Nucleation on SiO₂ during the Selective Chemical Vapor Deposition of Tungsten by the Hydrogen Reduction of Tungsten Hexafluoride

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ABSTRACT

A horizontal hot-wall chemical vapor deposition (CVD) quartz reactor with rectangular cross section was used to study the effect of different process conditions on the nucleation of tungsten on SiO₂ during selective WCVD by the H₂ reduction of WF₆. The experimental procedure included placing a metallic surface at the center of the reactor, and small samples of SiO₂ at different positions both upstream and downstream with respect to the metallic surface. Digitized scanning electron microscopy micrographs were used to determine the particle size distributions of nuclei on the SiO₂ surfaces. We found that the amount of nucleation on SiO₂ decreases when smaller metallic surfaces are present and for lower temperatures and shorter process times. Although nucleation was always greatest on SiO₂ samples closest to the metal sample, the effect of flow rate depended on the position of the SiO₂. A statistical nearest neighbor analysis indicated a clustering of W nuclei on the SiO₃. A simplified mathematical model was developed to predict concentration profiles of a gaseous intermediate generated at the metal surface during the thermal decomposition of the source gas. This intermediate has been proposed as being the reactive species that causes nucleation on SiO₂ surface. Qualitative agreement between experimental and theoretical results reinforce the proposed role of the intermediate with this species being characterized by a short lifetime.

Tungsten is a useful material to fill via holes in multilevel interconnections metallization for very large scale integration/ultralarge scale integration (VLSI/ULSI) technology because of its low resistivity and its ability to conform to high aspect ratio geometries.¹ Tungsten via-filling has the additional advantage of being a selective process,^{2.3} meaning that, at the right conditions, deposition occurs on the metal but not on the surrounding oxide.

Tungsten can be deposited by chemical vapor deposition (WCVD) which is carried out by the reduction of WF_6 through one of three different chemistries:

1. The silicon reduction $[2WF_6(g) + 3Si(s) \rightarrow 2W(s) + 3SiF_4(g)]$ yields high deposition rates but the growth is limited by the inability of the source gas to reach the silicon surface beyond a film thickness of about 15 nm.⁴ In addition, problems such as encroachment and wormholing have been reported.⁵

2. The hydrogen reduction $[WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)]$ eliminates the problems inherent in the silicon reduction, but reasonable deposition rates can be obtained only at temperatures above 500°C. The deposition mechanism for this system has been widely studied, and it has been determined that the deposition rate has a one-half-order dependence on the partial pressure of H₂ and a low (zero to one-sixth) order dependence on the partial pressure of WF_{6} . ^{1,24,6} 3. The silane reduction $[2WF_6(g) + 3SiH_4(g) \rightarrow 2W(s) + 3SiH_4(g) \rightarrow 2W(s)]$

3. The silane reduction $[2WF_6(g) + 3SiH_4(g) \rightarrow 2W(s) + 3SiF_4(g) + 6H_2(g) (Ref. 7) or WF_6(g) + 2SiH_4(g) \rightarrow W(s) + 2SiHF_3(g) + 3H_2(g) (Ref. 8)] combines the advantages of the two systems above by providing a gaseous source of silicon to yield high deposition rates. However, the higher deposition rates introduce difficulties for controlling the selectivity and also tend to yield mass-transfer limited deposition rates as characterized by a first-order dependence on silane. <math display="inline">^{9,10,11}$ More recent work suggests that the true kinetic rate may be more complicated than a simple power law rate expression. 12 The dependence of rate on temperature is more complicated with changes in the activation energy with pressure^{13} yielding negative activation energies at some conditions. 9,10

Because of the selective nature of WCVD, besides understanding the process of film formation, it is equally important to understand the mechanism for selectivity loss in order to propose rational processing strategies. Colgan and Chapple-Sokol¹¹ carried out a qualitative study of the selectivity loss during the silane reduction of WF₆ by comparing micrographs of samples that had experienced W deposition at different conditions. In summary, they observed more and larger W nuclei on the SiO_2 surface at higher temperatures, higher silane partial pressures, and lower WF₆ partial pressures; clearly, the conditions that result in higher deposition rates also contribute to a higher loss of selectivity.

In the case of the H₂/WF₆ system, different mechanisms for the loss of selectivity have been proposed. A reactive intermediate is assumed to be generated during the deposition process at the metal surface, and this intermediate diffuses toward the oxide where it reacts to produce tungsten nuclei. This argument is strongly supported by frequent observations that nucleation on SiO₂ tends to be higher when larger areas of metal are present.^{14,15} In one of the proposed mechanisms,^{15,16} a tungsten subfluoride (WF_x, x < 6) is the intermediate that causes the selectivity loss. Other papers^{4,14,17,18} propose as the intermediate the HF produced from the main reduction reaction; however, this contradicts experimental results^{16,19} in which the addition of HF did not have any effect on the nucleation of W on SiO₂.

Several attempts have been made to quantify the loss of selectivity for the H_2/WF_6 system. These attempts have focused on the development of mathematical models^{14,18,20-22} that are based on establishing the conditions at which the intermediate generation increases or decreases; predictions can then be made on what conditions will cause greater selectivity loss. More recently,²³ we presented a mathemati-



Fig. 1. Schematic diagram of the experimental system.

