

# High Power Pulse Reactive Sputtering of TiO<sub>2</sub>

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**Key Words:** Pulsed sputtering deposition      Reactive deposition  
Partial pressure control

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## ABSTRACT

Transition mode sputtering of TiO<sub>2</sub> was accomplished using High Power Pulse Magnetron Sputtering (HPPMS) in combination with rotatable magnetron cathodes and IRESS process control hardware. Pulses of 0.5 MW at a frequency of 100 Hz were used to reactively sputter TiO<sub>2</sub> from a metallic target. Results from HPPMS are compared to DC sputtering at similar conditions. While an increase in deposition rate is not seen, the indices of refraction of films deposited by HPPMS are higher.

## INTRODUCTION

High power pulsed magnetron sputtering (HPPMS) yields high plasma densities and high ionization of sputtered materials [1-3]. This has led to carbon film formations with higher densities than typical sputtering techniques [4].

In this paper we describe reactive sputtering of dielectric films with HPPMS. Until these experiments HPPMS has been confined to the sputtering of materials like carbon [4] and copper and the reactive sputtering of conductive films like CrN [5]. HPPMS consists of sputtering at a very high pulse power (0.5-1 MW) at a low frequency (50-100 Hz). In some configurations there is no additional power applied to the cathode in between pulses. Since the interval between pulses is so long, one theory is that a target will become fully reacted between pulses, making controllable reactive sputtering in the transition between metal mode and a fully reacted target impossible for dielectric films. The objective is to first determine if controllable reactive sputtering can be accomplished with HPPMS. The second objective is to determine the advantages and disadvantages of depositing optical quality TiO<sub>2</sub> with this sputtering method. Changes in rate, index of refraction, or crystalline structure would all be of interest to the application of large area glass coating for improvements of throughput or thin film quality. A comparison of metallic titanium films is also made.

## EXPERIMENT

The vacuum system used for this testing was of the in-line glass coating type. Glass substrates are capable of scanning in front of the magnetron. Testing was accomplished on a 90 mm

diameter Titanium rotary cathode with a 200 mm source to substrate distance.

Prior to any of the tests described, a base pressure of at least  $1 \times 10^{-5}$  Torr was achieved and the Ti target was pre-cleaned by direct current (DC) sputtering at 6 kW for 5 minutes at 4.5 mTorr in an Ar atmosphere.

To determine if reactive sputtering of dielectric films is possible using HPPMS, a number of hysteresis curves were created. Argon flow was held constant while oxygen partial pressure was increased and subsequently decreased. The oxygen partial pressure control was achieved using residual gas analyzer (RGA), high-speed MFC, and IRESS control [6]. During each hysteresis test, the system was allowed 60 seconds at each oxygen partial pressure condition to settle into a steady operating condition.

For film property tests, thin films were deposited at various oxygen partial pressures from zero oxygen to complete target oxidation. These tests were done with both DC and HPPMS to allow a direct comparison of the effects of both types of deposition. The optical and physical properties of these films were analyzed using a profilometer, ellipsometry, transmissive and reflective spectrophotometry, and x-ray diffraction (XRD).

To allow for a direct comparison between HPPMS and DC sputtering, it is important to determine the DC equivalent power of the HPPMS operation. The HPPMS power supply used for these tests consisted of a bank of capacitors charged by another set of power supplies. The average equivalent DC power ( $P_{avg}$ ), in watts, of the HPPMS pulses is determined from:

$$P_{avg} = \frac{0.5 * C * V^2 * f}{1000000}$$

Equation 1: HPPMS average power equivalent

where  $C$  is the capacitance in farads of the banks of capacitors (60  $\mu$ F),  $V$  is the voltage to which the capacitors are charged, and  $f$  is the pulse frequency in hertz. For the tests described in

this paper, pulse parameters for metallic mode and fully oxidized mode are shown in the table below. Transition mode pulses have voltages and currents between the two. Although pulse conditions at different voltages and frequencies were tested, the trends were consistent with the data discussed below.

Table 1: HPPMS Pulse Parameters.

