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KINETICS OF TIO_2 FILM GROWTH IN LOW PRESSURE SYSTEM USING TITANIUMTETRAISOPROPOXIDE (TTIP)

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ABSTRACT

TiO_2 thin films were grown by low pressure chemical vapour deposition from titaniumtetraisopropoxide (TTIP) as precursor in a horizontal hot wall reactor. Nitrogen (50 sccm) was employed as carrier gas and diluting gas (10 sccm), keeping the whole system at a total pressure of about 80 Pa. Titanium oxide films were grown in the range 350 – 430 °C with thickness in the range 300-600 nm.

A simple concept of mass transport in a horizontal tube reactor was applied to analyze the experimental data of TiO_2 film growth. Critical temperature and appropriate growth rate were estimated according to this approach. These dates are important for process simulation.

Keywords: low pressure MOCVD, TiO_2, titaniumtetraisopropoxide, film growth kinetics, modeling

1. INTRODUCTION

Kinetics of any CVD film growth is most complex and still far from satisfactory understanding [1]. Nevertheless, in this paper we explained our experimental data using simple concepts of mass transport in a horizontal tube reactor [2,3]. Also, we coupled and combined this approach with the elementary surface phenomena equation of Frank-Kamenetskii [4].

2. EXPERIMENTAL

The depositions were achieved in a low-pressure hot wall reactor, equipped with an in-line FT-IR spectrometer to monitor exhaust gases, as reported in [5]. The reactor was provided with a Pyrex pipe, inner diameter 4.8 cm, 31 cm long. Nitrogen (50 sccm) was employed as carrier gas and diluting gas (10 sccm), keeping the whole system at a total pressure of about 80 Pa ($Re \approx 0.5$: laminar regime). The temperature of the decomposition zone was monitored by a

thermocouple placed in a fixed position in the reactor tube; a previous calibration permitted to know the temperature profile in the reactor through an analytical relationship between position and the thermocouple temperature. So, the temperature profiles were fitted with a sole function in distance x, with temperature of the setting point T(set) as a parameter: $T = -0.1146\,x^2 + 2.95\,x - 12.97 + T(set)$. The central zone of the reactor, about 150 mm long, showed an almost uniform temperature with variations of ± 2°C.

Titaniumtetraisopropoxide (TTIP) was used as furnished from Aldrich (98%). All manipulations were carried out in a dry-box.

Titanium oxide films were grown in the range 350 – 430 °C with thickness between 300 and 600 nm. Soda-lime glass substrates were cleaned prior to the introduction into the reactor; they were immersed in soaped water, washed with distilled water, rinsed in isopropylic alcohol, and dried in air.

3. RESULTS

The variations of the TiO_2 deposition rate with the substrate temperature, Fig.1, suggested an Arrhenius-type dependence. So, the apparent activation energy (E_a) of the film growth process could be calculated from the slope of the straight lines. However, the activation energies calculated at different positions in reactor turned out to be so different that this simple approach did not permit a valuable evaluation of the deposition process and suggested a more complicated system. A large scattering of data for (E_a) ranging from 35 to 150 $kJmol^{-1}$ has been reported in the literature [6-9] depending mainly on the different experimental conditions. For example, the value of 20 $kJmol^{-1}$ in [6] is among the lowest in the literature obtained at quite low pessure below 250 Pa. In that case, the effect of the pressure on film deposition may be considerable, since the rate of gas-phase transport (i.e. the rate of diffusion through the boundary layer) of both reactant gases and byproduxt gases is low and overal reaction could be diffusion-limited.

The deposition rate, reported in Figure 1, was measured in 5 different positions in the reactor located at 3.5, 6.5, 10, 13.5 and 17 cm respectively away from the entrance.

In Figure 2, the ratios between the precursor concentration at the exit and entry of the reactor, obtained from IR intensities assuming the Beer law, are shown as a function of the reactor temperature. Intensities were normalised to 1 on the more intense bands. This ratio began to decrease above 390°C and und came down to zero near 430°C.

Summarizing, we had:

- at lower temperatures: (1) uniform growth of TiO_2 films along with the reactor x-coordinate, (2) lower growth rates and (3) a great amount of not used precursor.

• on higher temperatures: (1) non uniform growth of TiO_2 films along the reactor x-coordinate, (2) higher growth rates in some x- positions and (3) a good yield of precursor.

