

Modeling of the Kinetics in Copper Chemical Vapor Deposition from Cu(hfac)VTMS

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A new model is used to describe the surface kinetics in copper chemical vapor deposition from Cu(hfac)VTMS. This model is based on nonequilibria. It provides a mechanism that satisfactorily describes the kinetics. In this mechanism, next to the disproportional growth reaction, a parallel reduction reaction is proposed, which accounts for the observed growth-rate enhancement by hydrogen. The new model is herein more convenient than a conventional Langmuir-type model. The reaction-rate coefficients of all reactions in the mechanism are calculated. The *VTMS desorption appears to be fast. The reactions involving a Cu(hfac)-VTMS dissociation have a low reaction-rate constant. Both observations confirm results reported by several other authors.

Introduction

During the past decade, the interest in copper as a next generation material for metallic interconnects has increased.^{1–3} Up to now, aluminum has been generally used for interconnects in electronic microdevices, but modern requirements are better met by copper. The latter, which shows excellent electrical conductivity and a high electromigration resistance, has been the subject of much research.^{3–11}

In chemical vapor deposition (CVD) of copper, investigations have focused on the copper β -diketonates and their derivatives.^{3,4} One of these derivatives, copper(I) (1,1,1,5,5,5-hexafluoro-2,4-pentadionate) vinyltrimethylsilane (Cu(hfac)VTMS) is used in the present research. The overall reaction of this precursor is shown in eq 1.



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At a temperature of 120 °C conductive copper layers are already formed.¹² It is this low deposition temperature that fits Cu(hfac)VTMS for the coppering of plastics. Now, copper deposition by CVD is no longer restricted to refractory substrates such as TiN, Si, or SiO₂. Plastics such as polyimide and polyetherimide (PEI) can be metallized too.

Metallized plastics are used in the manufacture of several products such as car grills or computer housings, but also of more sophisticated applications as Printed Circuit Boards or Molded Interconnection Devices.

Metallization is often performed using galvanic processes. Better seed layers for galvanic metallization are the goal of CVD of metals on plastics.^{13,14} To understand this CVD process better, the present study is performed.

In this research the growth rate of copper in thermal CVD is monitored. Several reaction parameters are changed to establish the kinetics of this growth process. One of the parameters influencing growth is the hydrogen partial pressure.^{15–17} Jain et al. suggested two possible explanations for the observed growth-rate enhancement.¹⁷

Awaya et al.^{15,16} and Jain et al.¹⁸ used Langmuir-type models to describe the surface kinetics of copper CVD

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from Cu(hfac)VTMS. Girolami et al.¹⁹ described the reactions at the surface in more detail, using a molecular mechanistic approach, and Kim et al. used a numerical method to describe the transport phenomena.²⁰ Other authors who studied the influence of several process parameters did not provide a model.^{21–23}

An alternative model, recently developed in our group,²⁴ is applied to describe the present results. This model, in contrast to conventional models such as the Langmuir and Langmuir–Hinshelwood types,^{25,26} is based on the absence of equilibria and reactions between surface species. Because of the absence of equilibria, parallel reactions can be included in the mechanism. Moreover, the reaction-rate coefficients of all participating reactions can be calculated separately. Estimation of these coefficients at different temperatures will enable the calculation of the activation energies of the different reactions. This provides an extra check on the validity of the mechanism.

In this paper a reaction mechanism is proposed, on the basis of the new model. It will be shown to fit the experimental data satisfactorily. Our results are compared to those of other authors, who used different models.

Experimental Aspects

The growth-rate measurements are performed in a microbalance system, described previously.²⁷ For the present measurements, because less extreme experimental conditions are needed, several changes in this system were made. Pressures down to 5 hPa are achieved, while the reactor is operated at temperatures between 100 and 500 °C.

The gas delivery system consists of an evaporator system containing Cu(hfac)VTMS kept at 45 °C ($P_{\text{Cu(hfac)VTMS}} = 0.7$ hPa²⁸). In all cases nitrogen is used as an inert carrier gas at flow rates of 0–100 sccm. Deliberate changes in this rate are compensated for in a separate nitrogen line (flow range 0–100 sccm), so that a constant flow and pressure is maintained in the reactor system. Both gas flows, as well as the reactant gas H₂ (flow range 0–1000 sccm) and the diluent gas N₂ (flow range 0–1000 sccm), are adjusted and monitored by mass-flow controllers. The diluent gas is also used to purge the balance and protect it from unwanted deposition. Due to a bypass around the evaporator system, the reactor and its feeding lines can be purged, the flows adjusted, and the reactor heated and pressurized before the precursor is introduced.

