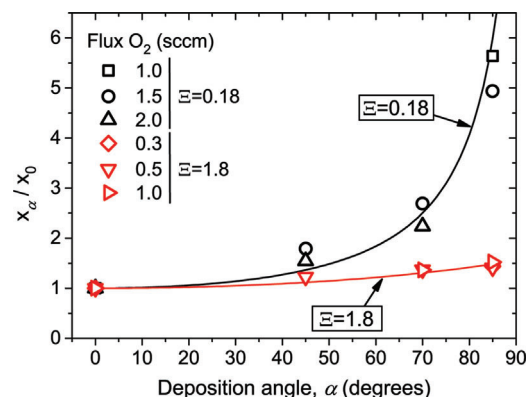


Stoichiometric Control of SiO_x Thin Films Grown by Reactive Magnetron Sputtering at Oblique Angles

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The deposition of SiO_x ($x \leq 2$) compound thin films by the reactive magnetron sputtering technique at oblique angles is studied from both theoretical and experimental points of view. A simple mathematical formula that links the film stoichiometry and the deposition conditions is deduced. Numerous experiments have been carried out to test this formula at different deposition pressures and oblique angle geometries obtaining a fairly good agreement in all studied conditions. It is found that, at low deposition pressures, the proportion of oxygen with respect to silicon in the film increases a factor of ~ 5 when solely tilting the film substrate with respect to the target, whereas at high pressures the film stoichiometry depends very weakly on the tilt angle. This behavior is explained by considering the fundamental processes mediating the growth of the film by this technique.



1. Introduction

The magnetron sputtering technique is a well-known and robust plasma-assisted deposition method typically employed to grow dense and compact coatings.^[1,2]

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Thanks to its versatility and efficiency, numerous works have appeared in the last decades aiming at improving the control over key aspects of the deposition, such as the thin film growth rate, surface roughness, crystallinity degree or preferential texture, among others.^[3,4] In the so-called reactive magnetron sputtering (rMS) technique,^[5] a certain amount of reactive gas (e.g., oxygen or nitrogen) is pumped into the plasma, affecting the film stoichiometry and allowing the growth of compound layers.^[1,6] Yet, and as a general issue of this technique, the reactive gas flow has to be constrained within certain limits in order to avoid the so-called target poisoning, i.e., the alteration of the chemical composition of the first monolayers of the target material, which causes process instabilities and a drop of the growth rate of the films.^[7–10] In fact, in the last years, much effort has been dedicated to minimize or

cancel the influence of this undesired effect, e.g., by evacuating the gases from the reactor at high pumping speeds or by pulsing the flow of gases.^[8,11] Moreover, in ref.^[12] we proposed a method to grow stoichiometric compound layers using low fluxes of reactive gas, thus avoiding target poisoning phenomena and demonstrating that the growth rate of TiO₂ layers improved ~400%. This method relied on the results of Nyberg et al.,^[13] who proved that operating at oblique angles (i.e., varying the angle between the substrate and the target surface) induced changes in the film stoichiometry in typical RMS conditions. In this paper, we quantitatively analyze the connection between growth conditions, oblique angle geometry and film stoichiometry, deducing a simple mathematical formula that links them all. This equation has been experimentally tested by growing SiO_x ($x \leq 2$) thin films under different experimental conditions, obtaining a good agreement in all the studied cases.

The oblique angle geometrical configuration has been widely explored in the last decades to grow thin films, mainly by the electron beam-assisted evaporation technique in absence of plasma, and its fundamentals are well established in the literature.^[14] For instance, it is known that the arrival of vaporized species at the substrate along a tilted direction enhances surface shadowing mechanisms and promote the formation of nanocolumnar arrays.^[15,16] This configuration has also been tested in magnetron sputtering depositions (MS-OAD), finding out a great diversity of thin film nanostructures, from purely compact to highly porous morphologies. In ref.,^[17] for instance, we analyzed the growth of gold thin films by MS-OAD and showed that, depending on the plasma gas pressure and substrate tilt angle, structures ranging from compact to highly porous columnar arrays could be achieved. This geometrical configuration has also been tested in the presence of a reactive plasma finding that, even under same experimental conditions, the film stoichiometry rapidly changed when varying the angle between the target and the film surface.^[12,13] In fact, these stoichiometric variations were associated to the existence of ballistic sputtered species, whose arrival rate at the film per unit area would depend on the relative angle between the target and the film substrate,^[18] while most reactive species would remain unaffected thanks to their approximately isotropic momentum distribution function in the plasma/gas. In this work, we analyze from both theoretical and experimental points of view the influence of the oblique angle geometry on the stoichiometry of SiO_x ($x \leq 2$) layers, and derive a simple equation that relates the value of x and the deposition conditions at oblique angles. We have particularly employed this material because of its relevance, its numerous applications in different fields and the extensive knowledge on its growth in the literature.^[19,20] Nevertheless, the main ideas presented in this

