Comparative study of RF reactive magnetron sputtering and sol-gel deposition of UV induced superhydrophilic TiOx thin films

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Abstract. TiOx and TiOx-like thin films were deposited on PEEK (Polyether ether ketone) substrates by low-temperature RF reactive magnetron sputtering and the sol-gel method. The resulting films were compared in terms of their properties and photoinduced hydrophilicity. Both techniques resulted in uniform films with good adhesion that can be switched to superhydrophilic after exposure to UVA radiation for similar time periods. In addition, the sputtered films can also be activated and switched to superhydrophilic by natural sunlight due to the higher absorption in the visible spectrum compared to the sol-gel films. On the other hand, the as deposited sol-films remain relatively hydrophilic for a longer time in dark compared to the sputtered film due to the differences in the morphology and the porosity of the two materials. Thus, depending on the application, either method can be used in order to achieve the desirable TiOx properties.

1. Introduction

It has been almost two decades since Wang et al. [1] revealed the unique photohydrophilic property of crystalline TiO2, i.e. its ability to become superhydrophilic upon UV irradiation [2], [3]. Nevertheless, low-temperature deposition methods are required for the deposition of photoinduced hydrophilic TiO2 films on thermosensitive substrates aiming to advanced applications, such as microfluidic and biomedical devices [4], [5]. The RF reactive magnetron sputtering is considered to be a promising low temperature method for deposition of high-quality TiO2 thin films [6], [7]. The sol-gel route of metal alkoxides is a widespread method due to the fact that it is a cost-effective, simple and equipment-free procedure for deposition of oxide films. However, dense and crystalline pure oxide thin films can be obtained only after intense post annealing. Thus, the choice of the deposition technique of functional coatings is of great significance, since it has a major impact on the properties and quality of the deposited film.

In this work, we deposited TiOx thin films on PEEK substrates by low-temperature RF reactive magnetron sputtering and the sol-gel method. The deposited films were compared in terms of their UV induced hydrophilicity, hydrophilicity persistence in dark, as well as their optical and structural properties. The differences in the latter properties were directly reflected on the radiatively induced

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superhydrophilicity and the dark storage recovery indicating that each of these techniques can be implemented, depending on the desired wettability properties of the TiO$_x$ films.

2. Experimental

2.1. Sol-gel spin coating deposition

For the deposition of TiO$_x$-like thin films, an isopropanol (iPrOH, PENTA 99.8%) solution of titanium tetraisopropoxide (TTiP, Sigma Aldrich 99.999%) and distilled water were used. The detailed procedure for the preparation of the deposition solution has been previously described in Ref. [8]. The molar ratios of TTiP and H$_2$O to iPrOH was 0.22 M and 1.38 M respectively, which corresponds to a hydrolysis ratio H = 6.3. The films deposited on PEEK were allowed to dry at room temperature, in dark storage for at least 24 hours resulting in TiO$_x$-like xerogel thin films.

2.2. RF reactive sputtering deposition

A magnetron source (ST-20, AJA International) with a 99.999% purity Ti metal target of two inches in diameter was used for the deposition of TiO$_2$ thin films. The total process pressure was kept at 3 mTorr by regulating the gas flows of argon and oxygen through two MKS mass flow controllers, and the partial pressure of oxygen was P$_{O_2}$/(P$_{Ar}$+P$_{O_2}$) = 0.35. The TiO$_2$ films were deposited onto unheated PEEK and microscope glass slides with dimensions 15mm × 15mm which were lying on a cyclical substrate holder at 100 mm above the Ti target. The experiments were carried out at different RF (13.56 MHz) power values (150 W, 250 W, 400 W, 500 W).

2.3. Thin film characterization

A DektakXT stylus profilometer was used for the film thickness measurements. The ir structure was determined by X-ray diffractometry (Siemens D-5000) using CuKa radiation (1.54 Å) at 40 kV and 30 mA at the 2θ range of 20° to 70°. The surface wettability was evaluated by carefully placing 2 μl distilled water drops on the surface and calculating the apparent contact angle using a Kruss DSA100S goniometer. The transmittance (%) spectra of the films were recorded by a UV-VIS spectrophotometer (Perkin Elmer l-35). The films morphology was monitored by using FE-ESEM (FEI QUANTA 250 FEG).

3. Results

Both methods resulted in transparent TiOx thin films. A 450-nm-thick xerogel TiOx-like film (SG) and the 400-W sputtered, 30-nm-thick TiO$_2$ film (SP-400W), which was deposited at a rate of 3.5 nm/min, were used for the comparison of the two deposition methods

3.1. Structure, morphology and optical transparency

The sol-gel films were amorphous due to the room temperature process and the absence of further annealing. In addition, a high content of organic groups in its network or as terminal groups will remain in the film [9]. On the other hand, the high-vacuum sputtering process resulted in crystalline oxide films.