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cal model which included a kinetic description of the relationship between the concentration of the intermediate and the number of tungsten nuclei. The parameters of the model were adjusted to fit data of W nuclei on SiO₂ reported by Kwakman and co-workers.^{14,18} By doing so, we reported that the nucleation process has a high order dependence of roughly 6 to 10 on the intermediate concentration. We proposed that this dependence indicates that 6 to 10 atoms of tungsten are necessary to obtain a stable cluster. In addition, a modified Damköhler number, introduced to compare the loss of the intermediate at the SiO₂ surface to the loss by diffusion between the metal and oxide surfaces, was determined to be small suggesting to us that, for this case, the life of the intermediate was long.

Although the preceding investigations have contributed to the understanding of the mechanism of selectivity loss, more data is needed to get a clear view of the WCVD process in order to produce more rational reactor designs. In this paper, we present an experimental procedure aimed at quantifying the selectivity loss during selective WCVD by the H₂ reduction of WF₆, by studying the effect of the process conditions on the amount of W nucleation on SiO₂. The experimental technique and results will also serve as the framework to address the problem of selectivity loss for the SiH₄/H₂/WF₆ system; this type of study is currently underway.

Equipment Description

A schematic diagram of the experimental setup is shown in Fig. 1. We used a hot-wall LPCVD reactor consisting of a quartz tube with rectangular cross section area. Quartz was selected because it should have little deposition on it during selective conditions. The tube, 51 cm long, 11 cm wide, and 4 cm high, has a simple enough geometry to allow a clear understanding of the flow patterns, and is characterized by short residence times which reduces depletion of reactants by operating the reactor in a differential mode. The ends of the quartz tube are sealed with stainless steel flanges using Viton o-rings.

A hot-wall configuration permits an accurate quantification and control of the temperature on the wafer surface. The reactor is heated with an Omega heating tape that wraps a 26 cm long central portion of the reactor. This hot region was designed to operate as a single-wafer isothermal furnace in which an extra length was added to heat up the gas through the chamber. A heat-transfer calculation showed that about 3 cm are required after the gas has entered this hot region to raise its temperature to within 10°C of the wall temperature. The two regions that remain unwrapped at each side of the hot zone keep the end flanges cold in order to keep them free of W deposition, and to protect the seals from the high temperatures required for the process. Aluminum plates are placed between the outer walls of the reactor and heating tape to make the temperature of the system more uniform. A J-type thermocouple is used to measure the temperature of the outer bottom wall; in situ measurements showed that there is at most a 5°C difference between the inner and outer walls, while calculations indicate that there is a 0.1°C difference between the wall temperature and the surface of the wafer. This estimate was obtained by equating the heat-transfer rate from the reactor wall to the wafer, and from the wafer to the gas. The heat-transfer coefficient between the wall and the wafer was obtained from Ref. 24. Furthermore, because of the hot-wall configuration and the relatively low temperatures typical of the WCVD process, radiative heat transfer was considered to be negligible in all of our design calculations. The temperature of the system is controlled with a Watlow 965 temperature controller connected to a Payne power controller. Glass wool was used to provide insulation.

The gases used were semiconductor grade tungsten hexafluoride from Air Products, semiconductor purity hydrogen from Matheson, and ultrahigh purity nitrogen from Matheson to provide a continuous purging of the system. The gas flow rates were measured and controlled with MKS



Fig. 2. Schematic diagram of the domain for the mathematical model describing tungsten intermediate formation and transport in a reactor of rectangular cross section.

1159B flowmeter controllers connected to an MKS 247C power supply; the flowmeter controller used for the WF₆ has Kalrez seals to reduce the swelling that this gas produces on elastomers such as Viton. The flowing lines consisted of 316 stainless steel 1/4 in. diameter tubing.

The system was evacuated with a Leybold D25B mechanical pump connected to the reactor with a 1.5 in. diam PVC hose. The pressure was measured with an MKS 122A capacitance manometer connected to an MKS PDR-D1 power supply with a resolution of 0.01 Torr; calibration of this instrument was monitored with a Hastings vacuum gage. A butterfly valve had been originally included to control the pressure of the system. However, we found that because of the large difference in molecular sizes between the WF₆ and H₂ molecules, the small opening formed upon partially closing the valve produced a molecular flow regime at the outlet, thus favoring the conductance of the smaller H₂ molecule. This led to an unknown concentration of H₂ that was lower than what was expected for the molar composition as determined from the ratio of the flow rates, with the net effect of having a lower deposition rate. This problem was eliminated by introducing sections of different lengths of 1/2 in. PVC hose at the outlet of the reactor to increase the pressure drop between the reactor and the pump with the final adjustment made by setting the total flow rate.

The residual gases coming out of the reactor were bubbled in a buffer solution before being released to the atmosphere to retain HF or WF₆. To prevent any moisture backstreaming into the pump, a moisture trap was placed before the bubbler.

A gravimetric technique was used to measure deposition rates on a Mettler balance with a resolution of 0.0001 g. The samples were analyzed with a Hitachi scanning electron microscope (SEM) coupled with a Niscan true-grayscale handscanner.

