Reactivities of TaCl_5 and H_2O as Precursors for Atomic Layer Deposition

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Abstract: Model calculations and time dependence of the deposit mass recorded by quartz crystal microbalance during atomic layer growth of tantalum oxide are used to determine sticking coefficients of TaCl_5 and H_2O , and diffusion coefficient of TaCl_5 in N_2 . It is shown that the reactivity of TaCl_5 towards H_2O -treated tantalum oxide surface is remarkably higher than the reactivity of H_2O towards TaCl_5 -treated tantalum oxide.

1. INTRODUCTION

Atomic layer deposition (ALD) is a method which provides a possibility for growing thin solid films with very precise thickness control on large areas [1]. A number of materials have been deposited using this method. However, in some cases serious problems arise with the choice of suitable precursors. As the solid film is formed by subsequent reactions between the solid surface and different precursors, reactivity of the precursors towards the surface is of significant importance in the ALD process.

In the simplest case the self-limited chemisorption needed for ALD can be characterized by the equation ([2])

$$dN/dt = kA(N_0 - N) - N/\tau, \quad (1)$$

where N is the number of precursor molecules adsorbed per unit area, N_0 is surface density of adsorption sites, A is the number of impacts of precursor molecules to one adsorption site per time unit, τ is the desorption time constant and k is the sticking coefficient.

The quantity which describes the reactivity of the precursors is k . It is obvious that the exposure time needed for deposition of an adsorbate monolayer is the shorter, the higher the value of k is. Therefore higher k enables to realize higher growth rate. It can also be shown that higher sticking coefficients result in higher utilization efficiencies of the precursors.

However, as a rule, there is no data about the sticking coefficients of precursors used for ALD. Particularly, it concerns the specific conditions at which ALD processes are carried out. Thus such measurements should be performed to characterize precursors for ALD quantitatively.

It was shown recently that sticking coefficient of precursor molecules can be estimated using whether the thickness profile of films grown in a channel-type ALD reactor [3] or chemisorption kinetics measured at the outlet of a channel-type ALD reactor [2]. In the present paper we demonstrate application of the latter method for determination of the sticking coefficients of TaCl_5 and H_2O on tantalum oxide.

2. EXPERIMENTAL

The experiments were performed in a horizontal flow-type low-pressure ALD reactor at 250°C using pure N_2 as the carrier gas. Plane substrates of tantalum foil were placed in the reactor tube with inner diameter of 35 mm in such a way that they formed slit-shaped channels between them (Fig. 1a). The length and height of the channels were 50 and 2.5 mm, respectively.

Figure 1: Experimental set-up for measurements of adsorption kinetics at the outlet of channels (a) and for determination of reactant pulse delays occurring in the inlet tube (b)

The chemisorption kinetics was measured at the outlet of the channels using quartz microbalance. Before starting the measurements 100 and 5 nm thick buffer layers of tantalum oxide were grown on the substrates and mass sensor, respectively. Single ALD cycles were used in order to study adsorption kinetics and to determine the sticking coefficients. Each cycle consisted of subsequent $TaCl_5$ and H_2O pulses separated by 4 s long purge time. During deposit mass measurements the fluctuations of the reactor temperature did not exceed 0.05°C.

The microbalance responses were recorded at different flow rates of the carrier gas while the total pressure inside the reactor (250 ± 20 Pa) as well as the partial pressure of $TaCl_5$ were kept constant. The temperature of $TaCl_5$ source ($70.5 \pm 0.5^\circ C$) and the flow rate of H_2O (170 ± 30 cm³ Pa/s) were somewhat lower than those used in the previous study [4].

In order to determine the reactant pulse delays occurring during the gas transport through the inlet tube, the substrates were removed from the reactor and the chemisorption kinetics was measured with the mass sensor located at the position corresponding to the location of the leading edges of the substrates (Fig. 1b).

3. RESULTS AND DISCUSSION

3.1. Adsorption kinetics

Time dependence of mass sensor signals after switching on the TaCl_5 and H_2O pulses was recorded 4-7 times for each flow rate of the carrier gas, $\bar{v}$. Single scans for each $\bar{v}$ were averaged. The results for $\bar{v} = 0.62$ and 0.28 m/s are demonstrated in Fig. 2. The shapes of the curves are very similar to those published in [5]. As one can see in Fig. 2, the deposit mass increases during TaCl_5 pulse and decreases during H_2O pulse. The increase is caused by adsorption of Ta-containing molecules. In general case surface intermediates with the Cl/Ta ratio different from that in TaCl_5 remain on the solid surface after this reaction step. The decrease of the deposit mass during the H_2O pulse is due to the exchange of the chlorine remained on the surface, with oxygen or hydroxyl groups which both are lighter than equivalent amount of chlorine.

Deposit mass

Figure 2: Experimental and calculated time dependences of mass sensor signals during TaCl_5 (a) and H_2O (b) pulses at two different velocities of carrier gas. Smooth curves represent time dependences of the surface coverage calculated for the values of k and D obtained in this work.

