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GROWTH OF TiO_x FILMS BY HIGH POWER PULSED MAGNETRON SPUTTERING FROM A COMPOUND $TiO_{1.8}$ TARGET

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Abstract. High power pulsed magnetron sputtering (HPPMS) has been employed for the growth of TiO_x (x > 1.8) films from a ceramic $TiO_{1.8}$ target in an Ar-O_2 ambient. The film properties have been compared to those deposited by dc magnetron sputtering (dcMS). Both HPPMS and dcMS films exhibit an amorphous structure and are transparent. Furthermore, films grown by HPPMS have improved properties, such as higher density, higher refractive index and smoother film surface, as compared to those deposited by dcMS.

1. INTRODUCTION

Titanium oxide (TiO_2) thin films are known for their transparency in the visible spectral range and their high refractive index [1]. Due to these properties they are extensively used in optical devices [2]. Other applications are in microelectronics [3], in chemical processes, such as photocatalysis [4] and gas detection [5], as well as in self-cleaning windows [6]. TiO_2 thin films exhibit two crystalline structures [7], the anatase and the rutile phase. However, when films grow at room temperature, an amorphous structure is often obtained [7]. In order to grow TiO_2 films, a number of deposition techniques, such as PVD [3,8], CVD [9], and sol-gel [10] are employed.

High power pulsed magnetron sputtering (HPPMS) is a novel ionized PVD technique [11]. In HPPMS, the power is applied to the target in unipolar pulses of low on-time and frequency. As a result, a high degree of ionization of the sputtered material is obtained [11,12]. This has been shown to result in improved film properties, in comparison to films produced by dc magnetron sputtering (dcMS), such as higher film densities [13], and smoother film surfaces [14]. HPPMS has been employed in order to deposit films from elemental [14,15] or compound [16] targets, in both non–reactive [16] and reactive modes [14,15]. Davis *et al.* [15] showed recently that TiO_2 films can be grown by HPPMS from a metallic Ti target resulting in films with a slightly higher refractive index, but lower deposition rate compared to films sputtered by dcMS. However, a study on the growth and characterization of TiO_2 films deposited by employing HPPMS from a compound target has so far not been done. The reactive sputtering from a compound target exhibits some interesting features, such as process stability and higher deposition rates, as compared to the reactive sputtering from a metallic target [17]

In the current study, TiO_x (x > 1.8) films are grown from a ceramic $TiO_{1.8}$ target employing reactive HPPMS at various pulse configurations in an Ar–O_2 ambient. The plasma characteristics are investigated. The structure, the composition and the surface morphology of the films are studied and

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their optical properties are investigated. The results are compared to those of films grown by dcMS.

2. EXPERIMENTAL PROCEDURE

TiO_x films were deposited on c-Si (100) substrates employing HPPMS. Depositions were carried out from a ceramic $TiO_{1.8}$ target (diameter 76 mm) with a Ti backing plate. High power unipolar pulses with a 50 μs pulse on-time and 1950 ms pulse off-time were applied to the target. Films were also grown in dcMS mode for comparison. In all depositions, the target was operating at a constant average current of 0.3 A. The power to the target was supplied by using an AE Pinnacle dc power supply coupled to a SPIK *2000A* pulsing unit from MELEC GmbH [18]. The target current and voltage were measured using a LEM LA205-S current transducer and a LEM CV3-1500 voltage transducer, respectively. A TDS2014 digital oscilloscope was used to monitor the target current and voltage, as well as the potential of a floating substrate. Films were grown at a distance of 70 mm from the target on floating substrates. An Ar-O_2 gas mixture with an Ar flow of 44 sccm and O_2 flow of 1.6 sccm was used.

In HPPMS, the target voltage, V_T, is applied in unipolar pulses, with the voltage kept constant during the pulse on-time. In order to study the target characteristics during the deposition process, the changes in the target voltage were monitored, while the O_2 flow was varied from 0 to 3 sccm. The Ar flow was accordingly adjusted in order to keep a constant total pressure of 0.8 Pa. The measurements were carried out at a constant average target current of 0.3 A.

The plasma composition was investigated employing time-resolved optical emission spectroscopy (OES). A *Mechelle 5000* Spectrometer equipped with an intensified CCD camera was used for this purpose. Light emission was collected using a fiber optic placed 30 cm from the target surface, at an angle of 45°. The time-resolved OES measurements were carried out by measuring the emission intensity in the spectral range 200-900 nm for a time of 70 μs from the beginning of the pulse.

