A Kinetic Study of Titanium Nitride Chemical Vapor Deposition Using Nitrogen, Hydrogen, and Titanium Tetrachloride

J. P. Dekker, A. P. J. van der Put, H. J. Veringa, and J. Schoonman

*Laboratory for Applied Inorganic Chemistry, Delft University of Technology, 2628 BL Delft, The Netherlands
ECN, Energy Research Foundation, 1755 ZG Petten, The Netherlands

ABSTRACT

The kinetics of the growth of titanium nitride (TiN) by hot-wall atmospheric pressure chemical vapor deposition (CVD) has been studied using titanium tetrachloride (TiCl₄) hydrogen (H₂), and nitrogen (N₂) as reactants. The growth rate as a function of reactant concentration at different reaction temperatures is determined. The growth rate dependence in the TiCl₄ input concentration changes from a positive to a negative order behavior with increasing reaction concentration, and the observed maximum growth rate shifts to a higher TiCl₄ input concentration with increasing reaction temperature. For the growth rate a square root dependence in the N₂ concentration is observed in all cases, and for the growth rate a positive order dependence in the H₂ concentration is observed which changes from 0.5 to 1.5. A reaction model has been proposed based on isothermal Langmuir adsorption behavior with mutual displacement on titanium sites at the surface, and an indirect mutual displacement on nitrogen sites at the surface. This reaction model consists of a set of elementary gas-phase, adsorption, and surface reactions which are quasi-equilibrated, and a rate-determining step involving the reaction at the surface between an adsorbed TiCl₄ species on a nitrogen site, and an adsorbed NH species on a titanium site. Using this model the experimental and reported growth rate data can be understood as a function of reactant concentration within the temperature region from 1000 to 1273 K.

Chemical vapor deposition (CVD) is a well-known synthesis method for producing titanium nitride (TiN) layers. These TiN layers are used, because of their electrical conductivity, structural properties such as wear and corrosion resistance. TiN layers can be used as a diffusion barrier between metal and silicon in electronic circuits. These layers are deposited in a cold-wall low-pressure CVD apparatus at substrate temperatures between 600 and 900 K using titanium tetrachloride (TiCl₄), ammonia (NH₃), and hydrogen (H₂) according to reaction 1

\[ 2\text{TiCl}_4(g) + 2\text{NH}_3(g) + \text{H}_2 \rightarrow 2\text{TiN}(s) + 6\text{HCl}(g) \]  

In general, this CVD reaction is not used for the synthesis of TiN layers for structural applications. Layers of TiN, required for mechanical purposes, are usually deposited in a hot-wall atmospheric pressure CVD apparatus using nitrogen (N₂), TiCl₄, and H₂ according to reaction 2

\[ 2\text{TiCl}_4(g) + \text{N}_2(g) + 4\text{H}_2(g) \rightarrow 2\text{TiN}(s) + 6\text{HCl}(g) \]  

A disadvantage of this chemical system is the necessity of applying a relatively high reaction temperature of over 1000 K.

A study on the kinetics of CVD of TiN using NH₃ has been reported by Srinivas et al. and Butting et al. Srinivas et al. found for the growth rate a zero-order dependence in the TiCl₄ concentration, and a second order dependence in the NH₃ concentration, whereas Butting et al. found for the growth rate a small negative order dependence in the TiCl₄ concentration, and a 1.3 order dependence in the NH₃ concentration. These differences are explained by the authors in terms of the formation of a TiCl₄ - NH₃ complex in the gas phase.

A study on the kinetics of CVD of TiN using N₂ has been reported by Fang et al. and by Nakanishi et al. They have performed growth rate measurements as a function of the reactant concentration at one temperature. All these kinetic studies are based on a gravimetric analysis of the deposition experiments. Fang's group has investigated the kinetics of CVD of TiN at 1273 K, whereas Nakanishi et al. have performed similar experiments at 1000 K. All these studies report for the growth rate a square root order dependence in the H₂ and N₂ concentration. For the growth rate Fang et al. have observed a positive order dependence in the TiCl₄ concentration at low TiCl₄ concentrations, and a negative order dependence in the TiCl₄ concentration at high TiCl₄ concentrations, whereas for the growth rate Nakanishi et al. have only observed a negative order dependence in the TiCl₄ concentration.

Fang et al. have reported two kinetic models based on the same experiments. The first model is based on isothermal Langmuir adsorption behavior assuming the following gas-phase thermodynamic equilibrium to be present

\[ \text{TiCl}_4(g) + \text{H}_2(g) + \text{TiCl}_4(g) + 2\text{HCl}(g) \]  

Based on thermodynamic equilibrium calculations Jung et al. assume that this reduction of TiCl₄ to titanium dichloride (TiCl₂) in the gas phase is substantial, and that the adsorption of TiCl₄ is a part of the growth rate mechanism. However, gas-phase thermodynamic equilibrium calculations performed by Nakanishi et al. and by Dekker et al. indicate that the TiCl₄ concentration can be neglected with respect to the TiCl₄ and TiCl₂ concentrations.