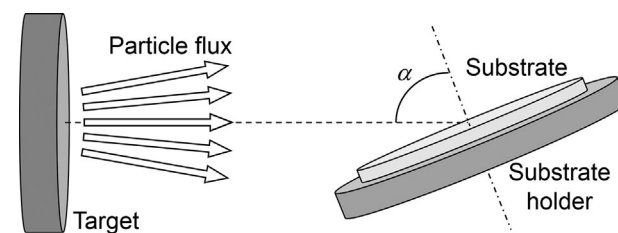
paper can be easily extrapolated to other conditions and materials.

2. Experimental Section

Amorphous SiO_x ($x \leq 2$) thin films were deposited onto silicon and highly oriented pyrolytic graphite (HOPG) substrates in a cylindrical vacuum reactor, pumped down to a base pressure lower than 5×10^{-4} Pa and equipped with a magnetron sputtering target device (Gencoa Ltd., Liverpool, UK). This base pressure was achieved by a combination of turbomolecular and rotary pumps. The working pressure was adjusted with a throttling valve, placed between the chamber and the turbo pump. A planar silicon target with a diameter of 3 in. and a thickness of 3 mm was used as sputtering source (see Figure 1). The film substrate was grounded and placed 70 mm apart from the target, its temperature around 350 K in all the cases. Experiments were carried out using a pulsed unipolar power DC supply at a frequency of 80 kHz, 2.5 μ s off-time, and a constant electromagnetic power of 300 W. A mixture of Ar (purity 99.995%) and O₂ (purity 99.995%) was used for the depositions. Two sets of films were grown at two different argon pressures, 0.15 and 1.5 Pa, while the relative angle between the substrate and the cathode, α , was varied between 0° and 85°. Oxygen fluxes between 0 and 2 sccm were used to change the stoichiometry of the samples. The chemical composition of the layers (i.e., the O/Si ratio) was characterized by Rutherford Backscattering Spectroscopy (RBS). The films used for this analysis were grown on graphite for a better quantification of the oxygen and silicon signals. Experiments were carried out in a 3 MeV tandem accelerator at the Centro Nacional de Aceleradores (CNA, Seville, Spain) with a beam of 1.5 MeV alpha particles, accumulated doses about 10 mC, 3 mm beam spot diameter, and a passivated implanted planar silicon (PIPS) detector located at 165° scattering angle. The RBS spectra were simulated with the SIMNRA software,^[21] whereas the film stoichiometry was obtained by dividing the measured areal densities of O and Si. Field emission scanning electron microscopy (FESEM) technique was used to characterize the film microstructure using a Hitachi S4800 at the Instituto de Ciencia de Materiales de Sevilla (CSIC-US, Seville, Spain).

3. Theory

We make use of the so-called effective thermalizing collision (ETC) model to describe the collisional transport of sputtered species from the target toward the film.^[18] This



■ Figure 1. Experimental setup.

simplifying theory considers that the progressive loss of kinetic energy and preferential directionality of sputtered atoms in the gas/plasma can be simplified by introducing a single effective collision, after which the sputtered particle becomes thermalized with the plasma gas. Relying on this idea, simple equations have been deduced in the last years to describe the film growth under classical (non-oblique) conditions, such as the well-known Keller-Simmons (K-S) formula,^[22] $r_0 = \Phi_0 (p_0 L_0 / p_g L) [1 - \exp(-p_g L / p_0 L_0)]$ that relates the mass deposition rate of sputtered atoms, r_0 , the pressure in the reactor, p_g , the flux of atoms stemming from the target, Φ_0 , and the distance between the target and the film, L . In this formula, the semi-empirical characteristic pressure-distance product, $p_0 L_0$, can be related to the mean free path for this single effective thermalizing collision, λ_T , by the relation $p_g L / p_0 L_0 = L / \lambda_T$,^[23] where