Target Mode	Metallic Mode	Oxide Mode
Charging Voltage	1500 V	1500 V
Pulse Frequency	100 Hz	100 Hz
Equivalent DC Power	6.75 kW	6.75 kW
Peak Pulse Voltage	980 V	280 V
Peak Pulse Current	460 A	840 A
Pulse Width	150 $\mu$ S	100 $\mu$ S

## RESULTS AND DISCUSSION

### Hysteresis

The creation of a hysteresis curve, Figure 1, indicates that controllable reactive sputtering can be accomplished using HPPMS on a rotary magnetron. The HPPMS curve, generated at a 6.75 kW equivalent DC power, is compared to a DC curve at 7 kW. The partial pressure of oxygen is listed in units of amps because this is the direct reading from the RGA sensor. The inability of the hysteresis curve to close upon itself when the partial pressure is reduced is due to outgassing of water vapor from the chamber walls that adds to the supply of oxygen in the chamber and reduces the required flow to reach a given setpoint. An increase in water vapor was indicated by an increase in  $H_2$  partial pressure during the hysteresis generation.

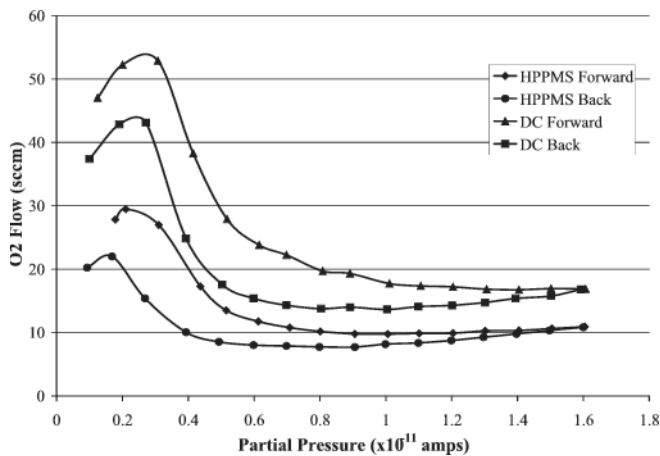


Figure 1: HPPMS and DC Sputtering Hysteresis.

The DC hysteresis uses more oxygen flow at a given partial pressure than HPPMS. Note that it seems to take a higher partial pressure of oxygen to achieve the fully poisoned condition with DC sputtering rather than pulsed sputtering. For instance, at a partial pressure of  $1 \times 10^{-11}$  amps, the pulsed hysteresis is flat and the DC hysteresis is still reducing slowly.

Interestingly, there is a decrease in peak pulse voltage between HPPMS in metal mode and fully oxidized mode (Table 1). This corresponded to an increase in peak pulse current and a reduction in pulse width. In comparison, all the DC hysteresis show about a 100V increase between metal mode and fully poisoned operation. The DC results agree with what has been seen previously in the industry [7]. An explanation for the peak pulse voltage decrease as the system transitions to oxide mode sputtering is still open.

Variations in pulse frequency, pulse voltage and operating pressure were also tested. For all the parameters tested, increasing the average power (increasing frequency or charging voltage) increases the  $O_2$  flow required by HPPMS to hold the same partial pressure of oxygen. This correlates well with standard DC sputtering.

### Deposition Rate

Thin films were deposited at various partial pressures along the hysteresis curves shown in Figure 1. The thickness of these films and deposition per pass is shown in Figure 2. All passes under the magnetron were done at 5 in./min.

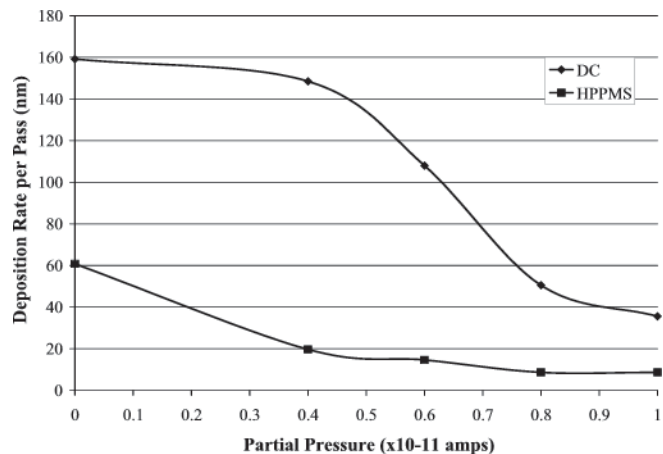


Figure 2: Deposition Rate per Pass of DC Sputtered and HPPMS  $TiO_x$ .

