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Controlled formation of anatase and rutile TiO₂ thin films by reactive magnetron sputtering

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We discuss the formation of TiO₂ thin films via DC reactive magnetron sputtering. The oxygen concentration during sputtering proved to be a crucial parameter with respect to the final film structure and properties. The initial deposition provided amorphous films that crystallise upon annealing to anatase or rutile, depending on the initial sputtering conditions. Substoichiometric films (TiO_{x<2}), obtained by sputtering at relatively low oxygen concentration, formed rutile upon annealing in air, whereas stoichiometric films formed anatase. This route therefore presents a formation route for rutile films via lower (< 500 °C) temperature pathways. The dynamics of the annealing process were followed by in situ ellipsometry, showing the optical properties transformation. The final crystal structures were identified by XRD. The anatase film obtained by this deposition method displayed high carriers mobility as measured by time-resolved microwave conductance. This also confirms the high photocatalytic activity of the anatase films. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4931925>]

Titanium dioxide (TiO₂) has been commercially produced from the early twentieth century and has traditionally been utilised as additives to polymeric binders,¹ toothpaste,² and sunscreens.³ In recent years, there has been an increasing interest in applications of TiO₂ related to environmental remediation⁴, energy generation⁵ and biomedicine.⁶

TiO₂ has three well-known polymorphs at atmospheric pressure: rutile, anatase and brookite. Brookite is hardly studied due to its metastable crystal structure and according difficulty in synthesis. The research to date has focused on anatase and rutile polymorphs instead. The properties of TiO₂ significantly depend on the microstructure and crystallographic phase. For instance anatase finds application in photovoltaics,⁷ electrodes for Li-ion batteries⁸ and photocatalysis⁹ for water and air purification. Rutile, due to its higher refractive index, is mostly studied for optoelectronics, semiconductor electronics¹⁰ and optical coatings.¹¹ Hence controlling the crystalline structure of TiO₂ is of paramount importance.

Titanium dioxide thin films can be synthesized by techniques including sol-gel,¹² suspension coating,¹³ electron beam evaporation,¹⁴ electrochemical deposition,¹⁵ sputtering,^{16,17} pulsed laser deposition (PLD)¹⁸ and many other methods.^{19,20} Among these, reactive sputtering provides accurate control regarding composition and morphology. The resulting TiO₂ thin films present high uniformity over large areas which makes them attractive for both industrial applications and fundamental studies.

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Regardless the synthesis route, the initial crystalline TiO_2 phase is usually the metastable anatase due to the faster recrystallization caused by its lower surface free energy compared to rutile. Generally, it is only possible to synthesize rutile at low temperatures by hydrothermal methods and precipitation of crystalline TiO_2 .^{21–23} Besides, rutile can be obtained through high-temperature treatment, above 600°C , by the non-reversible transformation of anatase to rutile (ART).^{24–28}

Besides ART, the rutile phase of TiO_2 was obtained by applying a negative bias on the substrate during reactive sputtering²⁹ or by modifying the RF power.³⁰ In addition, there are some attempts to modify the crystalline phase after deposition, e.g. by N^+ ion implantation.³¹

Here, we study the formation of rutile and anatase polymorphs of titanium dioxide by controlling the oxygen flow rate during DC reactive magnetron sputtering followed by annealing in air. The annealing process is analyzed through in-situ monitoring the ellipsometric parameter (ψ) for both sub-stoichiometric and stoichiometric TiO_2 using spectroscopic ellipsometry (SE). The optoelectronic properties of the films were studied using time resolved microwave conductance (TRMC) and were related to the photocatalytic characteristics.⁹