The reactor was cleaned *in situ* with an SF₆/dry-air plasma system. The system consisted of an ENI 2100L RF amplifier connected to a Krohn-Hite frequency generator, an L-type matching network, and a Bird 41 powermeter. The electrodes were two rectangular steel plates placed on the outer walls of the reactor, and they extended beyond the heated zone but remained far enough from the stainless steel end plates to prevent any sputtering. The gases used were etchant grade SF₆ and zero grade air from Air products. In this case, the pressure was controlled with the butterfly valve.

Mathematical Model

Based on the importance given to the role of the intermediate in causing loss of selectivity, in this section we describe a simplified mathematical model that predicts concentration profiles of the intermediate generated inside the reactor described in the previous section during selective WCVD. Figure 2 is the schematic diagram upon which such a model is based.

For developing the model we have assumed that the source gas flows across the reactor, and it reacts at a central



Fig. 3. Model predictions of the intermediate concentration profile for different total flow rates: (a) without gas-phase consumption ($K_G = 0$), (b) with gas-phase consumption ($K_G = 50$). The aspect ratio is 12.75, and the active area is located at 0.4912 $\leq \eta \leq 0.5088$.

region between x_1 and x_2 which can be denoted as the active surface. At the same time that the thermal decomposition of WF₆ occurs, the intermediate is generated, and it is carried away by diffusion in the *y*-direction, and combined diffusion and convection in the *x*-direction.

For simplicity, only the isothermal, hot region of the reactor is considered, in which case the density and diffusivity are constant. The velocity in the y- and z-directions are zero, while in the x-direction we have assumed that there is a fully developed parabolic velocity distribution. In addition, the active surface extends fully along the z-direction, which translates into a uniform generation eliminating any dependence of the concentration profile on this direction. Hence, a material balance for the intermediate can be written in terms of dimensionless variables as follows

$$\frac{\partial^2 C}{\partial \eta^2} + \alpha^2 \frac{\partial^2 C}{\partial \xi^2} - 4 \operatorname{Pe} \xi (1 - \xi) \frac{\partial C}{\partial \eta} - K_{\rm G} C = 0$$
 [1]

where $C = C_i/HG_s/D_i$) is the dimensionless concentration, $\eta = x/L$, $\xi = y/H$, $\alpha = L/H$ is the aspect ratio, $K_G = k_G L^2/D_i$ is a dimensionless first-order rate constant, and $\text{Pe} = v_{\max}L/D_1$ is the Peclet number. Because we do not know the exact structure of the WF_x intermediate, we used the diffusion coefficient (1100 cm²/s) for WF₆ at 1 Torr and 350°C as calculated with the Chapman-Enskog equation.²⁵

Solution of Eq. 1 requires appropriate boundary conditions. For the flowing stream, at the inlet and outlet ports, Danckwerts boundary conditions apply

$$-4\operatorname{Pe}\xi(1-\epsilon)C + \frac{\partial C}{\partial \eta} = 0 \quad \eta = 0 \quad 0 < \xi < 1$$
[2]

$$\frac{\partial C}{\partial \eta} = 0 \quad \eta = 1 \quad 0 < \xi < 1$$
[3]

Notice that Eq. 2 considers that the inlet concentration of the intermediate is zero. The consumption term of Eq. 1 accounts for all possible ways in which the intermediate could be depleted. Hence, any loss to the walls is neglected, and

$$\frac{\partial C}{\partial \xi} = 0 \quad 0 < \eta < 1 \quad \xi = 1$$
 [4]

$$\frac{\partial C}{\partial \xi} = 0, \quad \eta < \frac{x_1}{L} \quad \eta > \frac{x_2}{L} \quad \xi = 0$$
 [5]

A more detailed mathematical description should consider the heterogeneous loss of the intermediate that causes nucleation on the reactor wall and on the SiO_2 surface. In such a case, a reaction term would be added to Eq. 4 and 5.

Finally, in the absence of detailed kinetic information, and to keep the numerical calculations simple, we have assumed that the intermediate is generated at the active surface by a first-order reaction; hence, it is appropriate to use a Robin-type boundary condition for this region

$$\frac{\partial C}{\partial \xi} = -1 \quad \frac{x_1}{L} < \eta < \frac{x_2}{L} \quad \xi = 0$$
 [6]

A constant flux condition has been used for the results shown in this paper, however; constant concentration boundary conditions give similar results.

Equations 1 through 6 were solved with a finite difference technique using 401 uniformly spaced grids in the η -direction, and 21 uniformly spaced grids in the ξ -direction.

We used our model to predict the effect of total flow rate, magnitude of the homogeneous gas-phase loss, and size of the active surface, on the concentration profile of the intermediate along the reactor. The results of the simulations, presented in Fig. 3 and 4, show that there is an accumulation of the intermediate at the center of the reactor right above the active surface where it is generated. Back-diffusion causes a portion of the generated species to be present upstream from the active surface, while the rest is distributed along the downstream section as it is carried away from the flow.