This figure shows that at the same partial pressure of oxygen and the same average power, DC deposition has a 4-7 time greater deposition rate. It should also be noted that the 0.4 and 0.6 partial pressure DC deposited films looked metallic while

all the pulsed deposition conditions looked transparent, except where no oxygen was added into the system. One possible reason for the decrease in deposition rate is that some power used in HPPMS is consumed in the increased ionization of the sputtered material instead of being used to sputter material. Also, the ionized sputtered material will be attracted back to the target, reducing the amount of material headed towards the substrate. Quantitatively proving how much power is used to ionize sputtered material and how much ionized sputtered material is returned to the target is a subject for future research.

### Index of Refraction

A comparison of the index of refraction at 550 nm for the films discussed above is shown in Figure 3. This data was created by curve fitting the transmission and reflection data of the films. As was expected, the refractive index of the DC sputtered films starts high and reduces as the partial pressure during deposition increases. The refractive index for the HPPMS deposited films is consistently higher than DC at the same partial pressure.

The refractive index at 0.4 for DC films was unobtainable because the film was not transparent enough to yield a transmission curve.

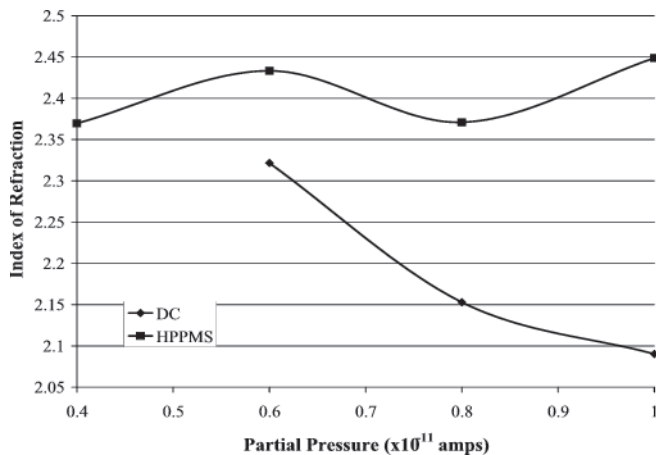


Figure 3: Index of Refraction for HPPMS and DC Deposition versus Partial Pressure of Oxygen.

Figure 4 shows the difference of the index of refraction between the HPPMS and DC deposited fully oxidized films as a function of wavelength. These films were deposited in poison mode for both pulsed and DC sputtering. The DC film was controlled at  $1.4 \times 10^{-11}$  amps while the pulsed film was controlled at  $1 \times 10^{-11}$  amps. The index of both films follows the expected pattern of the index, reducing as the wavelength increases.

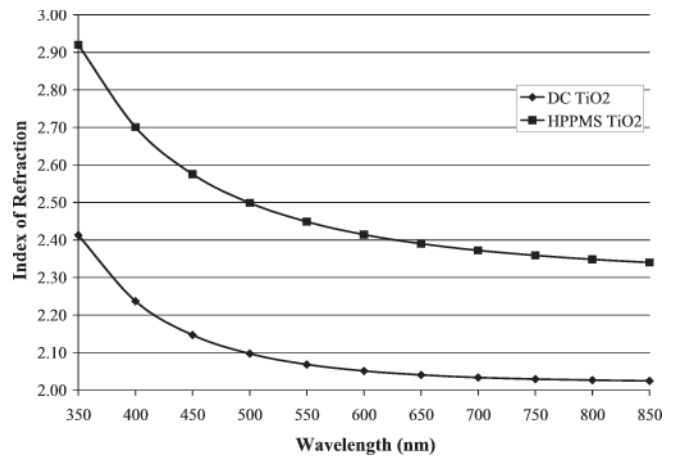


Figure 4: Index of Refraction for Fully Oxidized  $\text{TiO}_2$  DC vs. HPPMS.

Similar to the oxidized films the index of refraction for the metallic Ti deposited by HPPMS is higher than the index of refraction of metallic films deposited by DC sputtering (Figure 5).