In a later paper by Rong et al., Fang et al. have presented a different kinetic model based on the same experiments. In this paper they assume that the hydrogen chloride (HCl) concentration is determined by the conversion of TiCl₄ to TiN, and not by the reduction of TiCl₄ to TiCl₂ in the gas phase as postulated in their earlier papers. In order to obtain a growth rate expression as a function of input variables they assume that the HCl concentration near the surface is proportional to the growth rate. It should be noted that this proportionality is only valid if the growth rate mechanism has a first-order dependence in the TiCl₄ concentration. However, for the growth rate, their experiments reveal a change in the TiCl₄ concentration order behavior at high TiCl₄ concentrations. Hence, in this case, a mass balance equation considering the reactant concentrations as a function of residence time has to be solved in order to obtain an expression for the HCl concentration near the substrate as a function of the growth rate of TiN. This will often result in a growth rate with a nonlinear dependence in the HCl concentration at a given position in the reactor. Furthermore, Rong et al. assume a nonsteady-state behavior for an intermediate species (TiCl₃HCl) at the surface, which in fact is not confirmed by their experimental results.

Nakanishi et al. have presented a kinetic model based on isothermal Langmuir-Hinshelwood adsorption behavior. Their growth rate expression describes their experimental results very well at a reaction temperature of 1000 K, i.e.
Table I. Reported experimental standard conditions.

<table>
<thead>
<tr>
<th>P (10^5 Pa)</th>
<th>Inert carrier gas</th>
<th>Flow rate (mol/m^2 s)</th>
<th>N/H</th>
<th>p(TiCl_4) (Pa)</th>
<th>Temp. (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>1</td>
<td></td>
<td>1960</td>
<td>1223 to 1373</td>
<td>9</td>
</tr>
<tr>
<td>1</td>
<td>Ar</td>
<td>1.97</td>
<td>0.6</td>
<td>2630</td>
<td>1273</td>
<td>12 to 14</td>
</tr>
<tr>
<td>1</td>
<td>Ar</td>
<td>0.77</td>
<td>0.5 to 20</td>
<td>330</td>
<td>1000</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>Ar</td>
<td>74</td>
<td>0.7 to 10</td>
<td>1000</td>
<td>1273</td>
<td>17</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>0.77 to 0.85</td>
<td>1.5</td>
<td>3600</td>
<td>1173 to 1423</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>0.74</td>
<td>1.5</td>
<td>1370</td>
<td>1273</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>0.3</td>
<td>1</td>
<td>2400</td>
<td>1273</td>
<td>19</td>
</tr>
</tbody>
</table>

*Flow rate in mmol/s.

\[
R = \frac{p_{TiCl_4}^{1/2}}{(1 + (K_{Ar}p_{Ar})^{1/2} + (K_{N_2}p_{N_2})^{1/2} + K_{H_2}p_{H_2})^{1/2}}
\]  

(4)

where \( R \) is the growth rate, \( p_{TiCl_4} \) is the partial pressure of species \( xx \), and \( K_{Ar} \) is the adsorption heat of species \( xx \). This model is based on the assumption that a surface reaction between adsorbed atomic nitrogen and adsorbed atomic hydrogen is the rate-determining step (rde) of the process, and that there is a high surface coverage of adsorbed TiCl\(_4\), with respect to the other titanium containing intermediate species. For the growth rate this model predicts a zero to minus two-order dependence in the TiCl\(_4\) concentration. Hence, for the growth rate this model cannot explain the positive order dependence in the TiCl\(_4\) concentration as observed by Fang’s group\(^{10-14}\) at a reaction temperature of 1273 K.

Nakanishi et al.\(^{19}\) determined an apparent activation energy of 101 kJ/mol for low TiCl\(_4\) concentrations, whereas Fang et al.\(^{10-14}\) reported an apparent activation energy of 120 kJ/mol at high TiCl\(_4\) concentrations. Often differences in the observed apparent activation energy for CVD processes in which the same reactants are used are ascribed to differences in reaction mechanisms or reactor geometry.\(^{15}\) However, apparent activation energies determined at different reactant concentrations are not equal if the apparent concentration order dependence of the growth rate is not constant, because a change in reactant concentration order behavior also affects the contribution of the reactant adsorption heat to the apparent activation energy. Thus, a change in the apparent activation energy at different reactant concentrations does not necessarily imply that there is a change in reaction mechanism.

Hitherto, the experiments which have been discussed were performed in a differential mode, i.e., the total reactant conversion is low. Thus, there is a negligible depletion of reactant in the gas phase, and as a consequence the measured growth rate is determined by surface kinetics provided that the diffusional flux in the gas phase is fast relative to the surface reaction rate. If the depletion of the reactant becomes substantial then the growth rate at a given position in the reactor is determined by a combination of mass transfer in the gas phase and surface kinetics.

To our knowledge all other reports on the kinetics of the CVD of TiN are determined by a combination of mass transfer in the gas phase and surface reactions.\(^{1,2,15-19}\) The essential experimental standard conditions reported for the growth of TiN by CVD are summarized in Table I. All data are converted into SI units for comparison.

The reported apparent activation energies for the TiN CVD process changes from 25 kJ/mol to a value of more than 300 kJ/mol. These differences in apparent activation energies can be understood qualitatively by considering the influence of a feed rate limitation on the kinetics of the surface reaction as will be discussed. Furthermore, in the present paper experiments on deposition rate as a function of reactant concentration are conducted at different reaction temperatures. We have investigated the kinetics of this CVD process by gravimetric analysis of the synthesis experiments as a function of reactant concentration and reaction temperature. The experimental results along with the reported data on the kinetics of the deposition of TiN\(^{10-15}\) are evaluated by a model based on isothermal Langmuir-Hinshelwood adsorption behavior:

Experimental Aspects

CVD experimental aspects.—Two hot-wall CVD reactors have been used for the experiments. There are only minor differences in the design of the reactors. The experimental results in the two reactors were always comparable. The principle of the gas distribution system of one hot-wall CVD apparatus is given in a schematic drawing in Fig. 1. \( H_2 \) and argon (Ar) are purified over a copper catalyst and a 0.4 nm zeolite. \( H_2 \) is purified over a palladium catalyst and a 0.4 nm zeolite. Part of the \( H_2 \) is bubbled through heated liquid TiCl\(_4\) in order to saturate the hydrogen stream with reactant vapor. The temperature of the liquid TiCl\(_4\) was varied between 300 and 330 K depending on the desired concentration. The TiCl\(_4\) concentration in the \( H_2 \) stream is calculated assuming the TiCl\(_4\) vapor pressure to be in equilibrium with the TiCl\(_4\) liquid. The deviation in the TiCl\(_4\) gas concentration is less than 10% of the calculated value, as checked by monitoring the volume decrease in time of the TiCl\(_4\) liquid. The gas streams are mixed before they are introduced into the reactor. The reactor consists of a quartz tube with a length of 700 mm and a diameter of 50 mm. The quartz tube of the other hot-wall CVD apparatus is slightly smaller. The length of this reactor tube is 800 mm with a diameter of 42 mm. Inside the large quartz tube is a small tube of 200 mm. Through this tube the reactants are introduced into the hot zone of the quartz reactor. This tube is used to minimize depletion of reactants in the first half of the reactor.

The growth rates are measured on molybdenum (Mo) substrates with a surface area of 225 mm\(^2\). These substrates are placed in the hot-zone of the reactor where the axial temperature difference over the length of the substrate was less than 4 K. The conversion of reactants at the position in the reactor where the growth rate was measured was always less than 13%. Thus, it can be assumed that the reactant concentration near the substrate is approximately equal to the input reactant concentration. It should be当年
Table II. Gaseous species used for thermodynamic calculations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td></td>
</tr>
<tr>
<td>TiCl₄</td>
<td></td>
</tr>
<tr>
<td>N₂H₄</td>
<td></td>
</tr>
<tr>
<td>TiCl₃</td>
<td></td>
</tr>
<tr>
<td>TiCl₂</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
</tbody>
</table>

Table III. Observed reaction orders of gaseous input species.

<table>
<thead>
<tr>
<th>Reaction order</th>
<th>TiCl₄</th>
<th>N₂</th>
<th>H₂</th>
<th>HCl</th>
<th>Temperature (1/K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6</td>
<td>-0.5</td>
<td>0.5</td>
<td>1.15</td>
<td>1073, 1123, 1173</td>
<td>This paper</td>
</tr>
<tr>
<td>1.5, -2</td>
<td></td>
<td>0.5</td>
<td>-1</td>
<td>1273</td>
<td>12-14</td>
<td></td>
</tr>
<tr>
<td>-0.4, -1</td>
<td>0.5</td>
<td>-1</td>
<td>1000</td>
<td>15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results and Discussion

All deposits are crystalline as identified by x-ray diffraction (XRD) analysis and have a yellow gold color. According to Aggour et al., this color is found only for compounds close to the stoichiometric composition. The induction time before steady-state conditions are obtained is observed to be less than 600 s for the experiments at 1073, 1123, and 1173 K, using a TiCl₄ concentration of 1% and a N₂ over H₂ ratio of 1. Hence, it can be assumed that the growth rate derived from experiments where a process time of 3600 s is used is equal to the growth rate under steady-state conditions. Fang et al. observed similar induction times for their experiments, but Nakanishi et al. observed induction times of more than 3600 s. These long induction times can be ascribed to a simultaneous etching of the stainless steel substrates during their synthesis experiments. In this report a shorter induction time is observed, because chemically more stable Mo substrates are used. Apparently, a difference in substrate material has an influence on the observed induction time of the process.

The apparent activation energy for the growth of TiN by CVD using 1% TiCl₄, and a ratio of N₂ over H₂ of 1 is 100 kJ/mol in the temperature region between 1073 and 1273 K as can be seen in Fig. 2. Hence, from this observed high apparent activation energy in combination with the low conversion of reactants it can be concluded that the process is controlled by surface kinetics. This surface kinetics is studied by gravimetric analysis of the deposition experiments as a function of reactant concentration at three different temperatures. The observed reaction orders along with the reaction orders derived from literature data are given in Table III.

The growth rate dependence in the TiCl₄ concentration changes from a positive to a negative order with increasing TiCl₄ concentration at reaction temperatures higher than 1073 K. At a reaction temperature of 1000 K only a negative order of the growth rate dependence in the TiCl₄ concentration is observed. The observed maximum growth rate shifts to a higher TiCl₄ concentration with increasing reaction temperature. For the growth rate a square root dependence in the N₂ concentration is observed in all cases, and for the growth rate a positive order dependence in the H₂ concentr-
Fig. 4. Growth rate of TiN as a function of the square root of the hydrogen input concentration for three reaction temperatures with a \(p_{\text{CH}_4}\) input of 1000 Pa and an \(N_2\) concentration of \(0.5 \times 10^4\) Pa. The solid lines represent the nonlinear regression fit results of Eq. 21.

