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Titanium dioxide thin films from a low-frequency dual magnetron sputtering process

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ABSTRACT

TiO_2 films were sputtered by a bipolar pulsed-DC process from a pair of sub-stoichiometric TiO_x targets. By utilizing process gas analysis, we find that the largest impact on a reliable batch process lies in both the control of the adsorbed humidity and inlet of oxygen sputtering gas. After establishing this understanding, we show that high quality films can be deposited for any pulsing frequency between 0.5 kHz and 50 kHz with the lower frequencies having a beneficial impact on refractive index, the substrate temperature, and less energy losses at the sputtering power supply.

INTRODUCTION

Due to their opacity to ultraviolet light, high refractive index, and durability, titanium dioxide (TiO_2) films are a popular choice in glass coating applications as well as in fuel cells, displays, and photovoltaic devices. Increasingly, TiO_2 sputtering process designs utilize ceramic, sub-stoichiometric (TiO_x) targets to achieve high stability while at the same time providing a high sputtering rate [1,2]. These targets can be operated in various power configurations, whereby a DC-driven plasma usually offers the highest deposition rate [3]. DC sputtering of a single target is possible, yet due to the insulating nature of TiO_2 it might lead to a disappearing anode over time. Here, we operate a bipolar pulsed-DC sputtering process, where we apply frequencies as low as 0.5 kHz between the two rotatable sub-stoichiometric targets. We investigate the effect of this changing frequency on the film properties, as well as we investigate the process specifics of sputtering these films in a drum coater.

EXPERIMENTAL RESULTS

Deposition Procedure

Films were deposited in an industrial-sized drum coater, which is schematically depicted in Figure 1. It consists of a high-vacuum chamber with a rotatable drum of approximately 1.2 m diameter, subdivided into 15 same-sized segments. The height of the drum is 70 cm, while the length of the two rotatable TiO_x ($x = 1.8 – 1.9$) targets (supplied by GfE Fremat GmbH) is 60 cm. The rotatable targets were bipolarly powered by the pulsed-DC combination of Advanced Energy's Ascent AMS and Ascent DMS generators. An oscilloscope was utilized for measuring the differential voltage as well as the current between the targets. The oscilloscope probes were placed at the atmospheric site of the target endblocks. A high-pressure-capable quadrupole mass spectrometer (MKS HPQ3S) was mounted near the sputtering compartment.

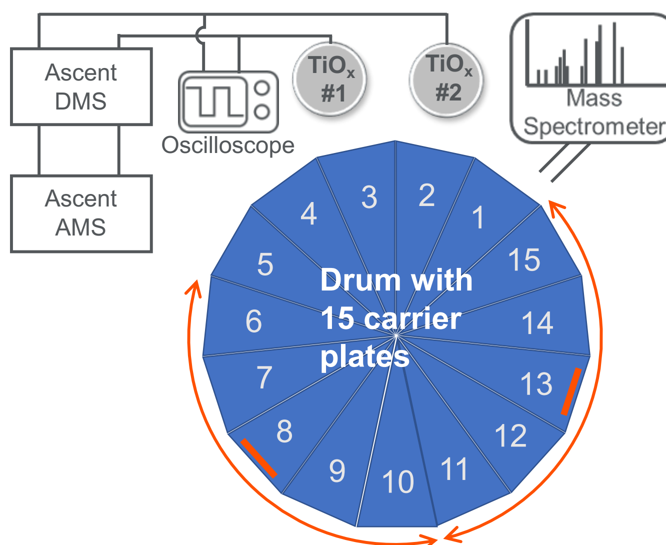

Figure 1. Top-view schematic of the experimental setup at the drum coater. Arrows depict the oscillating range of the drum during deposition of the samples at position 8 and 13, respectively.

