planes are already relevant from the sample with the lowest deposition time; the intensity of these peaks increase however with the deposition time.

**Set C**

For the deposition carried out at a temperature of 423 K, there is no evidence of a well crystallized phase: the application of a moderate substrate bias, up to -70 V, does not change, in a relevant way, the film structure and features (figure 3). A broad reflection corresponding to the (101) rutile plane is present in all the patterns presented in figure, at a 2θ angle of ~27.4°.

**Set D**

The diffraction patterns for the TiO\(_2\) coatings are grouped according to the arc current used during the deposition: figure 4 (a) and (b) are representative of the samples deposited with \( I_{\text{arc}} \) respectively of 100 and 200 A.

The reflections in the diffraction pattern of D01 (\( p_{\text{dep}} = \sim 6 \cdot 10^{-4} \) mbar, figure 4 (a)) are consistent with the presence of crystallized rutile. The peaks at ~27.4° (101), ~36.1° (101), ~39.2° (200), ~41.2° (111), ~44.1° (211), ~54.3° (211) and ~62.7° (002) do not correspond perfectly to the positions of the reference pattern, and this suggest the presence of residual stresses in the film. A reflection at ~25.3° suggests the presence of a small amount of anatase, with grains oriented in the direction (101). Decreasing the oxygen working pressure induces a decrease of the intensities of many rutile peaks. With a deposition pressure of ~6 \cdot 10^{-5} mbar (sample D03), the main rutile peak corresponding to (110) texture is still visible. For the same deposition pressure, and for a deposition temperature of 288 K, the coating is totally amorphous.

![Figure 4, (a) and (b). X rays diffraction patterns for samples of set D: (a) \( I_{\text{arc}} = 100 \) A and (b) \( I_{\text{arc}} = 200 \) A. See table 2 for the other experimental details.](image)

For a working pressure of ~6 \cdot 10^{-4} mbar, sample D05 deposited with an \( I_{\text{arc}} \) of 200 A presents reflections corresponding to rutile, the same pointed out for sample D01. In the range ~32° to ~37°, the irregular shape of the diffraction pattern can be ascribed to the superposition of several peaks, evidence of TiO\(_x\) phases with a lower oxygen amount than in rutile. Several small peaks can be attributed to Ti\(_2\)O\(_5\) (PDF 011-0193), at ~34.4°, ~35.7° and ~36.2°, related respectively to (-201), (102) and (-1-21) orientations. Other phases, like Ti\(_2\)O (PDF 011-0218), h-TiO (PDF 082-0803) or Ti\(_3\)O\(_5\) (PDF 040-0806), have reflections in the same angular range. Decreasing the deposition pressure, the intensity of reflections related to rutile also decrease. For deposition carried out at room temperature, only two broad peaks are present, in the range ~32° to ~37°, and a peak at ~61.1° (h-TiO (110)).
Electron microscopy
TEM micrographs (figure 5) show a sharp interface between the film and the substrate, suggesting coating good uniformity in depth. The structure of the film, for sample A04, present a fine columnar structure. The inset of figure 5 shows the selected area diffraction pattern (SADP). The presence of well crystallized rutile is confirmed for the highest deposition temperatures, and the rings corresponds to several orientations of the crystallites. SEM micrographs (an example is reported in figure 6), here representative of the structure of the film, shows the thickness of the film for sample D07. It was possible to estimate the thickness of the whole set of films: it ranges from few hundreds of nanometers, for most crystallized coatings, to some micrometers for the mainly amorphous ones. Increasing the deposition time from 60 to 240 min. Induces a thickness $t$ increase from $\sim$1.5 to $\sim$6 µm for group A samples and from $\sim$1.3 to $\sim$4.2 µm for group B samples. For group C samples, $t$ is $\sim$1.35 for C01, and it ranges between 0.7 ÷ 1.8 for C02 ÷ C04 coatings. In group D, $t$ shows the same trend for the two subgroups, even though its value is different for the two subsets: 0.3 to 0.5 µm for subgroup D01 to D04 and 0.5 to 0.9 µm for D05 to D08. In each group, the maximum thickness is reached for a pressure of $\sim$10$^{-4}$ mbar.

