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Reaction mechanism studies on atomic layer deposition process of AlF_3

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In this work, the reaction mechanism in the atomic layer deposition (ALD) process of AlF_3 thin films is studied with *in situ* quartz crystal microbalance (QCM) and quadrupole mass spectrometer (QMS). The depositions are done with AlCl_3 and TiF_4 as precursors. Similar to many metal fluoride films deposited by ALD, the growth rate of the AlF_3 is strongly temperature dependent. In addition, at low temperatures the growth rate is exceptionally high for a traditional ALD process. In this study, the reasons behind these characteristics are studied and a detailed step-by-step mechanism for the AlF_3 film growth process is presented.

I. INTRODUCTION

Atomic layer deposition (ALD) is a superior thin film deposition technique, which is based on sequential chemical reactions between alternately supplied precursor vapors on a substrate surface. With proper precursors and film growth conditions the reactions are self-limiting and pinhole free films with high purity and excellent uniformity and conformality can be deposited with film thickness control on a monolayer scale.^{1,2} The chemistry between the precursors determines the film growth, so only by studying the surface reactions an ALD process can be truly understood. The best way to study the reactions is to observe the changes of the film surface and the surrounding gas atmosphere already during the growth process. These kind of *in situ* studies have revealed insights on a wide range of different ALD chemistries, as can be seen on the comprehensive review articles published on the topic.³⁻⁵

An ALD process for AlF_3 using AlCl_3 and TiF_4 precursors has been published by Mäntymäki et al.⁶ TiF_4 as a fluorine source is a less hazardous alternative to the common fluorine ALD precursor of HF. Films were deposited at temperatures from 160 to 340 °C and good saturative ALD behavior was verified. Films were amorphous below 260 °C and showed increasing amounts of crystallinity at higher temperatures. They contained only small amount of titanium and chlorine impurities that decreased with increasing temperature so that both were less than 1 at.% at 280 °C. Earlier reaction mechanism studies on ALD AlF_3 ^{7,8} and other metal fluoride films⁹⁻¹¹ have been done only for processes which use HF,¹¹ HF/pyridine⁸⁻¹⁰ or SF_6 plasma⁷ as the fluorine sources.

In addition to the AlF_3 , ALD processes for LiF , CaF_2 , MgF_2 , LaF_3 , YF_3 and TbF_3 have been developed by using TiF_4 as the fluorine source.¹²⁻¹⁹ The processes are thought

to rely on a ligand exchange reaction between the metal precursor, usually Mthd, $M(\text{thd})_2$ or $M(\text{thd})_3$ (thd = bis(2,2,6,6-tetramethyl-3,5-heptanedionato),^{12–17,19} and TiF_4 from which a volatile $\text{Ti}(\text{thd})_4$ is formed as a byproduct. Similarly, the overall reaction in the AlF_3 process studied in this work has been thought to be a ligand exchange reaction between the metal halide precursors.

In many of the metal fluoride ALD processes the growth rates have been noticed to be strongly temperature dependent and exceptionally high at low deposition temperatures.^{6,13–16} This was the case also for the AlCl_3 and TiF_4 process for AlF_3 films where the growth rate decreased from 3 Å/cycle to 0.3 Å/cycle as the deposition temperature was increased from 160 to 340 °C.⁶ The mechanism proposed for explaining the exceptionally high growth rate is that during each pulse the precursors not only react with the functional groups on the surface, but also adsorb onto the freshly formed film. This kind of double monolayer type of growth can also make the process strongly temperature dependent, because the molecular adsorption is a reversible process unlike the common ligand exchange reactions in ALD. Herein we study the growth mechanism of AlF_3 to increase the understanding on this kind of reaction mechanisms.

The overall reaction is proposed to be a ligand exchange reaction between AlCl_3 and TiF_4 , which releases TiCl_4 as a gaseous byproduct and deposits AlF_3 film (reaction 1).

The reaction can proceed through a few possible routes. Either AlCl_3 adsorbs on AlF_3 surface without reaction (reaction 2) and AlF_3 and TiCl_4 form only during the TiF_4 pulse (reaction 3), or vice versa (reactions 4-5).

Another option is that AlF_3 and TiCl_4 are formed during both precursor pulses. In that case x amount of TiCl_4 is released during the AlCl_3 pulse (reaction 6) and the rest during the TiF_4 pulse (reaction 7).

