

Influence of the carrier gas in the growth kinetics of TiO₂ films deposited by aerosol assisted chemical vapor deposition with titanium-diisopropoxide as precursor

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Titanium dioxide thin films were deposited on crystalline silicon (100) substrates by delivering a liquid aerosol of titanium-diisopropoxide and by using oxygen and nitrogen as carrier gases. The crystalline and morphological features indicate that the films are deposited by a metal organic chemical vapor deposition process. This is strongly supported by the behavior of the growth rate r_g as a function of the deposition temperature, which indicates that the film formation is limited by both, the diffusion in gas phase of the precursor species to the surface substrate and reaction of those species at that surface. Even though the r_g line shape does not depend on the kind of carrier gas used to transport the aerosol, its absolute value and the activation energy E_A that characterizes the surface reaction do. A fitting procedure to an equation that takes into account both limiting mechanisms (gas phase diffusion and surface reaction) yields: $E_A \cong 26.4$ kJ/mol or $E_A = 21.4$ kJ/mol when oxygen or nitrogen is employed as carrier gas, respectively.

Keywords: Growth mechanisms; TiO₂ films; metal-organic chemical vapor deposition; spray pyrolysis.

Películas de dióxido de titanio fueron depositadas mediante la liberación de un aerosol líquido de diisopropóxido de titanio sobre substratos de silicio orientados (100), y empleando oxígeno y nitrógeno como gases de arrastre. Las propiedades cristalinas y morfológicas indican que el proceso de depósito se lleva a cabo mediante los vapores químicos de los precursores. Esto es fuertemente apoyado por el comportamiento de la tasa de crecimiento r_g como función de la temperatura de depósito, cuya forma de línea indica que el crecimiento está gobernado por la difusión de los precursores en fase vapor hacia el sustrato y la consecuente reacción de estos en la superficie. Aunque la forma de línea de r_g no depende del tipo de gas utilizado en el arrastre del aerosol, el valor absoluto de r_g y la energía de activación E_A que caracteriza a la reacción superficial sí. Un ajuste a una ecuación que toma en cuenta a ambos mecanismos (difusión de vapores y reacción de superficie) da como resultado: $E_A \cong 26.4$ kJ/mol o $E_A = 21.4$ kJ/mol cuando se utiliza oxígeno o nitrógeno como gas de arrastre, respectivamente.

Descriptores: Mecanismos de crecimiento; películas de TiO₂; depósito por vapores químicos; rocío porolítico.

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1. Introduction

Titanium dioxide (TiO₂) in thin film form has several properties that make it a material of interest for several applications [1]. Indeed, TiO₂ films can be used as coating in anti-corrosive protection [2], as catalysts in chemical industry and environmental purification phenomena [3–5], as a host matrix for luminescent devices [6] and, due to its photocatalytic properties, they have also been proposed as photochemical converters in solar energy conversion processes [3,7–9]. In most of these applications, films with good morphology and crystalline properties are required. Sol-gel, sputtering, chemical vapor deposition (CVD), plasma enhanced CVD and atomic layer deposition are deposition techniques that have been employed to produce titanium dioxide films with the properties mentioned above [10–14]. However, recently the simple and cheap ultrasonic spray pyrolysis (SP) technique has been explored to grow TiO₂ thin films by using titanium acetylacetonates or titanium diisopropoxide as precursor materials [15–16]. These results indicate that SP is a suitable technique for producing TiO₂ films with properties as good as those prepared by the more sophisticated techniques mentioned above. Therefore, by considering the importance of both TiO₂-film material and the deposition technique itself,

we think that it is worth making a detailed study of the physical phenomena involved in the deposition of these films by that technique.