After the reactor and its feeding lines are purged for about 1 h, the precursor is fed into the reactor, and the growth monitoring is started. When the growth rate has stabilized (typically after 45 min) the dependence of this rate on varying experimental parameters is studied.

At deposition temperatures below 180 °C, PEI substrates ($\sim 10 \times 15$ mm²) were used, cut, and milled to 1 mm from 4

Table 1. Experimental Conditions for CVD

parameter	symbol	value
reactor temperature	T	100–300 °C
total flow rate	Φ_T	300 sccm
reactor pressure	P_R	6.7 hPa
hydrogen pressure	P_{H_2}	2.2 hPa
precursor pressure	P_p	0.22 hPa

mm wafers of Ultem 1000, provided by GE Plastics. After being cleaned ultrasonically in 5% HNO₃ for 5 min, the substrates were attached to a 1-mm-diameter glass wire from the microbalance. Above 180 °C, the glass-transition temperature of Ultem 1000, silicon, or molybdenum substrates ($\sim 10 \times 15$ mm²) were used and cleaned in acetone and ethanol sequentially for 5 min each. On the silicon, the native oxide (SiO₂) was still present.

All experiments were carried out under the conditions summarized in Table 1, unless stated otherwise.

A New Model

The model we propose is quite different from the conventional models such as the Langmuir model. Because of its irreversible nature, and for convenience, it will be referred to as “monorhoic” (i.e., Greek for “only flowing in one direction”) model in this paper. The monorhoic model is applied in the same limiting regime of the CVD process as the Langmuir-type models, viz. the reaction-rate-limited regime.

Langmuir-type models were originally designed for use in heterogeneous catalysis. CVD and heterogeneous catalysis both deal with interactions between gases and surfaces. Therefore, the Langmuir model, which has been very successful in catalysis, is applicable to CVD processes. However, the differences between CVD and catalysis give sufficient reasons to search for a more convenient model.

The first, and most obvious, difference is in the process product. The product in most heterogeneous catalytic processes is a gas, whereas in CVD the most important product is a solid. This solid is deposited on a reactive surface, forming a new reactive surface itself. Thus, opposite to the situation in catalysis, the nature of the reactive surface changes during a CVD process.

Another difference, less obvious but more important, is found in the bonding strength of adsorbates to the surface. The bonding should be weak in catalysis, according to Sabatier's principle.²⁵ A weak bonding means a high mobility over the surface, and a fast desorption, resulting in an adsorption/desorption equilibrium. In CVD, this bonding is usually stronger. This leads to a slow desorption process, rendering the adsorption/desorption process irreversible.

Taking this into account, we assume the following for our monorhoic model: (1) no equilibria are present, (2) adsorbed species have no surface mobility, (3) the gas–surface reactivity depends on the species adsorbed, (4) the parameters are the reaction constants of the partial reactions, and (5) the variables are formed by the surface concentrations.

A monorhoic model, therefore, consists of a few irreversible reactions between the gas and the surface, with several adsorbates as the reacting species. As there are no reactions in equilibrium in our model, we are able to calculate all reaction-rate coefficients. In Langmuir-type models, nothing can be said about the reactions after the rate-determining step. Besides, the implemen-

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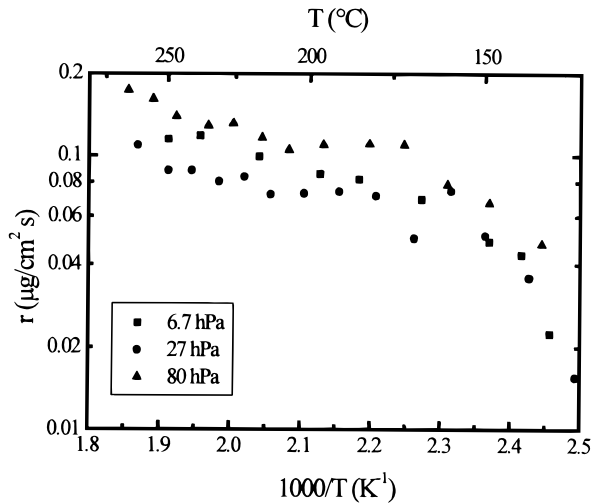


Figure 1. Arrhenius plots of copper deposition on Si, at different reactor pressures (P_R) of 6.7, 27, and 80 hPa. The other experimental parameters are given in Table 1.