Magnetron reactive sputtering deposition was conducted at constant target DC power of 500 W and constant process pressure of 6×10^{-3} mbar. The target was pre-sputtered for 2 minutes with a closed shutter. The substrate-target distance was set at 4.4 cm and the substrate was rotated at 5 rpm during the whole deposition process for enhanced uniformity. Thin films were sputtered on silicon p-type (100) substrates in Ar/O_2 atmosphere with additional controlled oxygen flow rate. The thickness of the deposited thin films were ~ 200 nm. All of the depositions were performed at room temperature without substrate heating. Following this, selected samples were annealed in an atmospheric environment for 1.5 - 8 h at 500°C with heating and cooling rates of 2°C min^{-1} . X-ray photoelectron spectroscopic (XPS) measurements were performed using Quantera SXM with monochromatic $\text{Al K}\alpha$ at 1486.6 eV X-ray source. All spectra were shifted to the binding energy of the adventitious C 1s peak at 284.8 eV. The crystal structure of the thin films was investigated by XRD (Bruker D2) using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA working in the θ - 2θ mode. Electroless time-resolved microwave conductance (TRMC) using X-band (8.2-12.4 GHz) microwaves (> 100 mW), generated by a voltage controlled oscillator (Sivers IMA-Sweden) were carried out at ca 8.4 GHz, i.e. the resonant frequency of the loaded cavity. For this measurement the depositions were carried out on quartz substrates due to their excellent transmission properties. A full description of the set-up is given elsewhere.³² The photocatalytic performance and intrinsic surface reaction rate constant were analyzed following the method described in our previous study.⁹

As seen in figure 1 two different sputtering modes; metallic and oxidized appeared as the oxygen flow rate increased. Up to oxygen flow rate of 4 sccm represents the metallic mode resulting in a sub-stoichiometric film. At higher flowrates, a stoichiometric film is obtained. The abrupt increase in

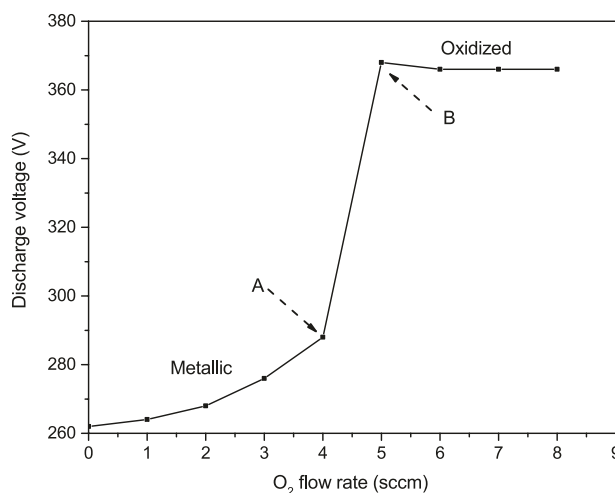


FIG. 1. Discharge voltage as a function of the oxygen flow rate during reactive magnetron sputtering.

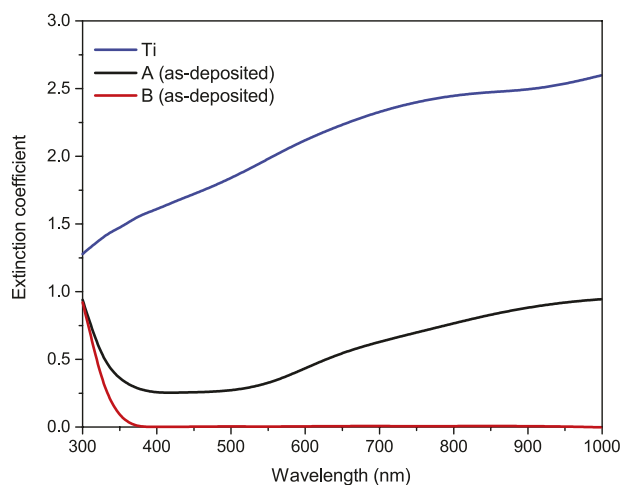


FIG. 2. Extinction coefficient spectra measured by ellipsometry on a metallic Ti film, as deposited film (A) sputtered at 4 sccm and as deposited film (B) sputtered at 5 sccm oxygen.

discharge voltage between these two regimes is due to the formation of TiO_2 on the target, requiring a higher discharge voltage.^{33,34}

Two samples, from here on named A and B, which were sputtered at 4 and 5 sccm oxygen flow rate respectively (figure 1), were selected and further analysed. The extinction coefficient spectra of A, B and Titanium (Ti), which was sputtered in absence of oxygen, are shown in figure 2.