Figure 3a shows concentration profiles for three different flow rates and for no depletion of the intermediate in the gas phase. At these conditions, higher concentrations can be expected throughout the reactor for the lower flow rates as a result of higher residence times. In contrast, for the case in which the intermediate is characterized by a short lifetime as a result of depletion in the gas phase, Fig. 3b shows that higher flow rates still produce lower intermediate concentrations near the active surface region and in the upstream portion of the reactor, but produce higher intermediate concentrations in downstream regions. These predictions would maintain the same qualitative features for the cases in which a first-order heterogeneous reaction term was introduced in Eq. 4 and 5. We have observed experimentally the type of behavior depicted in Fig. 3b as addressed in detailed in the Results and Discussion section.

The effect of varying the size of the active surface on the intermediate concentration is shown in Fig. 4. The size of the active surface was changed in our simulations by varying the proportion of the total length that corresponds to this region. Figure 4 shows that, throughout the entire reactor, the intermediate concentration directly depends on the size of the surface where it is generated. Therefore, the presence of larger metallic surfaces are expected to favor the nucleation of W on SiO₂.

The role of the intermediate in causing loss of selectivity during selective WCVD can be studied experimentally by evaluating the situations simulated with our model. Clearly, the degree of selectivity loss should follow the trends predicted for the intermediate concentration if, in

Fig. 4. Model predictions of the intermediate concentration profile for different sizes of the active surface. The aspect ratio is 12.75, Pe is 13.4, and the active surface is located at 0.4962 $\leq \eta \leq$ 0.5038, 0.4912 $\leq \eta \leq$ 0.5088, and 0.4812 $\leq \eta \leq$ 0.5188 for the 0.5 cm, 1.0 cm, and 2.0 metal widths, respectively.

fact, the intermediate plays the major role in causing the loss of selectivity. The experimental procedure described in the following section was designed based on these results.

Experimental

The types of wafers used in all the experiments consisted of p-type (100) silicon wafers with two different coatings: (*i*) 0.8 μ m of aluminum doped with 1% silicon and 0.3% copper, (*ii*) 0.7 μ m of phosphosilicate glass (PSG) densified at 865°C with 4.5% phosphorus. The samples were loaded into the reactor at room conditions. For each run, the samples consisted of an aluminum wafer strip 11 cm long, and four 2 cm² squares cut out of a PSG wafer. The aluminum strip was placed at the center covering the entire width, while two of the PSG samples were placed upstream (sample 1) and downstream (sample 2) adjacent to the metal and the remaining two at 5 and 10 cm downstream from the metal (samples 3 and 4, respectively); this arrangement is shown in Fig. 5.

With the samples loaded, the pressure was lowered by slowly opening the butterfly valve while nitrogen was flowing. At the same time, the power was turned on and the temperature was allowed to reach the setpoint. Then, the flow was turned off, and the system reached a base pressure of 0.002 Torr. The system was kept at the process temperature and base pressure for 20 min.

Before the run started, the hydrogen flow was allowed to stabilize, and the process time began at the moment the WF_6 was allowed to flow into the reactor. To end the run, the WF_6 flow was shut off. The hydrogen was purged out

Fig. 5. Positions of the SiO_2 and metal samples inside the CVD reactor.

from the lines, and the system was allowed to cool down to about 50° C before unloading the samples.

The thickness of the deposited W film was measured using a gravimetric technique by weighing the metal sample before and after the run. In order to account for possible errors caused by mishandling, the metal sample was divided prior to the run into three pieces which were weighed independently providing an extra check for the reproducibility of the measurements.

After every run there was some deposition on the reactor walls, and the tungsten was removed with an *in situ* plasma etch. An SF₆ discharge was used for the etching, and it was followed by a dry-air discharge to remove any remaining material on the surface and oxidize any possible open bonds left on the quartz walls. In the development of this cleaning procedure, a quartz sample was exposed to eight consecutive cleaning routines. No etching of the quartz was detected as determined by gravimetric measurements, and no contamination was observed as determined by x-ray a microanalysis.

During the early stages of our investigations, several preliminary depositions were carried out with their subsequent plasma clean. However, the reactor walls would be fully covered by W after every run. No treatment was given to the reactor upon receiving it from the manufacturer, and we believe that the original walls favored the formation of a thin layer of W that could not be removed solely with the plasma clean. We eliminated this problem by rinsing the reactor with 35% H_2O_2 . Nevertheless, consistent with earlier reports on cleaning of quartz tubes,²⁶ we had to recondition the reactor by performing seven 10 min runs with 5% WF₆ in H_2 at 350°C and 1.04 Torr, alternated with their corresponding plasma cleans, in order to regain reproducibility of the deposition rates.

The PSG samples were analyzed with the SEM with the objective of determining the particle size distribution and number density of tungsten nuclei in each sample as obtained by operating at different conditions. On each sample, four different locations were selected at random keeping track of the position with respect to the aluminum sample and the direction of the flow. Micrographs were taken with an amplification of 3000 times covering an area of 774 μ m² per screenful. The particle size distributions were obtained by scanning each micrograph into the computer with a resolution of 100 dots per inch, and the digitized images analyzed with the program IMAGE.²⁷ This program measures the area and determines the relative positions of regions whose pixels are contained within a user-specified grayscale threshold.