![Figure 5. Transmission electron micrograph of sample deposited with the following parameters: $T_{\text{dep}} = 773$ K, $p_{\text{dep}} = 6 \cdot 10^{-4}$ mbar, $U_{\text{bias}} = 0$ V, $t_{\text{dep}} = 90$ min.](image)

![Figure 6. Scanning electron micrograph of sample D07.](image)

Discussion
The rutile phase is formed by the reaction of the Ti$^+$ and O$_2^+$ [27], which are present in the plasma. The concentrations of the O$_2^+$ ions is higher for a lower total pressure, since they are produced through inelastic collisions with high-energy electrons. For lower pressure, the heating responsible for the formation of the rutile phase can be replaced by the energetic of depositing particles. Energetic particles can contribute to the nucleation of rutile crystallites, providing the necessary high mobility of adatoms and insuring the presence of migration effects [20]. Bendavid et al. pointed out also that rutile can also be obtained at room temperature, in presence of an high concentration of ionic species; the presence of such high amount of ionic species is a typical feature of plasma produced by FCA [20].

The ion total energy of the is due to several contributions, highlighted by Anders [28]: ions kinetic, excitation, ionization and cohesive energy, and the energy due to the application of a substrate bias, all play a role, and their relevance may vary with the deposition conditions. The distribution of kinetic energy, as a function of the applied arc current, is reported by Byon and al. [29], but in the range of arc current 100 to 400 A, it does not change in a relevant way. The ionization energies are, on the contrary, significant, especially for multiply charged ions. During FCA deposition, in the case of a bias applied to the substrate, the potential energy can exceed the kinetic energy [28].
Even though electron flux is responsible for chemical modifications of the surface [30], the plasma density is the major factor in the phase transformation [18]; in the present case, the dominant species is Ti\(^{++}\), but Ti\(^+\), TiO\(^+\) O\(^+\) and O\(_2\)^+ are also present [22]. The amount of metallic ions ejected by the cathode, and addressed as n\(_i\), i.e. plasma density without the contribution of external gases, is described by the following law: \( n_i \propto a_{arc} \). This relation describes the dependence of the metallic ion density in relation to the applied arc current, with \( a \) being the product of several constant, influenced by the deposition parameters and the geometry of the system.

The addition of a working gas changes the typology of ionic species in the plasma, the ion energy distribution [24] and the stoichiometric composition of the film. The overall gas pressure affects also the mean free path of the species of the plasma, so that the energy distribution of the plasma species can vary considerably [24, 31]. For example, in FCA deposition of TiN, Ivanov et al. [24] pointed out that the presence of nitrogen in the deposition chamber decreases \( r_{Ti} (Ti^{++}/Ti^+ \) ratio), probably for the enhanced energy transfer from doubly charged energetic Ti\(^{++}\) ions with N\(_2\).

When comparing groups A and B samples, we see that the transition between the fully crystallized rutile structure (\( T_{dep} = 773 \) K) and the quasi-amorphous phase obtained (\( T_{dep} = 288 \) K), is accompanied by a texture change of the deposited film. This texture change can be attributed to phenomena occurring at the surface of the sample, involving adatoms diffusion, nucleation and competitive growth of crystallites. The difference in thickness for A and B groups can be attributed to the different packing of Ti and O; in group B, only (101) and (111) preferred orientations are relevant, while in group A other relevant orientations are present. The prevalence of a specific texture clearly results in closer packing compared with the films without preferred orientation [32, 33].

For sets A and B, no bias was applied, and the only deposition parameter influencing the formation of different phases or states was the substrate temperature: this is responsible for atom diffusion, and rutile crystallite nucleation and growth, and other surface diffusing phenomena. Also in this case the oxygen pressure is sufficient for the formation of TiO\(_2\); the formation of rutile can be attributed to the creation of thermal spikes on the surface, as highlighted by Martin and co-workers [15]: a localized region, at the impact site, is melted and rapidly crystallized after the temperature drop during the following cooling stage. This effect plays an important role when the spike lifetime (\( 10^{-11} - 10^{-12} \) s) is higher than the lifetime of the collision cascade [18].

The results shown in Figure 3 are representative of the effect of a substrate bias. It is responsible for the formation of oxygen-deficient titanium oxides, TiO\(_x\) with \( x < 2\). The films deposited at even lower temperatures are amorphous. The thermal energy provided through the heating of the substrate in this case is too low to induce a consistent crystallization of the coating [34]. We detect the presence of a broad rutile peak, and of a peak attributed to an oxygen-deficient titanium oxides phase. This can be due a dominant ion bombardment effect. The increased energy provided from the bias to the ions can give a contribution for TiO\(_x\) with \( x < 2\). The thickness evolution for group C can be attributed to the concurrent phenomena of resputtering, more evident for C02, and of the increased ion flow for higher applied bias (sample C04).