$$\lambda_T = 1 / N \sigma_T, \quad (1)$$

with N the density of heavy particles in the plasma and σ_T the so-called thermalization cross-section. This latter quantity can be linked to the actual geometrical cross-section, σ_g , by the relation $\sigma_g = \nu \sigma_T$, or likewise, $\lambda_T = \nu \lambda_g$,^[24] where ν is the average number of subsequent collisions necessary to thermalize a sputtered atom in the gas, as calculated by Westwood in ref.^[25] and λ_g the actual mean free path of the sputtered species. Hence, by introducing the so-called thermalization degree of sputtered atoms, $\Xi = L / \lambda_T$, the K-S formula reads,

$$r_0 = \Phi_0 \frac{1 - \exp(-\Xi)}{\Xi}. \quad (2)$$

Using the ETC model, we have recently determined the deposition rate of sputtered atoms by MS-OAD for a given experimental configuration and for different tilt angles of the substrate, α .^[18] In that work, a fundamental relation was found between the deposition rate at oblique angles, r_α , and that in the classical (non-oblique) configuration, r_0 , that reads

$$r_0 - r_\alpha = \Phi_0 \exp(-\Xi)(1 - \cos \alpha), \quad (3)$$

and thus, whenever the K-S formula is applicable, using Equation (2) and (3), we find

$$\frac{r_\alpha}{r_0} = 1 - \frac{\Xi}{\exp(\Xi) - 1} (1 - \cos \alpha). \quad (4)$$

In order to deduce a simple relation to account for the variations of the film stoichiometry, we assume that the reactive species from the plasma gas arrive at the film surface following an isotropic momentum distribution, i.e., we neglect the influence of highly directed reactive species,

such as those sputtered from the target or reactive ions accelerated in the plasma sheath, an approximation that agrees with numerous results in the literature whenever the target is in non-poisoned conditions.^[26] In this way, the flux of the reactive species directed toward the film surface, F_R , is independent of α , and the deposition rate of reactive species onto the film, r_R , reads

$$r_R = s(x) F_R, \quad (5)$$

where $s(x)$ is the surface adsorption probability of reactive species. In general, the mathematical dependence of $s(x)$ on x can be quite complex,^[27,28] and strongly depends on the particular material, surface features, temperature as well as on the reactive species at play. In fact, much research is still required to analyze the adsorption of reactive species when the surface is not flat and its composition sub-stoichiometric. In this paper, we particularize Equation (5) to describe the deposition of SiO_x thin films as analyzed in ref.,^[29] where it was proposed that molecular oxygen was the main species responsible for the oxidation of the film, with an adsorption probability very weakly dependent on the particular value of x , whenever $x < 2$. This behavior clearly differed from a typical Langmuir adsorption regimen (where a linear dependence is expected between $s(x)$ and x).^[30] In fact, this weakly dependence of $s(x)$ on the surface coverage has been reported in several cases in the literature^[30–32] and has been generally explained by considering the incorporation of reactive species onto the film surface in two sequential steps: in a first stage, reactive species form a very weak bond with the film surface at the landing position, whereas, in a second stage, these species diffuse over the surface until they find an available site to bond.^[30] Assuming this weak dependence between $s(x)$ and x , the stoichiometric factor of a film grown at a deposition angle α reads $x_\alpha = r_R / r_\alpha$ which, using Equation (4) and (5), yields

$$\frac{x_0}{x_\alpha} = 1 - \frac{\Xi}{\exp(\Xi) - 1} (1 - \cos \alpha), \quad (6)$$

valid when $x_\alpha < 2$, with x_0 being the film stoichiometry for $\alpha = 0^\circ$ (note that, according to Equation (6), x_0 is always equal or below x_α). Equation (6) is the main theoretical result of this paper and demonstrates the intrinsic relation between the tilt angle of the substrate, the film stoichiometry and the deposition conditions.