![Figure 1. XRD patterns of the sol-gel derived TiOx-like film (SG) and the sputtered TiO$_2$ film (SP-400W) deposited on glass slides.](image-url)

The XRD pattern of the SP-400W TiO$_2$ film (figure 1) show mixed phases of anatase (101), (200) and rutile (110). It is also worth noticing that during the sputtering process at a 400-W input power, the substrate reached 100 °C due to plasma heating, surface reactions and ion bombardment. This temperature rise will favor the formation of nanocrystals [10]. The mean crystallite sizes (table 1) were estimated by applying Scherrer’s equation at the main peaks of the XRD pattern [11].
Table 1. Structural and optical characteristics of the sol-gel deposited xerogel TiOx film and the 400 W RF M sputtered TiO2 film.

| Method                     | Approximate mean crystallite size | Refractive index | Optical $E_g$ | Porosity |
|-----------------------------|----------------------------------|------------------|---------------|----------|
| RF M Sputtering (400 W)     | 22.3 (anatase 101) 18.6 (anatase 200) 17.3 (rutile 110) | 2.24 (450 nm) 2.1 (632.8 nm) | ~3.2 eV | 0.3 |
| Sol gel                     | Amorphous                       | 1.24 (450 nm) 1.15 (632.8 nm) | ~3.65 eV | 0.9 |

Moreover, the SG and SP-400W films exhibit very different surface morphology. The SEM image of the SG film shows a uniform smooth surface with nano-sized porosity, whereas the SP-400W film exhibits a denser nanocomposite structure (figure 2). In figure 3 we present the % transmittance spectra of the two films deposited on microscope glass slides. Both films are transparent throughout the visible range 400 nm – 700 nm, although the sputtered film exhibits interference fringes indicating differences in the refractive indices of the materials. A significant difference of the adsorption edge between the sputtered and the sol-gel film is also observed. The absorption edge of the SP-400W film is approximately at 380 nm, while the SG film is blue-shifted and absorbs light only at wavelengths below ~340 nm. The absorption shift to the lower wavenumbers for the SG film can be attributed to the reduction of the grains size (figure 2, SEM images) and can be interpreted as a quantum size effect [12].

The optical constants of the films were estimated using the Pointwise Unconstrained Minimization Approach (PUMA) for the fitting of the transmission data [13]. The SG film exhibits a low refractive index $n = 1.15$ (632.8 nm) which is closer to a polymer rather than an oxide film. Moreover, the porosity of the two films was calculated by equation [14]:

$$p = \frac{n_d - n_{meas}}{n_d - 1},$$

where $n_d$ is the refractive index of the dense anatase [15] and $n_{meas}$ is the calculated index of the films. The energy band gap ($E_g$) of the materials was calculated from Tauc’s relation [16]. The SP-400W $E_g$ is estimated at 3.2 eV, which is very similar to that of the pure anatase, while the SG film’s $E_g$ is much larger at 3.65 eV and confirms the inefficiency of this film to absorb the near visible range radiance.

### 3.2. Hydrophilicity

The contact angles of water with the as-deposited films were measured right after the sputtering deposition and after drying for 24 hours for the SG films. The as-deposited sputtered film is superhydrophilic with a contact angle <10°, while the contact angle of SG films ranges from 30° to 40°. Nevertheless, both surfaces suffer from aging, which is observed by the rise of
The contact angle mainly during the first 10 days after the deposition. The sputtered film changes to hydrophobic (CA >100°), whereas the SG film contact angle reaches a plateau at ~80°.

The evaluation of the photoinduced hydrophilicity was performed by measurements of the films CA during their illumination with intense UV light (254 nm, 8 mW/cm²), and also during their exposition to the day’s natural sunlight (figure 4a). Upon 15 to 20 minutes of UV illumination, both the SP-400 film and the amorphous SG xerogel film become superhydrophilic exhibiting a 0° contact angle, i.e. total wetting of their surface, no matter their initial wetting state (hydrophobic or relatively hydrophilic). On the other hand, during their exposure to the natural sunlight’s spectrum, only the sputtered film reaches superhydrophilicity after 3 h of illumination. The contact angle value of the SG film drops from 88° to 50° after 2 h of exposure, but lower CA cannot be achieved due to the high transmittance of the film in the UV-A and the near visible wavelengths range (figure 3).

Finally, in order to monitor the hydrophobic recovery of the illuminated (UV and sunlight) films, the materials were stored in dark and CA measurements were performed at specific time intervals. The SP-400W film exposed to UV radiation or to sunlight return to its hydrophobic state within 3 days. On the other hand, the SG films exposed to UV light remains hydrophilic for a longer period with CA ~50° for one week. Lee et al. [17], showed that the slow recovery of CA in dark is closely related to the higher surface roughness. The higher porosity of the SG xerogel film probably provides a larger surface area. Thus, the slow dark recovery rate of the SG film cannot be attributed to the surface roughness, but rather to a higher surface density of chemisorbed –OH after the UV-induced excitation.

4. Conclusions
The sol gel TiOx films deposited at room temperature without annealing exhibit good uniformity and transparency and also UV-induced superhydrophilicity. Despite the amorphous structure, the SG film
converts to superhydrophilic after 20 min of irradiation with UV light. The RF reactive sputtering results in crystalline TiO$_2$ films at low temperature, which also show UV-induced superhydrophilicity in a short exposure time (15 min).

The comparison of the photoinduced performance of the films shows two significant differences: (a) the sputtered film is suitable for outdoor applications, since it can become superhydrophilic also upon exposure to natural sunlight, while the SG film cannot be activated, and (b) the sputtered film’s wettability switches between hydrophobic (CA>100°) in dark and superhydrophilic upon UV or sunlight exposure, while the SG film is intrinsically more hydrophilic and remains hydrophilic for a longer time in dark. Depending on the application, both methods can result in good quality films.

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