

High-Rate Deposition of Stoichiometric Compounds by Reactive Magnetron Sputtering at Oblique Angles

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Target poisoning in reactive magnetron sputtering deposition of thin films is an undesired phenomenon, well known for causing a drastic fall of the process efficiency. We demonstrate that when this technique is operated at oblique angles, films with composition ranging from pure metallic to stoichiometric compound can be grown in non-poisoned conditions, thus avoiding most of the associated drawbacks. We have employed amorphous TiO_x , although the presented results can be easily extrapolated to other materials and conditions. It is found that the proposed method improves 400% the growth rate of TiO_2 thin films.



1. Introduction

The magnetron sputtering (MS) technique is a well-known plasma-assisted thin film deposition method widely employed in science and technology thanks to its simplicity, versatility, and high quality of the obtained layers.^[1–4] It makes use of a non-reactive plasma, usually made of argon,^[5] to physically vaporize a solid metallic target into atomic and molecular species that subsequently condensate on a substrate. In the so-called reactive magnetron sputtering (rMS) deposition, a variation of the

MS technique reported decades ago,^[6] a small amount of reactive gas is introduced into the plasma to alter the composition of the film, thus enabling the fabrication of compound materials. Yet, this technique faces a clear drawback when the amount of reactive gas surpasses a critical threshold, above which the chemical composition of the first monolayers of the target become chemically affected,^[7,8] leading to a significant drop of the process efficiency and growth rate of the layers. This phenomenon, dubbed target poisoning, is also responsible for the appearance of hysteresis phenomena and reactor instabilities (e.g., the presence of arcs in the discharge, pressure variations, etc.), that, upon fluctuation of process parameters, may lead to quite different growth conditions.^[9] In the last decades, different strategies have been proposed to minimize these instabilities, as for example evacuating the gases from the reactor at high pumping speeds or pulsing the flow of gases into the chamber, among others.^[9–11] In this letter, we present a versatile and easy-to-implement method that, relying on the oblique angle geometry, overcomes the aforementioned drawbacks and enables the growth of stoichiometric and sub-stoichiometric materials by rMS in the non-poisoned mode of the target.

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The oblique angle deposition (OAD) configuration has been extensively analyzed in the literature since more than a century ago,^[12,13] typically using the electron beam-assisted vapor deposition technique in the absence of plasma.^[14] Here, a sublimated flow of gaseous species arrives at a substrate along an oblique angular direction, causing the development of tilted columnar nanostructures,^[15] which are of special relevance for numerous applications.^[14] This configuration was recently tested in MS reactors by tilting the substrate with respect to the target, obtaining nanostructures qualitatively similar to those found by evaporation.^[16] Yet, the possible interaction among the plasma, sputtered species, and the film surface during growth^[17] has significantly widened the technique in terms of nanostructural possibilities.^[16,18] Remarkably, tilting the substrate with respect to the target also involves a change in the arrival rate of sputtered species at the film surface per unit time and area, whereas the arrival rate of other species in the gaseous/plasma phase that follow an isotropic momentum distribution^[19] remains unaffected. This interesting feature can be exploited in rMS depositions to tune the film stoichiometry^[20]: in this letter, we show that, if deposition conditions are properly chosen, stoichiometric films can be prepared by rMS at oblique angles using a relatively low amount of reactive gas, thus avoiding target poisoning. This possibility suggests that this method may potentially outmatch the classical (non-oblique) approach. To test this idea, we have grown a large set of TiO_x (with $x \leq 2$) thin films by rMS using both, the classical approach and the oblique angle configuration. This choice has been dictated by the interest of titanium oxide, a widely-studied material of relevance for numerous applications (see for instance ref.^[21,22]), and because of the characteristics of the hysteresis curve when growing this material by rMS, which permits a straightforward extrapolation of the proposed method to other conditions and materials.

2. Experimental Section

A set of amorphous TiO_x thin films were grown using the deposition setup described in ref.^[18]. A 3 inches diameter titanium target was employed, placing the substrate holder at a distance $L = 7$ cm. An argon pressure of 0.2 Pa was maintained for all depositions. In Table 1, we gather the utilized conditions, labeling each sample with letters (A, B, C, D, and E) according to the flow of oxygen, followed by the tilt angle of the substrate, α (in the classical, non-oblique configuration $\alpha = 0$). In these conditions, the thermalization mean free path of Ti atoms in a pure Ar gas, λ_T , defined as the distance a Ti atom has to cover in the Ar gas to become thermalized, can be estimated (in m) by using the formula $\lambda_T \sim 0.08/p_g$, with p_g the argon pressure (in Pa).^[23] For an argon pressure of 0.2 Pa, we can then estimate $\lambda_T \sim 40$ cm, that is, more than five times the target-film distance. This implies that, in our conditions, most Ti atoms arrive at the film surface along a preferential direction and with kinetic energies much above thermal values.

