Supporting information:

Synthesis of anatase(core)/rutile(shell) nanostructured TiO$_2$ thin films by magnetron sputtering methods for dye-sensitized solar cell applications

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1. Magnetron sputtering in DC and high pulse peak regime

In magnetron sputtering techniques, it is possible to tune the phase constitution of titania thin films for example by biasing the substrate during the growth[1]. However, our previous results show that the use of a substrate bias leads to the densification of the nanosculpted material[2]. Alternatively, it is also possible to obtain different phases in titania thin films using ionized plasma such as the one generated in High Power Impulse Magnetron Sputtering (HiPIMS)[3]. In a recent work[4], the authors have correlated the normalized energy flux during the growth with the phase constitution of the coatings evolving from a pure anatase phase to a pure rutile when increasing this normalized energy, which corresponds to the energy transferred to the growing film by the impact of charged and neutral particles, chemical reactions and the bombardment by infrared radiations. So, the use of DC and HiPIMS discharges enable to grow anatase and rutile titania, respectively.

2. Glancing angle deposition technique (GLAD)

We reported in[2] that Reactive Magnetron Sputtering technique in glancing angle configuration (RMS-GLAD) enables the engineering of nanosculpted and crystallized TiO_2 films. Basically, by tilting (α angle) and rotating the substrate during deposition, different types of nanostructures can be obtained. Inclined columns are obtained when working with a fixed α angle higher that 60°; (ii) zig-zag are generated when rotating the substrate by successive rotation of the substrate by a 180° angle in the latter configuration and plots or helical structures can be grown continuously rotating the tilted substrate during deposition (substrate rotation speed is thus labelled as ϕ)[2]. Each nanostructure is characterized by a given porosity (inter-columnar space) that depends on the columnar tilt. Using these nanosculpted films as photo-anode is expected to insure a better charges transport as they provide a more direct pathway towards the external circuit so that recombination at the grain boundaries and exposure to the electron acceptors in the electrolyte is avoided. In this way, faster transport and a slower recombination rate lead to a minimization of charge losses. So, we have decided to combine DC or HiPIMS discharges with GLAD technique to grow the desired anatase(core)/rutile(shell) nano-pillars.

3. Experimental setup

All experiments were carried out in a cylindrical stainless steel chamber (see **Figure Figure** S1). A dry primary pump is combined with a turbo-molecular pump (Edwards nEXT400D 160W) to evacuate the chamber down to a residual pressure of 10^{-6} Torr. The introduction of argon and oxygen is performed using two distinct mass flow meters. The total flow is kept constant to 15 sccm (standard cubic centimeter per minute) and the $O_2/(Ar + O_2)$ flow ratio (labeled as $O_2\%$) can be varied from 0 to 100%. The gases are mixed prior to being injected in the vacuum chamber. For the deposition experiments, $O_2\%$ is always set to 17% in order to grow stoichiometric TiO_2 films as the discharge is maintained, in every case, in the oxidized regime. The total working pressure is continuously maintained at the set point value of 0.13 Pa (1 mTorr) by a throttle valve in order to have a ballistic flux which allows a shadowing effect. An unbalanced magnetron cathode was placed in front of the substrate, at the top of the chamber on which a 2-inch in diameter and 0.25-inch thick Ti target (99.99% purity) was connected. The target/substrate distance was fixed at 10 cm for dense films ($\alpha = 0°$) and 7 cm for the nanostructured ones ($\alpha = 85°$). In these cases, the pressure–distance product equals 1.30 Pa·cm and 0.91 Pa·cm, respectively. Silicon single crystals with (100) orientation and whose resistivity is 5.10^{-3} Ω·cm were used as substrates and are placed at the ground potential and at ambient temperature.
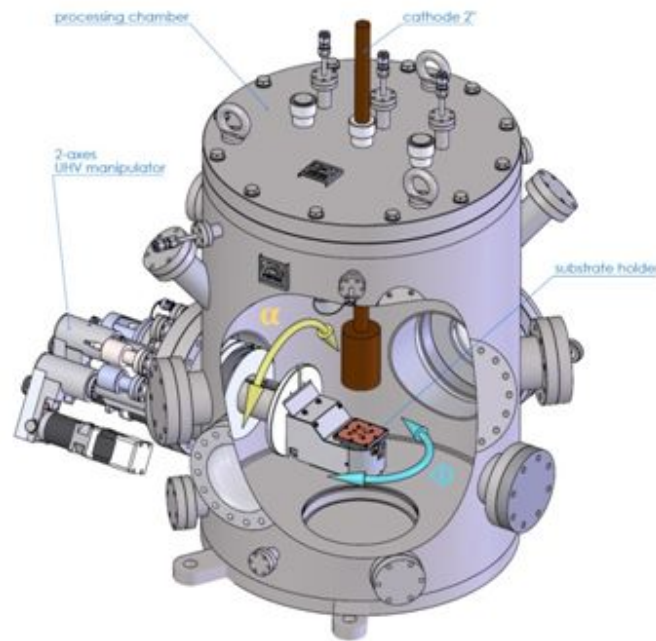

