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Modelling of Precursor Flow and Deposition in Atomic Layer Deposition Reactor

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Abstract. A calculation model to study atomic layer deposition (ALD) in low-pressure channel-type CVD reactor with many parallel substrates is described. The calculations are based on continuity equation and kinetic equation for surface coverage. Formation of a steady-state adsorption wave propagating between the substrates during a precursor pulse is studied. The effect of diffusion and sticking coefficients, carrier gas flow rate and growth temperature on formation and propagation of the steady-state adsorption wave is analyzed.

1. INTRODUCTION

Atomic layer deposition (ALD) - the technique at which the different constituent elements of a solid compound are deposited during alternate precursors pulses, allows to obtain thin film structures of high quality. In addition to the possibility to grow uniform films on profiled substrates and unique multilayer structures, ALD has demonstrated to be a proper technique for characterization of the growth kinetics and evaluation of the quantities related to that.

The experimental methods used for investigation of the growth kinetics in chemical vapor deposition (CVD) and ALD equipment include optical methods [1-5], mass spectrometry [5-7], spectro-ellipsometry [8], deposit mass monitoring by quartz microbalance [9-11] and gravimetry [12]. Data about the gas phase consistency or the surface coverage are obtained from these measurements. Furthermore, comparing the data to some theoretical model, the quantities characterizing surface (or gas phase) reactions can be calculated.

Propagation of precursors and film growth in low-pressure CVD equipment has been investigated using various computational models, e.g. [13-16]. However, the models are related to specific circumstances, such as reactor geometry, transport of the substances and the reactions on the growing surface as well as in the gas phase. In case of ALD the precursors and the growth conditions are chosen to accord to self-limited growth. Precursors react only with the substance adsorbed on the solid surface during the exposure of the growing film to the other precursor, and cannot be deposited more than one monolayer during every reaction step. For this reason the adsorption process can be described more exactly and the data concerning with the surface reactions should be more reliable in case of ALD rather than in case of conventional CVD.

However, the theoretical model has to be fitted with geometry of reactor used for experimental research.

It has been shown that channel-type ALD reactors have some advantages in investigation of growth kinetics [17, 18]. Therefore, a calculation model to describe the ALD growth in this type of reactor is presented below. The model is used to study the propagation and adsorption of a precursor. The effect of the carrier gas flow rate, sticking and diffusion coefficients of the precursor and reactor temperature on the length and formation rate of the steady-state adsorption wave is investigated. Finally, surface coverage of the substrates and mean values of precursor concentration as the parameters available from experiments are calculated for different growth conditions.

2. THEORETICAL

We consider the ALD growth in a low-pressure gas-transport reactor where substrates are located parallel to one another and to the gas flow direction whereas the distance between the substrates is small compared with the width of the substrates (Fig. 1). Continuous flow of carrier gas passes through the reactor and the both precursors are added to that alternatively. In order to prevent gas phase reactions the reactor is purged from the surplus of the reactants by pure carrier gas flow between subsequent reactant pulses. The gas flow is assumed to be viscous and laminar.

Figure 1: Schematic diagram of the ALD reactor (a) and a channel between two substrates (b).

Carrier gas flow rate, total pressure and temperature in the channels between the substrates are assumed to be constant. Variation of the precursor concentration, c (in moles per unit volume), is described by the continuity equation

$$\frac{\partial c}{\partial t} + \text{div } \vec{N} = R, \quad (1)$$

where $\vec{N}$ is the molar flux of the precursor, i.e. the number of moles passing through unit area per time unit, and R is the number of moles emitted in unit volume per time unit. When diffusion of the precursor in the carrier gas is taken into account, the following relationship can be written for $\vec{N}$,

$$\vec{N} = \frac{c}{c + c_c} (\vec{N} + \vec{N}_c) - (c + c_c) D \text{grad} \left(\frac{c}{c + c_c} \right), \quad (2)$$

where $\vec{N}_c$ and c_c are the flux and the concentration of the carrier gas, respectively, and D is the diffusion coefficient of the precursor in the carrier gas. Assuming that c_c is constant and $c \ll c_c$, and taking into account that $\vec{N}_c = \vec{v}c$ where $\vec{v}$ is the velocity of the carrier gas, Eq.(2) gives

$$\vec{N} = c\vec{v} - D \text{grad } c. \quad (3)$$

We also assume that the distance between the substrates, h (Fig. 1b) is small compared to the width of the substrates. Therefore, two-dimensional case is considered in the following. Using Eq.(3), Eq.(1) obtains the form