Table 1. List of samples and experimental conditions analyzed.

#Sample	O ₂ flow (sccm)	Substrate angle (°)
#A0	0	0
#B0	1.5	0
#C0, #C45, #C70, #C85	2	0, 45, 70, 85
#D0, #D30, #D45, #D60, #D70, #D80, #D85, #D87.5	2.4	0, 30, 45, 60, 70, 80, 85, 87.5
#E0	2.8	0
#Ref TiO ₂	3	0

Electromagnetic power was always 200 W in the DC mode and the argon partial pressure 0.2 Pa.

Deposition time in each case was chosen to grow films with thicknesses around 700 nm, obtained by means of cross-sectional Field Emission Scanning Electron Microscopy (FESEM) images of the layers. These were also characterized by Rutherford Backscattering Spectroscopy (RBS) to assess the O/Ti ratio in the films, x . Experiments were carried out in a 3 MeV tandem accelerator at the Centro Nacional de Aceleradores (CNA, Seville, Spain). RBS measurements were done with a beam of 2.0 MeV alpha particles, and a passivated implanted planar silicon (PIPS) detector located at 165° scattering angle. The RBS spectra were simulated with the SIMNRA software.^[24] NRA measurements, using the ¹⁶O(d, p₁)¹⁷O nuclear reaction, were performed with a deuteron ion beam of 0.9 MeV and a PIPS detector located at 150° angle. A 13 μm Mylar foil was inserted in front of the detector to avoid the arrival of deuteron ions backscattered in the sample. The growth rate of each film, r , had been obtained by dividing the areal density of Ti atoms in the material, as obtained by RBS, by the deposition time. Moreover, since the inherent error in the experimental RBS analysis does not allow a clear differentiation between a fully oxidized TiO₂ layer and a highly oxidized sub-stoichiometric TiO_x film, UV-vis absorption spectroscopy was employed to assess their stoichiometry. In this regard, it is well known that TiO₂ thin films deposited on quartz substrates are fully transparent beyond the optical absorption edge of this material (i.e., 3.2 eV) and in the case of dense films, their spectra are modulated by interference oscillations with amplitude and frequency that depend on the thickness and compactness of the material. On the contrary, TiO_x thin films, even for x values very close to 2, are known to absorb in the visible and IR regions of the spectra.^[25,26] The transmittance spectra of the TiO₂ films were analyzed by a home-made MATLAB-based software, OPTIFIT, freely available in our webpage,^[27] to estimate the refractive indexes of the layers.

3. Results and Discussion

Figure 1(a) shows the value of the total gas pressure in the deposition reactor as a function of the flow of oxygen during the rMS deposition of TiO_x ($x \leq 2$). This curve was obtained in one run by increasing/decreasing the oxygen flux in

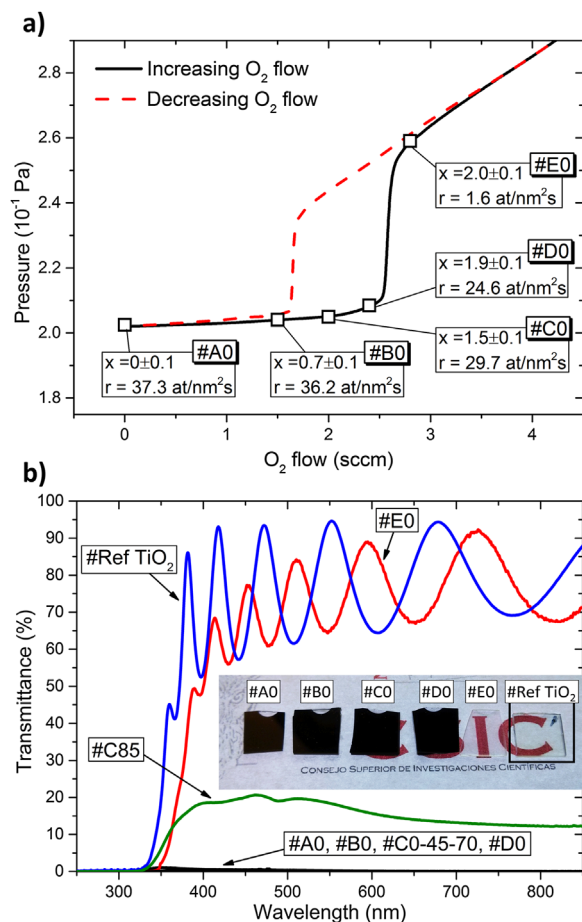


Figure 1. (a) Total pressure in the deposition reactor as a function of the flow of oxygen for the films listed in Table 1, grown in the classical (non-oblique) configuration, including the deposition rate in each case. (b) Optical transmittance spectra of samples #A0, #B0, #C0, #D0, #E0, #C45, #C70, #C85 in Table 1 and a reference TiO₂ sample. The inset presents the photographs of these films.