Figure 2 shows the available stoichiometric variation range, x_α / x_0 , as a function of α , as predicted by Equation (6). In this way, when the thermalization degree is very low, i.e., in the limit where sputtered particles do not experience any collision in the gas phase and all of them arrive at the film surface along a preferential direction, the trend $(x_\alpha / x_0)_{\Xi \ll 1} \sim 1 / \cos \alpha$ is obtained. Moreover, at very high

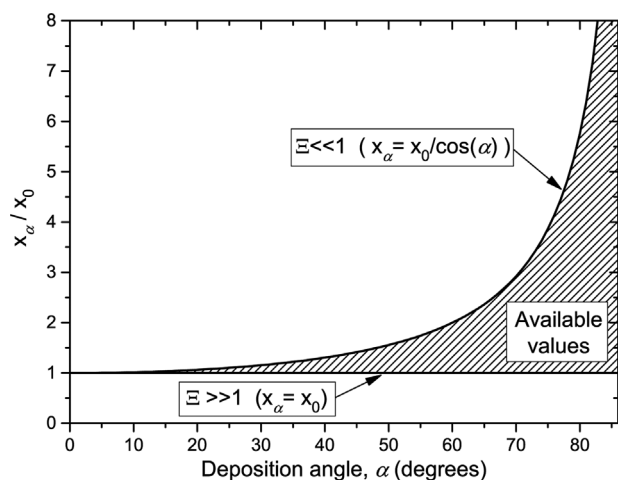


Figure 2. Accessible stoichiometries of the SiO_x thin films upon the variation of the tilt angle.

thermalization degrees, the relation $(x_0/x_\alpha)_{\Xi \gg 1} \sim 1$ is found, no matter the particular value of α . Under these conditions, sputtered atoms arrive at the film surface following an isotropic momentum distribution function and, hence, the stoichiometry of the film is independent of the tilt angle of the substrate. Interestingly, Figure 2 anticipates that the most important stoichiometric variations should occur for tilt angles above $\sim 45^\circ$.

4. Results and Discussion

Figure 3 presents the stoichiometry of the SiO_x films as a function of α , for an argon partial pressure of $p_g = 0.15$ Pa

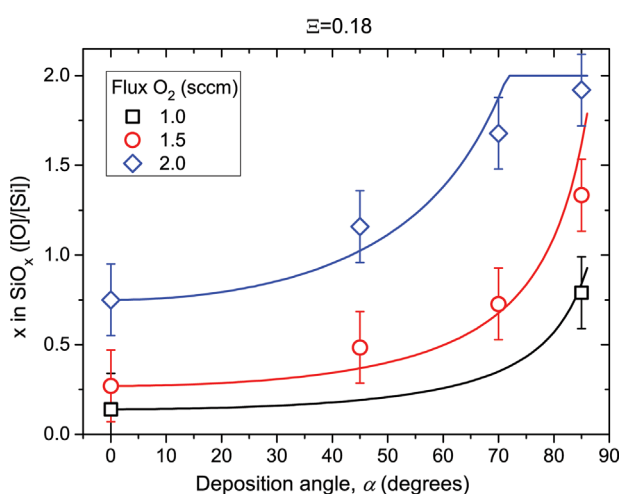


Figure 3. Film stoichiometry for different tilt angles of the substrate at different fluxes of reactive gas and an argon partial pressure of 0.15 Pa, together with the theoretical trend predicted by Equation (6).

and different oxygen fluxes, F_{O_2} , into the reactor. As expected, in classical non-oblique conditions (i.e., for $\alpha = 0^\circ$), the value of x_0 increases with F_{O_2} , from $x_0 = 0.15$ when $F_{O_2} = 1$ sccm to $x_0 = 0.8$ when $F_{O_2} = 2$ sccm. However, when solely tilting the substrate for a given oxygen flux, values as high as $x_{85} = 0.8$ can be achieved for $F_{O_2} = 1$ sccm, i.e., the proportion of oxygen in the film increases by a factor of ~ 5 relative to non-oblique conditions, whereas the saturated value, $x_{85} = 2$, is achieved when $F_{O_2} = 2$ sccm. In Figure 3, we have also included the results for an intermediate oxygen flux, $F_{O_2} = 1.5$ sccm, showing that the film stoichiometry ranges now from $x_0 = 0.3$ to $x_{85} = 1.4$, i.e., same factor as before (~ 5) when increasing the deposition angle. These results clearly show the potential of the OAD configuration to control the film composition using low fluxes of reactive gas. For instance, and according to Figure 3, an oxygen flow of $F_{O_2} = 2$ sccm is required to deposit SiO_{0.8} thin films in the normal configuration, whereas only half of the oxygen flux ($F_{O_2} = 1$ sccm) is required when $\alpha = 85^\circ$. Likewise, $F_{O_2} \sim 3$ sccm is required to grow SiO₂ thin films in non-oblique conditions, while the full stoichiometry is obtained for $F_{O_2} = 2$ sccm and $\alpha = 85^\circ$.