Generally speaking, depending on the precursors and on deposition conditions, the SP technique represents a deposition process by means of liquid droplets or by chemical vapors (as in chemical vapor deposition). Actually, in the latter case, the SP technique is sometimes classified as “aerosol-assisted” chemical vapor deposition (AA-CVD) [17]; and the important point in distinguishing between SP and AA-CVD is the thermodynamic phase (liquid or vapor) in which the initial aerosol droplets, or spray, reach the substrate surface. For example, by using inorganic compounds such as nitrates or chlorates (dissolved in water), which have high boiling points, the aerosol solution usually arrives at the surface substrate in the liquid phase, while by employing precursors of low boiling point, such as the metal-organic compounds, the precursors reach the vapor phase [18–20]. These processes produce films with different qualities. Indeed it has been found, for example, that if the deposition process is achieved by means of liquid droplets, the films will have a rougher surface than if this is achieved by chemical vapors [17]. Hence, the good surface and crystalline quality of the TiO₂ films reported in Refs. 15 and 16 seem to indicate

that, in those cases, SP behaves like an AA-CVD process; or, since metal-organic precursors were employed, this could be referred to as an “aerosol-assisted metal-organic chemical vapor deposition (AA-MOCVD)” process. Nevertheless, in a more quantitative way, when the precursors are delivered in aerosol form, the best way to obtain the mechanisms that control the film formation would be to study the behavior of the deposition rate as a function of temperature [17]. Indeed, this type of study gives clues not only as to the thermodynamic phases in which the precursors reach the substrate surface, but also as to the physical and chemical phenomena that occur during an MOCVD process also [17,21-23], namely, thermodynamics, gas phase reaction, mass transport, and reaction at the substrate surface. Recently, by correlating the crystalline and morphology properties with the behavior of the growth rate r_g (nm/min), the physical mechanisms that control the TiO₂ film formation by delivering an aerosol of Ti-diisopropoxide onto a hot substrate, were elucidated [24]. The present study is addressed to clarifying the influence of the carrier gas on the growth kinetics of TiO₂ films deposited by means of an aerosol of Ti-diisopropoxide.

2. Experimental

The possible modes of the spray pyrolysis techniques have been summarized in the book by T. Kodas [17], and the generation of a spray by ultrasonic means has been described elsewhere [18–19]. In the present study, an ultrasonic generator set at 0.8 MHz, which produces droplets of 1–5 μm in average size [19,25], was used to produce the aerosol. The starting solution was prepared with titanium diisopropoxide-bis-(2,4 pentanedionate) (TIPO) dissolved in ethanol (EtOH), at a molar ratio of 0.0162. Oxygen and nitrogen were used, separately, as carrier gases to conduct the aerosol to the substrate (through a glass nozzle of 12 mm in diameter). In both cases, the carrier gas flux was fixed at a constant value of 3.5 l/min and the substrate was heated at a fixed Temperature T_s , with an auto-adjustable temperature controller, at values between ~ 453.15 –823.15 K (180–550 °C). At the beginning, films were deposited on (111) and (100)-oriented crystalline silicon substrates, but no detectable dependence on the substrate orientation was observed; therefore the present results refer to films grown on Si-(100). The deposition rate r_g was evaluated by measuring the film thickness (nm) and the deposition time (min) and subsequently normalizing it to the volume (mL) that each sample consumed.

The crystallization process was examined with a standard X-ray powder diffractometer ($\text{CuK}\alpha$ $\lambda = 1.5418 \text{ \AA}$) in the grazing angle mode from 10° to 70° in 2θ . The surface morphology and roughness were evaluated with an atomic force microscope (VEECO auto probe CP-II), with a 10 nm curvature radius gold tip. In this technique, the images were verified by scanning in both x and y directions in the tapping mode ($\sim 13 \text{ nN}$), thus avoiding drift effects. UV-visible reflectance spectroscopy, performed in the 200–900 nm wavelength range (1-nm resolution), was employed to measure the film thicknesses through interference effects.