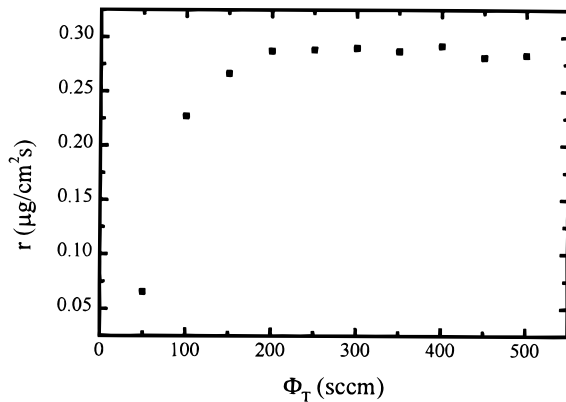


Figure 2. Growth rate versus total flow rate (Φ_T) on Ultem 1000 at 145 °C.

tation of two parallel reactions is easily achieved, something which is quite difficult in Langmuir-type models where it will lead to many additional reactions and parameters.

Results and Discussion

According to several authors^{18,21–23} the transition between diffusion-rate and reaction-rate limitation can be found at ± 200 °C, as estimated from an Arrhenius-type plot. Below 200 °C, therefore, one expects surface kinetic measurements to be meaningful.

In Figure 1, Arrhenius-type measurements at different reactor pressures are shown. Indeed, the transition point is present under our experimental conditions (Table 1). From Figure 1 it is not clear whether the position of the transition point depends on reactor pressure. Lee et al. found a lower transition temperature at lower reactor pressure between 0.33 and 1.3 hPa,²³ but this trend is not confirmed here.

Although the shape of the Arrhenius curve is similar to that reported by Awaya et al.,¹⁵ it is still no proof of a transition between two limiting regimes. This proof can be obtained from the measurements shown in Figures 2 and 3. In the former, the growth rate increases with flow till about 250 sccm, while in the latter the growth increases even at very large flows. From these

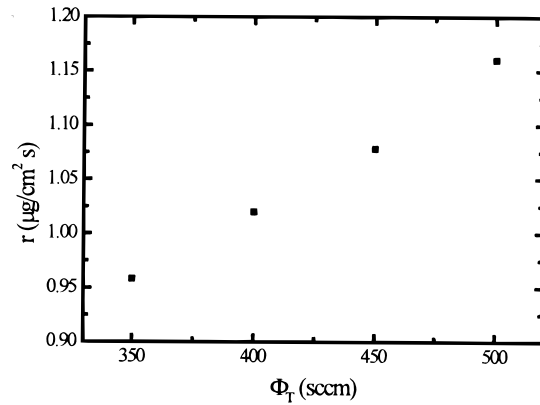


Figure 3. Growth rate versus total flow rate (Φ_T) on molybdenum at 265 °C.

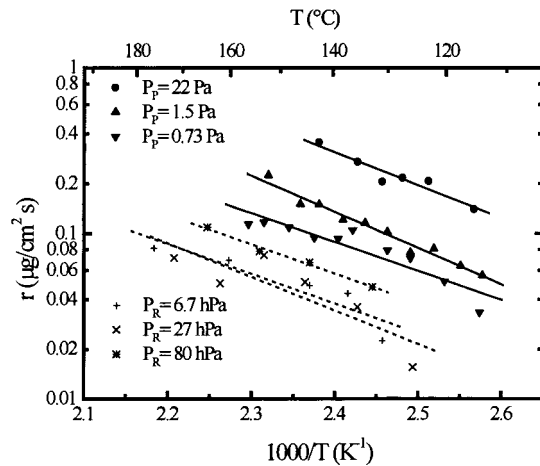


Figure 4. Arrhenius plots at different precursor partial pressures (P_p) and reactor pressures (P_R). The solid lines indicate deposition rates on Ultem 1000, and the dashed ones, on silicon. The other experimental parameters are given in Table 1.

measurements, we conclude that the experimental parameters (Table 1) result in experiments within the reaction-rate-limited regime and, therefore, are suitable for our kinetic measurements.

