

Selectivity loss during tungsten chemical vapor deposition: The role of tungsten pentafluoride

J. R. Creighton

Citation: *Journal of Vacuum Science & Technology A* **7**, 621 (1989); doi: 10.1116/1.575854

View online: <http://dx.doi.org/10.1116/1.575854>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvsta/7/3?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

[Area selective metalorganic chemical vapor deposition of gold on tungsten patterned on silicon](#)

J. Vac. Sci. Technol. A **8**, 1411 (1990); 10.1116/1.576892

[Summary Abstract: Mechanisms for selectivity loss during tungsten chemical vapor deposition on Si and SiO₂](#)

J. Vac. Sci. Technol. A **5**, 1739 (1987); 10.1116/1.574522

[New insights on nucleation of tungsten on insulators during selective chemical vapor deposition](#)

Appl. Phys. Lett. **50**, 965 (1987); 10.1063/1.98000

[Diffusion barrier properties of thin selective chemical vapor deposited tungsten films](#)

J. Vac. Sci. Technol. B **4**, 1369 (1986); 10.1116/1.583460

[Barrier effect of selective chemical vapor deposited tungsten films](#)

J. Vac. Sci. Technol. B **4**, 1175 (1986); 10.1116/1.583478



Instruments for Advanced Science

 <p>Gas Analysis</p> <ul style="list-style-type: none">dynamic measurement of reaction gas streamscatalysis and thermal analysismolecular beam studiesdissolved species probesfermentation, environmental and ecological studies	 <p>Surface Science</p> <ul style="list-style-type: none">UHV TPDSIMSend point detection in ion beam etchelemental imaging - surface mapping	 <p>Plasma Diagnostics</p> <ul style="list-style-type: none">plasma source characterizationetch and deposition process reactionkinetic studiesanalysis of neutral and radical species	 <p>Vacuum Analysis</p> <ul style="list-style-type: none">partial pressure measurement and control of process gasesreactive sputter process controlvacuum diagnosticsvacuum coating process monitoring
--	---	---	---

Contact Hiden Analytical for further details:
W www.HidenAnalytical.com
E info@hiden.co.uk
CLICK TO VIEW our product catalogue

Selectivity loss during tungsten chemical vapor deposition: The role of tungsten pentafluoride

J. R. Creighton

Sandia National Laboratories, Albuquerque, New Mexico 87185

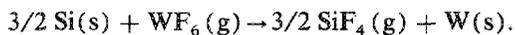
(Received 16 December 1988; accepted 9 January 1989)

Our previous studies found evidence for a selectivity loss mechanism that is initiated by desorption of tungsten subfluorides formed by the reaction of WF_6 with metallic tungsten surfaces. When a hot ($\approx 600^\circ\text{C}$) tungsten surface is exposed to WF_6 , a nonvolatile subfluoride, apparently WF_4 , will accumulate on a nearby SiO_2 surface held at $\approx 30^\circ\text{C}$. Disproportionation of this tungsten subfluoride upon heating above 350°C produces a reactive state of tungsten that induces rapid selectivity loss when exposed to chemical vapor deposition conditions. The net effect of this tungsten subfluoride desorption-disproportionation mechanism is the transport of tungsten from a tungsten surface to the silicon dioxide surface. Isolation of a higher tungsten subfluoride, apparently WF_5 , has been accomplished by cooling the SiO_2 surface to $\approx -45^\circ\text{C}$ under otherwise similar experimental conditions. Preliminary Auger spectroscopic results yield a stoichiometry of $F/W = 4.9 \pm 0.5$ for this subfluoride, and temperature programmed desorption results are consistent with the behavior of tungsten pentafluoride. Upon heating WF_5 multilayers, most of the compound desorbs, but some reaction and disproportionation occurs leaving a reduced state of tungsten on the SiO_2 surface. It seems likely that tungsten pentafluoride is the key volatile species in a tungsten transport mechanism that can initiate selectivity loss.

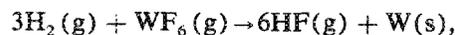
I. INTRODUCTION

Low-pressure chemical vapor deposition (CVD) of tungsten by reduction of WF_6 has many promising applications for the fabrication of very large scale integrated (VLSI) devices.¹⁻⁶ These applications include formation of diffusion barriers and planarization for multilevel interconnects. Tungsten CVD is attractive for most applications because of the selective nature of the deposition chemistry, i.e., deposition occurs on silicon and tungsten (and some other metals) but not on SiO_2 or other typical insulators. The selective nature of the deposition produces self-aligning structures and therefore significantly reduces the number of steps required for a metallization process. Unfortunately, it is not always possible to maintain selectivity indefinitely as tungsten may nucleate and grow on the insulator surfaces.