Results and Discussion

The experimental procedure described above allowed us to evaluate the nucleation rates as a function of position in the reactor, area of the metal surface, gas flow rates, time, and temperature. This information allowed us to determine the validity of the intermediate theory as described in the following paragraphs.

Figure 6 shows an Arrhenius plot of the deposition rates obtained at different temperatures. The observed rates, and an activation energy of 62.4 kJ/gmol are consistent with previously reported data² obtained at similar conditions in a hot-wall system, and they compare favorably to results using cold-wall systems^{1.6} with activation energies of 73 and 57.5 kJ/gmol, respectively.

As explained in the previous section, we studied the selectivity loss by determining the particle size distribution of W on SiO₂. Figure 7 shows the cumulative particle size distribution obtained on eight different locations that can be distinguished from the four-sample configuration described in Fig. 5. These locations correspond to the edges of the samples facing the metal strip (-0.0, 0.0, 5.0, 10.0 cm), and about 0.5 cm away from this edge into the sample (-0.5, 0.5, 5.5, 10.5 cm); the negative distances correspond to the sample located upstream from the metal strip.

The general trends seen in Fig. 7 are observed for all our experiments. For the samples downstream of the metal sur-

Fig. 6. Arrhenius plot of tungsten deposition rate vs. temperature.

face, the nucleation of W is the greatest on the SiO₂ closest to the metal. There is a significant drop in the number of nuclei from 0.0 to 0.5 cm on sample 2. Nevertheless, the amount of nucleation at either position on sample 2 was so great that we could not distinguish individual particles contained in large clusters; these clusters were counted as particles with radii greater than 0.35 µm, which is roughly the thickness of the film deposited on the metal. The number of nuclei continue to drop going further downstream (from sample 3 to 4) but the nuclei counts seem to level off enough that there is no significant difference between the downstream or upstream edge for either sample 3 or 4. For this reason, for the results presented later, we have lumped any data for locations 5 and 5.5 cm together to be the results at 5 cm. Similarly we have lumped the results for locations 10 and 10.5 cm together as results at 10 cm. For sample 1 upstream of the metal surface, again the nucleation rate dramatically drops off as we get further away from the metal so that the nucleation at -0.0 is much higher than that at -0.5 cm.

These results are consistent with the proposed mechanism for nucleation growth because the experimentally observed nuclei mimic the expected variation in intermediate concentration as shown in Fig. 3 and 4. The high nuclei counts observed closest to the metal surface are due to the high intermediate concentration expected there. The very sharp decrease in nucleation with position upstream of the sample is due to rapid decrease in intermediate concentra-

Fig. 7. Cumulative particle size distribution as a function of position in the reactor with respect to the metal. The distributions are given in terms of the particle radius.

tion as the intermediate tries to diffuse back into the flowing stream.

Figures 8a and b show the cumulative frequency distributions in samples 3 and 4 (5 and 10 cm from the metal) for different total deposition times. In this case, the particle radius has been replaced in the x-axis by the theoretical time at which a given particle was initially formed. This format followed the one used by Kwakman et al. 18 who proposed that the radius of the particles created on the SiO₂ surface grow at the same rate as the film on the metal. Hence, the theoretical time is calculated by subtracting from the total time the ratio between the particle radius and the deposition rate of W on the metal. If this is a valid method for determining when the nuclei were created, all of the curves in Fig. 8a and b should lie on top of one another for the different total deposition times. The fact that these curves are offset from one another indicates that the mechanism governing the growth of the individual particles on the SiO_2 is different from the one of the film growth. In general, the nuclei appear to grow slower than the bulk film.

The results of the effect of the process conditions on the growth of W nuclei on SiO_2 can be conveniently presented in terms of the fraction of the samples that are covered with tungsten. This number does not require the ability to distinguish different nuclei that may have merged together, nor is it very sensitive to our ability to measure particles below about a 0.06 μ m radius. This format is first shown in Fig. 9, in which the dotted vertical line separates the upstream and downstream regions with respect to the metal strip. The conclusions that can be drawn from this figure are basically the same as in Fig. 7, but it is possible to see more clearly that the amount of nucleation is more uniform on the samples that are far downstream.

Figure 10 shows the fraction area of the SiO_2 samples covered with W nuclei at the end of different total process time. The general trend observed is that nucleation becomes more significant for longer process times. The more than four orders of magnitude increase in the nucleation going from 10 to 25 min is an indication of an autoacceleration phenomenon caused by an increase of the metal area as tungsten deposits on the SiO_2 surface as well as on the reactor walls, therefore favoring the generation of larger amounts of intermediate.

Experiments were carried out by varying the width of the aluminum strip, while maintaining its length extending from side to side in the reactor; this configuration is the same as that simulated in the Mathematical Model section. Our simulations showed that there is a direct relationship between the concentration of the intermediate in the system and the size of the surface where it is generated. The experimental results presented in Fig. 11 are consistent with the idea showing that there is an increase in the fraction area of SiO₂ covered with W for larger widths of the metal strip. In addition, the fraction area covered with W increases approximately proportional with the area of the metal strip to the 2 to 4 power which can be obtained from a log-log plot. We see that it is a weaker relationship than the one we had predicted²³ for the data by Kwakman et al., but it is still a high order dependence.