To deposit TiO_2 films, the plasma was ramped over 15 min to a power of 24 kW, which here always refers to the power measured with the oscilloscope. Depending on the pulse frequency, the set power at the DC generator thus had to be adjusted accordingly and was between 24.4 kW for up to 3 kHz and up to 25.8 kW for 50 kHz. During the ramp-up and pre-sputtering phase, the drum was oscillating around a position where there is no deposition on the actual samples at positions 8 and 13. The samples are centimeter-sized pieces of 525 µm

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thick Si(100), Si with 500 nm thermal oxide, and 110 µm thick glass, which were then coated by oscillating the drum in a way that the samples pass the sputtering compartment 18 times with an angular speed of the drum of 1 rpm – an in-line speed of ca. 3.77 m/min. The substrate temperature during sputtering was recorded by means of thermocouples attached to 300 µm thick glass wafers. As described above, per each pumping-down of the chamber repeatably two samples were deposited.
The resulting films on the silicon pieces were optically analyzed with an ellipsometer (J.A Woollam alpha-SE) to accurately obtain thickness and refractive index. The model used for the TiO_2 film was a single Tauc-Lorentz oscillator with a band gap of $E_g \approx 3$ eV [4]. For the minority of the films with an apparent absorption in the visible range, the Tauc-Lorentz model gives a poor fit and a B-Spline model was used instead. The films on the 110 µm thick glass slides led to a bending of that substrate, which was then used to calculate the residual film stress.

Influence of Oxygen and Water

The films in this paper were deposited at a constant argon flow of 200 sccm as well as a smaller amount, between 8 to 22 sccm, of oxygen. Although gas flows and pumping speed remained constant during deposition of a film, it became apparent from the gas analysis that partial pressures of the relevant gases are far from constant. This is related mostly to the adsorption and release of water vapor from the drum and chamber walls. Factors that influence the water content during sputtering include, but are not limited to, base pressure, duration of chamber opening, amount of pre-sputtering, and outside humidity and temperature. As the drum coater had to be regularly opened for sample exchange, pumping to a very low base pressure where the water content might be negligible was unfeasible.

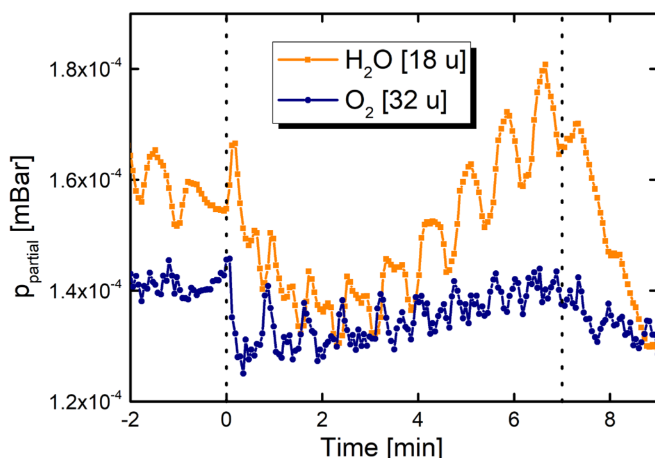

Figure 2. Water and oxygen partial pressures during deposition of a TiO_2 films in the drumcoater. Vertical lines show the beginning and end of the sample oscillating in front of the cathodes.

An example of water and oxygen partial pressures during a film deposition can be seen in Figure 2. We can see that at the onset of deposition, the apparent partial pressures of both gases decrease. This is due to the already warmed up sputtering compartment being faced by the still cold surface of the drum in the sample's vicinity. The released water from the sputtering compartment thus finds a place where it can firstly adsorb. During deposition, the drum surface around the sample warms up significantly, releasing adsorbed water again into the gas phase, visible as the increase in water partial pressure during the second half of the deposition time.

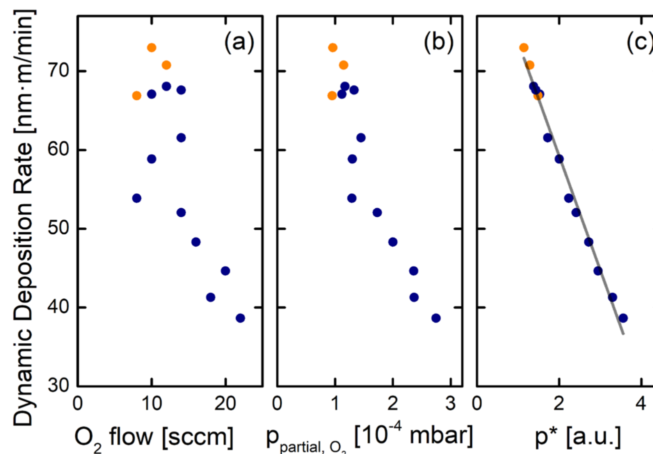

Figure 3. Dynamic deposition rate for films deposited at 20 kHz under various oxygen flows and base pressures. Absorbing films are plotted in orange.