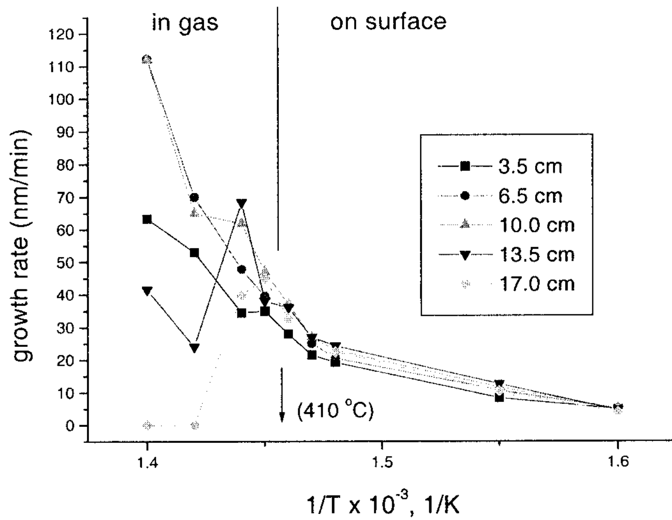


Figure 1 - Temperature dependence of overall rate constant

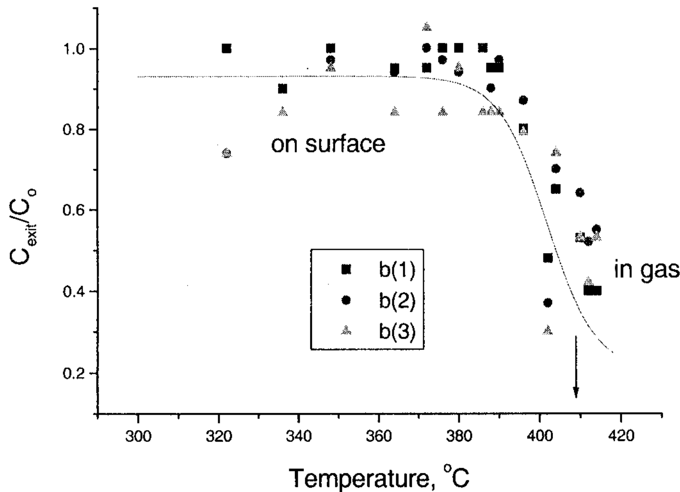


Figure 2 - Ratio between the precursor concentration at the exit (C_{exit}) and entry (C_o) of the reactor obtained from FT-IR bands (b(1) 1601 cm^{-1}; b(2) 1535 cm^{-1}; b(3) 1696 cm^{-1}) as a function of the reactor temperature at 80 Pa.

4. MODELING

In first step, we can start as explained in [2] and official modeling procedure of members of CVD project [3] (Society of Chemical Engineers of Japan), presenting the elements of mass transport as in Fig.3.

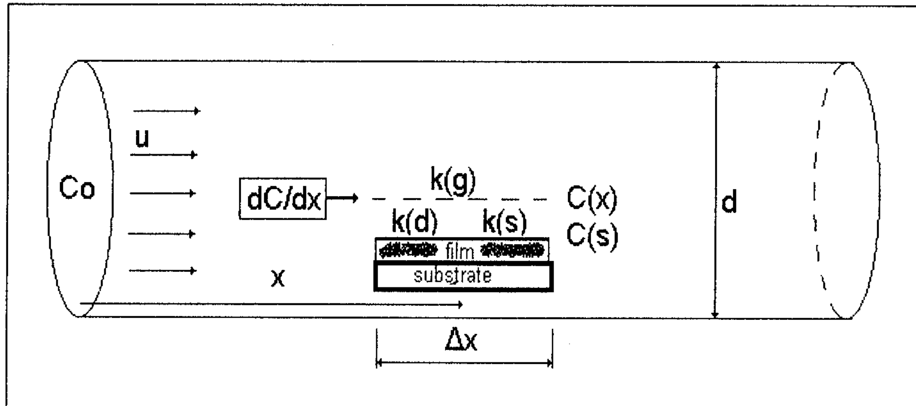


Figure 3 - Elements of mass transport in a horizontal hot-wall tubular reactor (simplified description)