The measurements discussed here were performed using several different substrates, viz. silicon, molybdenum, and Ultem 1000. We expected that this is not of any influence on the final growth mechanism, because after a certain time, the substrate will be all copper, regardless of the underlying substrate. In Figure 4, it is shown that this indeed is the case, as the slopes of the curves are virtually equal. Here the deposition rate is measured as a function of temperature in the surface reaction-rate-limited regime at different substrates and reaction parameters. The solid lines represent measurements on Ultem 1000, whereas the dashed lines are measured on silicon. For clarity, we did not include results on molybdenum, which show the same behavior. The other experimental conditions can be found in Table 1. The experimental conditions are the same for two experiments, viz. on Ultem 1000 at $P_p = 22$ Pa ($- \cdot -$) and on silicon at 6.7 hPa ($- + -$). The growth rate, however, is not. This discrepancy probably results from the error in the estimation of the deposited area. This error might be large. Therefore absolute values for different measurements cannot be compared.

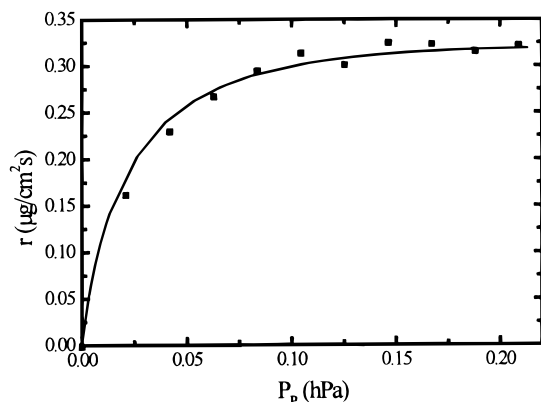


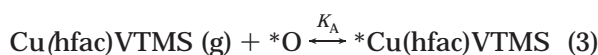
Figure 5. Growth rate versus precursor partial pressure (P_p) on Ultem 1000, at 150 °C, 6.7 hPa reactor pressure, 2.2 hPa H_2 pressure, and 300 sccm total flow rate. The solid squares represent the experimental values, and the solid line, the fit by the monorhoic mechanism.

From the slope of the curves represented by

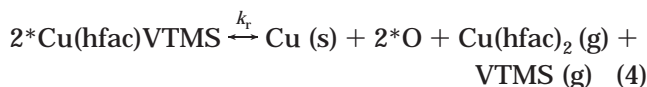
$$r = Ae^{-E_a/RT} \quad (2)$$

the activation energies, E_a , can be calculated and vary from 33 ± 5 to 42 ± 2 kJ/mol.

The influence of both precursor partial pressure and hydrogen pressure on the growth rate was studied. In Figure 5, the results for the Cu(hfac)VTMS partial pressure are shown. The solid line in this graph represents the growth rate calculated from the monorhoic model, which is explained below. The behavior represented by the experimental points can clearly be fitted with a simple Langmuir-type model. The first reaction, for example, is an adsorption reaction, which is in equilibrium:



Here $*O$ denotes a free surface site, whereas $*A$ indicates a species A adsorbed to the surface. The second reaction in this simplified model is a surface growth reaction:



A fit of this model to the data results in $k_r = 1.3$ mg/cm²s, and $K_A = 0.066$ mTorr. These values agree within an order of magnitude. With this simple model, however, it is not possible to fit the behavior in Figure 6, the effect of the hydrogen pressure. Growth at zero pressure implies a parallel reaction, not easily accounted for in a Langmuir-type model. The implementation of parallel reactions would lead to an additional amount of parameters, resulting in a complex model.

The influence of the hydrogen pressure is not large, but definitely present.¹⁶ The solid line in Figure 6 again shows the calculated growth rate, obtained from fitting the monorhoic model to the observed growth rate.

Apparently, two gas-phase species affect the growth rate. Therefore, both should be included in the monorhoic model. We propose the mechanism to consist of

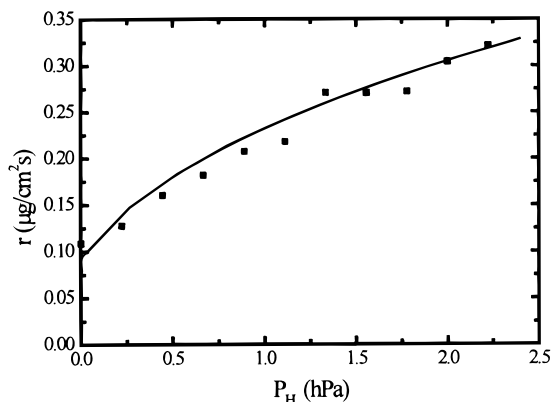
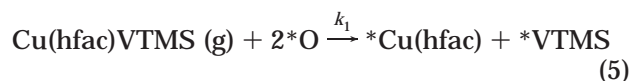


