KINETICS AND MECHANISM OF TUNGSTEN LPCVD USING WF₆ AND SIH₄ STUDIED BY IN-SITU GROWTH RATE MEASUREMENTS

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ABSTRACT

In-situ growth rate measurements, using a tungsten CVD reactor equipped with a microbalance, have shown that the kinetics of SiH₄ reduction of WF₆ are determined by the ratio of reactant partial pressures. At p(SiH₄)/p(WF₆) ≤ 0.3 first order in p(SiH₄) and a small negative order in p(WF₆) have been observed. The dependence changes into almost second order in p(SiH₄) and minus first order in p(WF₆) in the range of 0.5 ≤ p(SiH₄)/p(WF₆) ≤ 1.0. From the zero order dependence on p(H₂), it appears that dissociative SiH₄ adsorption must be regarded as an irreversible step in the reaction mechanism. Consequently, reaction pathways involving several irreversible steps have been proposed. Rate equations, derived from steady-state approximations, show qualitative agreement with the observed kinetic behaviour.

INTRODUCTION

Reduction of tungsten hexafluoride (WF₆) by silane (SiH₄) offers a tungsten LPCVD process not suffering from several adverse effects associated with the hydrogen reduction of WF₆, i.e., silicon consumption, formation of voids in contact regions, and encroachment at the Si/SiO₂ interface [1]. According to Kobayashi et al. [2] the overall reaction can be expressed as:

\[ \text{WF}_6 + 2 \text{SiH}_4 \rightarrow \text{W} + 2 \text{SiH}_3 + 3 \text{H}_2 \]  

(1)

The reaction:

\[ 2 \text{WF}_6 + 3 \text{SiH}_4 \rightarrow 2 \text{W} + 3 \text{SiF}_4 + 6 \text{H}_2 \]  

(2)

represents a minor pathway.

High growth rates can be obtained at temperatures in the range of 250 to 400°C. However, regarding the kinetics of the deposition process, many uncertainties have remained. Reports on growth rate measurements that have appeared in the literature [3-6] do not provide a consistent set of data with respect to the dependence of deposition rate on wafer temperature and partial pressures of reactant gases. McNamara et al. [7] have shown that the growth rate may be limited by mass transfer rather than surface reaction kinetics, resulting in quasi-first and zero order dependences on partial pressures of SiH₄ and WF₆, respectively, and low values of the apparent activation energy.

In this paper we report on an investigation of tungsten LPCVD from SiH₄ and WF₆ using a hot wall reactor setup designed for growth rate studies. The reactor is equipped with a microbalance enabling in-situ growth rate measurements by monitoring the sample weight during tungsten film deposition. Care has been taken to avoid mass transfer limitations in these experiments. The present work focuses on the determination of the influence of partial pressures of SiH₄, WF₆ and H₂ on the deposition rate. The results provide a more detailed knowledge of the reaction mechanisms involved. Possible reaction pathways will be discussed.
EXPERIMENTAL

Details of the microbalance and CVD setup have been presented elsewhere [8]. Silicon substrates (10x15 mm) were cut from (100) oriented 3" wafers. They were cleaned in HF solutions and dipped in a buffered hydrofluoric acid (BHF) solution prior to the deposition experiment. Once reactant gas flows, tube temperature, and pressure had attained stable values, measurements were performed by monitoring the sample weight during deposition. Film growth rates were calculated from the constant slope of weight increase vs time.

RESULTS

Different rate limiting regimes can be observed if process parameters are varied. The influence of total flow rate has been investigated at constant values of total pressure, temperature, and feed gas ratio. At low flow rates the growth rate increases with increasing flow. At sufficiently high flow rates the deposition rate becomes independent of flow, indicating transition from a mass transfer limited to a surface reaction controlled deposition rate. The measurements presented hereafter have been performed in the latter regime.

At SiH₄/WF₆ ratios lower than or equal to one, deposited films consisted of polycrystalline α-W. Increasing the ratio to values higher than one resulted in formation of a mixture of α-W and β-W. The rate measurements in this investigation have been performed in the α-W deposition regime.