The growth rate is observed which changes from 0.5 to 1.5. It should be noted that when these dependencies are observed the reactant concentrations are different. Apparently, the reaction mechanism has a complex dependence on the reactant concentrations. From these observations it is clear that a reaction mechanism model can be useful to clarify this type of growth rate behavior. Here, in Eq. 5 one overall gas-phase reaction is proposed, and a set of elementary reactions involving the TiN surface in Eq. 6 to 12 which might be responsible for the growth of TiN using TiCl\(_4\), \(N_2\), and \(H_2\)

\[
2\text{TiCl}_4(g) + H_2(g) \xrightleftharpoons[k_{-3}]{k_{3}} 2\text{TiCl}_3(g) + 2\text{HCl}(g) \tag{5}
\]

\[
H_2(g) + 2s^* \xrightleftharpoons[k_{-6}]{k_6} 2\text{H} \cdot s^* \tag{6}
\]

\[
N_2(g) + 2s^* \xrightleftharpoons[k_{-7}]{k_7} 2N \cdot s^* \tag{7}
\]

\[
\text{TiCl}_4(g) + s^* \xrightleftharpoons[k_{-3}]{k_3} s^* \cdot \text{TiCl}_3 \tag{8}
\]

\[
\text{TiCl}_4(g) + s^* \cdot \text{TiCl}_3 + \text{Cl} \cdot s^* \xrightleftharpoons[k_{-9}]{k_9} \text{Cl} \cdot s^* + \cdot \text{TiCl}_3 + \text{N} \cdot s^* \tag{9}
\]

\[
\text{Cl} \cdot s^* + \cdot \text{H} \cdot s^* \xrightleftharpoons[k_{-10}]{k_{10}} \text{HCl}(g) + 2s^* \tag{10}
\]

This proposed set of reactions is based on thermodynamic calculations, literature data on heterogeneous chemistry involving TiN or the individual gaseous reactants, and some assumptions which are common in heterogeneous catalysis. The rational for this set of reactions will be discussed.

Gas-phase reactions.—In the gas phase intermediate species are supposed to be formed, and they can contribute to the growth mechanism. Thermodynamic equilibrium calculations have been performed in order to conclude which intermediate species are stable in the gas phase. The equilibrium concentration of \(H_2\) and \(N_2\) remains virtually unaffected on heating. Only a relatively small amount of \(H_2\) and \(N_2\) is consumed by the formation of \(\text{HCl}\) and \(\text{NH}_3\). However, the reduction of \(\text{TiCl}_4\) to \(\text{TiCl}_3\) by \(H_2\) is substantial. At equilibrium \(\text{TiCl}_3\) becomes the most abundant titanium containing species in the gas phase at a temperature between 1050 and 1250 K depending on the input ratios of the species. Similar results have been reported by Nakanishi et al. Thus, the presence of \(\text{TiCl}_4\) in the gas phase should not be excluded. Therefore, reaction 5 is assumed to be one of the prime reactions in this system.

Adsorption and desorption reactions.—Adsorption and desorption processes are dependent on the nature of the gaseous species and surface. It is assumed that only adsorption of the gaseous species \(H_2\), \(N_2\), \(\text{TiCl}_4\), \(\text{TiCl}_3\), and \(\text{HCl}\) on TiN are important for the reaction mechanism. The concentrations of the other species, as determined by the gas-phase thermodynamic equilibrium calculations, are negligibly small. Hence, their adsorption is neglected.

Adsorption of \(H_2\) involves dissociative chemisorption on the surface involving an interaction with the d-orbitals of the titanium atoms in the lattice at the surface as described in Eq. 6, where \(s^*\) denotes an active titanium site at the surface. The presence of such a dissociative chemisorption is based on catalytic reactions on TiN involving \(H_2\). This dissociative chemisorption is notable in the activation energy of the fit parameters.

Fig. 5. Growth rate of TiN as a function of the square root of the nitrogen input concentration for three reaction temperatures with a \(p_{\text{CH}_4}\) input of 1000 Pa, and an \(H_2\) concentration of \(0.5 \times 10^4\) Pa is used. The solid lines represent the linear regression fit results of Eq. 21.

Fig. 6. Arrhenius plot of the three fit parameters of Eq. 21. The solid lines represent the least squares fit to determine the activation energy of the fit parameters.
whereas nitrogen atoms have a relative negative charge in the TiN lattice.

There is no direct evidence for a dissociative chemisorption of N\(_2\) on the surface as described in reaction 7. However, we assume that the adsorption mechanism of N\(_2\) on TiN can be expressed as an elementary reaction involving dissociative chemisorption, because this kind of dissociative chemisorption of N\(_2\) on several metals has been observed in catalysis studies.

We propose that chemisorption of TiCl\(_4\) involves an interaction between a titanium ion of the gaseous species and a nitrogen atom in the lattice at the surface, and that chemisorption of titanium-containing species on titanium sites is negligible. This chemisorption can be described as

\[
\text{Ti} + \text{Cl}_2 \rightarrow \text{TiCl}_2 + \text{N}_2
\]

where \(s^d\) denotes an active nitrogen site at the surface. The dot between the nitrogen site and the Ti species of the TiCl\(_4\) molecule in reaction 8 indicates that there is an interaction between these two species.

The chemisorption mechanism of a TiCl\(_4\) molecule is postulated to be similar as described for the TiCl\(_4\) molecule. However, the formation of an adsorbed TiCl\(_4\) species from gaseous TiCl\(_4\) has to be preceded by a transition state, because the titanium ion is shielded by four chlorine atoms in the TiCl\(_4\) molecule. Therefore, the TiCl\(_4\) molecule chemisorbs at the surface involving an interaction between a chloride ion of the TiCl\(_4\) molecule and a titanium site. Instantaneously, this transition state is followed by a dissociation of the TiCl\(_4\) molecule to the surface and an adsorbed atomic chlorine on a titanium site. An adsorbed TiCl\(_4\) molecule on a nitrogen site, because of the strong interaction between the chlorine atom and the titanium site, the adsorbed TiCl\(_4\) species is expected to be very unstable. Thus, the dissociative chemisorption reaction of TiCl\(_4\) can be expressed as an elementary reaction as described in Eq. 9.