3. Results and discussion

Regardless of the carrier gas, if the films are deposited at temperatures $> 225^\circ\text{C}$ (498.15 K), they develop the anatase phase, see Fig. 1. However, for the higher T_s values, different phases of the TiO₂-anatase start to appear. In particular, the presence of TiO₂-rutile is evident in films prepared with nitrogen, and the emergence of peaks around $2\theta \sim 29$ – 30 indicates the appearance of spurious phases, which, despite having only two peaks, might be identified with a TiO (PDF 23-1078). Figure 2 and Fig. 3 show the surface morphology of samples deposited at 588° K and 773° K (315°C and 500°C) from both oxygen and nitrogen as carrier gases. In both cases, as the films are deposited at higher temperatures, the grains become slightly larger. This gives an indication of the influence of this parameter on the kinetics of grain growth. Although no exact correlation was found between the grain size D observed in AFM images and those evaluated with the full width at half maximum of the XRD peaks, a general tendency can be noted. Actually, by using the (101) and (200) diffraction peaks, an average $D \sim 210 \text{ nm}$ was obtained for both kinds of films deposited at 500°C; which roughly coincides with the grains observed in Fig. 2b and Fig. 3b.

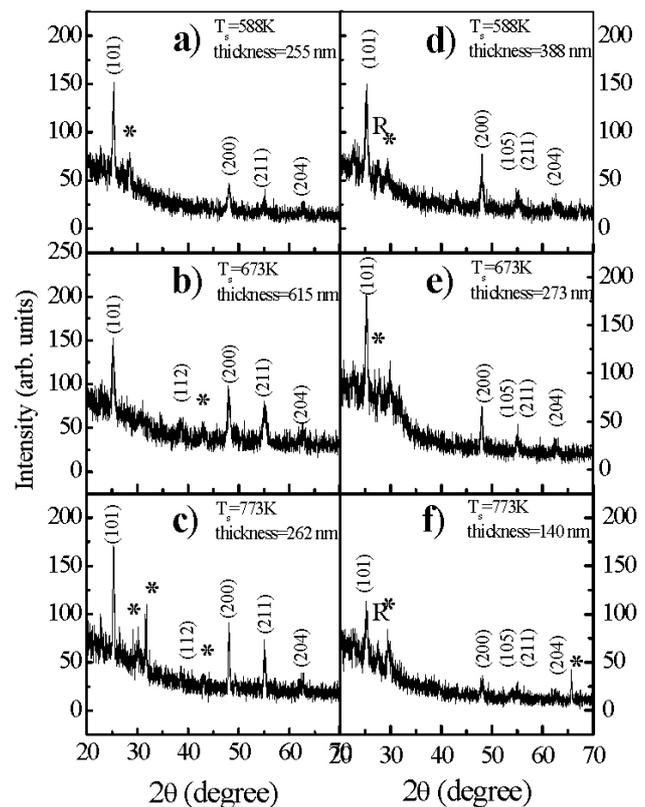


FIGURE 1. XRD experiments in grazing angle mode for TiO₂ films deposited from a TIPO/EtOH solution by using oxygen (a, b, c) and nitrogen (d, e, f) as carrier gases. Indexed peaks correspond to the TiO₂-anatase phase, R-index correspond to rutile and * peaks may be identified with TiO.

As has been discussed in Ref. 24, the most important point from Fig. 1, Fig. 2 and Fig. 3 is to observe that the morphological and crystalline features of our TiO₂ films are quite similar to those grown from sources delivered in vapor phase (CVD) [10-12]. This indicates that when titanium-diisopropoxide (dissolved in ethanol) is delivered in aerosol form, the liquid droplets evaporate before they reach the substrate, and the initial SP becomes an AA-MOCVD process. However, as was mentioned in the introduction, the best way to reveal the phenomena that limit film formation is to study the behavior of the growth rate as a function of the temperature. Fig. 4 shows the behavior of the normalized r_g as a function of T_s for the TiO₂ films reported in this work. Different curves correspond to different carrier gases. Regardless of the carrier gas and contrary to the spray pyrolysis behavior, r_g increases, reaches a maximum (~ 670 K for oxygen and ~ 630 K for nitrogen) and then decreases. The initial increase of r_g clearly indicates that the deposition is achieved by chemical vapors and not by liquid droplets [17,22]. Indeed, the deposition process by liquid droplets can be analyzed in terms of a binary liquid mixture (dissolvent/sol-