Figure 12 shows the nucleation obtained by varying the residence time of the intermediate in the reactor; this was achieved by changing the total flow rate at constant pressure. Notice that the higher upstream intermediate concentration for the lower flow rates predicted by our simulations, translates into higher nucleation on sample 1. This dependence remains present on sample 2 because of the larger residence times at the smaller flow rates. However, further downstream the phenomenon is reversed with higher nucleation for the higher flow rate, indicating that the intermediate is consumed in the gas phase further upstream at the lower velocities. The small differences seen in Fig. 3b for different flow rates get amplified to give large changes in the fraction area covered due to the high order dependence of nucleation intermediate concentration. The results shown in Fig. 12 are in direct contradiction with our

Fig. 8. Cumulative particle size distribution as a function of total process time at 5 cm (sample 3) and 10 cm (sample 4) downstream from the metal. The distributions are given in terms of the theoretical time as proposed by Kwakman *et al.*¹⁸ The conditions are 350° C, 1.04 Torr, 500 sccm, 5% WF₆, 95% H₂, and 1 cm metal width.

early theoretical results²³ that were based on the data by Kwakman *et al.*, ¹⁸ which indicated that the intermediate had a long lifetime. Instead, a comparison of the experimental results of Fig. 12 with the simulations presented in Fig. 3b, lead to the conclusion that the intermediate is in fact characterized by a short lifetime.

The effect of temperature on the W nucleation is shown in Fig. 13. The total process time was adjusted to attain the same film thickness in the different runs and to study the effect that different process conditions have while producing similar films. The experimental results show that nucleation is an activated process with higher values as the temperature increases.

Finally, a nearest neighbor analysis was performed on our nucleation data. This analysis consists of comparing the expected mean distance [$\delta = 0.5(A/n)^{0.5}$] between particles that are nearest neighbors, and that have been randomly placed on a surface, to the actual experimentally observed mean distance. Hence, it is possible to determine if W preferably nucleates on SiO₂ forming clusters of particles or not.^{28,29} In order to eliminate edge effects for analyzing areas which are not infinitely large, we used the equations by Donelly³⁰ to calculate δ and its standard error, as follows

$$\delta = \frac{1}{2} \sqrt{\frac{A}{n}} + \left(0.514 + \frac{0.412}{\sqrt{n}}\right) \frac{P}{n}$$
^[7]

$$S_{\delta}^{2} = 0.07 \, \frac{A}{n^{2}} + 0.035 P \, \frac{\sqrt{A}}{n^{5/2}}$$
[8]

Fig. 9. Fraction area of SiO_2 covered by tungsten nuclei as a function of position in the CVD reactor for three different runs at the same conditions.

The distribution of δ is normal, providing n > 6.²⁸ Hence, we made *Z*-tests ($Z = |d - \delta|/S_{\delta}$) at the 95% level of significance for the nucleation data obtained from our samples. We found that in 95% of the cases W tended to nucleate in clusters on the SiO₂ surfaces, meaning that the presence of a nuclei seems to favor the formation of subsequent nuclei in a close vicinity or that particular local areas of SiO₂ are thermodynamically favorable for nucleation.

Conclusions

An experimental procedure was developed for studying the phenomenon of selectivity loss during selective WCVD by the H_2 reduction of WSF₆. The information gathered from our results reinforce the argument that an intermediate generated during the thermal decomposition of the source gas is what causes the selectivity loss.

We found that the amount of nucleation of W on SiO₂ decreases on positions located further from the metal surface, as well as for smaller metallic surface areas. This effect is consistent with the predicted high order dependence of nucleation on the intermediate concentration. Lower flow rates produce higher nucleation on SiO₂ surfaces located upstream and immediately downstream from the metal; however, this behavior is reversed on positions further downstream. We developed a simplified mathematical model for predicting intermediate concentration profiles in our reactor and were able to qualitatively reconcile the experimental results with our simulations only if the intermediate is characterized by a short lifetime. We also found that nucleation on SiO₂ is favored at higher temperatures and increases as the process time progresses. By comparing cumulative frequency distributions of different runs with

Fig. 10. Fraction area of SiO₂ covered with tungsten nuclei as a function of process time at different distances from the metal.

Fig. 11. Effect of the metal surface area on the fraction area of SiO₂ covered with tungsten nuclei at different positions from the metal.

different process times, we concluded that the processes of nuclei and film growth occur through different mechanisms. Finally, a nearest neighbor analysis indicates that W nuclei preferentially form clusters as they deposit on the SiO₂ surfaces.

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LIST OF SYMBOLS

- area of the map for the nearest neighbor analysis, μm^2 А
- \overrightarrow{C}_{i} intermediate dimensionless concentration
- intermediate concentration, mol cm⁻
- $\hat{D_{i}}$ intermediate diffusivity coefficient, $cm^2 s^{-1}$
- generation rate of the intermediate, mol cm⁻² s⁻¹ G
- Hreactor height, cm
- $k_{
 m g} K_{
 m G}$ first-order gas-phase rate constant, s⁻¹
- dimensionless first-order gas-phase rate constant
- reactor length, cm L
- number of particles n
- Pe Peclet number $r_{\rm G}$ gas-phase reaction, mol cm⁻³ s⁻¹

flow rate (sccm)

Fig. 12. Effect of the total flow rate on the fraction area of SiO_2 covered with tungsten nuclei at different positions from the metal.