An increase of the argon pressure in the reactor promotes a higher thermalization degree of sputtered species in the plasma gas: in Figure 4, we present the obtained stoichiometries for an argon pressure of $p_g = 1.5$ Pa at different oxygen fluxes and tilt angles. This time, the oxygen fluxes were set to 0.3, 0.5, and 1 sccm to ensure the sub-stoichiometric character of the layers in the classical configuration. In these conditions ($\alpha = 0^\circ$), x_0 increases with the oxygen flux from $x_0 = 0.4$ to $x_0 = 1.2$, indicating

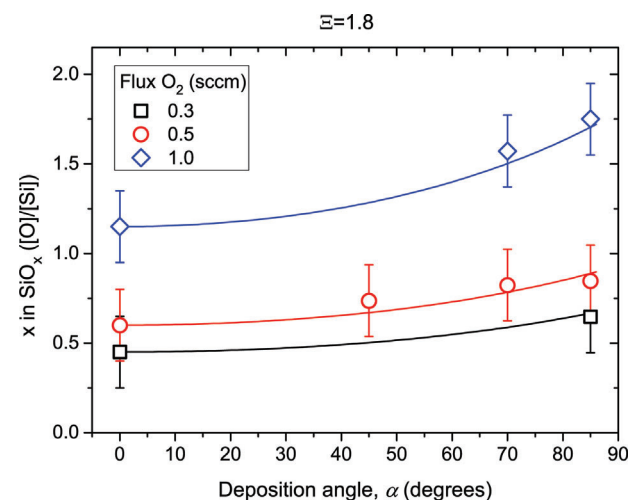


Figure 4. Film stoichiometry for different tilt angles of the substrate at different fluxes of reactive gas and an argon partial pressure of 1.5 Pa, together with the theoretical trend predicted by Equation (6).

the validity of the classical approach to grow SiO_x by pumping more reactive gas in the reactor. In Figure 4, we also note that when the OAD geometry is employed, the value of x changes lightly with α , namely from 0.4 to 0.6 for $F_{\text{O}_2} = 0.3$ sccm, from 0.6 to 0.9 for $F_{\text{O}_2} = 0.5$ sccm, and from 1.2 to 1.8 for $F_{\text{O}_2} = 1$ sccm, resulting in a factor of ~ 1.5 between the $\alpha = 0^\circ$ and the $\alpha = 85^\circ$ cases. This factor is remarkably smaller than the one obtained in the lower pressure cases (~ 5), suggesting that the higher thermalization degree of sputtered species makes them arrive at the film surface with a more isotropic momentum distribution, thus precluding a significant dependence of their arrival rate per unit area on α .

In order to compare Equation (6) with the experimental data in Figures 3 and 4, a quantitative relation between Ξ and our experimental conditions must be estimated. This relation can be calculated by considering that, by definition, $\Xi = L/\lambda_T$ with $L = 7$ cm and λ_T given by Equation (1), where $N = p_g/k_B T_g$ is the density of heavy particles in the plasma gas with $T_g \sim 350$ K the temperature of the gas, and $\sigma_T \sim 8.3 \times 10^{-20} \text{ m}^2$ is the thermalization cross-section for an elastic scattering event of a Si atom on an Ar heavy particle (here, we neglect the unlikely collision of a Si sputtered species with an oxygen species in the plasma gas).^[33] Following these assumptions, we deduce that, if p_g is in Pa, $\Xi \sim 1.2 \times p_g$, i.e., $\Xi \sim 1.2 \times 0.15 = 0.18$ for the low pressure case and $\Xi \sim 1.2 \times 1.5 = 1.8$ for the higher one. By introducing the calculated value of Ξ and the corresponding value of x_0 in Equation (6) as input parameters, we have obtained the expected values of x_α . These are depicted in Figures 3 and 4, where we notice the fairly good agreement with the experimental data in all studied cases. Interestingly, Equation (6) predicts that, in the low pressure cases, the full stoichiometry is achieved for $\alpha \sim 70^\circ$ and an oxygen flux of $F_{\text{O}_2} = 2$ sccm, whereas, in the higher pressure cases, the full stoichiometry is never achieved, at least for tilt angles between $\alpha = 0^\circ$ and $\alpha = 85^\circ$.

