Preparation and Characterization of MOCVD-Fabricated TiO$_2$ Thin Films Deposited on Titanium for Biomedical Applications

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Titanium oxide (TiO$_2$) thin films devoted to biomedical application were obtained using the chemical vapour deposition method. The films were deposited on titanium substrate using a low-pressure reactor with various precursor molar fractions and deposition temperatures. The influence of these parameters on film properties was studied by using electron microscopy images, roughness measuring, X-ray diffraction, contact angle measuring and cyclic polarization tests.

Keywords: titanium, TiO$_2$, MOCVD, thin films

Titanium is still the most commonly used metal material to manufacture orthopaedic prostheses on account of its very good mechanical properties, corrosion resistance and biocompatibility [1].

Titanium surface properties are important factors due to the interactions between the implants and biological environment occur at the surface after implantation. [2] The metal surface can be modified by forming or adding an oxide layer of which morphology and thickness strongly depend upon initial treatment [3-5]. It is widely recognized that the presence of an oxide film is crucial to the application of titanium [6]. There is a number of scientific and technical knowledge published about the oxide film [7-10].

The technique of chemical vapour deposition is one of the various industrial processes to deposit a thin film on a substrate. The procedure, consisting using of metalo-organic compound as a precursor (MOCVD), results in relatively low deposition temperatures and generally nature-friendly processes [11]. The surface of objects with complicated shapes (as are implants and prostheses) can be conformally coated by operating at low pressure (LP-MOCVD) [12,13]. Varied film morphologies and microstructures can be obtained by selecting several experimental parameters: nature of the precursor, nature of the carrier gas, optional use of an additional reactive gas, deposition temperature ($T_{\text{deposition}}$), total pressure ($P_{\text{total}}$), precursor molar fraction ($X_{\text{precursor}}$), gas flow rates ($Q_{\text{total}}$, $Q_{\text{precursor}}$) [11,14].

We have used the LP-MOCVD technique to grow TiO$_2$ thin films on titanium with varied morphologies and micro- (nano-) structures in order to study the influence of film characteristics on cell cultures and on the protection of Ti substrates against corrosion by biological fluids. We present here our results about films preparation, as well characterization and corrosion tests.

Experimental part

Preparation of Ti substrates

The substrate samples were 1mm thick discs sliced from 10 mm diameter titanium rods (99.6% purity, Good Fellow Ltd.). The deposition surface of the discs was mechanically polished with wetted metallographic SiC paper grade 4000 (grain size 5 µm). The discs were ultrasonically cleaned in acetone, then in boiling alcohol, and finally rinsed with distilled water.

Deposition of thin films by the LP-MOCVD technique

The method known as Metal-Organic Chemical Vapor Deposition (MOCVD) consists in making the vapour of a metal-organic complex (the precursor) to react with a heated surface (the substrate) so that the solid reaction product deposits and progressively forms a thin film on the substrate surface.

The MOCVD system used in this study was built as a hot wall reactor (fig. 1). The precursor was titanium isopropyl oxide [Ti(OCH(CH$_3$)$_2$)$_3$] (TTIP), a liquid at room temperature. TTIP vapour phase was carried to the reactor by bubbling pure nitrogen (99.9992% purity) through the precursor placed in a thermo-stated bath. The partial pressure of TTIP vapour was fixed at constant value by the temperature of the bath. Nitrogen...
was also used as a dilution gas. Dilution and carrier gas flows were controlled by flow rate meters. The deposition temperature was measured with a thermocouple K plugged into the reaction zone. The overall pressure was controlled by means of a vacuum pump equipped with a butterfly valve, controlled with an automatic system. Once deposition was achieved, the reactor was purged with nitrogen for about 20 min.

TiO₂ thin films were grown at varied temperatures and TTIP ppm concentrations, the operating conditions being presented in tables 1-3.

### Scanning electron microscopy (SEM)
Observation of films surface topography was carried out with a LEO-435 scanning electron microscope, operating at 15 kV and a source current intensity of 99 pA. The working distance has varied between 10 and 20 mm. The images were analyzed at magnifications of 5000X, 10000X and 15000X.