As shown in Fig. 1, the dependence of growth rate on p(SiH₄) appears to be determined by p(WF₆). After an initial linear increase of deposition rate with p(SiH₄), a transition to a higher order dependence is observed at higher p(SiH₄). The range in which the transition occurs moves to lower p(SiH₄) values as p(WF₆) decreases. According to Fig. 2, the deposition rate decreases with increasing p(WF₆). At relatively high p(WF₆) the dependence becomes less strong. Here, the order transition range depends on the value of p(SiH₄).

Similar behaviour of WF₆ has been observed at 260°C, 270°C, and 360°C. From Fig. 3 it can be seen that the influence of p(H₂) in the range of 0 to 200 mTorr is negligible, at several SiH₄/WF₆ ratios. The effect of temperature on deposition rate has been presented elsewhere [8]. From Arrhenius type plots it appeared not possible to determine an apparent activation energy for the deposition process. Maximum rate values have been observed near 300°C.

From the measurements it is evident that the kinetics of the process are determined by the ratio of p(SiH₄) and p(WF₆). Two regimes can be distinguished. A least-squares fit of the data results in the following empirical rate equations:

At p(SiH₄)/p(WF₆) ≤ 0.3 (region I)

\[
R = k_1(T) \left( \frac{p(\text{SiH}_4)}{\text{mTorr}} \right)^{0.06} \left( \frac{p(\text{WF}_6)}{\text{mTorr}} \right)^{-0.16} \left( \frac{p(\text{H}_2)}{\text{mTorr}} \right)^{0.8} \]  

(3)

At 0.5 ≤ p(SiH₄)/p(WF₆) ≤ 1.0 (region II)

\[
R = k_1(T) \left( \frac{p(\text{SiH}_4)}{\text{mTorr}} \right)^{0.82} \left( \frac{p(\text{WF}_6)}{\text{mTorr}} \right)^{0.94} \left( \frac{p(\text{H}_2)}{\text{mTorr}} \right)^{0.0} \]  

(4)

in which R denotes the deposition rate; \(k_1(T)\) and \(k_1(T)\) are rate constants. The standard deviations in the orders of reaction range from 0.03 to 0.08. Rate constants at 310°C are \(k_1 = 24.7 \pm 0.7\) and \(k_1(T) = 46.7 \pm 0.3\).
DISCUSSION

Kinetics

Comparison of the results obtained in this work with those reported by others reveals significant differences. In several cold-wall reactor studies first order in $p(SiH_4)$ and zero (or slightly negative) order in $p(WF_6)$ has been observed \[3,4,5\] covering the entire range $0 \leq p(SiH_4)/p(WF_6) \leq 1.0$. According to McInerney et al. \[7\], mass transfer limitation may readily occur, and this phenomenon probably accounts for the apparent first order in $p(SiH_4)$ in these reported studies. The almost first order in $p(SiH_4)$ observed in region I of the present study is not caused by feed rate limitation, since these measurements have been performed in the flow rate independent regime, as explained above. Hence, the observed dependence in region I is determined by surface reaction kinetics, and not by mass transfer limitation.

Recently published papers on selective tungsten deposition are consistent with our observations. Holleman et al. \[9\] observed increasing reactive sticking coefficients at certain values of $p(SiH_4)$, indicating an order higher than one. Van der Jagd et al. \[10\] found an order of approximately 1.7 with respect to $SiH_4$ at $p(SiH_4)/p(WF_6) \approx 0.7$.

Surface Reaction Mechanism

Two kinetic regions can be distinguished in the range of operating conditions considered in this investigation. A surface reaction model should explain the observed dependence of deposition rate on reactant partial pressures, and account for the transition from kinetics according to Eq. 3 to kinetics according to Eq. 4. Proposed mechanisms of CVD processes are usually based on the Langmuir-Hinshelwood (L-H) model. In tungsten CVD, the model has been applied to the $W_2/\text{WF}_6$ process by McDonica et al. \[12\]. Within the L-H treatment \[12\], reactant gases are generally assumed to attain adsorption/desorption equilibrium at the surface, whereas one of the elementary surface reactions or product desorption is considered as the rate determining step, all other elementary steps being at equilibrium.