The extinction coefficient of the metallic Ti film is evidently the largest. Film A (4 sccm oxygen flow rate) displays some reminiscence of extinction, while film B (5 sccm oxygen flow rate) is completely transparent in the visible region of the light spectrum. The visible light absorption in film A is due to the presence of oxygen vacancies.^{35,36} No further differences in terms of extinction coefficient were observed at oxygen flow rates higher than 5 sccm. Figure 3 presents high resolution XPS scans of the Ti 2p for sample A before and after annealing in air. Sample B, which was sputtered in the oxidized region, matches with Ti 2p scan of stoichiometric TiO_2 both before and after annealing.³⁷ The presence of the shoulder peaks in Ti 2p (Ti^{3+}) of the unannealed sample A indicate oxygen deficiencies.³⁷ The shoulder peaks disappeared following the annealing and matched to sample B suggesting the formation of stoichiometric TiO_2 .³⁷

In addition to the XPS scans of the Ti 2p and O 1s core level, the compositional measurement following 4 nm removal of surface by an Ar gun on sample A reveals $\text{TiO}_{1.8}$ and TiO_2 before and after annealing, respectively. It is observed that the extinction coefficient of sample (A) strongly reduces in the visible range after annealing. The film becomes stoichiometric TiO_2 with absorption in the UV region of the light spectrum.³⁴

The in-situ extraction of the refractive index and extinction coefficient changes during annealing of the sub-stoichiometric sample (A) has proven challenging. This is probably due to strong alterations of the sample's optical properties during the process. In particular, a composition gradient in the normal direction as a result of the oxidation reaction develops. To capture this adequately, such a gradient would require grading the B-spline optical model by, for instance, segmenting the sample in several layers with distinct optical properties. This however would introduce a large number of fitting parameters making the procedure less reliable. For similar reasons, attempts to elucidate morphological or structural changes within the sample in the in-situ process proved unreliable. Therefore, in figure 4 the dynamic evolution of raw ellipsometry data (ψ parameter, the amplitude component of the complex reflectance ratio) at 3 different wavelengths is shown during annealing in air (from 25 °C to 500 °C with 5 °C/min ramp rate). The different wavelengths are chosen to represent 3 distinct regions of the sample optical response. At 230 nm both the as-deposited and annealed samples are absorbing, 365 nm represents the approximate position of the band gap of the annealed sample, and 800 nm represents the far visible light. The examination of the ψ dynamics shows that the oxidation onsets at around 150 °C and proceeds to full conversion