It is evident that a desorption of adsorbed chlorine atoms is obligatory. Otherwise, a steady-state growth of TiN could be observed. Presumably, gaseous HCl instead of gaseous diatomic chlorine in the desorption reaction is formed, because gaseous HCl is far more stable than gaseous diatomic chlorine under our deposition conditions as determined by the multistep thermodynamic equilibrium calculations. The elementary reaction for desorption of HCl is given in Eq. 10.

**Surface reactions.**—In principle, at least one adsorbed TiCl\(_4\) molecule, one adsorbed nitrogen molecule, and two titanium sites are necessary in one elementary reaction to form TiN given the adsorption reactions as discussed. However, an elementary reaction involving four species is rather unlikely. Therefore, the surface reaction to form TiN is split into two elementary reactions. The first reaction involves the formation of an ammonia radical at the surface where the interaction between an adsorbed hydrogen atom and a titanium atom in the lattice at the surface is broken to form a bond between a hydrogen species and an adsorbed nitrogen as described in Eq. 11.

TIN is deposited involving a reaction between an adsorbed TiCl\(_4\) species and an adsorbed NH species as described in Eq. 12. In the transition state of this reaction a TiCl\(_4\) is formed at the surface under the release of HCl, and the adsorbed Ti containing species as well as the adsorbed nitrogen species are immobilized, because of their interaction. At the same time a chlorine is released to an empty active titanium site at the surface. At this stage the titanium and nitrogen species of the TiN have become indistinguishable from the surface, hence, these two species have to be denoted as \(s^d\) and \(s^d\) on the right side in reaction 12, respectively.

This set of elementary reactions given in Eq. 5 to 12 represents a multiple path reaction for depositing TiN. It can be formed by a dissociative adsorption of TiCl\(_4\) and a subsequent reaction of \(s^d\)TiCl\(_4\) with \(s^d\)NH, i.e., reaction path-

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**Table V. Experimental and calculated apparent activation energies.**

<table>
<thead>
<tr>
<th>Experimental apparent activation energy (kJ/mol)</th>
<th>Calculated apparent activation energy (kJ/mol)</th>
<th>Temperature region (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>105</td>
<td>1073 to 1173 This paper</td>
<td>14</td>
</tr>
<tr>
<td>100</td>
<td>175</td>
<td>1173 to 1273</td>
<td>12-14</td>
</tr>
<tr>
<td>101</td>
<td>101</td>
<td>1000 to 1150</td>
<td>15</td>
</tr>
</tbody>
</table>

* Derived from figure in Ref. 14.

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**Fig. 7. Growth rate of a hypothetical chemical system concordant to Eq. 35 as a function of reactant concentration at five reaction temperatures.**

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**Table VI. Experimental and calculated apparent activation energies.**

<table>
<thead>
<tr>
<th>Experimental apparent activation energy (kJ/mol)</th>
<th>Calculated apparent activation energy (kJ/mol)</th>
<th>Temperature region (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>(1 \times 10^9)</td>
<td>1223 to 1273</td>
<td>8</td>
</tr>
<tr>
<td>176 to 251</td>
<td></td>
<td>1223 to 1273</td>
<td>10</td>
</tr>
<tr>
<td>25 to 51</td>
<td></td>
<td>1223 to 1273</td>
<td>16</td>
</tr>
<tr>
<td>209</td>
<td>235</td>
<td>1173 to 1223</td>
<td>7</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>1273 to 1425</td>
<td>17</td>
</tr>
<tr>
<td>108*</td>
<td></td>
<td>1173 to 1273</td>
<td>10</td>
</tr>
<tr>
<td>239</td>
<td>170</td>
<td>1173 to 1273</td>
<td>10</td>
</tr>
</tbody>
</table>

* Not enough data to calculate apparent activation energy.

* Derived from figure in Fig. 18.

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**Fig. 8. Growth rate of a hypothetical chemical system concordant to Eq. 35 as a function of reactant concentration for five reaction temperatures.**
Fig. 9. Arrhenius plot of the growth rate derived from Fig. 7 in order to obtain the apparent activation energy when the growth rate is affected by a feed-rate limitation (B), and when the depletion of a reactant can be neglected (A).

In principle, the overall reaction rate is determined by the respective reaction rate constants of the elementary reactions and the site conservation equations. To our knowledge there are no data available on the adsorption and desorption reaction rate constants and surface reaction rate constants. However, adsorption measurements of TiCl₄ on silicon and equilibrium adsorption measurements of TiCl₄, N₂, and H₂ on TiN powder are discussed by Mendicicci and Seebauer,²⁶ and by You et al.,²⁷ respectively. Mendicicci and Seebauer²⁶ made a qualitative statement in that the desorption of chlorine becomes substantial at temperatures higher than 840 K. The adsorption data reported by You et al.²⁷ could be reasonably well described by an isothermal Langmuir adsorption behavior. The adsorption equilibrium constants of the individual reactants on TiN are reported to be on the order of 10⁻³ Pa⁻¹ for TiCl₄, and 10⁻⁷ Pa⁻¹ for H₂ and N₂ at a temperature of 900 and 950 K.²⁷

The turnover rate of the reaction to form TiN, i.e., the number of monolayers TiN deposited per unit time has a maximum of typically 1 s⁻¹ at the measured reaction temperatures. Therefore, we suggest that it is reasonable to assume that the reaction mechanism can be described as a quasi-equilibrium system.