Selectivity is the result of a deposition mechanism that is strongly controlled by heterogeneous processes. Dissociative chemisorption of hydrogen and tungsten hexafluoride are thought to be necessary heterogeneous steps in the deposition mechanism.^{2,7} Several researchers have noted that a selectivity loss usually first occurs on surfaces near but not necessarily contiguous with areas of tungsten deposition.^{5,8,9} This observation strongly suggests that a volatile reaction product, by-product, or intermediate is initiating selectivity loss. For deposition on silicon, the first reaction occurring is the reduction of tungsten hexafluoride by silicon; i.e.,



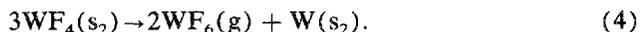
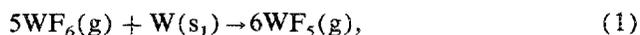
Several authors have postulated that silicon tetrafluoride or other silicon-bearing species produced by this initial reaction may contribute to selectivity loss.^{5,9} We note that if such a mechanism exists, it could not explain the selectivity loss often observed during deposition when there is initially no exposed silicon. The primary reaction responsible for tungsten deposition is the hydrogen reduction reaction, i.e.,



in which a large amount of hydrogen fluoride is produced. Hydrogen fluoride is known to react with silicon dioxide under some conditions and has also been suspected of initiating selectivity loss.⁸ However, our experiments investigating the role of HF failed to establish a definitive link between the HF partial pressure and the degree of selectivity loss.¹⁰ We have instead found convincing evidence for a tungsten transport mechanism that first involves the formation of volatile tungsten subfluorides (WF_x , $x < 6$) on tungsten surfaces.¹⁰ These subfluorides desorb from the tungsten surfaces and may diffuse through the gas phase. The adsorption and disproportionation of the tungsten subfluorides on SiO_2 surfaces then produces a reactive state of tungsten that can immediately catalyze the hydrogen reduction of tungsten hexafluoride.

For example, when a hot ($\approx 600^\circ\text{C}$) tungsten surface is exposed to WF_6 , a nonvolatile subfluoride, apparently WF_4 , will accumulate on a nearby SiO_2 surface held at $\approx 30^\circ\text{C}$. Tungsten tetrafluoride disproportionates upon heating above 350°C producing a reactive, essentially metallic, state of tungsten that induces rapid selectivity loss when exposed to CVD conditions. Given the physical properties (e.g., low volatility) of tungsten tetrafluoride,^{11,12} it seems unlikely that it is the dominant *gas-phase* species participating in the tungsten transport mechanism. Several factors indicate that tungsten pentafluoride WF_5 would be the most likely gas-phase intermediate involved in the tungsten transport mechanism. These factors include its volatility, the conditions for which it can be formed, and its propensity to disproportionate into lower subfluorides.^{13,14} By modifying our experimental conditions, we have now isolated a higher tungsten subfluoride, evidently WF_5 , and studied its thermal properties by temperature programmed desorption (TPD) and its

elemental composition by Auger spectroscopy. Our results are consistent with a tungsten transport mechanism that is initiated by formation of tungsten pentafluoride from the reaction of WF_6 with metallic tungsten [see reaction (1)].



The tungsten pentafluoride is volatile even at room temperature and may easily diffuse through the gas phase. Upon contact with another surface the tungsten pentafluoride may disproportionate into tungsten tetrafluoride and tungsten hexafluoride [see reactions (2) and (3)]. At temperatures greater than 200 °C, tungsten tetrafluoride may disproportionate further into tungsten hexafluoride and metallic tungsten,^{10-12,15} [reaction (4)]. Note that the sum of reactions (1) to (4) gives no net production of new species; the only change is that tungsten has been transported from one surface (s_1) to another (s_2).

II. EXPERIMENTAL

These experiments were performed in a multilevel vacuum system composed of a reaction chamber and an UHV analysis chamber. The analysis chamber was equipped with a cylindrical mirror analyzer (CMA) for Auger spectroscopy and a quadrupole mass spectrometer for TPD. This chamber was pumped with a turbomolecular pump to a typical working base pressure of 5×10^{-10} Torr. The reaction chamber was also pumped by a turbomolecular pump to a base pressure of $\approx 1 \times 10^{-9}$ Torr. Because relatively high pressures (5 mTorr) of WF_6 were used during the subfluoride generation experiments, the turbopump for the reaction chamber was normally throttled to give a nitrogen pumping speed of ≈ 1 l/s.