We have attempted to interpret the kinetics of the $SiH_4/\text{WF}_6$ process on the basis of the L-H model. However, the rate equations derived from the procedure described above do not predict the kinetics correctly. To show the effect of $p(H_2)$, equilibrated adsorption of $SiH_4$ can be formulated as:

$$ \text{SiH}_4(g) + 2* \rightarrow \text{SiH}_3^* + \text{H}^* $$ \hspace{1cm} (5)

or:

$$ \text{SiH}_4(g) + * \rightarrow \text{SiH}_2^* + \text{H}_2(g) $$ \hspace{1cm} (6)

and:

$$ 2 \text{H}^* \rightarrow \text{H}_2(g) + 2* $$ \hspace{1cm} (7)

where "*" symbolizes a free surface site, and $X^*$ a chemisorbed species occupying a surface site. In case of equilibrated $H_2$ adsorption/desorption, $p(H_2)$ is expected to have a significant influence on the concentration of $\text{SiH}_n^*$ species and, therefore, a non-zero order in the rate equation. In contrast to this prediction, our experiments have shown a negligible influence of $p(H_2)$. Indeed, a zero order in $p(H_2)$ may be obtained if the forward reaction of (7) is the irreversible step in the reaction mechanism. However, assuming equilibrium in all other steps, the predicted influences of $p(SiH_4)$ and $p(WF_6)$ on growth rate do not agree with the observed kinetics. It appears that these simplifying assumptions cannot be applied to the $SiH_4/\text{WF}_6$ process. In fact, adsorption of $SiH_4$ must be regarded as a non-equilibrated, or even irreversible step in the surface reaction mechanism. Sault and Goodman \[13\] reported that
the rate of dissociative SiH₄ adsorption on a W(110) surface is not influenced by the presence of adsorbed hydrogen atoms. Hydrogen is displaced from the surface, and will not compete in the occupation of surface sites.

In order to model the kinetics adequately, we will attempt to develop a model comprising more than one irreversible elementary step. In this type of mechanism, one cannot discern a single rate limiting step, and the rate expression is obtained from a steady state approximation [14,15].

In their theoretical model of N₂ reduction of WF₆, Arora and Pollard [16] have shown WF₆ species to be adsorbed predominantly on pairs of adjacent surface sites, i.e., on dual sites (*₂). Here, this fluorine-bridged bond configuration is represented by WF₆*-₂. Single fluorine atoms can be adsorbed on dual sites as F*-₂. However, the occupation of so-called hollow sites by fluorine atoms (F*-₂) is thermodynamically more favorable [16]. We have adopted the most significant steps of the sequence of adsorption and subsequent dissociation of WF₆ according to [16] in Eqs. (8) to (13) of the following reaction mechanism:

\[
\begin{align*}
WF₆(g) + *₂ & \rightarrow WF₆*-₂ \quad (8) \\
WF₆*-₂ + *₂ & \rightarrow WF₆*-₂ + F*-₂ \quad (9) \\
WF₆*-₂ + *₂ & \rightarrow WF₆*-₂ + F*-₂ \quad (10) \\
WF₆*-₂ + 2*₂ & \rightarrow WF₆*-₂ + F*-₂ + 2F*-₂ \quad (12) \\
F*-₂ + *₂ & \rightarrow WF₆*-₂ \quad (13)
\end{align*}
\]

Dissociative adsorption of SiH₄, removal of fluorine atoms from the surface, and adsorption of gaseous reaction products is represented by:

\[
\begin{align*}
SiH₄(g) + * & \rightarrow SiH₂* + H₂(g) \quad (14) \\
SiH₂* + * & \rightarrow SiH* + H* \quad (15) \\
SiH* + F*-₂ & \rightarrow SiHF* + *₂ \quad (16) \\
SiHF* + F*-₂ & \rightarrow SiHF₂* + *₂ \quad (17) \\
SiHF₂* + F*-₂ & \rightarrow SiHF₃(g) + *₂ + * \quad (18) \\
2H* & \rightarrow H₂(g) + *₂ \quad (19)
\end{align*}
\]

The concentration of free dual sites is proportional to the square of the concentration of free single sites [11,14], i.e., [*₂] = [*]². In steady state, the rate of (11) is proportional to the rate of (16):

\[
R = k_{14}p(SiH₄)[*] = 2k_{11}[WF₆*-₂][*]² (20)
\]