A number of analytical techniques were employed in order to study the film properties. In all cases, films with thicknesses varying between 50 and 70 nm were studied. The composition was identified by means of Rutherford backscattering spectroscopy (RBS). The RBS spectra were analyzed using the XRUMP [19] software. X-Ray Reflectometry (XRR) was employed in order to determine the film thickness and, consequently, also the deposition rate. In addition, XRR was used for the calculation of the film density and the roughness both at the surface and at the interface. The structural properties of the films were investigated by means of X-Ray Diffraction (XRD) in both Bragg-Brentano (BB) and grazing incidence (GI) geometry. The X-Ray measurements were carried out using a Philips X'Pert Diffractometer. The optical properties of the films were determined by employing variable angle spectroscopic ellipsometry (VASE). A Woolam M-2000UI rotating compensator ellipsometer was used. The ellipsometric spectra were recorded in the range 0.73 – 5.13 eV. The five angles of incidence 70°, 72°, 74°, 76°, and 78° were used in order to enhance the accuracy of the analysis. The spectra were analyzed using the WVASE32 [20] software by fitting to a model consisting of a TiO_x film on a c-Si substrate. The optical response of the TiO_x film was described using a Tauc-Lorentz term [21]. The optical response of the substrate was described using a measured spectrum of a c-Si (100) wafer. Furthermore, a Bruggeman layer [22] consisting of 50% of the TiO_x film and 50% voids was added as a top layer above the Tauc-Lorentz layer that describes the optical response of the TiO_x film. The Bruggeman layer was considered in order to describe the effect of the film surface on the measured spectra. This ef-

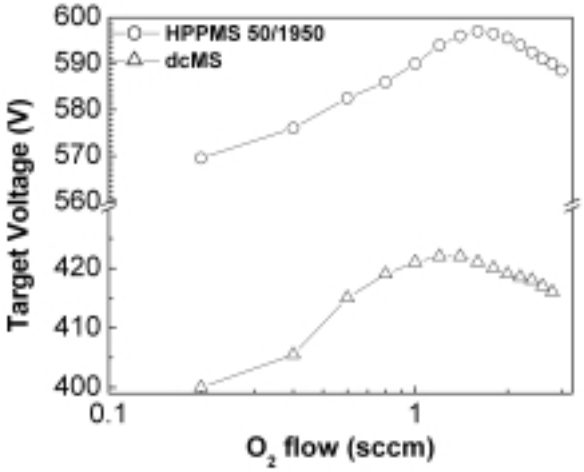

Fig. 1. Target voltage (V_T) versus O_2 flow (q_{O2}) for HPPMS 50/1950 configuration (circles) and dcMS (triangles).

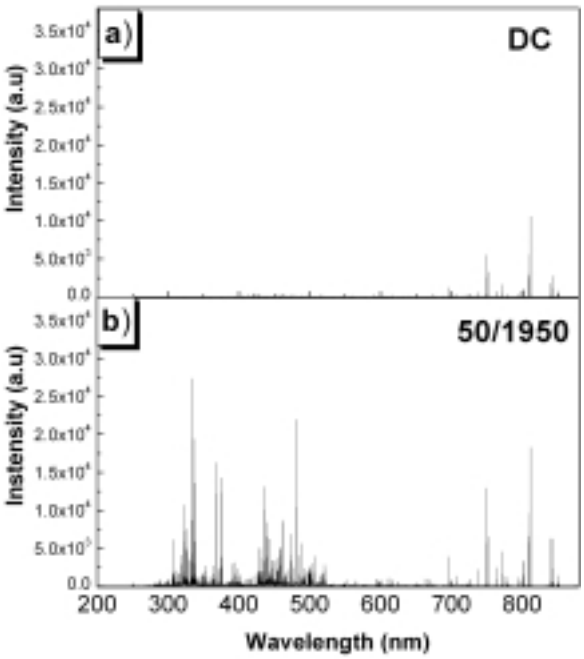

Fig. 2. Optical emission spectra of a (a) dcMS and a (b) HPPMS 50/1950 glow discharge. The intense peaks in the range 300 – 500 nm in Fig. 2 (b) are attributed mainly to Ti^+ species.

fect was particularly significant at high photon energies (>4 eV) where the penetration depth of the used electromagnetic radiation in the film is small. The thickness of the Bruggeman layer was calculated by the fitting procedure. In order to determine the refractive index of the films in the transparent range with high precision, the experimental data were also fitted to the Cauchy model [20]. The extinction coefficient was considered to be $k = 0$. The refractive index was described as $n(\lambda) = A+B/\lambda^2$. Here, λ is the wavelength of the light used and A, B constants.

3. RESULTS

3.1. Process characteristics and plasma properties

Fig. 1 shows the target voltage (V_T) as a function of the O_2 flow (q_{O2}) for dcMS and HPPMS in the pulse configuration 50/1950, i.e., 50 μs on-time and 1950 μs off-time. It is seen that in both cases V_T increases as the O_2 flow is increased, up to a qO2 value of ~1.6 sccm, corresponding to a transition from a less oxidized to a more oxidized target [23]. In addition, similar V_T values were measured for increasing and decreasing O_2 flow (not shown in Fig. 1), which is indicative of a hysteresis-free target operation and process stability over the full q_{O2} range.

The potential of a floating substrate was measured and found to be ~18 V for the dcMS discharge. In the case of the HPPMS discharge, the substrate potential was time-dependent, ranging from high negative potential (tens of volts) at the beginning of the pulse to a value close to zero after the pulse ends. We estimated the mean value to be ~40 ± 5 V during the pulse on-time.