The averaged experimental curves show that at the beginning of a deposition pulse the deposit mass is rapidly varied whereas the variation rate depends on the flow rate of the carrier gas. After some time variation rate of the deposit mass decreases and then obtains a constant value which is the same for all carrier gas flow rates. This constant value is obtained faster in case of higher $\bar{v}$. Finally, intensity of the mass sensor signal obtains the value which remains constant in the following. Therefore we conclude that at least two different processes with different time constants take place during adsorption of TaCl_5 as well as H_2O . There is no simple explanation to this phenomenon because CVD-type deposition and temperature fluctuations [6] as well as two-step surface reactions can be responsible for the slower change of mass sensor signal. However, the faster process clearly dominates at the beginning of the both pulses. Therefore we apply the calculation model [2] which takes into account only one self-limited reaction to the faster process in case of each pulse.

3.2. Determination of diffusion coefficient and precursor concentration

It has been shown that besides the sticking coefficient, the diffusion coefficient of the precursor molecules in gas phase, D , influences the shape of mass sensor signal recorded at the outlet of channel-type ALD reactor [2]. There are reliable data concerning with the diffusivity of H_2O in N_2 , e.g. [7,8]. Unfortunately, no data were available for the diffusion coefficient of TaCl_5 . However, diffusion coefficients of some other chlorides, e.g. AlCl_3 and SnCl_4 which have also

Figure 3: Calculated and experimental dependences of delay time on reciprocal velocity of carrier gas, $1/\bar{v}$. Solid curves are calculated at $D = 0.0075 \text{ m}^2/\text{s}$ and $c_0/N_0 = 12 \text{ m}^{-1}$ for TaCl_5 , and $D = 0.026 \text{ m}^2/\text{s}$ and $\bar{v}c_0/N_0 = 26 \text{ s}^{-1}$ for water.

been used as precursors for ALD, could be determined from the data available for us [8-10]. In the present work we determined the diffusion coefficient of TaCl_5 using our experimental data and considering the value of the diffusion coefficient of SnCl_4 in N_2 , $0.0059 \text{ m}^2/\text{s}$, as the initial data for our approximation.

We have shown earlier [2] that gas phase diffusivity of a precursor can be found from the dependence of the delay time on the velocity of the carrier gas, $\bar{v}$ (Fig. 3). The calculations have also shown that the delay time is inversely proportional to the precursor concentration at the channel inlet, c_0 . Thus we obtained the values of D and c_0/N_0 for TaCl_5 and $\bar{v}c_0/N_0$ for H_2O by fitting the calculated curves to the experimental points. As a result of the best approximation the values $D = 0.0075 \text{ m}^2/\text{s}$ and $c_0/N_0 = 12 \text{ m}^{-1}$ for TaCl_5 , and $\bar{v}c_0/N_0 = 26 \text{ s}^{-1}$ for H_2O were determined. The solid lines in Fig. 3 are calculated based on these values. The curve for TaCl_5 significantly differs from that for H_2O because the precursor concentration was kept constant in the former case while the precursor flow rate was constant in the latter one.

3.3. Determination of sticking coefficients

Model calculations have shown that the surface coverage as a function of time depends on the sticking coefficient [2]. This circumstance lies on the basis of determination of k in this study whereas the maximum slope of the mass sensor signal, M , is used as a quantity characterizing the time dependence of surface coverage. Comparing the experimental values of M with the maximum slope of surface coverage calculated at different k we obtained the best fit at $k = 0.02$ and $k = 0.0004$ in case of TaCl_5 and H_2O , respectively (Fig. 4). As one can see, there is a significant deviation of experimental points in Fig. 4. Thus, the value of k can be estimated only roughly. We do not know about other similar measurements of the sticking coefficient. Some indirect data refer to that the sticking coefficients in atomic layer chemical vapor deposition from chlorides and water must be small. S.B.Desu, growing TiO_2 films from TiCl_4 and water by successive layer-wise chemisorption at pressure and temperature close to ours, used very long pulse times (20 minutes) [11]. In most cases high precursor concentrations and carrier gas flow rates are used to achieve the complete monolayer coverage in a growth cycle [2, 12]. Achieving full monolayer in a cycle at high $\bar{v}$ and c_0 and short pulse times even if the sticking coefficient is very small, is in accordance with our calculations. However, although producing of films by ALD is possible in spite of k is very small, the value of k will be useful in future investigation of the chemisorption.

Figure 4: Calculated and experimental dependences of maximum slope of surface coverage variation, M , on reciprocal velocity of carrier gas, $1/\bar{v}$.

Although the values of k are determined very roughly, our results enable to confirm that the sticking coefficient of TaCl_5 on H_2O -treated tantalum oxide surface is much higher than that of H_2O on TaCl_5 -treated tantalum oxide.

4. CONCLUSIONS

The data presented above demonstrate that the sticking coefficients of precursors as well as the gas phase diffusion coefficients can be evaluated using deposition kinetics recorded by quartz microbalance at the outlet of channel-type ALD reactor.

We have shown that the reactivity of TaCl_5 towards H_2O -treated tantalum oxide is higher than reactivity of H_2O towards TaCl_5 -treated oxide.

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