### X-ray diffraction (XRD)
X-ray diffraction patterns were recorded using a vertical diffractometer (Seifert 3000t) equipped with a graphite monochromator and a Cu anticathode (λCuKα = 1.54098 Å). The patterns were recorded using the θ-θ mode, analyzed with the Analyze program and compared with the corresponding JCPDS files.

### Wettability
Water contact angles were measured using a DIGIDROP Contact Angle Meter (GBX Scientific Instruments). For each specimen, the measurement was performed at three different places of the surface by lying 10 µL of distilled water. The contact angle was measured immediately after drop deposition, with a digital camera, using the program Windrop.

### Roughness
Surface roughness of the specimens was measured with a profilometer Tencor. Three measurements were made for each specimen and a mean value was calculated. The surface area analyzed was of 0.4 mm². Profile traces were recorded both in the center and at the periphery of the specimen.

### Cyclic voltammetry
Cyclic curves were recorded with a VOLTALAB equipment, using simulated body fluid (SBF) as an electrolyte. Platinum and Ag/AgCl electrodes served as an auxiliary electrode and a reference electrode, respectively. The electrode potential was cycled between –800 mV and +4000 mV, at a scan rate of 2 mV/s. Prior to measurements, the specimens were maintained in the solution for 30 min.

### Results and discussion
#### Films thickness
The films show a good uniformity with different bright colors depending on their thickness (interferential colors). Films thicker than 1500 nm are almost opaque. Reflectance variation presents oscillations of which amplitude and periodicity are related to film thickness, roughness and optical indices (fig. 2). Optical indices used for TiO₂ were refractive index n = 1.37019 and k = 1.63088. This method loses accuracy on increasing film thickness (hence opacity) because the oscillations flatten.

Obviously, the two techniques used to measure film thickness have their limits. This fact leads to relatively

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**Table 1**

<table>
<thead>
<tr>
<th>Characterization of the samples</th>
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</table>
| To determine the thickness of the films, the substrates were weighted before and after deposition. A first value e₁ was derived for the film thickness by combining film mass (m), substrate area (A) and we took for the density (d) of bulk titanium oxide: e₁ = m/Ad. This technique does not take into account the porosity of the film and the amount of side-deposited oxide. Neglecting porosity results in a slightly underestimated thickness. For a height of 1 mm and a diameter of 10 mm, the side area of the substrate is equal to 40% of the area of the disc. The film deposited on the side surface of the substrate is certainly not as uniform and thick as the film deposited on the disc surface. However, its neglect is likely to appreciably overestimate the thickness of the film deposited on the disc surface. The thickness of the TiO₂ films was also estimated optically (e₂) by recording the reflectance versus wavelength on a NC-UV-VIS Ocean Optics instrument and using the program NanoCalc. A mirror polished Ti surface was used as a reference. |"
large difference in plotting the growth rate variation (fig. 3).

Kinetics of film growth. We have noticed that the two major parameters influencing the growth of TiO₂ coatings: are the deposition temperature and the molar fraction of the precursor. Figure 3a shows the effect of deposition temperature on the growth rate as an Arrhenius plot [11]. To complete the study, we have performed growth measurements for a sample prepared at 300°C - 350°C. Between 300°C and 350°C, the growth rate increases much more rapidly than at higher temperature, meaning that the reaction rate is kinetically limited. Above 350°C, the limiting step is the diffusion through the static boundary layer. These observations are in agreement with data reported by Zhang et al. [15] and Conde-Gallardo et al. [16]. One can notice on the graphs of figure 3 that the discrepancy between the two sets of measurements (weighting and reflectometry) increases with thickness increasing, in agreement with the above remarks about the limits of each two methods.

Film morphology. Scanning electron microscopy was carried out on films deposited at different temperatures and molar fractions to examine the surface morphology. The observed morphologies vary from fine-grained equiaxed (fig. 4a) to columnar (fig. 4b,c), depending on the growth conditions. The low growth rate, due to either low temperature or low molar fraction, produced a fine-grained equiaxed structure. Moderate growth rates produced columnar microstructure with segmentation along grain boundaries. High growth rates produced fully dense, highly oriented columnar microstructure.