The thickness variation in group D is due to the increased amount of Ti ions available with higher arc currents; these energetic ions impinging on the substrate also contribute to change the structure of the coating, making it amorphous, and increasing consequently its thickness [12, 32, 33]. For this set of samples, when a \( I_{arc} = 100 \) A is applied, the formation of a crystallized rutile is observed, even for a temperature of 473 K and an oxygen pressure of \( \sim 6 \cdot 10^4 \) mbar, while at the same pressure and temperature, with a \( I_{arc} = 400 \) A is applied at the cathode, there is no crystallized rutile [21]. Decreasing the oxygen partial pressure in samples D01 \( \div \) D04 does not prevent the rutile crystallization, even though the reflection intensity decreases, and reflections due to the presence of poorly crystallized phases are still present. For samples D05 to D08, substoichiometric oxides are present when the pressure is decreased. This behaviour can be attributed to the higher Ti ions amount in D05 to D08 samples than in D01 to D04, because of the higher arc current applied [18]. On the other side, the working pressure is an important parameter in filtered cathodic vacuum arc (FCVA) deposition, because an increasing pressure of the process gas is responsible for decreasing the average
charge state and the average energies [23, 25, 35]. When $I_{arc}$ is increased up to 400 A, the coating is almost totally amorphous (sample C01). With the same parameters, that is $I_{arc} = 400$ A and $p_{O_2} = 6 \cdot 10^{-4}$ mbar, Zhirkov and coworkers [22] deposited a set of sample, with a crystallinity degree increasing with increasing temperature. In these conditions, Ti and O amounts are sufficient for the formation of rutile.

According with XRD patterns for samples D01 and D05, crystalline rutile was achieved also with lower arc currents. This means that for $I_{arc} = 100$ to 200 A, the involved ion energy is somewhat higher, allowing the crystallization of rutile and of a small amount of anatase. This outcome is apparently in contrast with results presented by other authors. Bendavid and coworkers [18] states that a critical ion current density (CICD) is needed for a phase transformation. The crystalline phase is formed for higher ion current densities than the critical one, which was 0.5 mA/cm$^2$. CICD depends on plasma ion density, which is related to the arc current used for deposition [18]. New investigations and experiments are needed to better understand the phenomena which contributed to this particular result (Ti ions - reactive O gas interaction, charge state and ion energy plasma distribution, substrate resputtering, etc.).

Conclusions
Thin titanium oxide films were deposited with a filtered cathodic arc system. Effects of substrate temperature and bias were investigated in the present work. Rutile/amorphous transition was achieved, by means of thermal energy and without any substrate biasing. A rutile structure is obtained for temperatures higher than 773 K and an amorphous phase for temperatures below 423 K.

Different mechanisms can be responsible for the structure of the films: (1) thermal energy, provided by substrate heating, (2) energetic ion bombardment from the plasma, (3) arc ion current, responsible for the amount of titanium ejected from the cathode, and (4) amount of oxygen. Thermal energy and substrate bias can affect the properties of the coating; in particular, for a $t_{dep} = 473$ K and a $I_{arc} = 100$ A well crystallized rutile was obtained, while for the same temperature, with an $I_{arc} = 400$ A poorly crystallized films were obtained. By decreasing the pressure, well crystallized rutile was obtained even for low arc currents.

The formation of titanium oxides like Ti$_3$O or Ti$_2$O$_3$, for low temperature and substrate biasing up to 70 V, can be attributed to the synergy of several phenomena, such as resputtering, bombardment of metallic energetic ions and reduced atom mobility due to the low amount of thermal energy. The mechanisms involved in the formation of amorphous films, even for a high ion current density corresponding to $I_{arc} = 400$ A, has to be clarified. Further experiments needs to be carried out, taking into account different deposition parameters, to better understand the formations of the preferred orientations at higher temperature deposition.

Acknowledgements
The research was performed as part of the “Interuniversity Attraction Poles” IAP-PAI program financed by the Belgian government (BELSPO). The authors would like to thank the EXCELL Network of Excellence (NMP3-CT-2005-515703) for its support.

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