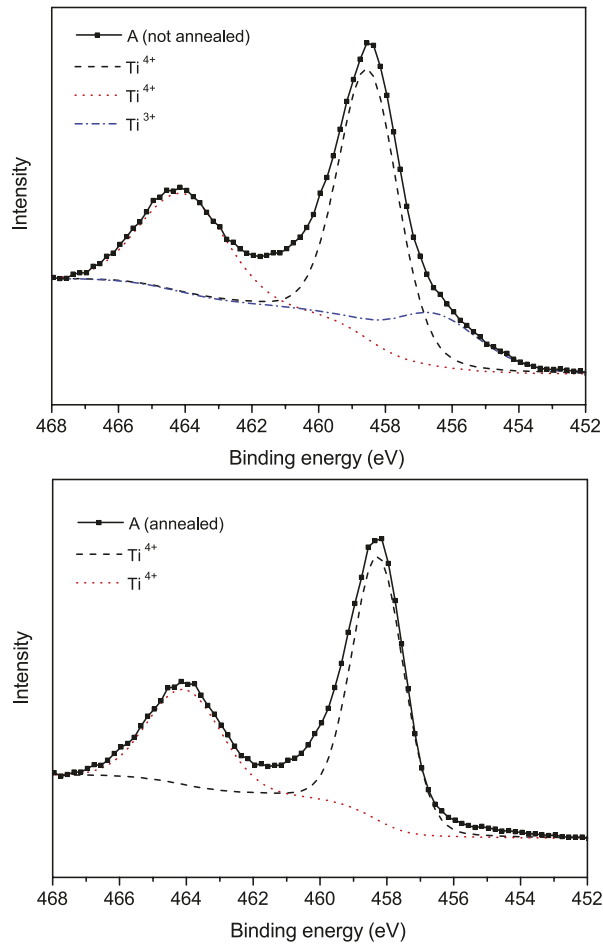


FIG. 3. High resolution XPS scan of the Ti 2p core level and their de-convolutions of the as-deposited and annealed thin film (A) sputtered at 4 sccm oxygen flow rate.

in about 1 hour after reaching 500 °C, after which it slightly change during the cooling ramp. In particular the large variation in 800 nm data signify the rapid development of transparency as the oxidation reaction proceeds. The inset shows the resulting extinction coefficients before and after annealing.

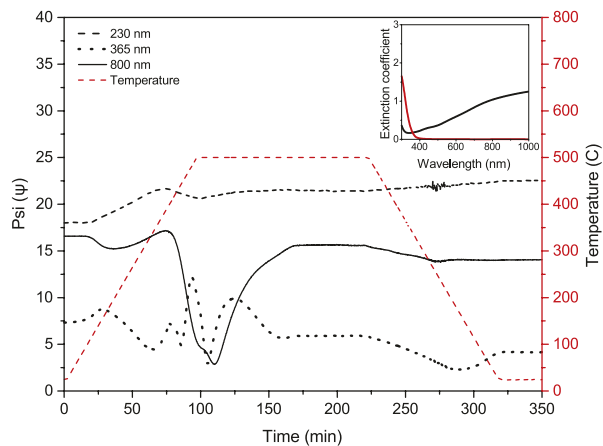


FIG. 4. Ψ (ψ) for film (A) at three different wavelengths during annealing in air with indicated temperature ramp. The inset shows the extinction coefficient before (black) and after (red) annealing in air.

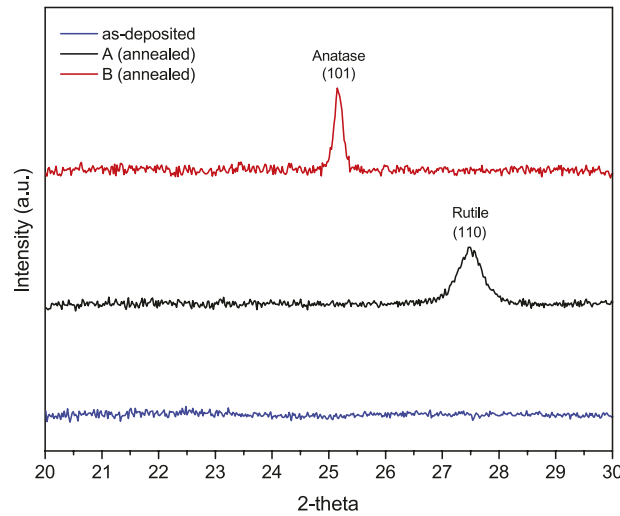


FIG. 5. X-ray diffraction patterns of the sputtered thin films as-deposited, (A) deposited at 4 and (B) 5 sccm oxygen flow rate after annealing in air.