The assumption that the system is quasi-equilibrated makes it possible to use the theory of Langmuir adsorption with mutual displacement. At low reactant concentrations a positive reaction order behavior is found for each individual reactant. Thus, the elementary reaction which is the r.o. of the reaction mechanism should contain intermediate species which originate from these three individual reactants given this set of adsorption reactions. Hence, reaction 12 has to be the r.o. and not reaction 11, as was suggested by Nakanishi et al.¹⁴ Furthermore, given this set of elementary reactions it has to be assumed that \([s]²\) is proportional to \([s][s]\), this assumption is based on a similar argument as discussed by Boudart et al.²⁸ for the probability of finding two similar sites as neighbors. Consequently, an expression for the growth rate can be written as in Eq. 16.

\[
R = \frac{K_{p,eq,p}^{1/2} \cdot P_{Ti}^{1/2}}{1 + (K_{p,eq,p}^{1/2} + K_{p,eq,n}^{1/2} + K_b \cdot P_{H_2}^{1/2} + K_C \cdot P_{N_2}^{1/2}) \cdot (1 + K_d \cdot P_{Cl_2}^{1/2})}
\]

where \(K_{p,eq,p}\) is the thermodynamic equilibrium partial pressure of species \(X\), and \(K_i\) is the equilibrium constant of reaction (i), i.e., equal to \(k_i/k_{-i}\), Equations 16 describes the growth rate of both reaction pathways. It is assumed that adsorbed atomic chlorine is the most abundant surface intermediate (MASI) on the titanium sites of the process, otherwise, given this reaction model no negative order in the titanium containing species can be observed. Hence, Eq. 16 can be reduced to Eq. 21:

\[
R = \frac{K_{p,eq,p}^{1/2} \cdot P_{Ti}^{1/2}}{1 + K_b \cdot P_{H_2}^{1/2} \cdot P_{N_2}^{1/2} \cdot (1 + K_d \cdot P_{Cl_2}^{1/2})}
\]

All experimental results can be understood qualitatively using this proposed reaction rate mechanism. This can be illustrated by discussing a few extreme experimental conditions at low reaction temperatures with minor reduction of TiCl₄ in the gas phase, i.e., the experimental conditions with very low surface coverage or fully covered surface.

At low coverage of titanium and nitrogen sites growth rate Eq. 21 is simplified to Eq. 22 by substitution of equilibrium constant \(K_i\)

\[
R \propto (P_{Ti})^{1/2} \cdot (P_{Cl_2})^{1/2}
\]
where $p_{TiCl}$ is the input partial pressure of TiCl. The model predicts for the growth rate a three-quarter order dependence in the H$_2$ concentration. Unfortunately, no experimental data are currently available to evaluate this dependence.

At high coverage of titanium sites and low coverage of nitrogen sites the growth rate expression can be simplified to Eq. 23 by substitution of equilibrium constant $K_e$:

$$R = \frac{P_{H_2}}{P_{TiH}}$$

[23]

whereas at high surface coverage of all active sites the growth rate expression can be simplified to Eq. 24:

$$R = \frac{P_{H_2}}{P_{TiH}}$$

[24]

From these observations it can be concluded that, at a low reaction temperature, the growth rate dependence on the TiCl$_4$ concentration decreases from a positive square root to a negative square root or minus one order, whereas the growth rate dependence on the H$_2$ concentration increases from a three-quarter order to one, or five-fourths order with increasing TiCl$_4$ input concentration. Apparently, the growth rate order behavior with respect to the H$_2$ and TiCl$_4$ concentrations is a function of the surface coverage of nitrogen sites as well as titanium sites. At high reaction temperatures the growth rate expression cannot be simplified as easily as discussed above, because the TiCl$_4$ and HCl concentrations are no longer proportional to the square root of the input TiCl$_4$ concentration.

The experimental results are fitted concordant to Eq. 21 by a three-parameter nonlinear regression method taking into account the gas-phase equilibrium. The fit results with respect to concentration dependence, fit constants, and overall temperature dependence will be discussed separately.

**Concentration dependence.**—The growth rate as a function of the individual reactants are presented in Fig. 3 to 5 for three different reaction temperatures. All experimental results along with the literature data$^{[15-18]}$ could be fitted reasonably well. All experimental data did fall within the 90% confidence region of the fit.

**Fit constants.**—The three fit constants are presented in an Arrhenius plot in Fig. 6. The fit constants $K_b$ and $K_d$ in the denominator of the growth rate Eq. 21 reveal an Arrhenius-type behavior. $K_d$ represents the adsorption constant of TiCl$_4$ on TiN. The adsorption heat of this species is 131 kJ/mol. The adsorption constant of TiCl$_4$ on TiN can be obtained by a combination of Eq. 18 and 20, and the equilibrium constant of reaction 5:

$$K_e = K_b K_d K_{a}$$

[25]

The adsorption heat of this species is 107 kJ/mol. This adsorption heat is similar to the value of 105 kJ/mol obtained from equilibrium adsorption measurements of TiCl$_4$ on TiN powder.$^{[19]}$ The reason for the non-Arrhenius-type behavior of $K_d$ in Fig. 6 is not clear. However, possible explanations for this observed temperature dependence could be, first, that the presented model is physically not realistic, or second, that the apparent activation energy of fit constant $K_a$ consists of several adsorption heats and activation energies of surface reactions as illustrated in Eq. 17. It might also be possible that the adsorption heat of N$_2$ is a function of the surface coverage, which would result in a non-Arrhenius type behavior. This kind of behavior has been observed indeed for the adsorption of N$_2$ on several metals,$^{[20]}$ third, that the value of $K_a$ is a direct consequence of the type of growth rate measurement. The shape of the fit curves is determined by the reactant concentrations and the fit constants in the denominator, whereas $K_e$ in the numerator only determines the absolute value of the growth rate. In all experimental studies on the growth rate of TiN the growth rate is derived from a gravimetric analysis of the substrates assuming that the substrates have a constant accessible surface area. However, it might very well be possible that the growth rates derived in this paper are too low, because the substrates present on the bottom of the horizontal reactor did not have a well-defined accessible surface area, whereas the growth rates reported by the group of Fagh and by Nakashima et al.$^{[15-18]}$ were derived from substrates hanging on a wire in a vertical reactor.