Formation of mixed halides, such as TiFCl_3 , TiF_2Cl_2 and TiF_3Cl , is also possible if all the ligands do not exchange in the reaction.

II. EXPERIMENTAL

The depositions were done in a F120 SAT flow-type ALD reactor by ASM Microchemistry Ltd. to which an *in situ* quartz crystal microbalance (QCM) and quadrupole mass spectrometer (QMS) are attached. The details of this unique ALD reactor are described elsewhere.²⁰ The deposition area of the reactor is enlarged compared to a regular F120 ALD reactor to ensure high enough amount of byproducts for detection by QMS. During the measurements the deposition chamber is loaded with glass

substrates so that overall the substrates and the glass walls make an area of 3500 cm^2 .²⁰ The pressure drop from the working pressure of the ALD reactor (1-5 mbar) to the required pressure in the QMS chamber (around 10^{-5} mbar) is done by differential pumping through a $150 \text{ }\mu\text{m}$ orifice. QMS measurements were done with a Hiden HAL/3F 501RC mass spectrometer using an ionization energy of 70 eV. The reference mass spectra are from NIST Mass Spectrometry Data Center.²¹ The QCM is placed in between the glass substrates and the QMS inlet, and the measurements are done on a gold coated quartz crystal with a Maxtek TM 400 with a sampling rate of 20 Hz. Before the measurements a thin layer of AlF_3 was deposited on the gold coated crystal.

The depositions were done at the temperature range of $160 - 320 \text{ }^\circ\text{C}$ using AlCl_3 (Acros Organics, 99%) and TiF_4 (Strem Chemicals, Inc. 98 %) as precursors. Both precursors were heated in open glass boats inside the reactor and pulsed by inert gas valving to the reaction chamber. The sublimation temperature of AlCl_3 was $90 \text{ }^\circ\text{C}$ and that of TiF_4 $140 \text{ }^\circ\text{C}$.

III. RESULTS AND DISCUSSION

In the original paper by Mäntymäki et al, it was noted that the growth rate of AlF_3 in the AlCl_3 - TiF_4 process is strongly temperature dependent and at low temperatures exceptionally high for an ALD process, around $3 \text{ }\text{\AA}/\text{cycle}$ at $160 \text{ }^\circ\text{C}$.⁶ The suggested reason for the unusual growth rate is that at low temperatures the precursors would not only react with the surface groups but also adsorb onto the new film formed.⁶ At higher temperatures the adsorption would rapidly decrease, thereby explaining the strong

temperature dependence of the growth rate. The question is that which precursor, or both, would be adsorbing this way.

FIG. 1. QCM close up on two ALD cycles of AlF_3 at deposition temperatures a) 160 °C, b) 200 °C, c) 240 °C, d) 280 °C and e) 320 °C.

Mass changes during the deposition of AlF_3 were measured with QCM at each selected temperature (Figure 1a-e). The mass increase during the AlCl_3 pulse is sharp throughout the whole temperature range, and only a slight decrease in m_1 , measured after the following purge, was observed at 320 °C (Figure 1e). The mass change during the TiF_4 pulse on the other hand is clearly temperature dependent. At low deposition temperatures, from 160 to 240 °C, the mass increases also during the TiF_4 pulse (Figure 1a-c). At higher temperatures (>240 °C) the mass increase during the TiF_4 pulse is much lower and the overall mass change after one whole ALD cycle (m_0) is on the same level (Figure 1d) or even lower (Figure 1e) than after the AlCl_3 pulse and purge (m_1). As a result, m_0 that represents the growth rate is strongly temperature dependent (Figure 2) similar to the results in the work of Mäntymäki et al.⁶

These results imply that molecular adsorption of TiF_4 on AlF_3 is taking place at low temperatures, and this adsorption decreases as the temperature is increased. The mass change during the AlCl_3 pulse is less temperature dependent than that during the TiF_4

pulse, hence no molecular AlCl_3 adsorption on AlF_3 is suggested to occur. The slight decrease of m_1 at higher temperatures presumably originates from the decreased amount of the reactive TiF_4 molecules on the surface.

FIG. 2. The mass increase after one whole ALD cycle (m_0) as a function of the deposition temperature.