Firstly, samples with a variation in oxygen gas flows as well as base pressures ranging from 4.1×10^{-7} mbar to 5.0×10^{-5} mbar were sputtered at a constant frequency of 20 kHz. The dynamic deposition rate as a function of simply the oxygen flow, see Figure 3(a), shows that higher gas flows are to be associated with a slower deposition rate, however with a large scatter. The rates could be different by ca. 20 % for the same oxygen flow. Looking at the time-averaged oxygen partial pressures during the deposition instead of the flow, see Figure 3(b), the scatter already reduces, yet there are still variations of ca. 10 % of deposition rate for the same oxygen partial pressure. By a pairwise comparison between films with similar oxygen partial pressure but different water partial pressures and vice versa, we find that oxygen partial pressure has a roughly 3-5 times larger effect on the deposition rate than water partial pressure. To link both values together, we introduce the dimensionless pressure parameter p*, which is a weighted sum of the oxygen and water partial pressures:

$$p^* = \frac{p_{partial,\ O2} + 0.3\times p_{partial,\ H2O}}{10^{-4}\ \text{mbar}}$$

This merges partial pressures of both relevant gases into a single parameter by assigning them relative weights based on

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their influence on the deposition rate. As can be seen in Figure 3(c), the dynamic deposition rate as a function of this pressure parameter then follows a monotonic trend with much higher predictability, a linear fit results in a decrease of (15±1) nm·m/min per unit of p*.

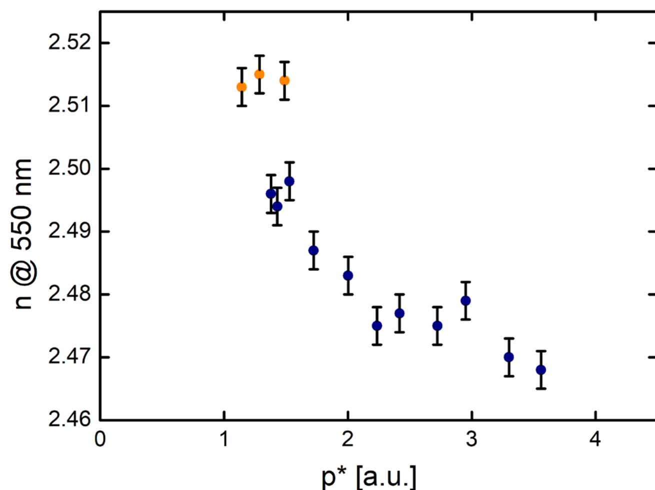

Figure 4. Refractive index of TiO_2 films sputtered at 20 kHz as a function of parameter p*. Absorbing films are plotted in orange.

The refractive index at 550 nm wavelength of the deposited ca. 290 nm thick films can be seen in Figure 4, plotted as a function of p*, showing a decreasing trend. For p*<1.3 the films have a non-negligible absorption in the visible range, while for p*>1.5 all films are transparent. In the intermediate range transparency depends on whether p* stems from a higher amount of oxygen with little water (transparent) or vice-versa (non-transparent). The highest refractive index for a transparent film obtained in this set of samples is 2.498.w

Influence of Pulsing Frequency

A second set of films was deposited with pulsing frequencies between 0.5 kHz and 50 kHz, while keeping the base pressure, the oxygen flow, as well as the partial pressure of water before the first deposition approximately constant between the samples. Naturally, the second sample in each batch always had a lower level of water due to the ongoing warming-up of the chamber surfaces. Yet, the oxygen flow was kept constant for all samples at 12 sccm, leading to transparent samples without compromising much on the deposition rate.