It is observed that the surface morphology of the films does not change considerably in the temperature range 350-600°C, taking into account that the thickness of the film is around 1µm. Figures 4c,d,e show surfaces resulting from experiments performed with the same concentration χ = 260 ppm at different temperatures. They show small crystals, about 100 to 300 nm in size, rather uniformly and densely packed. Increasing the ppm concentration leads to bigger crystals size, as seen from figures 4a,c,b.

The surface roughness values for the samples are presented in table 4. These results are in accordance with the values found for commercially available implant components. Wennerberg et al. [17] suggested that the roughness can be described as smooth for abutments, minimally rough for roughness from 0.5 to 1µm, moderately rough for 1 to 2µm, and rough for 2 to 3µm. Roughness has been shown to be a key feature for the quality of cell growth. From in vitro studies, it was found that osteoblasts develop better on rough surfaces [6,18]. In contrast, epithelial cells and fibroblasts were better attached to the smoother surfaces than the rougher.

![Figure 3](image3.png)

**Fig. 3.** Variation of the growth rate of TiO₂ films on titanium with the deposition temperature (χ_{TTIP}=260 ppm), (a) and the TTIP ppm concentration (T_{deposition}=350°C) (b)

<table>
<thead>
<tr>
<th>Sample</th>
<th>χ_{TTIP} (ppm)</th>
<th>T_{precursor} (°C)</th>
<th>Thickness (nm) (mass weighing) (e₁)</th>
<th>Thickness (nm) (reflectometry) (e₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T350/76</td>
<td>76</td>
<td>25</td>
<td>477</td>
<td>340</td>
</tr>
<tr>
<td>T350/260</td>
<td>260</td>
<td>41</td>
<td>1273</td>
<td>950</td>
</tr>
<tr>
<td>T350/1035</td>
<td>1035</td>
<td>60</td>
<td>2836</td>
<td>1650</td>
</tr>
</tbody>
</table>

<p>| Table 3 |
|---------|----------------|-------------------|----------------------------------|----------------------------------|</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>T_{deposition} (°C)</th>
<th>Deposition time (min)</th>
<th>Thickness (nm) (mass weighing) (e₁)</th>
<th>Thickness (nm) (reflectometry) (e₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T350/260</td>
<td>350</td>
<td>180</td>
<td>1273</td>
<td>950</td>
</tr>
<tr>
<td>T450/260</td>
<td>450</td>
<td>120</td>
<td>955</td>
<td>800</td>
</tr>
<tr>
<td>T600/260</td>
<td>600</td>
<td>120</td>
<td>1000</td>
<td>910</td>
</tr>
</tbody>
</table>
Film composition. Figure 5 presents the XRD patterns for samples prepared with $\chi = 260$ ppm at different temperatures. The films are crystalline. Three phases show up: the titanium substrate and two allotropic forms of TiO$_2$, namely anatase and rutile. The oxide grown at 350°C is anatase only. Increasing amounts of rutile are observed in the films grown at 450°C and 600°C, respectively.

Wettability. The TiO$_2$ thin films appear very hydrophilic, after exposition to natural light. The hydrophilic character of TiO$_2$ exposed to UV light is very well documented in the literature [21].

Once deposited on the surface, the water drop spreads rapidly. Measured contact angle for the two series of experiences are presented in table 5.

The titanium oxide surface in contact with water is highly hydroxylated. The prevalence of hydroxide groups and the fact that the surface does not carry a strong electric charge might account for the excellent biocompatibility of titanium oxide surfaces. This is an important feature with respect to the interaction of the surface with ions such as calcium and phosphate that can modify the charge properties of the surface, as well as the interactions of the surface with amino acids, peptides and proteins, which generally contain domains of different electric charges [6].