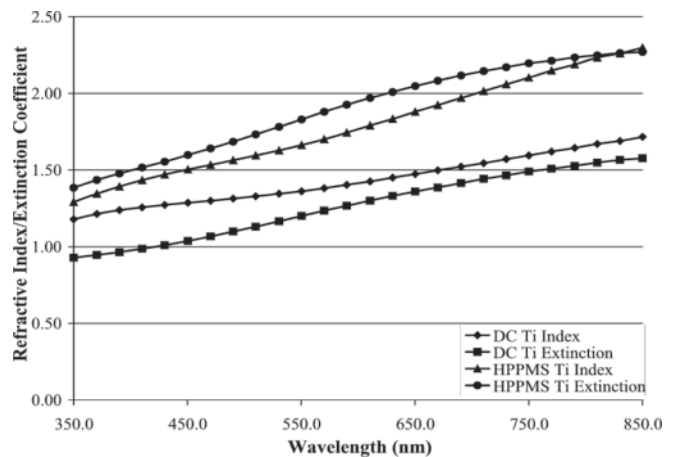


Figure 5: Index of Refraction and Extinction Coefficient of HPPMS and DC Deposited Ti.

The consistently higher index of refraction for fully oxidized, partially oxidized and metallic films indicates that some part of the HPPMS process changes the films. While the exact mechanism is not understood one possible reason is increased density of the deposited films. The increase in density could be caused by higher energy reflected neutrals impinging the substrate (caused by the high pulse voltage), ionized target material impinging the substrate or increased photons from the plasma striking the substrate.

## X-ray Diffraction

X-ray Diffraction (XRD) measurements of all the films deposited with any partial pressure of oxygen showed no crystallinity, regardless of whether the film was deposited with DC sputtering or HPPMS. Film thicknesses ranged from 50 nm to 200 nm. Figure 6 shows a representative XRD scan of one of the TiO<sub>2</sub> films. This scan looks just like the one of a bare glass slide.

There is a difference in the crystallinity of the metallic Ti films (Figure 6). The film deposited by DC sputtering show peaks at  $2\theta = 38^\circ$  and  $53^\circ$ , which correspond to crystal structure of (004) and (012) respectively. The film deposited by HPPMS shows only one peak at  $2\theta = 38^\circ$  with a strong (004) preferred orientation. The peak for the HPPMS film has much higher signal strength compared to the DC sputtered film.

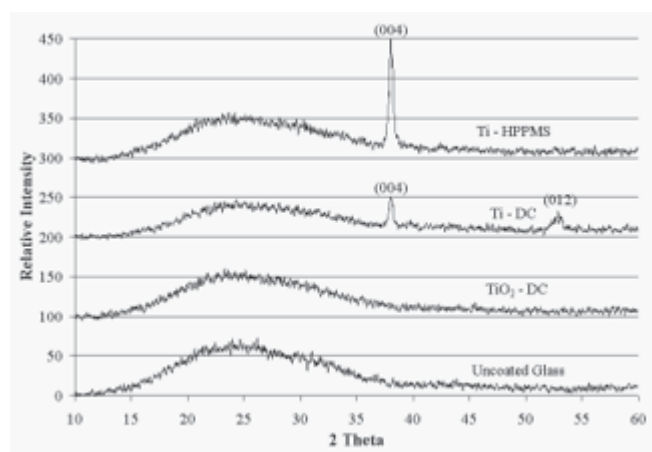


Figure 6: XRD Scans of DC sputtered and HPPMS Ti Films.

## Mid-Frequency TiO<sub>2</sub>

In many commercial coating systems TiO<sub>2</sub> is deposited by mid-frequency reactive sputtering of metal targets or DC sputtering from recently developed ceramic targets. The index of refraction at 550 nm for these methods of deposition is typically around 2.5 [8], which is slightly higher than the 2.45 found for HPPMS. If the index of refraction is the most important characteristic in a given process, HPPMS could be a viable alternative to mid-frequency reactive sputtering or DC sputtering from a ceramic target.

## CONCLUSION

It has been shown that controllable reactive sputtering of dielectric thin films is possible with HPPMS on a rotary magnetron. The pulsing characteristics of HPPMS reduce the deposition rate compared to DC sputtering but an increase in the index of refraction is also seen. While the oxide films are amorphous the metallic Ti films see a strong increase in (004) preferred structure with HPPMS.

## ACKNOWLEDGMENTS

Many thanks to Karin Witting, Applied Films GmbH, for the measurement of optical properties including index of refraction measurements.

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