steps of 0.1 sccm, and waiting until pressure stabilizes in each case. This graph defines a typical hysteresis plot characterized by two curves when either increasing or decreasing the flow of oxygen.^[10] The fundamentals of this behavior are well explained in the literature in connection with the target poisoning mechanisms^[9–11]: for low oxygen flows, the metal target composition is little affected and the films only incorporate a little proportion of reactive atoms, whereas for an oxygen flow of ~2.6 sccm, the partial pressure in the deposition reactor increases sharply due to the target poisoning mechanism, the associated drop of the sputtering rate of Ti and the lower getter activity at the reactor walls. For illustration purposes, we have grown the films #A0, #B0, #C0, and #D0, for increasing oxygen flows, obtaining TiO_x films with $x = 0.0 \pm 0.1$, $x = 0.7 \pm 0.1$, $x = 1.5 \pm 0.1$, and $x = 1.9 \pm 0.1$, respectively, and a similar deposition rate of Ti per unit time and area of $r \sim 30$ atoms nm⁻²s⁻¹ (specific values in each case are given in

Figure 1a). Yet, sample #E0, grown using an oxygen flow of $F_{O_2} = 2.8$ sccm possesses a stoichiometric parameter $x = 2.0 \pm 0.1$, but grows at a remarkably lower rate, $r = 1.6$ atoms nm⁻²s⁻¹, that is, about ~20 times lower than in non-poisoned conditions. In agreement with these values, the transmittance spectra in Figure 1(b) confirm that films #A0, #B0, #C0, and #D0 are clearly sub-stoichiometric, whereas #E0 corresponds to fully oxidized TiO₂^[25] (the sample photographs in the inset of Figure 1(b) confirm this assessment on the film stoichiometry).

Figure 1(a) illustrates the inherent difficulty to grow fully stoichiometric films at high rates by rMS due to (i) the higher pressure of reactive gas and, consequently, the lower mean free path of sputtered species in the plasma, and (ii) the target poisoning phenomenon. To overcome this limitation we propose to use rMS in the OAD configuration, which we analyze next: experiments were carried out for $F_{O_2} = 2$ sccm, varying α from 0° to 85° (samples #C0, #C45, #C70, and #C85 in Table 1). Figure 2(a) shows that while the deposition rate decreases with α , the value of x clearly rises up to $x = 2.0 \pm 0.1$ for samples #C70 and #C85, characterized by growth rates of $r = 11.2$ atoms nm⁻²s⁻¹ and $r = 6.8$ atoms nm⁻²s⁻¹, respectively. However, the transmittance spectra of these films in Figure 1(b) reveal that samples #C70 and #C85 are clearly sub-stoichiometric. This behavior can be corroborated in the inset in Figure 2(a), that shows the colored aspect of these samples.

To test our hypothesis and achieve a fully stoichiometric TiO₂ thin film, we have utilized an oxygen flow of $F_{O_2} = 2.4$ sccm, just below the threshold required to poison the target in Figure 1(a), for increasing values of α (samples #D0, #D30, #D45, #D60, #D70, #D80, #D85, and #D87.5). The determined film stoichiometry in these cases ranged between $x = 1.9 \pm 0.1$ and $x = 2.0 \pm 0.1$, meaning that only the optical analysis can reveal whether the films have attained full oxidation or not. The comparison in Figure 2(b) of the transmittance spectra of these films and that of a TiO₂ reference sample clearly proves that for angles above $\alpha \sim 80^\circ$, fully oxidized TiO₂ layers have been obtained. This is confirmed by the photographs in the inset of Figure 2(b), illustrating the high transparency of the films prepared with $\alpha \geq 80^\circ$. Figure 2(a) also shows that the film growth rate decreases with the deposition angle, as seen in the cases presented for $F_{O_2} = 2$ sccm, and in agreement with the expected dependence with α for particles coming from a preferential direction. In particular, the deposition rate of Ti is $r = 5$ atoms nm⁻²s⁻¹ for $F_{O_2} = 2.4$ sccm and $\alpha = 80^\circ$, meaning that the OAD rate for stoichiometric TiO₂ improves ~400% the classical (non-oblique) approach.