Corrosion resistance. Because of the contact with body fluids for long periods of time, resistance against corrosion is an important parameter to consider in choosing an implant material [22]. The films resistance against corrosion was tested in a simulated body fluid (SBF). Figure 7 shows the potential-current density curves for polished and TiO$_2$ coated commercially pure Ti samples with a scan rate of 2 mV/s.

It was noticed from this figure that for uncoated Ti sample, the potential range of passivity extends from 0 to 2200 mV while for coated samples the passivity domain increases up to 2800 mV for the film grown at 450°C. Above approx. 2200 mV polarization, the current density increases for all the samples, but it increases much more for uncoated Ti. In all cases, the current densities in the range of the body potential (400–500 mV) are in the domain of passivity, which means that no destruction process can affect the material surface. It can be seen that samples with TiO$_2$ film obtained by
Table 4
CHARACTERIZATION OF SURFACE ROUGHNESS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ra(μm)</th>
<th>Rq(μm)</th>
<th>Sample</th>
<th>Ra(μm)</th>
<th>Rq(μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T350/76</td>
<td>0.122±0.030</td>
<td>0.189±0.030</td>
<td>T350/260</td>
<td>0.077±0.020</td>
<td>0.151±0.040</td>
</tr>
<tr>
<td>T350/260</td>
<td>0.077±0.020</td>
<td>0.151±0.040</td>
<td>T450/260</td>
<td>0.060±0.015</td>
<td>0.114±0.013</td>
</tr>
<tr>
<td>T350/1035</td>
<td>0.646±0.020</td>
<td>1.341±0.060</td>
<td>T600/260</td>
<td>0.543±0.050</td>
<td>0.890±0.015</td>
</tr>
</tbody>
</table>

*R is the average surface roughness of all points from a plane fit to the test part of the surface, and Rq is the square-root of the average of the measured height deviation.

Table 5
THE VALUES WATER CONTACT ANGLE MEASURED IN THE FIRST SECONDS AFTER DEPOSITION OF THE DROP

<table>
<thead>
<tr>
<th>Sample</th>
<th>T350/76</th>
<th>T350/260</th>
<th>T350/1035</th>
<th>T450/260</th>
<th>T600/260</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle</td>
<td>13</td>
<td>10</td>
<td>9</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>degrees</td>
<td></td>
<td></td>
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</table>

Fig. 6. Drop and contact angle for water on: a) cleaned titanium substrate; b) TiO₂ - MOCVD coating on titanium – T350/260 surface sample

Fig. 7. Potentiodynamic curves obtained in SF solution for mechanically polished Ti and two samples with TiO₂ deposited by MOCVD at 350°C, 260 ppm and 450°C, 260 ppm

Conclusion
Thin films of TiO₂ have been deposited by low-pressure MOCVD on titanium substrates at temperatures ranging from 350°C to 600 °C using titanium isopropyl oxide [Ti(OCH(CH₃)₂)₄] as a precursor. The results indicate that the films are crystalline and consist of anatase at 350°C and of mixed anatase and rutile at 450 and 600°C. In this temperature range a diffusion kinetic regime was observed.

SEM images show that homogeneous coatings, with minor roughness were obtained by using a simple equipment and MOCVD technique. Grain size increases markedly with increasing precursor concentration from 76 to 1035 ppm at 350°C. Increasing the temperature...
from 350 to 600°C had a less marked effect on grain size. The films prepared at 350 and 450°C and with precursor concentration of 76 and 260 ppm are smooth. The roughness is about 7 times higher when either the deposition temperature is 600°C or the concentration is 1035 ppm. All TiO$_2$ films are strongly hydrophilic, exhibiting water contact angles between 13 and 6°.

Titanium resistance against corrosion in SBF was improved by the MOCVD TiO$_2$ coatings. A film prepared at 350°C, showed better protection than a film prepared at 450°C.

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Bibliography
2. ANSELME, K., Biomaterials, 21, 2000, p. 667
9. SUL, Y.T., Biomaterials, 24, 2003, p.3893
20. BOYAN, B.D., HUMMERT, T.W., DEAN D., SCHWARTZ, Z., Biomaterials 17, 1996, p.137

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