As a final test to prove the validity of Equation (6), we have analyzed the ratio x_α/x_0 as a function of α whenever $x_\alpha < 2$. According to this equation, a relation solely dependent on Ξ should be found, independent of the particular flux of oxygen or, likewise, the value of x_0 . Moreover, and according to Figure 2, the ratio x_α/x_0 should be constrained within the curves $x_\alpha/x_0 \sim 1/\cos \alpha$ and $x_\alpha/x_0 \sim 1$. In Figure 5, we show a representation of the experimental (for $x_\alpha < 2$) and theoretical results, where it is evident that all the experimental data collapse along the theoretical curves obtained for each of the two values of the argon pressure (thermalization degree). Overall, the results in Figures 3–5 confirm the validity of Equation (6) to describe the growth of SiO_x thin films by rMS at oblique angles. Furthermore, these results corroborate that the stoichiometric variations obtained at different background pressures are mediated by the different thermalization

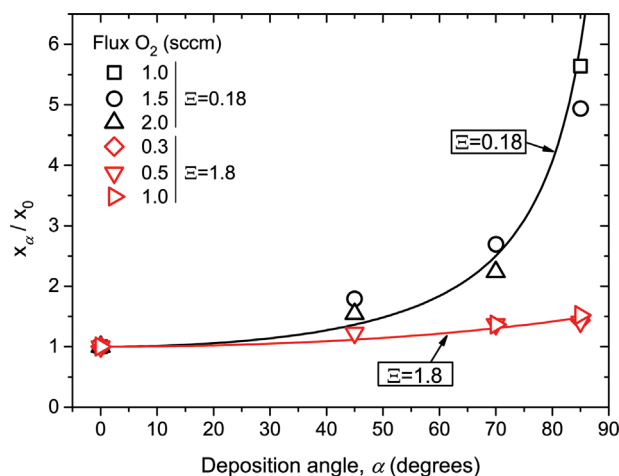


Figure 5. Value of x_α/x_0 as a function of α for all experimental cases studied in this paper, whenever $x_\alpha < 2$, together with the trend predicted by Equation (6). Note that the cases with $x_\alpha = 2$ have not been plotted.

degrees, and hence by the isotropy of the momentum distribution functions of sputtered species.

An additional issue in this paper is the high impact of the OAD geometry on the thin film microstructure, which may lead to the development of different bulk and surface patterns depending on the nominal angle of incidence of the deposition species.^[14,34] Even though these structures can be easily removed by applying an electric bias to accelerate plasma ions toward the film,^[35–39] it is of relevance to illustrate the clear microstructural differences among the SiO_x thin films analyzed in this work. In Figure 6, we show the cross-sectional FESEM images of selected films for $p_g = 0.15$ Pa ($\Xi \sim 0.18$), $F_{\text{O}_2} = 1.5$ sccm, and $\alpha = 0^\circ, 45^\circ, 70^\circ, 85^\circ$, respectively. In all these cases, the deposition time was chosen to obtain films with thicknesses of about 500 nm. Clearly, a compact microstructure is obtained for $\alpha = 0^\circ$ and $\alpha = 45^\circ$, while a well-developed columnar microstructure with large open pores at the surface is present for the $\alpha = 70^\circ$ and $\alpha = 85^\circ$ cases. This behavior qualitatively agrees with that reported for Au thin films grown by MS-OAD at low pressures,^[17] where a smooth transition from compact to columnar morphologies were reported. The cross-sectional images of the films grown at a higher pressure, $p_g = 1.5$ Pa ($\Xi \sim 1.8$), are also shown in Figure 6, where a clear porous microstructure with vertically aligned column-like structures is evident in all the cases. The deposition time was set to 30 min for the $\alpha = 0^\circ$ and $\alpha = 45^\circ$ cases, 45 min for the $\alpha = 70^\circ$ case, and 40 min for the $\alpha = 85^\circ$ case. This kind of thin film microstructure matches with that reported for SiO_2 thin films grown at the backside of the substrate in the classical MS configuration, and has been widely reported whenever the film growth is governed by the shadowing-dominated