Mass balance for a source precursor in an isothermal tubular reactor is:

$$u(dC/dx) - kC = 0 \quad (1a)$$

with solution:

$$C_{(x)} = C_{(x=0)} \exp(-kx/u) \quad (1b)$$

where k is first order deposition rate constant [s^{-1}]. This constant depends on the rate-limiting step [3]:

$k = k_g$ (*gas-phase reaction limited*)

$k = (S/V)\, k_s = (4/d)\, k_s$ (*surface reaction limited*)

$k = (S/V)\, k_d = (4/d)\, k_d = Sh\, (4/d^2)\, D$ (*diffusion limited*)

where:

u: gas velocity, [cm/s]; C: concentration of precursor, [mol cm^{-3}]; x: distance from inlet, [cm]; d: reactor diameter, [cm]; k_g: gas-phase reaction rate constant to produce intermediates; k_s: surface reaction rate constant of the film precursors; k_d : diffusion rate constant (D : diffusion coefficient of the film precursor, Sh : Sherwood number, Sh = 3.66 for laminar tube flow [2]).

Dependences on temperature and reactor diameter for k_g, k_s, and k_d are shown on Table 1.

***Table 1** - Dependences on temperature and reactor diameter for k_g, k_s, and k_d*

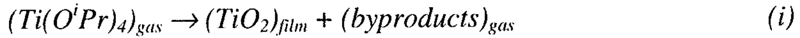
Constant	Dependence on temperature	Dependence on reactor diameter
$\mathbf{k_g}$ (gas-phase reaction rate)	Arrhenius type	-
$\mathbf{k_s}$ (surface reaction rate)	Arrhenius type	1/d
$\mathbf{k_d}$ (diffusion rate)	$T^{3/2}$	$1/d^2$

4.1. Proposed models

Two possibilities were taken into consideration, described as Variant (I) and (II)

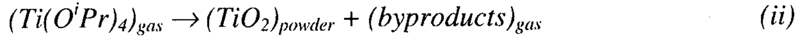
4.1.1. Variant (I)

We developed [5] a model that includes the overall heterogeneous reaction:



$$(Ti(O^iPr)_4)_{gas} \rightarrow (TiO_2)_{film} + (byproducts)_{gas} \qquad (i)$$

and a parasitic gas phase reaction



$$(Ti(O^iPr)_4)_{gas} \rightarrow (TiO_2)_{powder} + (byproducts)_{gas} \qquad (ii)$$

Reaction (i) is a global process of film formation whose mechanism includes the effects of decomposition products such as water and isopropanol. Reaction (ii) is a schematic way of representing many possible decomposition reactions that are ineffective to film growth, but which could result in TiO_2 powder and volatile product formation. A small amount of powder was found in the trap after depositions. For this case mass balance is:

$$u(dC/dx) - (k^{film} + k^{pwd})C = 0 \qquad (2a)$$

with solution:

$$C = C_{(x=0)} \exp[-(k^{film} + k^{pwd})x/u] \qquad (2b)$$

Thus, deposition rate is

$$r = d\delta/dt \text{ (nm/min) or } r = C_{(x)}\, L\, k^{film}(W_{TiO2}/\rho) \qquad (2c)$$

where: W_{TiO2}: molecular weight of TiO_2, ρ: density of the film, and L is the ratio reactive on superficial area. In this variant, the value of the apparent activation energy for the E_a^{film} is 126 kJ/mol and for powder formation E_a^{pwd} 370 kJ/mol, but only for temperatures up to 410°C.

4.1.2. Variant (II)

For more complex and/or mixed situations for temperatures above 410°C, we suggest mass balance (I) coupled with Frank-Kamenetskii model (II) [4]:

- in gas : $u(dC/dx) - k_gC = 0$ with solution: $C_{(x)} = C_{(x=0)} \exp(-k_gx/u)$ (I)
- on surface: $k_{s(x)}C_{s(x)} = k_{d(x)}(C_{(x)} - C_{s(x)})$ (II)

where: $C_{(x)}$: concentration at x position; $C_{(x=0)}$: concentration at inlet, $C_{s(x)}$: surface concentration at x position.

