MOCVD FILM GROWTH OF Al$_2$O$_3$ INSIDE HOT WALL TUBULAR REACTOR

GIOVANNI A. BATTISTON[1], ROSALBA GERBASI[1], KARLO T. RAIĆ[2]

[1]*Istituto di Chimica Inorganica e delle Superfici del C.N.R., Corso Stati Uniti, Padova, Italy,* [2]*Faculty of Technology and Metallurgy, Belgrade University, Beograd, Serbia and Montenegro*

ABSTRACT

The deposition kinetics for MOCVD film growth of Al$_2$O$_3$ was investigated in a range of common process parameters during laminar flow in horizontal hot wall tubular reactor. Particular attention was paid to the relationship between growth rate and reactor dimensions as well as process temperature. The development of the modeling procedure permitted to predict growth rates and precursor concentrations at different experimental conditions.
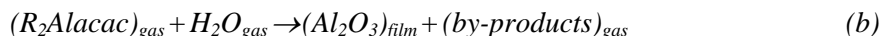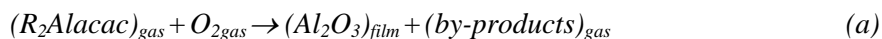
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1. INTRODUCTION

Kinetics of any CVD film growth is most complex and still far from satisfactory understanding (1). Nevertheless, in our investigations we have tried to explain our experimental data using the concept of mass transport in a horizontal tube reactor (2,3). In that sense, we coupled and combined this approach with the elementary surface phenomena equation of Frank-Kamenetskii (4). Evidence was based on our experimental date of Al$_2$O$_3$ films deposition.

Dimethyl, diethyl and di*iso*-buthyl aluminium acetylacetonate (R$_2$Alacac, R = Me, Et, *iso*-But; Acac = C$_5$H$_7$O$_2$) were synthesised to deposit Al$_2$o$_3$ films by a hot LP-MOCVD system (5-7). Growths of alumina were carried out in the temperature range 400-520°C under an oxygen or vapour atmospheres. A kinetic model ("first model") was applied to analyze the experimental data related to the three precursors and to compare their properties. The model supported by FT-IR measurements, well individuated the rate determining step of the heterogeneous process with kinetic constant correlated to the precursor

molecular structure. Also, we developed a new kinetic model ("second model") (8), which included the overall heterogeneous reaction in the two different experimental conditions (a: O_2/N_2; b: H_2O/N_2):

$$(R_2Alacac)_{gas} + O_{2gas} \rightarrow (Al_2O_3)_{film} + (by\text{-}products)_{gas} \qquad (a)$$

$$(R_2Alacac)_{gas} + H_2O_{gas} \rightarrow (Al_2O_3)_{film} + (by\text{-}products)_{gas} \qquad (b)$$

Such overall reactions actually consisted of a series of reaction steps, some in the gas phase (homogeneous) and some on the surface (heterogeneous). Each reaction step had a rate determined by an activation energy and process conditions, and any one could be the step which controls the film deposition rate. Our assumption was that the rate determined step was a thermally controlled reactions near the surface. Either oxygen in (a) or water vapour in (b) was in large stoichiometric excess; therefore the reaction rate depends on the concentration of a single reactant and a pseudo first-order kinetic in precursor concentration was postulated. A steady state analysis was carried out in one dimension, on the basis of the high uniformity of the film thickness in the radial direction.

In this paper we presented the growth rate of Al_2o_3 films from dimethilaluminium isopropoxide (($CH3$)2Al(iPr), synthesised in our lab, Figure 1. Summarising, in all cases, we usually had:

- at lower temperatures: (i) uniform growth of films along with the reactor x-coordinate, (ii) lower growth rates and (iii) a great amount of not used precursor.

- on higher temperatures: (i) non uniform growth of films along the reactor x-coordinate, (ii) higher growth rates in some x- positions and (iii) a good yield of precursor.

On the other hand, our "first model" has not always been in agreement with experimental data, so it was a reason to develop a new approach ("second model"), shortly presented in this paper.

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 (5-7). The reactor was provided with a Pyrex pipe, inner diameter 4.8 cm, and 31 cm long. Nitrogen (50 sccm) was employed as carrier gas and diluting gas (10 sccm), keeping the all 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 for Al$_2$O$_3$ example (Figure 1):

T = -211.6018 x^2 + 175.9463643x - 8.01385 + T(set), x are normalised coordinates x= (distance from origin in cm)/31cm. The central zone of the reactor, about 150 mm long, showed an almost uniform temperature with variations of ± 2°C.