Fig. 2 illustrates representative emission spectra of a dcMS and a 50/1950 HPPMS plasma (Figs. 2a and 2b, respectively). The spectrum of the HPPMS plasma was recorded at a time 50 μs from the beginning of the pulse. This is the point of the pulse, where the maximum target current (peak current) is measured. Fig. 2 reveals substantial differences between the DC and the HPPMS plasma. In particular, the DC spectrum exhibits only weak peaks at the right end of the spectrum. On the other hand, the HPPMS spectrum exhibits stronger peaks at the same range, while a group of intense peaks at the spectral range 300 – 500 nm also appears. These last peaks are mainly attributed to emission by Ti^+ ions and Ti neutrals [24].

3.2. Film properties

HPPMS and dcMS grown films exhibited a similar composition with respective [O]/[Ti] ratios of 2.2 and 2.1 as determined by the RBS analysis. Furthermore, the XRD analysis revealed amorphous films in all cases. The respective deposition rates for dcMS and HPPMS grown films were determined by XRR and were found to be 0.08 nm/s and 0.10 nm/s, respectively. In addition, XRR provided the density of the films, which were found to be 3.71 gcm^{-3} and 3.83 gcm^{-3} for dcMS and HPPMS deposition respectively. Moreover, the surface roughness (s_s) of the films grown by HPPMS was calculated to be 0.5 nm, while the corresponding value for the films grown by dcMS was 1.3 nm. The analysis of ellipsometric spectra based on the Tauc-Lorentz model revealed that both HPPMS and dcMS films were transparent with respective band gap values of 3.25 eV and 3.21 eV. This fact enabled us to fit the experimental ellipsometric data to the Cauchy model in the spectral range 0.73 eV – 2.5 eV and to calculate the refractive index n within an error margin of 10^{-4}. The resulting refrac-

Table 1. Summary of film properties grown by HPPMS and dcMS. The symbols E_g, σ_s, ρ and *n* stand for the band gap, the surface roughness, the film density and the refractive index, respectively.

	Structure	[O]/[Ti]	E_g (eV)	σ_s (nm)	ρ (gcm^{-3})	*n* (550 nm)
HPPMS	Amorphous	2.1	3.21	0.5	3.83	2.47
dcMS	Amorphous	2.2	3.25	1.3	3.71	2.38

tive indices for the films grown by HPPMS and dcMS are presented in Fig. 3. Higher values were obtained for the HPPMS grown films, as compared to the dcMS ones. In particular, the films deposited by HPPMS exhibited an *n* value of ~2.47 at an energy of 2.25 eV (550 nm), while the corresponding value achieved in the dcMS mode was 2.38. The films properties for both HPPMS and dcMS cases are summarized in Table 1.

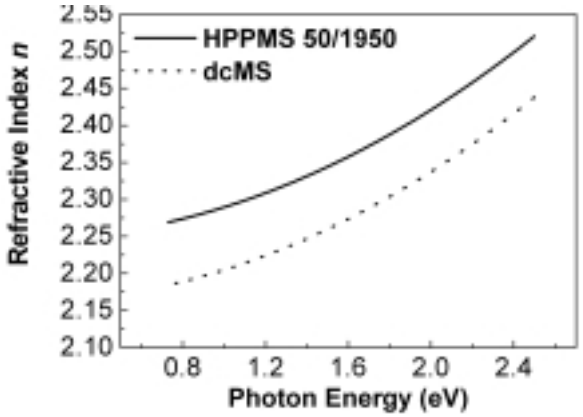

Fig. 3. Refractive index of HPPMS (solid line) and dcMS (dotted line) grown films as derived by fitting the experimental ellipsometric data to the Cauchy model.

4. DISCUSSION AND SUMMARY

It was shown that the stoichiometry of the films is similar, irrespective of the deposition method chosen. This can explain the fact that transparent films with similar E_g values are deposited in all cases. In HPPMS, the Ti^+ ion density is higher, as compared to dcMS, as demonstrated by the OES results presented in Fig. 2. Thus, in HPPMS a higher flux of positive ions is available to bombard the growing film. In addition, in HPPMS the energy that the positive ions gain upon incidence on the substrate is higher, since a higher negative substrate potential was measured in comparison to the HPPMS. These results manifest a more intense energetic bombardment of the growing film. The intensification of the bombardment, in turn, is known to contribute to the adatom mobility leading to a higher adatom diffusion length [25] and smoother surfaces [26]. In fact, significantly lower surface roughness was found for the films grown by HPPMS (Table 1). Furthermore, the film smoothening is known to result in denser films [26], which is also demonstrated in Table 1. Finally, the higher density of the films grown by HPPMS is consistent with the higher refractive index [27], as compared to the films grown by dcMS.

In summary, in this work TiO_x films were deposited employing reactive HPPMS and compared to films deposited by dcMS. In both cases, amorphous and transparent films with similar [O]/[Ti] ratios and comparable deposition rates were obtained. In addition, the HPPMS films were found to have a density of 3.83 gcm^{-3}, a refractive index of 2.48 at 550 nm, and a surface roughness of 0.5 nm. The corresponding values for the dcMs films were 3.71 gcm^{-3}, 2.38, and 1.3 nm, respectively. The improvement of the properties of the films grown by HPPMS has been attributed to the more intense energetic bombardment during the HPPMS deposition.

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