Figure 6. Growth-rate versus hydrogen partial pressure (P_{H_2}) on Ultem 1000, at 145 °C, 6.7 hPa reactor pressure, 0.22 hPa precursor pressure, and 300 sccm total flow rate. The solid squares represent the experimental values, and the solid line, the fit by the monorhoic mechanism.

five different steps. This mechanism is analogous to the one proposed by Farkas et al.²⁹

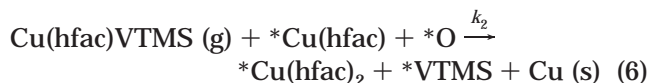
Gas-phase reactions are not possible in the monorhoic model. Therefore, the first reaction step should be a precursor adsorption step. Here, it is assumed that the precursor decomposes upon adsorption:



The monovalent $*Cu(\text{hfac})$ has been observed by several authors.^{19,29} Popovici et al. observed a divalent copper species upon adsorption on Teflon.³⁰ Apparently, the adsorption reaction is surface-dependent.

Another possibility for the first step could be the adsorption of an intact Cu(hfac)VTMS molecule at the substrate, as proposed by many authors.^{19,21,29,31} This is not possible here, as it would induce a subsequent reaction of this $*Cu(\text{hfac})VTMS$ with an empty surface site to create $*VTMS$, which has been observed at the surface in adsorption experiments.²⁹ The monorhoic model does not allow such a reaction.

The adsorption of hydrogen to a metallic copper substrate is not favorable.^{32,33} Besides, there is no need for hydrogen to adsorb, as reactions between adsorbates do not exist in the monorhoic model. This leaves only two growth mechanisms. First, the adsorbed, dissociated precursor can react with an impinging precursor molecule from the gas phase. This disproportionation reaction is analogous to reaction 1:



The other growth mechanism, accounting for the observed hydrogen influence, would be a reduction reac-

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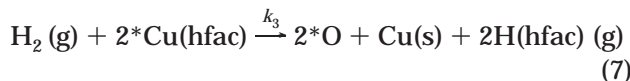
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tion. Here, we assume the reaction of hydrogen to be with two adjacent precursor molecules:



The validity of this reaction is not known, as the system $\text{H}_2\text{-Cu}(\text{hfac})\text{VTMS}$ has not been subject of any surface-chemistry studies, yet. Other possibilities exist. The $\text{H}(\text{hfac})$ compound could stick to the surface, or H_2 could react with only one $^*\text{Cu}(\text{hfac})$ species. Both possibilities would result in more complex calculations, and are not considered here. Besides, the reaction of H_2 with only one monovalent copper species would lead to a free hydrogen atom or radical.

The gaseous $\text{H}(\text{hfac})$ compound formed in the reduction reaction is directly transported away from the surface and, therefore, of no influence on the reaction.

Surface species that do not react in any way should desorb, to avoid poisoning:



This mechanism results in four coupled differential equations. Herein the reaction-rate coefficients are the parameters, and the surface concentrations, the variables. As we assume the total amount of surface sites to be 100%, three out of four surface concentrations are independent. Therefore, three differential equations suffice to describe the whole system:

$$\frac{d[^*\text{O}]}{dt} = -2k_1 \cdot [^*\text{O}]^2 \cdot P_p - k_2 \cdot [^*\text{O}] \cdot [^*\text{Cu}(\text{hfac})] \cdot P_p + 2k_3 \cdot [^*\text{Cu}(\text{hfac})]^2 \cdot P_{\text{H}_2} + k_4 \cdot [^*\text{Cu}(\text{hfac})_2] + k_5 \cdot (1 - [^*\text{O}] - [^*\text{Cu}(\text{hfac})] - [^*\text{Cu}(\text{hfac})_2]) \quad (10)$$

$$\frac{d[^*\text{Cu}(\text{hfac})]}{dt} = k_1 \cdot [^*\text{O}]^2 \cdot P_p - k_2 \cdot [^*\text{O}] \cdot [^*\text{Cu}(\text{hfac})] \cdot P_p - 2k_3 \cdot [^*\text{Cu}(\text{hfac})]^2 \cdot P_{\text{H}_2} \quad (11)$$

$$\frac{d[^*\text{Cu}(\text{hfac})_2]}{dt} = k_2 \cdot [^*\text{O}] \cdot [^*\text{Cu}(\text{hfac})] \cdot P_p - k_4 \cdot [^*\text{Cu}(\text{hfac})_2] \quad (12)$$