If reactions (8) to (10), and (13) are assumed to be equilibria, the concentration of adsorbed WF₆*-₂ species, i.e., [WF₆*-₂], can be expressed in terms of \( p(WF₆) \), [*] and [F*-₂]::

\[
[WF₆*-₂] = \frac{KP(WF₆)[*]^{10}}{[F*-₂]²} \quad (21)
\]

in which \( K' \) represents an overall equilibrium constant. Substitution of (21)
in (20), assuming the surface to be predominantly covered by thermodynamically most favorable \( P_{\text{d}} \) species, yields an expression for \([\ast]\):

\[
[\ast] = \frac{k_{\text{d}}p(\text{SiH}_4)}{2k_{11}K'p(\text{WF}_6)^{\frac{1}{2}}}
\]

From (22) and (20) the rate equation is obtained:

\[
R = \left[ k_{\text{d}}p(\text{SiH}_4) \right] \frac{1}{2k_{11}K'p(\text{WF}_6)^{\frac{1}{2}}}
\]

The resulting reaction orders agree with the experimentally found kinetics according to Eq. (3) in region I, i.e. an order slightly higher than one in \( p(\text{SiH}_4) \) and a small negative order in \( p(\text{WF}_6) \). This approximation may be valid as long as the \( p(\text{WF}_6) \) is sufficiently high for adsorption equilibrium to be established. However, if \( p(\text{WF}_6) \) is lowered, \([\ast]\) will increase. Consequently, the rate of \( \text{SiH}_4 \) adsorption will increase, and therefore the overall deposition rate will rise to a value at which \( \text{WF}_6 \) adsorption equilibrium cannot be attained. Adsorption and dissociation of \( \text{WF}_6 \) must now be regarded as irreversible processes, and in steady state the forward rate of (8) is equal to the rate of (14):

\[
R = k_{\text{d}}p(\text{SiH}_4)[\ast] = 2k_{\text{d}}p(\text{WF}_6)[\ast]^2
\]

From (24) \([\ast]\) can be found:

\[
[\ast] = \left[ \frac{k_{\text{d}}p(\text{SiH}_4)}{2k_{\text{d}}p(\text{WF}_6)} \right]^{\frac{1}{2}}
\]

The following equation is obtained for the overall reaction rate:

\[
R = \left[ k_{\text{d}}p(\text{SiH}_4) \right] \left[ 2k_{\text{d}}p(\text{WF}_6) \right]^{-1}
\]

This result fairly agrees with the empirical rate equation valid in region II, given by Eq. (4), showing almost second and minus first order in \( p(\text{SiH}_4) \) and \( p(\text{WF}_6) \), respectively.

The model described here reasonably explains the experimentally observed kinetics. However, modified assumptions may result in similar rate equations. For instance, if decomposition of \( \text{WF}_6 \text{P}_2 \) is considered to be irreversible, or \( \text{P}_2 \) is the dominant adspecies instead of \( \text{P}_{\text{d}} \), small negative orders in \( p(\text{WF}_6) \) are obtained, as found in region I. Moreover, models can be formulated in which dissociative \( \text{SiH}_4 \) adsorption requires two surface sites. A general rate expression is:

\[
R = k(T)p(\text{SiH}_4) \left[ \frac{p(\text{SiH}_4)}{p(\text{WF}_6)} \right]^n
\]

with \( n = 0 \) at high fluorine surface coverage, and \( n = 1 \) at low coverage.
CONCLUSIONS

In contrast to several previous literature reports, marked deviation from first and zero order dependences with respect to $p(\text{H}_2)$ and $p(\text{WF}_6)$, respectively, in the range of $0.5 \leq p(\text{H}_2)/p(\text{WF}_6) \leq 1.0$, has been obtained from in-situ growth rate measurements. Simple Langmuir-Hinshelwood mechanisms appear to be unsuitable in modeling the kinetics of the process. Instead, models have been proposed involving several irreversible reaction steps, and rate equations have been derived from quasi-steady-state approximations. These rate equations qualitatively agree with the observed kinetics in the two regions.

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