Fig. 13. Effect of the temperature on the fraction area of SiO₂ covered with tungsten nuclei at different positions from the metal.

- gas-phase rate, mol $cm^{-2} s^{-1}$ velocity, cm s^{-1} $r_{\rm S}$
- v
- x-direction space variable, cm x
- location of the upstream end of the active surface, cm x_{1}
- location of the downstream end of the active surface, x_2 cm
- y direction space variable, cm y
- aspect ratio α
- δ expected mean distance between nearest neighbors, μm
- x-direction dimensionless space variable η
- ξ y-direction dimensionless space variable

REFERENCES

- C. M. McConica and K. Kristnamani, This Journal, 133, 1. 2542 (1986)
- 2. E. K. Broadbent and C. L. Ramiller, ibid., 131, 1427 (1984).
- M. L. Green and R. A. Levy, ibid., 132, 1243 (1985). 3
- 4. Y. Pauleau and Ph. Lami, *ibid.*, **132**, 2779 (1985).
- 5. W. T. Stacy, E. K. Broadbent, and M. H. Norcott, *ibid.*, 132, 444 (1985)
- H. Körner, Thin Solid Films, 175, 55 (1990).
- M. L. Yu and B. N. Eldridge, J. Vac. Sci. Technol., A7, 7. 625 (1989)
- 8. N. Kobayashi, Y. Nakamura, H. Goto, and Y. Homma,
- J. Appl. Phys., 73, 4637 (1993).
 J. E. J. Schmitz, A. J. M. van Dijk, and M. W. M. Graef, in Proceedings of the Tenth International Conference on Chemical Vapor Deposition, G. W. Cullen and J. M. Blocher, Editors, PV 87-8, p. 625, The Electrochemical Society Proceedings Series, Pennington, NJ (1987).
- 10. R. S. Rosler, J. Mendonca, and M. J. Rice, J. Vac. Sci. Technol., B6, 1721 (1988).
- 11. E. G. Colgan and J. D. Chapple-Sokol, ibid., B10, 1156 (1992)
- J. A. M. Ammerlaan, P. J. van der Put, and J. Schoon-man, J. Appl. Phys., 73, 4631 (1993).
 H. Gockce, J. T. Sears, and T. Sahin, Paper 32j pre-
- sented at Fall National Meeting of the American Institute of Chemical Engineers (1991).
- 14. L. F. Tz. Kwakman, W. J. C. Vermeulen, E. H. A. Granneman and M. L. Hitchman, in Proceedings of the Workshop on Tungsten and Other Refractory Metals for VLSI Applications II, E. K. Broadbent, Editor, p. 377, Materials Research Society, Pittsburgh, PA (1987)
- 15. C. M. McConica and K. Cooper, This Journal, 135, 1003 (1988).
- 16. J. R. Creighton, *ibid.*, **136**, 271 (1989).
- 17. C. M. McConica, in Proceedings of the Workshop on Tungsten and Other Refractory Metals for VLSI Ap-plications II, E. K. Broadbent, Editor, p. 51, Materials
- Research Society, Pittsburgh, PA (1987). 18. L. F. Tz. Kwakman, W. J. C. Vermeulen, E. H. A. Granneman and M. L. Hitchman, in Proceedigns of the Workshop on Tungsten and Other Refractory Metals for VLSI Applications III, V. A. Wells, Editor, p. 141, Materials Research Society, Pittsburgh, PA (1988).

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- I. Hirase, T. Sumiya, M. Schack, S. Ukishima, D. Rufin, M. Shishikura, M. Matsura, and A. Ito, *ibid.*, 133.
- 20. C. M. McConica, J. K. Hunter, K. Tan, and M. D. Szczepaniak, *ibid.*, 125.
- 21. J. I. Ulacia, S. Howell, H. Körner, and Ch. Werner, *Appl. Surf. Sci.*, **38**, 370 (1989). 22. C. Werner, J. I. Ulacia, C. Hopfmann, and P. Flynn, *This*
- Journal, 139, 566 (1992).
- 23. C. Chang, N. Desatnik and B. E. Thompson, in Proceedings of the Twelfth International Conference on Chemical Vapor Deposition, CVD-XII, K. F. Jensen and G. W. Collen, PV 93-2, p. 244. The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
- D. L. Smith, in *High Pressure Etching*, N. E. Einspruch and D. M. Brown, Editors, Plasma Processing for VLSI, Academic Press, Inc., New York (1984).
- 25. R. B. Bird, W. E. Stewart, and E. D. Lightfoot, Transport Phenomena, John Wiley & Sons, Inc., New York (1960)
- 26. Ph. Lami and Y. Pauleau, This Journal, 135, 980 (1988).
- 27. Image 1.49 Users's Manual, National Institute of Health (NIH) (1992). 28. P. J. Clark and F. C. Evans, *Ecology*, **35**, 445 (1954).
- B. D. Ripley, Spatial Statistics, John Wiley & Sons, Inc., New York (1981).
- 30. J. C. Davis, Statistics and Data Analysis in Geology, 2nd ed., John Wiley & Sons, Inc., New York (1986).