vent) [26]. The phase diagram of that mixture indicates that, for a given dissolvent/solvent molar ratio, as the temperature increases the volatile compound (solvent) removes more and more dissolvent (film precursor). Therefore, in the SP process, as the temperature increases, the liquid droplets have less and less precursor material for the film formation and, hence, r_g decreases. Thus, in agreement with the morphology of the films, the initial line shape in Fig. 4 indicates a deposition of the precursors by the chemical vapors. However, it is important to stress that the results of Fig.4 cannot be explained by the evaporation rate ($\sim \exp(-\Delta H_{evap}/RT)$) of our precursors, in that TIPO and EtOH have low boiling points ($\sim 100^\circ\text{C}$, $\sim 78^\circ\text{C}$) [27]; therefore, it must be one of the phenomena that work in MOCVD, such as those associated with a surface-activated catalysis and/or adsorption, that should be involved here.

In the surface-reaction-limited regime of MOCVD, the growth rate r_g increases with T according to a thermally ac-

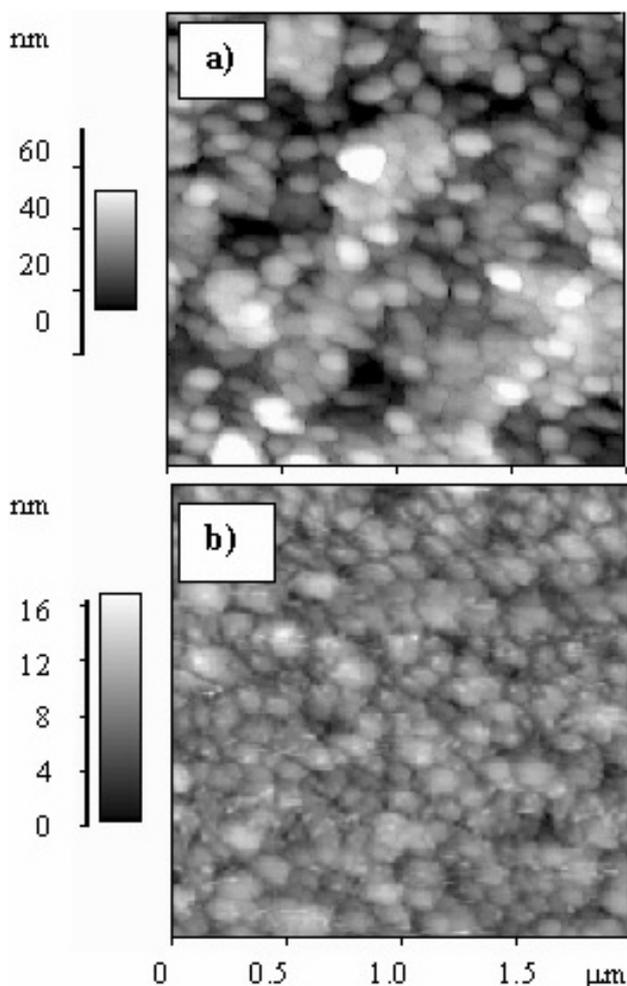


FIGURE 2. AFM images of TiO₂ films deposited at $T_s=588$ K and $T_s=773$ K with oxygen as carrier gas.