**Overall temperature dependence.**—The fit results are used to calculate the apparent activation energy of the process. The calculated apparent activation energies agree very well with the experimental activation energies as can be seen in Table V.

It can be concluded that the present model describes the reaction for depositing TiN very well. However, the present model is not unique. Another reaction model based on isothermal Langmuir adsorption behavior similar to the discussion above can be presented. The elementary quasi-equilibrated reaction of this alternative reaction mechanism are given in Eq. 26 to 31.

$$H_2(g) + \frac{K_{Ti}}{p_{H_2}} \rightarrow 2H.s$$

[26]

$$N_2(g) + \frac{K_{Ti}}{p_{H_2}} \rightarrow 2N.s$$

[27]

$$TiCl_4(g) + s \rightarrow s.TiCl_4$$

[28]

$$TiCl_4(s) + 2s.TiCl_4 + s.Cl.s\rightarrow 2s.Cl.s + HCl(g)$$

[29]

$$Cl.s + H.s \rightarrow HCl(g) + 2s$$

[30]

$$s.TiCl_4 + s.NH.s \rightarrow 2s.Cl.s + HCl(g)$$

[32]

and the site conservation is given by Eq. 33:

$$1 = [s] + [s.TiCl_4] + [Cl.s] + [s.NH] + [H.s] + [N.s]$$

[33]

where $[L]$ is the total number of sites per unit surface area. From this set of equations an expression for the growth rate can be derived. If it is assumed that the surface is covered by adsorbed TiCl$_4$ and adsorbed chlorine then the expression for the growth rate becomes very similar to expression 21 as discussed earlier.

$$R = \frac{\frac{K_{Ti}^{1/2}P_{H_2}^{0.5}}{P_{TiH}^{0.5}}}{1 + K_{Ti}^{1/2}K_{a}^{1/2}P_{H_2}^{0.5}P_{TiH}^{0.5}P_{NH}^{0.5}}$$

[34]

The differences in the fit results of the proposed model, i.e., Eq. 21 and Eq. 34 are only marginal. However, there is a tendency that the alternative model predicts a growth rate order dependence with respect to the TiCl$_4$ concentration which is too negative at high concentrations of TiCl$_4$. These kinds of differences in growth kinetics can never be evaluated by a thermogravimetric analysis alone. As long as no further experimental data are available concerning the growth kinetics of TiN the proposed reaction model is quite adequate, because all reported experimental and present data obtained in differential mode can be understood by the reaction model as presented in this paper.

Furthermore, the proposed model can be used to evaluate all the reported apparent activation energies for the growth of TiN.$^{[15]}$ The activation energies derived from literature data along with the calculated activation energies of the reaction model are summarized in Table VI.

The experimental apparent activation energies given in Table VI are obtained under experimental conditions where the growth rate is influenced by a feed-rate limitation. Apparently, a feed-rate limitation in a reactor will not
necessarily result in a lower apparent activation energy than the apparent activation energy derived from experiments conducted in a reactor in differential mode. Often, these differences in activation energies are explained in terms of different kinetics, or differences in reactor geometry.\textsuperscript{16-18} However, this phenomenon can be understood considering the following illustrative example in which the influence of feed rate on the apparent activation energy for an imaginary CVD process is taken into account.

A hypothetical growth mechanism is assumed which can be described by an isothermal Langmuir-Hinshelwood adsorption behavior as in Eq. 35

\[
R_m = \frac{K_m p_c}{1 + K_m p_c}
\]

where \( R_m \) is the growth rate, \( k_m \) a reaction rate constant, \( K_m \) an adsorption constant, and \( p_c \) a reactant concentration. All these parameters are in arbitrary units (a.u.). It is assumed that only \( k_m \) and \( K_m \) on the right side of Eq. 35 are temperature dependent. By solving the Van’t Hoff equation, the apparent activation energy for the growth rate can be obtained for two extreme conditions, i.e., low surface coverage and high surface coverage. At low surface coverage the apparent activation energy is equal to the heat of the adsorption step and the activation energy of the reaction rate when times the adsorption heat. Thus, the apparent activation energy is a function of the surface coverage, and if this surface coverage is a function of the reactant concentration. With increasing temperature the apparent activation energy will also change as a consequence of a decrease in surface coverage. This can be induced by a depletion of reactant in the reactor, but due to this depletion the actual concentration at a given position in a reactor is unknown. However, the decrease in reactant concentration can be calculated by solving the mass balance of the process.