Figure 5 presents the XRD patterns of the as-deposited film, film (A) and film (B) after annealing. What is interesting in this figure is that although the both films are similar in terms extinction coefficient and composition after annealing, film A and B display diffraction peaks that correspond to rutile (110) and anatase (101), respectively.³⁸ The extracted refractive index of film A and B after annealing is 2.75 and 2.54, respectively, being in close agreement with reported refractive indices for rutile and anatase phases.^{39,40} The extracted band gaps after annealing are 3.08 and 3.2 eV which also corresponds to the value for the rutile and anatase polymorphs respectively.^{41,42}

Figure 6 shows the intensity normalized photoconductance transients obtained on pulsed optical excitation at $\lambda=300$ nm for sample A (insert) and B, both after annealing corresponding to rutile and anatase respectively. Since the photon energy used is well above the bandgap of both polymorphs, optical excitation leads to the formation of mobile carriers resulting in a fast rise of the microwave signal. The decay of the signals is due to immobilization of mobile carriers in trap states or electron hole recombination. The incident laser intensity was varied from 4×10^{12} photons/cm² to 167×10^{12} photons/cm² per pulse. It is important to note that although normalized photoconductance transients are shown, the maximum signal size increases first from about 2×10^{-3} cm²/Vs to

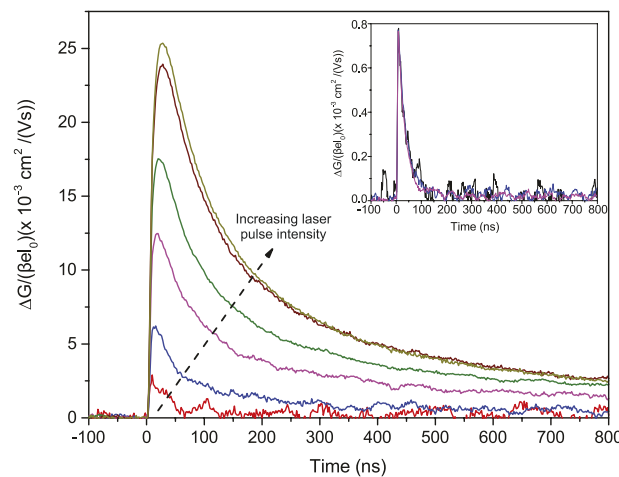


FIG. 6. Intensity normalised photoconductance transients after excitation by laser pulse at different intensities on sample A (insert) and B after annealing.

about $25 \times 10^{-3} \text{ cm}^2/\text{Vs}$ with increasing intensity. This has been observed previously for various anatase nanostructured TiO_2 and is attributed to trap filling.^{43–46} When using even higher laser intensities, the signal decreases again due to the fact that multiple charge carrier pairs are generated per particle leading to rapid sub-nanosecond charge carrier recombination. With higher intensities also the lifetime of the charge carriers reduces. Interestingly, the TRMC signals recorded for sample A (rutile) display a very different photophysical behavior. The maximum signal sizes are more than an order of magnitude smaller which can well be explained by the fact that for rutile the charge carrier mobilities are lower. More importantly, the lifetimes are much smaller ($<100 \text{ ns}$) limiting the period the photo-induced carriers are available for consecutive reactions. All is in full agreement with reduced photocatalytic activity found previously for rutile thin films.⁴⁷ The anatase thin film demonstrated significantly high photocatalytic activity as reported in our previous study.⁹

To conclude, our findings provide a methodology for deposition of thin films of TiO_2 with selective crystal phase based on the oxygen concentration during reactive magnetron sputtering. Thin films of TiO_2 were deposited at low (A) and high (B) oxygen flow rates, resulting in sub-stoichiometric and stoichiometric films respectively. During annealing in air these films correspondingly turn into anatase and rutile, as confirmed by XRD and spectroscopic ellipsometry. The anatase film furthermore displayed high photoconductance with long lifetime charge carriers and consequently strong photocatalytic activity.

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