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial y} - D \left(\frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) = R, \quad (4)$$

where v denotes the y -component of $\vec{v}$. Since the gas flow is viscous, v depends on the value of z . This velocity dependence may be expressed through the mean flow rate $\bar{v}$ as

$$v = 6 \bar{v} \left[\frac{z}{h} - \left(\frac{z}{h} \right)^2 \right]. \quad (5)$$

When the adsorption on the channel walls is self-limited, as it is inherent to ALD, the surface coverage, Θ , can be calculated from the relationship

$$\frac{d\Theta}{dt} = \frac{k(1 - \Theta) \langle v \rangle c}{4 N_0} - \frac{\Theta}{\tau}, \quad (6)$$

where k is the sticking coefficient, $\langle v \rangle$ is the mean thermal velocity of precursor molecules, N_0 is the density of adsorption sites on the growing surface and τ is the desorption rate constant. Further the desorption rate is assumed to be small, so that the second term on the right side of Eq.(6) is neglected in the following considerations.

We assume that at $t = 0$ the surface coverage of the substrates and precursor concentration are equal to zero everywhere in the channel, while concentration is assumed to be equal to c_0 at the inlet of the channel where $y = 0$. Precursor concentration is assumed to retain the value c_0 at the channel inlet during the pulse. Eq.-s (4) and (6) are used to determine c in the channel and Θ for next time moments. To solve Eq.-s (4) and (6), the channel is divided into small parts, as shown in Fig. 1b, and c and its derivatives, as well as variation of Θ are calculated for all these parts at time moments separated by sufficiently small time intervals.

It is taken into account that adsorption is the reason for precursor molecules to leave the gas phase and it takes place in the rectangles adjacent to the channel walls. In these rectangles,

$$R = - \frac{N_0}{\Delta z} \frac{d\Theta}{dt}, \quad (7)$$

while $R = 0$ in the other rectangles.

3. CALCULATION RESULTS AND DISCUSSION

Some facilities of the model calculations are demonstrated below. It is shown how a steady-state adsorption wave is formed between the substrates and how this process depends on the sticking and diffusion coefficients of the precursor, on the mean flow rate of the carrier gas and on reactor temperature.

Besides the surface coverage, the precursor concentration $\bar{c}$ averaged over the distance between the substrates is under consideration.

3.1 Formation of a steady-state adsorption wave

Time dependence of Θ and $\bar{c}$ calculated for definite growth parameters and certain values of y is demonstrated in Fig. 2.

Figure 2: Time dependence of the surface coverage, Θ , (a), and of the averaged relative precursor concentration, $\bar{c}/c_0$, (b). $\bar{v} = 20 \text{ m/s}$, $D = 0.03 \text{ m}^2/\text{s}$, $k = 0.1$, $h = 2.4 \text{ mm}$, $\langle v \rangle = 640 \text{ m/s}$, $c_0/N_0 = 2 \text{ nr}^{-1}$.

As one can see, Θ and $\bar{c}$ increase rapidly near the channel inlet at the beginning of the pulse. Simultaneously the propagation rate of the precursor slows down until a region with a stable concentration profile (steady-state concentration wave) is formed. A certain surface coverage profile corresponds to every concentration profile and they both move with the same (constant) rate towards the reactor outlet when the formation of steady-state profiles is completed.

The effect of the growth parameters on the propagation rate of the steady-state adsorption wave was analyzed in our previous paper [18] while the effect of $\bar{v}$, k and D on the length and formation time of that will be discussed below. In order to characterize the initial stage of propagating the adsorption wave we calculated the time t^* necessary to obtain the surface coverage $\Theta = 0.97$ at $y = 5 \text{ mm}$ and a parameter l_s which is the length of the region where Θ varies

from 0.9 to 0.1. The dependence of t^* and l_d on k and $\bar{v}$ is presented in Figs. 3 and 4, respectively, for two values of D .

Figure 3: Formation time, t^* , (a) and length, l_d , (b) of steady-state adsorption wave as functions of sticking coefficient, k . $h = 2.4 \text{ mm}$, $\langle v \rangle = 640 \text{ m/s}$, $c_0/N_0 = 2 \text{ m}^{-1}$.

Figure 4: Formation time, t^* , (a) and length, l_d , (b) of steady-state adsorption wave as functions of velocity of carrier gas, $\bar{v}$. $h = 2.4 \text{ mm}$, $\langle v \rangle = 640 \text{ m/s}$, $c_0/N_0 = 2 \text{ m}^{-1}$, $k = 0.1$.