The deposition rates, reported in Figures 1, were 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.
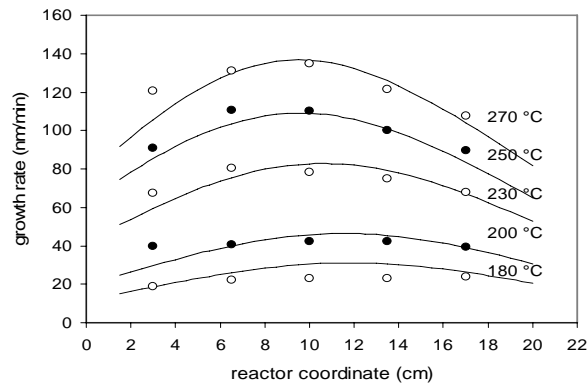

Fig. 1 - Deposition rate of the Al$_2$O$_3$ film growth for various temperatures, as a function of reactor x-coordinate. Symbols represent experimental data, lines the calculated trends

Proposed (”Second”) Model (8)

For most complex and/or mixed situations we suggest mass balance (I) coupled with Frank-Kamenetskii model (II) (4):

- in gas : u(dC/dx) – k$_g$C = 0 with solution:

$C_{(x)} = C_{(x = 0)} \, exp(-k_g x/u)$ *(I)*

- on surface:

$k_{s(x)}C_{s(x)} = k_{d(x)}(C_{(x)} - C_{s(x)})$ *(II)*

On the other side, surface deposition rate at some position (x) is

$r_s = (W/\rho) \, k_{s(x)} \, C_{s(x)}$ *(1)*

Starting deposition rate at x = 0 is

$r_{(x=0)} = (W/\rho) \, \Sigma k_{(x=0)} \, C_{(x=0)}$ *(2)*

where: $C_{(x)}$: concentration at x position; $C_{(x = 0)}$: concentration at inlet, $C_{s(x)}$: surface concentration at x position, W: molecular weight of the film, ρ: density of the film, $r = d\delta/dt$ (nm/min): deposition rate, $\Sigma k_{(x=0)} = [(k_g \, k_{s(x=0)} \, k_{d(x=0)})/(k_g + k_{s(x=0)} + k_{d(x=0)})]$: overall transport coefficient.

Finally, we get:

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

or

$$[r_{s(x)}/r_{(x = 0)}] = (k_{s(x)} / \Sigma k_{(x=0)})[exp(-K\xi)]/[1 + z_{(x)}] \tag{4}$$

where: $[C_{s(x)}/C_{(x = 0)}]$: relative surface concentration; $[r_{s(x)}/r_{(x = 0)}]$: 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 ref.(8)).

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, Figure 2. Also, we are in position to explane the exact deposition rate at any position.
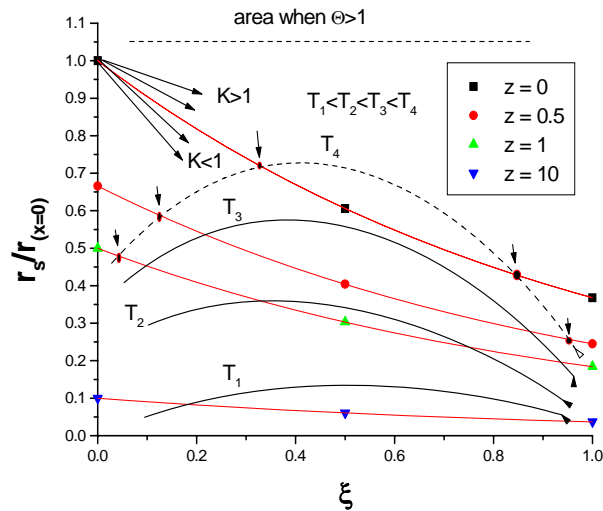

Fig. 2 - Relative deposition rate vs normalized reactor x-coordinate for z = 0; 0.5; 1 and 10 (k_s and k_d : constant values at any x position; ($\Theta = k_{s(x)} / \Sigma k_{(x=0)}$) ≈ 1; K = 1 ; T = T_4 = const) compared with possible experimental data at different temperatures. Areas for K<1 and K>1 are indicated but only for z = 0. Area when $\Theta = k_{s(x)} / \Sigma k_{(x=0)} > 1$ is above the straight doted line.

3. CONCLUSION

A model of deposition kinetics for MOCVD film growth of Al$_2$O$_3$ was developed for the horizontal hot wall tubular reactor under laminar regime (Re $\approx$ 0.5). The modeling procedure permitted to predict growth rates and precursor concentrations at different experimental conditions. In other words, we have had the possibility to take into account the influence of $\mathbf{k_g}$ (gas-phase reaction rate constant), $\mathbf{k_s}$ (surface reaction rate constant) and $\mathbf{k_d}$ (diffusion rate constant) on overall deposition process as well as to explain the exact deposition rate at any position of the horizontal hot wall tubular reactor.

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