The formation of TiCl_4 as a byproduct was clearly detected with QMS at each measured temperature (Figure 3a). Several m/z values from the fragmentation pattern of TiCl_4 were observed (Table I) and the intensities of the measured fragments are in accordance with the reference mass spectrum.^{21–23} Closer consideration is given for $m/z = 153$ because it has the highest intensity in the mass spectrum of TiCl_4 . In the measurements shown in Figure 3a, TiF_4 is pulsed alone prior to the ALD sequence for reference to see if certain m/z would originate from the precursor itself. Similar reference pulsing was done for AlCl_3 after the ALD pulses. It was noticed with QCM that at lower temperatures TiF_4 needs higher dose, i.e. longer pulse time to saturate the surface than at high temperatures, which is why the cycling times vary in Figure 3a.

Fragments corresponding to other possible reaction byproducts, i.e. mixed halides TiCl_3F , TiCl_2F_2 and TiClF_3 , were followed as well (Table I). The fragmentation patterns of these halides overlap to some extent with each other and with TiCl_4 . However, no ions corresponding specifically to the mixed halides were visible and hence the recurring m/z are assigned to TiCl_4 and no other byproduct is identified in the process. However, the lower the vapor pressure is for a suggested byproduct, the more difficult it is to detect, so some formation of mixed halides cannot be absolutely excluded. The major byproduct in the process is anyway TiCl_4 .

TiCl_4 formation was especially clear during the AlCl_3 pulse at each temperature (Figure 3b). This indicates that after the TiF_4 pulse the surface is always $-\text{TiF}_x$ terminated, even though TiF_4 adsorbs on to the AlF_3 surface less at high temperatures as discussed earlier. As less $-\text{TiF}_x$ groups exist on the surface at higher temperatures, not all the chlorides in AlCl_3 are able to exchange and form TiCl_4 already during the AlCl_3 pulse. The unreacted chlorides remaining on the surface react during the TiF_4 pulse, which is observed in QMS as a release of TiCl_4 also during the TiF_4 pulse at temperatures $\geq 200^\circ\text{C}$. At the low temperature of 160°C almost all TiCl_4 is formed during the AlCl_3 pulse, presumably because the surface contains a high amount of TiF_4 in the beginning of the AlCl_3 pulse. This deduction based on the QMS observations is in line with the QCM results which also implied that AlCl_3 does not adsorb on AlF_3 similarly as TiF_4 does.

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FIG. 3. a) QMS measurements of $m/z = 153$ (TiCl_3^+) at each deposition temperature and b) a close up on measurements done at 160, 240 and 320 °C.

TABLE I. The measured m/z values, observations and possible fragments. The measurements were done at 240 °C.

m/z	Observation	Fragment	m/z	Observation	Fragment
48	yes	$[\text{}^{48}\text{Ti}]^+$	153	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_3]^+$
100	no	$[\text{}^{27}\text{Al}^{35}\text{Cl}^{19}\text{F}_2]^+$	155	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_2^{37}\text{Cl}]^+$
102	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}^{19}\text{F}]^+$	156	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_2^{19}\text{F}_2]^+$
116	no	$[\text{}^{27}\text{Al}^{35}\text{Cl}_2^{19}\text{F}]^+$	157	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}^{37}\text{Cl}_2]^+$
118	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_2]^+$	172	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_3^{19}\text{F}]^+$
120	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}^{37}\text{Cl}]^+$	188	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_4]^+$
121	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}^{19}\text{F}_2]^+$	190	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_3^{37}\text{Cl}]^+$
137	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_2^{19}\text{F}]^+$	192	yes	$[\text{}^{48}\text{Ti}^{35}\text{Cl}_2^{37}\text{Cl}_2]^+$
140	no	$[\text{}^{48}\text{Ti}^{35}\text{Cl}^{19}\text{F}_3]^+$			

According to the results presented in this study, during the first precursor pulse of the ALD cycle AlCl_3 goes through a ligand exchange reaction with TiF_4 terminated surface resulting in $\text{F}_x\text{AlCl}_{3-x}$ surface species and formation of gas phase byproduct TiCl_4 (reaction 6). The reaction is observed in QCM as a sharp mass increase during the AlCl_3 pulse and in QMS as a very clear release of TiCl_4 . During the second precursor pulse of the ALD cycle TiF_4 then reacts with the remaining chlorides on the $\text{F}_x\text{AlCl}_{3-x}$ surface forming AlF_3 . In addition, TiF_4 adsorbs on to the AlF_3 surface recreating TiF_4 terminated surface and the next ALD cycle is ready to begin (reaction 7). As was seen with QCM, the adsorption of TiF_4 is strongly temperature dependent, which leads to the strong temperature dependence of the growth rate of the process.