Finally, we get:

$$C_{s(x)} = [C_{(x=0)} \exp(-k_g x/u)]/[1 + (k_{s(x)}/k_{d(x)})] \quad (3a)$$

or

$$[C_{s(x)}/C_{(x=0)}] = [r_{s(x)}/r_{(x=0)}] = [\exp(-K\xi)]/[1 + z_{(x)}] \quad (3b)$$

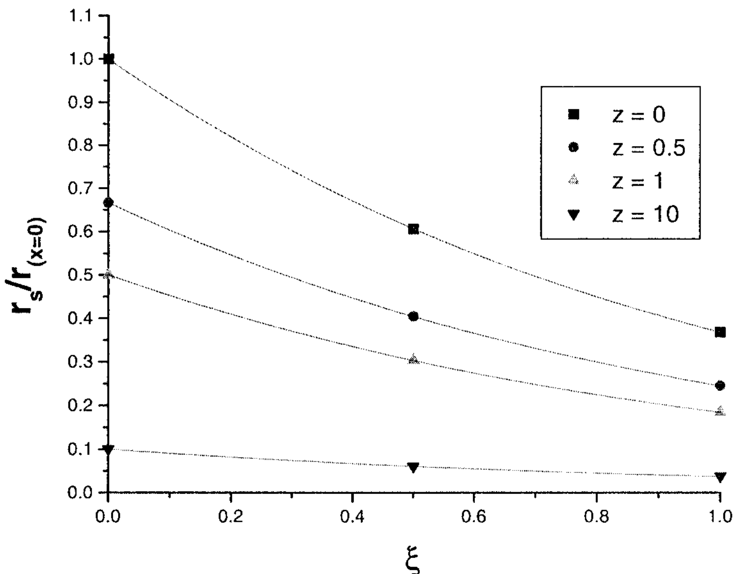


Figure 4 - Relative deposition rate vs normalized reactor x-coordinate for $z = 0$; 0.5; 1 and 10 (k_s and k_d : constant values at any x position; $K = 1$; $T = const.$)

where: $[C_{s(x)}/C_{(x=0)}]$: relative surface concentration; $[r_{(x)}/r_{(x=0)}]$: relative deposition rate; $K = (k_g x_{ref}/u)$: dimensionless gas rate group; $\xi = x/x_{ref}$: normalized position; $z_{(x)} = (k_{s(x)}/k_{d(x)})$ or in simplified form: $z = (k_s/k_d)$, when k_s and k_d are constant values at any x position (for characteristic values see Table 2.) and deposition rates: $r_{s(x)} = C_{s(x)} k^{film}(W_{TiO2}/\rho)$; $r_s = C_s k^{film}(W_{TiO2}/\rho)$; $r_{(x=0)} = C_{(x=0)} k^{film}(W_{TiO2}/\rho)$; $r_{(x)} = C_{(x)} k^{film}(W_{TiO2}/\rho)$

Now, we have the possibility to take into account the influence of k_g, k_s (or $k_{s(x)}$) and k_d (or $k_{d(x)}$) on overall deposition process, Fig. 4.

Table 2 - Characteristic relationships when $z_{(x)}$ or $z = 0; = 1; > 1$

$z_{(x)} = 0$ $z = 0$	$k_{s(x)} << k_{d(x)}$ $k_s << k_d$	$C_{s(x)} \doteq C_{(x)}$ or $r_{s(x)} = r_{(x)}$ $C_s = C_{(x)}$ or $r_s = r_{(x)}$
$z_{(x)} = 1$ $z = 1$	$k_{s(x)} = k_{d(x)}$ $k_s = k_d$	$C_{s(x)} = 0.5C_{(x)}$ or $r_{s(x)} = 0.5r_{(x)}$ $C_s = 0.5C_{(x)}$ or $r_s = 0.5r_{(x)}$
$z_{(x)} > 1$ $z > 1$	$k_{s(x)} > k_{d(x)}$ $k_s > k_d$	$C_{s(x)} < 0.5C_{(x)}$ or $r_{s(x)} < 0.5r_{(x)}$ $C_s < 0.5C_{(x)}$ or $r_s < 0.5r_{(x)}$

5. CONCLUSIONS

The deposition kinetics for TiO_2 growth is investigated and a range of common process parameters are obtained. Particular attention was paid to the relationship between growth rate and reactor temperature. The development of the modeling procedure permits to predict growth rates and precursor concentrations at different experimental conditions. In variant (I), a model includes the overall heterogeneous reaction and parasitic gas phase reaction. However, in variant (II) we have the influence of k_g, k_s, and k_d on overall deposition process incorporated into deposition rate equations (3a) and (3b).

According to this analysis the critical temperature when the mass transport is moving from surface into the gas phase is about 410°C.

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