FTIR Studies of the Adsorption/Desorption Behavior of Cu Chemical Vapor Deposition Precursors on Silica

III. Re-examination of (1,1,1,5,5,5-hexafluoroacetylacetonato)(vinyltrimethylsilane)copper(I),

(hfac)Cu(VTMS)

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ABSTRACT

The reaction of (hfac)Cu(VTMS) with SiO₂ surfaces with varying surface concentrations of isolated and hydrogen-bonded surface hydroxyl groups and four-membered SiO rings has been investigated. The adsorbed (hfac)Cu(VTMS)(where hfac = 1, 1, 1, 5, 5, 5-hexafluoroacetylacetonate and VTMS = vinyltrimethylsilane) reacted with the hydrogen-bonded surface hydroxyl groups and the strained siloxane sites and interacted with the isolated surface hydroxyl groups. The VTMS ligand was completely liberated from the adsorbed compound between 125 and 175°C depending on the relative VTMS ligand was completely liberated from the adsorbed compound between 125 and 175°C depending on the relative ratios of the reactive surface sites. Because all SiO₂ surfaces have some combination of these reactive sites, dissociation of (hfac)Cu(VTMS) to give "(hfac)Cu" and VTMS is always expected. Selective chemical vapor deposition (CVD) relies on the slow nucleation of Cu on SiO₂ which involves a number of steps in series including adsorption, dissociation, and reaction to give Cu atoms and physical nucleation to give stable nuclei. This suggests that selective CVD must rely on slow adsorption, dissociation, reaction, or physical nucleation to limit the formation of Cu clusters on the nongrowth, SiO₂ surface. Results from this work and the literature suggest that most of these steps are slower on SiO₂ than on Cu surfaces. However, the rates of these steps can be increased sufficiently by increasing temperature and precursor partial pressure to result in loss of selectivity. result in loss of selectivity.

Selective chemical vapor deposition (CVD) is a process by which a material can be deposited on one surface, usually referred to as the growth surface, and not on another surface, usually referred to as the nongrowth surface. Selective CVD of copper has attracted much attention because it provides an alternative to blanket deposition and subsequent etching as a method for obtaining patterned copper films for interconnects in multilevel ultralarge-scale integrated (ULSI) circuits.¹⁻³ The most promising precursors for blanket and selective CVD of Cu are $Cu(\beta$ -diketonate)₂ and $(\beta$ -diketonate)CuL compounds. The experiments results regarding the selective CVD of copper onto various metals and diffusion barriers vs. SiO₂ using these precursors are often conflicting.¹⁻⁴ This motivated us⁵⁻⁷ and others⁸ to study systematically the interaction of Cu(hfac)₂ and (hfac)CuL compounds with silicon dioxide surfaces using FTIR spectroscopy.

Of the precursors in the (hfac)CuL family, the CVD of Cu from (hfac)Cu(VTMS) has been studied most extensively and varying degrees of selectivity depending on the deposi-tion conditions have been observed.⁹⁻¹² A previous Fourier transform infrared spectroscopy (FTIR) study of the interaction of (hfac)Cu(VTMS) with silicon dioxide surfaces⁸ implied a higher reactivity with surfaces rich in hydrogenbonded surface hydroxyl groups relative to surfaces where only isolated hydroxyl groups were present. These data suggested that the conflicting results for selective deposition may be due to different amounts of hydrogen-bonded hydroxyl groups on the different SiO₂ surfaces.

As a part of our FTIR studies of a series of (hfac)CuL compounds, where L = 2-butyne, 1,5-COD, PMe₃, and Cu(hfac)₂, with SiO₂ surfaces, we re-examined the interaction of (hfac)Cu(VTMS) with silicon dioxide. The experiments were carried out in the same manner as for the compounds $Cu(hfac)_2$ and (hfac)CuL, L = 2-butyne, 1,5-COD and PMe₃, which was different from the methodology used in the previous study of (hfac)Cu(VTMS).8 Our experimental data are consistent with a new interpretation and provide a broader understanding of the interaction between (hfac)Cu(VTMS) and silicon dioxide surfaces. The goal of this paper is to report these findings and to correlate them with the deposition behavior of (hfac)Cu(VTMS).

Experimental

The experimental setup, the collection of the gas- and solid-phase data, and the preparation and treatment of the silica surface were described in the preceding papers of this series.^{5.6} Briefly, transmission FTIR spectroscopy was used to study the interaction of different adsorbates on highsurface-area Cab-O-Sil. A half-inch SiO_2 pellet made from about 10 mg Cab-O-Sil was then pressed onto a 0.3 mm thick tantalum mesh. The temperature was measured with a thermocouple spot-welded to the mesh approximately 2 mm from the pellet. The mesh was wired directly to a current source for resistive heating. The sample assembly was mounted on a stainless steel cube (2.75 in.) equipped with KBr windows. The sample cell was connected to a