Although the propagation rate of the steady-state adsorption wave is almost independent of k [18], t^* and l_d both increase rapidly with decreasing k . This result shows that less than a complete monolayer of the compound grows per cycle if the pulse time is too short while the film thickness variation from the inlet to the outlet can be still small because l_d increases with decreasing k , as well. At low velocities of the carrier gas the formation time of the steady-state adsorption wave increases rapidly with decreasing $\bar{v}$, while at high values of $\bar{v}$ the effect of $\bar{v}$ on

t^* is weak. At the same time l_d increases with $\bar{v}$. As one can see in Fig. 4, the longitudinal diffusion is significant at low velocities of the carrier gas while the values of l_d are higher and the steady-state adsorption wave is formed faster at higher D values. Lower l_d corresponds to high D at high $\bar{v}$ showing that transversal diffusion plays some role in this region. This effect increases with increasing distance between the substrates. The calculations show that at low $\bar{v}$ the surface coverage reaches the value 0.97 remarkably faster than $\bar{v}/c_0$, but at high velocities it occurs on the contrary. Consequently, the precursor is blown through the channel even when the surface coverage is still rather low.

3.2 Effect of temperature

It is obvious that the sticking and diffusion coefficients as well as the thermal velocity of precursor molecules depend on temperature. However, it is rather difficult to predict the effect of temperature on the sticking coefficient because the mechanisms of surface reactions can be very different at different temperatures. Thus, we concern with the effects caused by temperature dependence of $\langle v \rangle$ and D ,

$$\langle v \rangle = v_0 (T/T_0)^{1/2}, \quad (8)$$

$$D = D_0 (T/T_0)^{3/2}, \quad (9)$$

where v_0 , D_0 and T_0 are constants. To study the temperature dependence, their values were chosen assuming that $\langle v \rangle = 640 \text{ m/s}$ and $D = 0.1$ or $0.01 \text{ m}^2/\text{s}$ at $T = 600 \text{ K}$.

First, the coverage profile was calculated for different temperatures at the same time moment (Fig. 5).

Figure 5: Surface coverage profiles at various temperatures T for $\bar{v} = 20 \text{ m/s}$ (a) and $\bar{v} = 5 \text{ m/s}$ (b). $k = 0.1$, $h = 2.4 \text{ mm}$, $c_0/N_0 = 20 \text{ m}^{-3}$.

We can see that temperature affects the propagation rate of the precursor at low values of $\bar{v}$ when increase of the longitudinal diffusion rate accompanies the temperature increase. At high $\bar{v}$ longitudinal diffusion and temperature have no effect on the precursor propagation rate, although l_d depends on temperature (Fig. 6).

Figure 6: Temperature dependence of the length of steady-state adsorption wave, l_d , for $D_0 = 0.1 \text{ m}^2/\text{s}$ (a) and $D_0 = 0.01 \text{ m}^2/\text{s}$ (b). $h = 2.4 \text{ mm}$.

It is interesting that the temperature dependence of l_d is essentially effected by D . At sufficiently high values of D , the increase of l_d with T is caused by increasing longitudinal diffusion which has particular importance in case of low $\bar{v}$. At low values of D , l_d decreases with increasing temperature. This behavior may be caused by two circumstances. First, increase of D with increasing T causes increase of transversal diffusion and, secondly, mean thermal velocity $\langle v \rangle$ increases with T . The both effects are remarkable at high flow rates. In general, the effect of temperature on l_d is stronger at lower sticking coefficients.

4. CONCLUSIONS

Our calculations show that surface coverage profile and, consequently, the thickness profile of the growing film depend significantly on diffusion and sticking coefficients of precursor molecules, flow rate of carrier gas and reactor temperature. Both, the formation time of the steady-state profile and the length of this profile increase significantly with decreasing sticking coefficient. Therefore rather uniform films can be grown using insufficient precursor doses at high flow rates of the carrier gas. As a result no unambiguous information about the self-limitation of adsorption can be obtained from thickness profiles when precursors with very low sticking coefficient are used.

Our calculations also demonstrate that the behavior of surface coverage profile with changing temperature depends significantly on the flow rate of the carrier gas, gas phase diffusivity of precursor molecules and distance between the substrates. The length of nonuniform thickness profile increases with increasing temperature at low values of $\bar{v}$ and high values of D while that decreases with increasing temperature at high values of $\bar{v}$ and low values of D . This phenomenon can be explained by different contributions of diffusion and thermal motion of gas molecules to the adsorption process and propagation of the adsorption wave.

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