Looking at the dynamic deposition rate, see Figure 5(a), we can see that it remains constant for all pulsing frequencies with a measured average value of 60.6 nm·m/min and a standard deviation of 2.2 nm·m/min. Due to the rate being greatly affected by the gas composition, we can use the linear dependence determined earlier in Figure 3(c) to adjust the values to an average p* = 1.82 for all the films. After this adjustment the dynamic deposition rate remains stable, yet with a much smaller standard deviation of 0.9 nm·m/min.
Similarly, the residual stress of the films remains unaffected by the pulsing frequency, see Figure 5(b). The refractive index stays nearly constant at a value of ≈2.493 for frequencies below 7 kHz and drops beyond this frequency down to a value of ≈2.482 at 50 kHz, see Figure 5(c). The substrate temperature as shown in Figure 5(d), increases by 125 K for frequencies below 3 kHz with an even larger rise at higher frequencies, up to 131 K for pulsing at 50 kHz.

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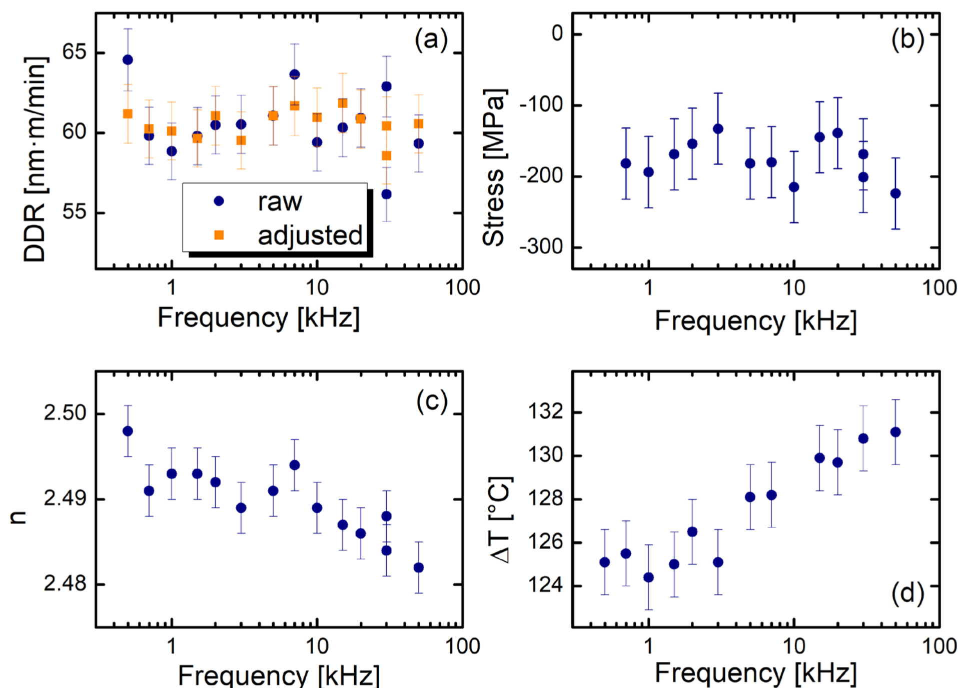

Figure 5. Dependence of (a) dynamic deposition rate, (b) residual stress, (c) refractive index, and (d) temperature rise at the substrate as a function of bipolar pulsing frequency.

CONCLUSIONS

TiO_2 films sputtered from pre-oxidized TiO_x targets with a bipolar pulsed-DC waveform show a remarkably robust film quality and deposition rate with the deposition rate being virtually independent from the pulsing frequency. A much larger effect on deposition rate and refractive index stems from the present reactive gases in the sputtering compartment. Besides the intentionally introduced oxygen, the unavoidable water content also must be considered for a highly repeatable process. In a production tool a control loop would be advisable, which regulates the oxygen gas flow based on the measured partial pressures of oxygen and water. If one requires a high refractive index and/or a lower heat load to the substrate, pulsing frequencies of 3 kHz and lower would yield the best results. Lowering the frequency below 3 kHz while keeping the nominal power at the power supply constant, as it is possibly already at its maximum, will lead to a higher power at the magnetrons and thus to an increase in deposition rate without sacrificing film quality or process stability.

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FOR FURTHER INFORMATION

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