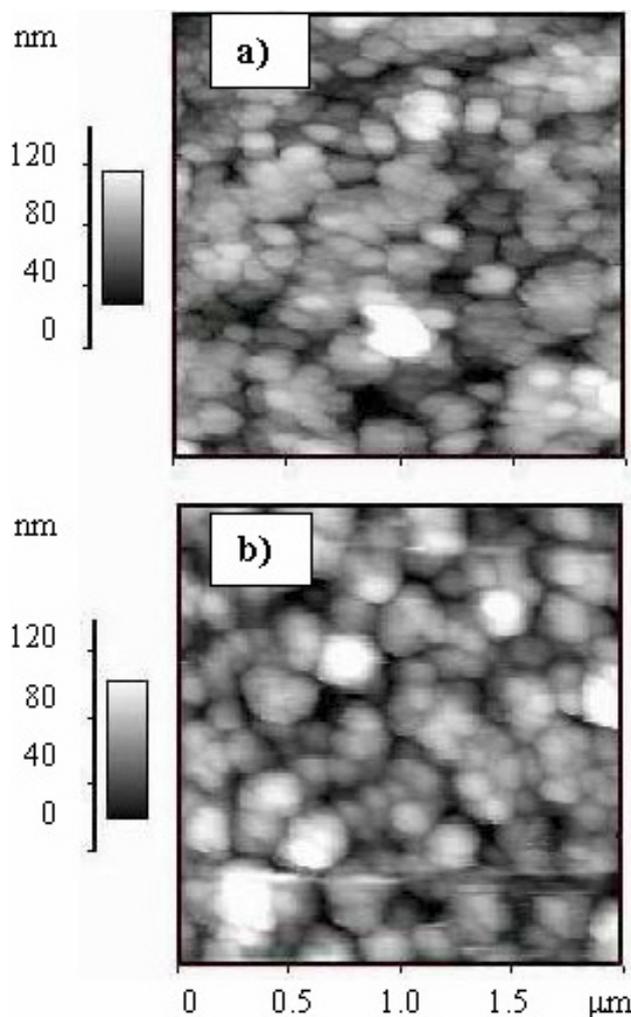


FIGURE 3. AFM images of TiO₂ films deposited at $T_s=588$ K and $T_s=773$ K with nitrogen as carrier gas.

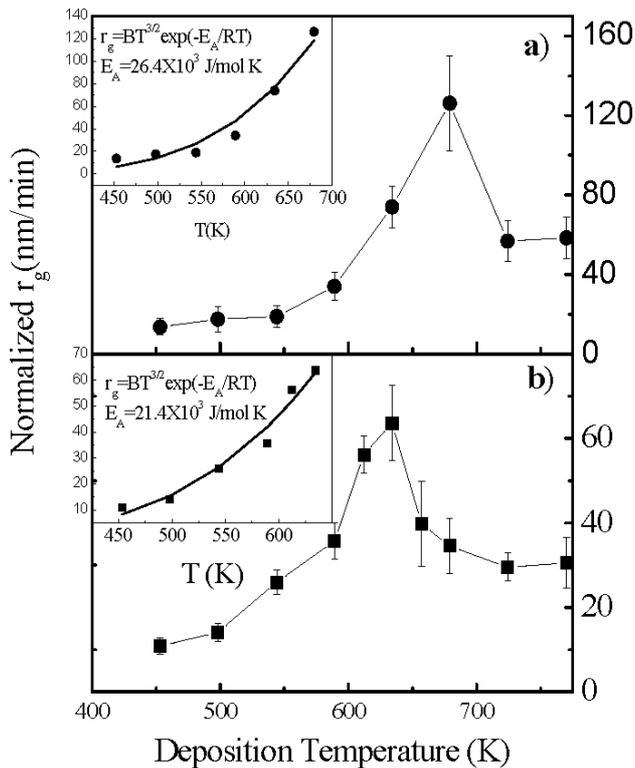


FIGURE 4. Normalized growth rate for TiO_2 films deposited with an aerosol of titanium-diisopropoxide conducted with two different carrier gases: a) oxygen and b) nitrogen.

tivated process [17,22-24]:

$$r_g = K_s C_r V_m = k_0 C_r \exp(-E_A/RT),$$

where K_s is the surface reaction rate constant (cm/sec), T the surface substrate temperature (K), C_r is the reactant concentration (molecules/cm³), V_m the volume of the deposited species (cm³), k_0 the pre-exponential constant, R the gas constant (J/K-mol), and E_A the activation energy of a surface activated reaction process of the metal-organic precursors. Although this equation fits the greater increasing part of our experimental data, as has been argued in Ref. 28, the proportionality of the reactant concentrations (TIPO/EtOH ratio) is not maintained; in fact, there it has been shown that although the reactant concentration (TIPO) is increased \sim four times, r_g increases only \sim 1.7. Therefore, in agreement with Refs. 28 and 24 we can say that, in the present case, independently of the carrier gas, the process is limited by a complex combination of the diffusion of molecular species through a boundary layer (formed by the residual gases near the substrate surface ($r_g \sim D_0 T^{3/2}$)) and surface reaction of these species. Actually (see insets in Fig. 4), the greater in its increasing part of the experimental data of the present study fit the following expression:

$$r_g = BT^{3/2} \exp(-E_A/RT), \quad (1)$$

where B is the pre-exponential factor that takes into account the reactant concentration and all the mass transport coefficients in the gas phase [17,24,28]. Therefore, this clearly

shows that, regardless of the carrier gas, we are dealing with an AA-MOCVD process and that those two phenomena must be considered as the limiting mechanisms for the film formation. Consistently, it should be observed that surface reaction phenomena are thermally-activated processes that have an observable dependence on temperature only at low values (the lower the T values, the lower the rate of the process), but at higher temperatures there is enough energy for any surface reaction to be achieved, and the dependence on T diminishes. Thus, in the process described above, at higher temperatures the boundary layer formed by the residual gases becomes thicker and the gas phase diffusion process dominates over the surface reaction and, therefore, a change of regimen occurs, as observed in both curves of Fig. 4.

The differences observed in Fig. 4 indicate a surface dissociation of the precursors that depends on the ambient [29]. A peak at lower temperatures in the r_g curve for films grown with nitrogen simply indicates that the dissociation of the initial molecule is easier when this gas is employed to conduct the precursors to the substrate than when oxygen is. In fact, by leaving B and E_A as free parameters in a least-square nonlinear regression fitting procedure in Eq. (1), the values obtained for the activation energy E_A are: $E_A \cong 26.4$ kJ/mol and $E_A=21.4$ kJ/mol for oxygen and nitrogen, respectively. By the way, it is important to observe that these E_A values are much lower than either the heat of adsorption of the Ti-O species (~ 500 kJ/mol) on solid substrates [1,29] or the enthalpy of formation of Ti-diisopropoxide in the gas phase ($\Delta H_f(\text{gas}) \sim 1 \times 10^3$ kJ/mol) [27]; therefore, as has already been mentioned, they must be associated with the surface-induced catalysis of some Ti-Rn organometallic molecular complexes (Rn-organic molecule) and not to those other surface phenomena. However, the molecular decomposition occurs in parts [30], and by the moment it would be difficult to associate these E_A value to the dissociation of a particular portion of TIPO ($\text{Ti}[(\text{CH}_3)_2\text{CHO}]_2[\text{CH}_3\text{C}(=\text{O})\text{CHC}(=\text{O})\text{CH}_3]_2$). Whichever the case, the differences in the E_A values can be explained by considering that the presence of nitrogen near the substrate surface probably induces a titanium-rich surface (working with several positive valences) that breaks up more easily into the TIPO molecules. On the other hand, oxygen would produce a neutral surface and therefore higher temperatures would be necessary to complete the surface catalysis. What nevertheless, under this scheme, a nitrogen environment automatically implies a lower oxidation rates and, therefore, lower growth rates also, as observed in Fig. 4.

4. Conclusions

When in the ultrasonic spray pyrolysis technique, titanium diisopropoxide is employed as precursor in the starting solution, TiO_2 thin films grow with a smooth surface and good crystalline qualities regardless if oxygen or nitrogen is used

as carrier gas. In any case, the correlation between the growth rate and surface properties of the films indicates that the films grow through chemical vapor and not by liquid droplets of the precursors. From the various phenomena that can control the film formation, the behaviour of the deposition rate as a function of the deposition temperature, indicates that the process is governed by the competition of surface reaction and gas-phase diffusion of the precursors. When oxygen or nitrogen is used as carrier gas, the values for the activation energy E_A of a surface reaction differ just slightly (~ 26.4 kJ/mol and 21.4 kJ/mol respectively), indicating that it is more easy

to break the precursors in nitrogen than in oxygen ambient. However, a nitrogen environment implies a lower oxidation rate and, therefore, lower growth rates.

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