At lower temperatures more TiF_4 adsorbs on AlF_3 and almost no TiCl_4 is formed during the TiF_4 pulse. This means that at 160°C x in reactions 6-7 should be close to 3. When the temperature increases, less TiF_4 is adsorbed, and x decreases. The reaction coefficient x is estimated from the QCM results using the mass change ratio m_1/m_0 , and from the QMS results by comparing the amounts of TiCl_4 released during the AlCl_3 pulse (A) and the TiF_4 pulse (B).

Based on the reactions 6 and 7, after the AlCl_3 pulse and purge the mass change of the film is $m_1 = 4 * m(\text{AlCl}_3) - x * m(\text{TiCl}_4)$. After one complete ALD cycle the mass increase should be $m_0 = 4 * m(\text{AlF}_3)$. The masses can be replaced with the corresponding molar masses ($M(\text{AlCl}_3) = 133.3 \text{ g/mol}$, $M(\text{TiCl}_4) = 189.7 \text{ g/mol}$ and $M(\text{AlF}_3) = 84.0 \text{ g/mol}$). From the ratio m_1/m_0

$$\frac{m_1}{m_0} = \frac{4 * M(\text{AlCl}_3) - x * M(\text{TiCl}_4)}{4 * M(\text{AlF}_3)} \quad (1)$$

x is solved as

$$x = \frac{4 \cdot M(\text{AlCl}_3) - 4 \cdot M(\text{AlF}_3) \cdot \frac{m_1}{m_0}}{M(\text{TiCl}_4)} \quad (2)$$

In the reactions 6 and 7, x amount of TiCl_4 is released during the AlCl_3 pulse and $3-x$ during the TiF_4 pulse. In the proportion below (Equation 3) the ratio of these quantities is compared to the intensity ratio of the byproducts observed with QMS. A is the integrated area of $m/z = 153$ during the AlCl_3 pulse and B the integrated area of $m/z = 153$ during the TiF_4 pulse. As already noted, the intensity of $m/z = 153$ is used because it is the strongest fragment in the TiCl_4 mass spectrum.

$$\frac{A}{B} = \frac{x}{3-x} \quad (3)$$

from there x can be solved as

$$x = \frac{3 \cdot \frac{A}{B}}{1 + \frac{A}{B}} \quad (4)$$

The calculated m_1/m_0 and A/B ratios for each measurement temperature and x defined from them are listed in Table II. The trend of decreasing x with increasing temperature is clear for both measurement techniques. The values themselves correspond better at temperatures 200, 240 and 280 °C than they do at either extremes of 160 and 320 °C. However, these measurements must be considered as only estimations to support the qualitative observations on the mechanism. For comparison m_1/m_0 for reactions 2 and 3 would be 1.6, and for reactions 4 and 5 m_1/m_0 would be -0.1.

TABLE II. The mass change ratios m_1/m_0 , the ratios of released amount of TiCl_4 A/B and x defined from QCM and QMS results at each temperature.

T ($^{\circ}\text{C}$)	m_1/m_0	x according to QCM	A/B	x according to QMS
160	0.54	1.8	4.5	2.5
200	0.61	1.7	2.2	2.0
240	0.80	1.4	0.86	1.4
280	1.1	0.93	0.61	1.1
320	1.2	0.60	0.44	0.92

IV. SUMMARY AND CONCLUSIONS

In this work, the reaction mechanism of the ALD process of AlF_3 was studied with *in situ* QCM and QMS. The growth occurs via ligand exchange reaction between AlCl_3 and TiF_4 forming volatile TiCl_4 as a byproduct. No other byproducts were detected. The growth rate of the AlF_3 process is strongly temperature dependent, and especially at lower temperatures the growth rate is higher than expected for a traditional ALD process. The high growth rate was found to occur because after reacting with the $\text{F}_x\text{AlCl}_{3-x}$ surface created by the previous AlCl_3 pulse, TiF_4 adsorbs molecularly on the freshly formed AlF_3 . On contrary to the earlier presumptions, the effect was observed only for TiF_4 whereas AlCl_3 did not adsorb molecularly on AlF_3 . TiF_4 adsorption was found to be strongly temperature dependent, which leads to the strong temperature dependence of the mass increase during the TiF_4 half reaction and thereby to strong temperature dependence of the growth rate.

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DATA AVAILABILITY

The data that is used in this study are available upon request from the corresponding author and from the first author (heta-elisa.nieminen@helsinki.fi).

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