Figure S1 : Sketch of the deposition chamber used in this work.

In order to modify the phase constitution of the TiO_2 films, the Ti target was sputtered either in DC mode or in HiPIMS regime. For the DC mode, an Advanced Energy MDK 1.5 K power supply was used. The power was fixed at 150 W, corresponding to a power density on the target surface of 7.5 W/cm² which was calculated taking into account the target surface exposed to the plasma ($\sim$ 20 cm²). In HiPIMS regime, a Lab-made power supply based on a one-quadrant chopper topology has been used allowing the generation of short high power pulses at the cathode [5]. A wide bandwidth 1 MHz Tektronix TCP303 Hall effect current probe combined with a TCPA300 amplifier has been connected to a Tektronix TDS2024B digital oscilloscope to measure the discharge current while the discharge voltage has been measured with a high voltage probe P5100. We have to highlight that the discharge voltage is measured at the output of the Lab-made power supply, not directly at the cathode. The pulse duration and the time-averaged power were fixed at 15 µs and 150 W, respectively, but the repetition frequency (f) and the discharge voltage (V_D) were modified independently.

4. Optimization of the growth parameters

Based on the results obtained by Cormier *et al.* on the influence of the discharge mode on the phase constitution of TiO_2[4], we studied the growth of TiO_2 by DCMS and HiPIMS in order to define the optimal parameters to grow anatase and rutile TiO_2 films. These experiments are performed in conventional configuration ($\alpha = 0°$).

Figure Figure S2 shows the HiPIMS current and voltage signals for the two experimental conditions studied in the present work. These conditions differ by the pulse frequency (f) and the associated peak current (i.e. the time-average power and the pulse length are fixed at 150 W and 15 µs, respectively, and the discharge voltage weakly varies). Based on these curves, we can measure that when f = 4 kHz, the peak current is of 12 A, defined as a low ionization rate situation, while for f = 2 kHz, it is of 30 A, defined as the high ionization rate situation. It is indeed reported that the ionization rate of a HiPIMS discharge is associated with the peak current value[3,6].
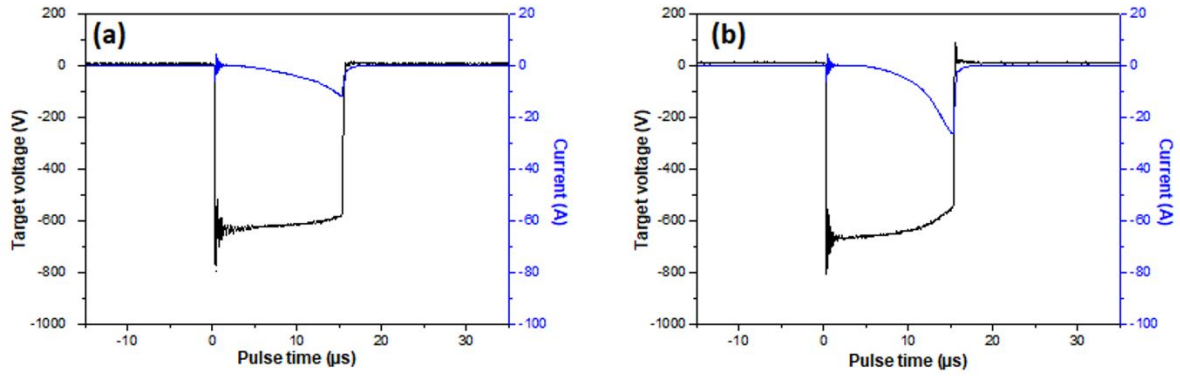
Figure S2 : HiPIMS signal when the pulse frequency is set to (a) 4 kHz; (b) 2 kHz.