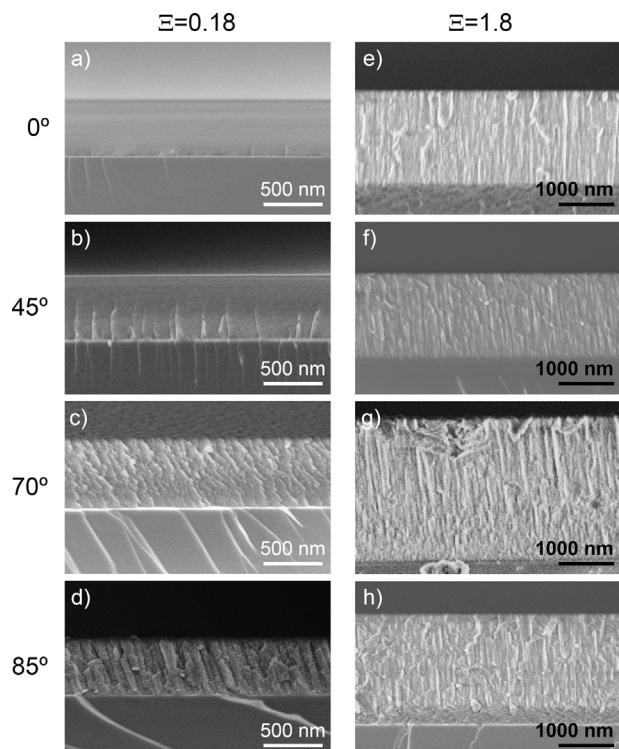


Figure 6. Cross-sectional FESEM images of SiO_x films deposited in different conditions: a) $F_{O_2} = 1.5\text{sccm}$, $\alpha = 0^\circ$ and deposition time 10 min; b) $F_{O_2} = 1.5\text{sccm}$, $\alpha = 45^\circ$ and deposition time 15 min; c) $F_{O_2} = 1.5\text{sccm}$, $\alpha = 70^\circ$ and deposition time 30 min; d) $F_{O_2} = 1.5\text{sccm}$, $\alpha = 85^\circ$ and deposition time 30 min; e) $F_{O_2} = 0.5\text{sccm}$, $\alpha = 0^\circ$ and deposition time 30 min; f) $F_{O_2} = 0.5\text{sccm}$, $\alpha = 45^\circ$ and deposition time 30 min; g) $F_{O_2} = 0.5\text{sccm}$, $\alpha = 70^\circ$ and deposition time 45 min; and h) $F_{O_2} = 0.5\text{sccm}$, $\alpha = 85^\circ$ and deposition time 40 min.

deposition of low energy vapor species that follow an isotropic momentum distribution function in the plasma/gas.^[17,40] Moreover, film thicknesses are approximately proportional to the deposition time, with a growth rate of $\sim 50\text{ nm min}^{-1}$, no matter the tilt angle of the substrate, a fact that agrees with our result above regarding the weak dependence of the film stoichiometry on the tilt angle of the substrate in these conditions. Finally, it is worth mentioning that film exposure to the atmosphere causes the oxidation of its first monolayers, a phenomenon that may increase the average content of oxygen in the material, especially for layers with such a large specific surface as those presented in Figure 6. As discussed in ref.,^[12] atmospheric oxygen affects a $\sim 4\text{ nm}$ thick layer of material on the surface, which in our conditions lead toward a variation of the film stoichiometry below 2%, much lower than the experimental error of the presented data.

The deduction of Equation (6) has been made by considering numerous simplifying assumptions, e.g., the introduction of an effective thermalizing collision

between sputtered and heavy plasma species, the negligible role of reactive ions or the existence of an oxygen absorption probability independent of the surface stoichiometry, among others. In this regard, Equation (6) has to be considered as a simple formula that provides meaningful insights on the deposition dynamics and that puts together aspects as different as the reactor geometry, the nature of the sputtered and reactive species or the plasma conditions by means of a simple mathematical relation.

5. Conclusion

In this paper, we analyze how the oblique angle geometry influences the film stoichiometry in reactive magnetron sputtering depositions. We have shown that, at low pressures, the oblique angle configuration may promote the growth of compound thin films with a stoichiometric factor about five times higher than in the normal configuration. At higher pressures, the film composition shows a weakly dependence on the tilt angle due to the higher isotropy of the momentum distribution function of sputtered particles in these conditions. We explain this behavior by analyzing the progressive thermalization and directionality loss of sputtered species for increasing background pressures, deducing a simple formula that relates the stoichiometry of SiO_x thin films and the tilt angle of the substrate. This equation reproduces all experimental data fairly well at low and at high deposition pressures. Although this paper is focused on the growth of SiO_x thin films, the main ideas herein are general and can be easily applied for the growth of other compound materials by RMS.

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