The influence of such a feed-rate limitation on the apparent activation energy can be illustrated considering the mass balance for this hypothetical chemical system in a tubular reactor. The depletion of reactant at a given position in the reactor will increase with increasing temperature, and thus, the growth characteristics will change. The growth rate at different reaction temperatures for the two extreme situations are given in Fig. 5 and 8. In these figures the intersections between the growth rate curves T1 to T5, and line A represent the observed growth rate where the depletion of reactant is negligible, whereas the intersections between the growth rate curves T1 to T5, and line B represent the observed growth rate where the growth rate is affected by a mass-transfer limitation. These growth rates at different temperatures are plotted in an Arrhenius plot as can be seen in Fig. 9 and 10. Apparently, at a low input reactant concentration where the growth rate has a positive order dependence with respect to the reactant concentration the apparent activation energy will decrease with increasing depletion of reactant, whereas at a high input reactant concentration where the growth rate has a negative order dependence in the reactant concentration the apparent activation energy will increase with increasing depletion of reactant.

From these observations the rationale for the high observed experimental activation energies can be obtained. If the growth rate shows a negative order dependence in the reactant concentration at a given position in the reactor then the apparent activation energy will increase with increasing depletion of reactant, and if the growth rate shows a positive order dependence in the reactant concentration at a given position in the reactor then the apparent activation energy will decrease with increasing depletion of reactant. Indeed, this is found for experiments with a substantial depletion of reactants.\textsuperscript{16,17} It should be noted that the Damköhler \( \Pi \) number is small under the experimental conditions which are typical for the growth of TiN. Thus, the growth of TiN can never be limited by a diffusion mass transfer, but instead has to be determined by the heterogeneous kinetics as proposed in our reaction model, or by a combination of heterogeneous kinetics and a feed-rate limitation.

Conclusions

A combination of literature data and experimental results presented in this paper on the growth of TiN by CVD using TiCl\(_4\), N\(_2\), and H\(_2\) reveals that the growth is limited by surface kinetics within the temperature region from 1000 to 1273 K. The growth-rate dependence in the TiCl\(_4\) input concentration changes from a positive to a negative order behavior with increasing TiCl\(_4\) concentration, and the observed maximum growth rate shifts to a higher TiCl\(_4\) input concentration with increasing reaction temperature. For the growth rate a square root dependence in the N\(_2\) concentration is observed in all cases, and for the growth rate a positive order dependence in the H\(_2\) concentration is observed which changes from 0.5 to 1.5.

The reaction mechanism has a complex dependence on the reactant concentrations. A reaction model for the growth of TiN using TiCl\(_4\), N\(_2\), and H\(_2\) has been proposed based on Langmuir adsorption behavior with mutual displacement on titanium sites at the surface, and an indirect mutual displacement on nitrogen sites at the surface. This reaction model consists of a set of elementary gas-phase, adsorption, and surface reactions which are quasi-equilibrated, and a rate-determining step involving the reaction between an adsorbed TiCl\(_3\) species on a nitrogen site, and an adsorbed NH species on a titanium site at the surface. All reported growth rate data as a function of reactant concentration can be understood within the temperature region of 1000 and 1273 K, and all these growth rate data did fall within the 90% confidence region of the fit concordant to the reaction model. Thus, the proposed reaction model for the growth of TiN is quite adequate.

The reaction model predicts an adsorption heat of 131 kJ/mol for gaseous TiCl\(_4\) on TiN, and an adsorption heat of 107 kJ/mol for gaseous TiCl\(_4\) on TiN. These values are close to the adsorption heat of TiCl\(_4\) of 105 kJ/mol derived from equilibrium adsorption measurements on TiN powder. An apparent activation energy ranging from 100 to 183 kJ/mol depending on the reactant concentration can be predicted from the reaction model.

Furthermore, the reported differences in the activation energy when the growth rate is affected by a feed-rate limitation can be understood qualitatively. The apparent activation energy increases with increasing domination of the feed-rate limitation as long as the growth rate dependence shows a negative order with respect to the reactant concentration in the vicinity of the substrate. Whereas the apparent activation energy decreases with increasing domination of the feed-rate limitation as long as the growth-rate dependence shows a positive order with respect to the reactant concentration in the vicinity of the substrate.

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LIST OF SYMBOLS

\( E(l) \) reaction in equation (l) 
\( E_a \) activation energy (kJ/mol) 
\( k_e \), \( k_r \) reaction rate constants of reaction in equation (l) 
\( K_t \) thermodynamic equilibrium constant in equation (l) 
\( K_a \) product of reaction rate and thermodynamic equilibrium constants, Pa\(^{-2}\) g/(m\(^2\)s) 
\( K_b \) product of thermodynamic equilibrium constants, Pa\(^{-1}\) 
\( K_c \) product of thermodynamic equilibrium constants, Pa\(^{1}\) 
\( K_{c0} \) adsorption constant of a species xx, Pa\(^{-1}\) 
\( K_{c0} \) adsorption constant of a hypothetical species 
\( L \) total number of active surface sites 
\( L^+ \) total number of active nitrogen surface sites 
\( L^+ \) total number of active titanium surface sites 
\( MASI \) most abundant surface intermediate
$p_c$ partial pressure of a hypothetical species c
$P_{xx}$ thermodynamic equilibrium partial pressure of a species xx, Pa
$P_{eq}$ partial pressure of titanium tetrachloride, Pa
$P$ reactor pressure, Pa
$s$ active site at the surface of TiN
$s^*$ active titanium surface site of the TiN lattice
$S(i)$ stoichiometric number of the reaction in equation (i)
$R$ growth rate of TiN, g/(m² s)
$r_{ds}$ rate-determining step
$r_g$ growth rate of a hypothetical species
$T$ temperature, K
$T_n$ reaction temperature of the hypothetical species

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