Here, P_p is the precursor partial pressure, and P_{H_2} the hydrogen partial pressure. The symbols between brackets represent the concentrations of the surface species. The growth rate from this model is

$$r = k_2 \cdot [^*\text{O}] \cdot [^*\text{Cu}(\text{hfac})] \cdot P_p + k_3 \cdot [^*\text{Cu}(\text{hfac})]^2 \cdot P_{\text{H}_2} \quad (13)$$

The mechanism results in a satisfactory description of the measured growth rates, as shown by the solid lines in Figures 5 and 6. This fit is obtained by numerically solving the differential equations, starting from an arbitrary initial surface occupation. Time is then increased until stationary solutions are found. Next, the reaction-rate coefficients k_i are changed and

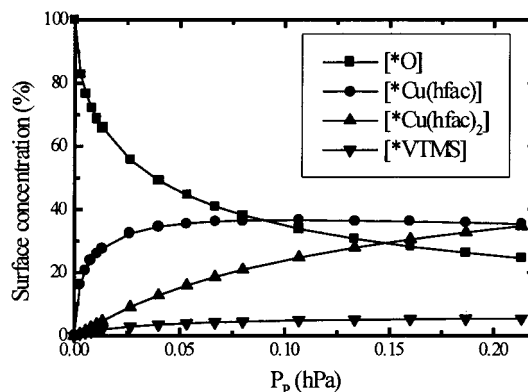


Figure 7. Surface concentration changes with changing precursor partial pressure.

Table 2. Calculated Reaction-Rate Constants

k_1	0.033 $\text{cm}^2/\mu\text{g hPa s}$
k_2	0.008 $\text{cm}^2/\mu\text{g hPa s}$
k_3	0.0005 $\text{cm}^2/\mu\text{g hPa s}$
k_4	0.32 s^{-1}
k_5	8 s^{-1}

the equations solved again until an acceptable fit is obtained.

The final reaction-rate coefficients found are shown in Table 2, and exhibit some striking features. The largest value is found for the desorption of the VTMS ligand (eq 9). Apparently this desorption is rather fast. This is in good agreement with Gross' and Donnelly's finding,² although several authors claim otherwise.^{15,19}

A very small reaction-rate coefficient is found for the reduction reaction (eq 7). This indicates that this reaction is of influence only at large hydrogen pressures. Jain et al. gave two possible explanations for the hydrogen enhancement.¹⁷ As we observe the growth-rate enhancing effect of hydrogen without using it as a carrier gas, their explanation concerning a lower viscosity of hydrogen and a higher precursor transfer in the bubbler is not confirmed by our experiments. Their other explanation, a chemical reduction of the copper(I), seems indeed more plausible.

Low k values are found also for the adsorption and the disproportionation reaction (eqs 5 and 6). These reactions have the dissociation of a precursor molecule in common, which might account for the low reaction-rate coefficient. Girolami et al. showed the precursor dissociation to be the rate-limiting step in a Langmuir-type approach of the $\text{Cu}(\text{hfac})\text{VTMS}$ system.¹⁸ To distinguish between dissociation and adsorption or reaction would be interesting, but would result in the implementation of surface reactions, which are not allowed in our model.

Besides the reaction-rate coefficients, the surface concentrations are calculated with our model. In Figure 7, these concentration profiles are shown. This figure shows that even at high precursor partial pressure, surface poisoning by $^*\text{Cu}(\text{hfac})_2$ and $^*\text{VTMS}$ is not an issue. From this picture it is also clear that the desorption of $^*\text{VTMS}$ is faster than that of $^*\text{Cu}(\text{hfac})_2$.

Conclusions

With the new monorhoid model, the surface chemistry of copper CVD from $\text{Cu}(\text{hfac})\text{VTMS}$ is described satis-

factorily. Even the enhancement with hydrogen flow can be fitted, something which is not as easily achieved using a Langmuir-type model. From our measurements we can conclude that the growth-rate enhancement by hydrogen is not the result of a higher precursor transfer in the bubbler, but of a reduction reaction at the surface. However, the enhancement is not large, as shown by the high hydrogen pressure needed to achieve any increase at all.

The fast *VTMS desorption confirms earlier results by other authors, indicating that our model is chemically reasonable. The same conclusion can be drawn from the

fact that both reactions containing a Cu(hfac)VTMS dissociation have a low reaction-rate constant. This dissociation has been shown earlier to be the rate-limiting step in a Langmuir-type approach.

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