These two HiPIMS conditions, as well as standard DCMS sputtering, have been utilized to grow TiO_2 films. **Figure Figure** S3 shows the XRD pattern measured for each of the deposited films. In DC mode, a constant negative voltage is applied to the target leading to deposited species at a moderate energy and the film is slightly crystallized under the anatase structure (JCPDS card N° 84-1286). Hence, the thin films must be annealed at 500 °C for 2 hours in air atmosphere in order to obtain bigger anatase crystals. On the other hand, this energy can be as 6 times higher by applying high pulse peak voltage and current to the target in HiPIMS mode, promoting the growth of the rutile phase (JCPDS card N° 88-1175), without annealing, which is the high-temperature phase of the titania[7].
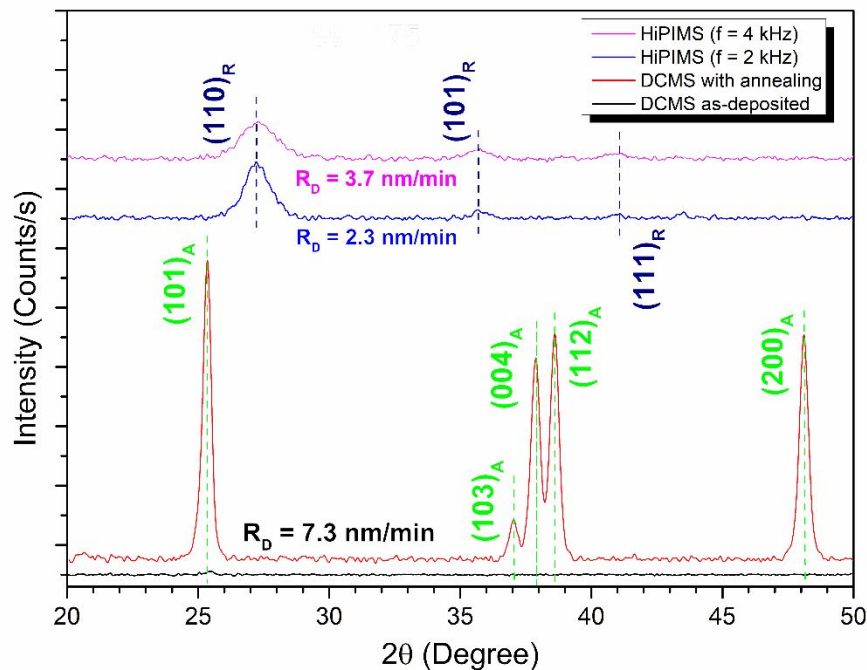

Figure S3 : GIXRD patterns of TiO₂ thin films synthesized by DCMS before annealing (black line) and after annealing (red line) and by HiPIMS with pulse frequency of 2 kHz and 4 kHz (blue and pink lines, respectively).

The prize to pay when using HiPIMS is a strong decrease of the deposition rate (R_D) from ~ 7.3 nm/min in DCMS to ~ 3.7 nm/min in HiPIMS (f = 4 kHz) and ~ 2.3 nm/min in HiPIMS (f = 2 kHz). In the HiPIMS community, it is accepted that this decrease is attributed to the non-linear energy dependence of the sputtering yields. This induces the self-sputtering target by metallic ions produced in the dense plasma created close to the sputtering target. Consequently, these are trapped toward the cathode surface by the high negative voltage. If the self-sputtering yield is inferior to unity, the deposition rate decreases because of less metallic ions reach the substrate surface. Furthermore, gas rarefaction has been highlighted during high current pulse inducing a decrease of the argon density in the neighborhood of the sputtering target[8,9]. Through these prelaminar data, we conclude that we can indeed tune the phase constitution of the TiO_2 films by choosing the adapted plasma conditions.

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