Figure 2(a and b) demonstrate that an OAD configuration can be employed to grow fully oxidized TiO₂ thin films in the metallic mode of the target, that is, under conditions where the undesired hysteresis-induced instabilities can be avoided and, as evidenced by the reported experiments, at

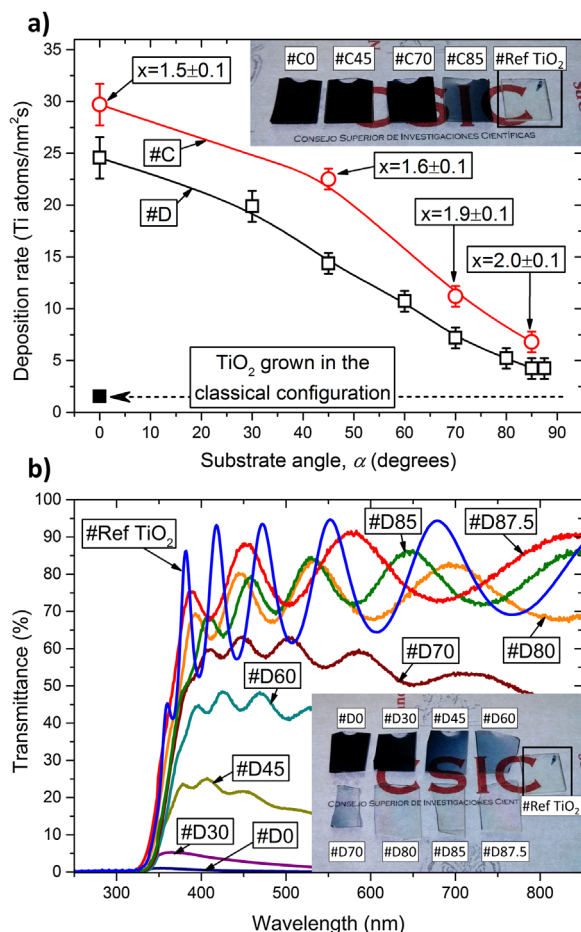


Figure 2. (a) Deposition rate of Ti atoms per unit time and area when tilting the substrate for oxygen flows $F_{O_2} = 2$ sccm (circular symbols and red curve) and $F_{O_2} = 2.4$ sccm (square symbols and black curve). For $F_{O_2} = 2$ sccm, the film stoichiometry is given for each condition, while for $F_{O_2} = 2.4$ sccm, the value of x , as determined by RBS, always yielded $x = 1.9 - 2.0 \pm 0.1$. (b) Optical transmittance spectra of a reference TiO₂ sample and the #D0–87.5 series in Table 1, for an oxygen flow of $F_{O_2} = 2.4$ sccm. The inset shows the images of these films.

relatively high deposition rates. Yet, it is important to mention that unlike films grown by other plasma-assisted techniques, such as PECVD in typical conditions^[28] or classical rMS,^[29] the rMS-OAD configuration promotes the growth of nanostructured thin films formed by tilted columns.^[18] Indeed, the different refractive indexes of the TiO₂ layers in Figure 2(b) indicate the different microstructure in either case: while the reference TiO₂ (compact) layer possesses a refractive index of ~ 2.4 , the #D80, #D85, and #D87.5 cases are characterized by a value around ~ 1.9 . Even though this value is mediated by the water uptake capability and hydrophilicity of the layers, the observed difference can be mainly attributed to a different porosity. In any case, this (porous) columnar nanostructure can be removed in our conditions by applying a low substrate bias

to attract the plasma ions and densify the films (see for instance ref.^[30,31]).

It is worth mentioning that oxygen content in the layers can be slightly overestimated due to their exposure to air during manipulation, a phenomenon that can be enhanced by the existence of columnar nanostructures with large specific surfaces. In order to check whether this phenomenon is of relevance, we have measured how deep a pure compact Ti layer may become affected by atmospheric oxygen: we have performed Nuclear Reaction Analysis (NRA) of this layer, obtaining that the first 4 nm of material may become affected by oxidation (analysis not shown). In this way, even if columns are covered by a 4 nm thick conformal layer with composition TiO₂, the stoichiometric variation on a typical 50 nm diameter column with composition TiO_{*x*} can be estimated around 2%, that is, much below the error bar, which corroborates the little influence of atmospheric oxygen in the film stoichiometry in the presented results. Also, as it is apparent in Figure 2(b), some films show a small inhomogeneity in transparency. This effect is caused by the different distance between each side of the film and the target when the substrate is tilted. This issue is intrinsically associated to the characteristics of the experimental setup, which was specifically designed to coat small substrates. In any case, this effect can be minimized by rotating the layers during growth, so that the distance of each side of the film to the target becomes averaged.

4. Conclusions

The relevance of the proposed method to grow stoichiometric films is clear from both scientific and technological points of view. We have shown that it clearly improves both the growth rate of the films and the process efficiency by avoiding hysteresis-associated instabilities in comparison with the classical approach. Finally, it must be stressed that beyond the growth of TiO_{*x*} thin films, which is the object of the present work, our method can easily be implemented to effectively grow other compound materials by adjusting the flow rate of the reactive gas just below the threshold required to poison the target, and tilting the film substrate accordingly.

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