The samples were 2 cm \times 1 cm \times 0.5 mm rectangular slices of 0.4 Ω cm Si(100) that were covered with 400 Å of thermally grown silicon dioxide. Samples were etched for 15 s in a 20:1 NH_4F/HF solution and rinsed with distilled water. Cross-section transmission electron microscopy (TEM) shows that ≈ 270 Å of oxide remains after this step. These samples were mounted on a long-throw manipulator by means of tantalum clips that allowed direct resistive heating to above 800 °C, if desired. The samples could be cooled below room temperature by adding a cryogen to a Dewar to which the sample was in thermal contact. For temperature measurements, a Chromel–Alumel thermocouple was attached to the top edge of the samples with a small drop of ceramic cement (Aremco No. 516). By opening a gate valve, a sample could be moved from the reaction chamber into the UHV chamber for surface analysis within a few minutes after high-pressure experiments were finished.

A polycrystalline tungsten foil was also mounted in the reaction chamber and served as an independent source of reaction products and intermediates. This foil could be positioned from ≈ 0.5 to 5 cm from the SiO_2/Si sample, and this experimental arrangement proved essential for this study. The foil was heated resistively, and the temperature was

measured with a Chromel–Alumel thermocouple spot welded to the middle of the foil. To condense any tungsten pentafluoride produced, it is necessary to cool the SiO_2/Si sample well below room temperature. However, the necessity of having a background ambient of WF_6 during the subfluoride formation procedure precludes the use of liquid nitrogen as a cryogen, since any surface at that temperature would condense the WF_6 at the pressures used. For this reason we used liquid CHF_3 (bp = -82 °C) as a cryogen. Due to imperfect thermal contact the sample would typically cool to only ≈ -60 °C.

When performing Auger electron spectroscopy (AES) on fluorinated tungsten species, it is particularly important to minimize electron beam damage. Low electron beam currents (0.2–0.3 μA) were used, and the beam was defocused until it was slightly less than the area analyzed by the CMA (≈ 100 - μm -diameter spot). Since electron beams usually result in the desorption of fluorine from the surface, the fluorine region of the spectra were typically scanned first to obtain the highest possible fluorine signal.

TPD was performed with a multiplexed mass spectrometer, typically monitoring six to eight masses, and a sample heating rate of 10 K/s. The sample was normally placed about 2 in. in front of the mass spectrometer ionizer. A liquid-nitrogen-cooled cryoshroud surrounded the ionizer portion of the mass spectrometer, and this served to reduce the scattered component of the TPD signals, thus enhancing detection of the line-of-sight component.

III. RESULTS AND DISCUSSION

The experimental procedure used in this study to produce the tungsten subfluoride is similar to the procedure we used to isolate tungsten tetrafluoride.^{10,11,15} A steady-state flow of tungsten hexafluoride was established in the reaction chamber at a pressure of 5 to 6 mTorr. The SiO_2/Si sample was positioned about 1 cm away from the hot (600–700 °C) tungsten foil. In our previous work, the SiO_2/Si sample was normally kept at 30–40 °C which resulted in the accumulation of tungsten tetrafluoride on its surface. In this study, the SiO_2/Si sample was first cooled to ≈ -60 °C (as described in Sec. II). However, when the sample was positioned in front of the hot tungsten foil, radiation and/or conduction caused the sample temperature to rise from ≈ -60 °C to a range from -50 to 35 °C. The variation from -50 to -35 °C was enough to cause reproducibility problems with the amount of subfluoride adsorption, since this was the temperature range where desorption was becoming appreciable. Under proper conditions, thick films could be deposited as evidenced by color changes of the sample under white light. During a long deposition run, the sample color would change from silver grey (clean sample) \rightarrow purple \rightarrow blue \rightarrow pale green \rightarrow yellow \rightarrow golden yellow. This observation is consistent with the deposition of a film of WF_5 , as solid tungsten pentafluoride is reported to be yellow.^{13,16} The intermediate colors observed are likely due to thin-film interference effects rather than differences in chemical composition. A typical experimental result will now be described. A clean SiO_2/Si sample was positioned in front of the tungsten foil, and the WF_6 pressure was brought up to 5.5 mTorr. The

tungsten foil was then heated to 700 °C for 45 min, after which it was allowed to cool and the WF_6 flow terminated. During this procedure, the SiO_2/Si sample warmed to a maximum temperature of -46 °C. The resulting film appeared purple under white light. The sample was lowered into the analysis chamber, and Auger spectra were recorded at several points across the film. A representative spectrum is displayed in Fig. 1, curve (a), along with a spectrum of tungsten tetrafluoride, curve (b), from Ref. 10. The two curves have been scaled to have the same tungsten peak height, and the fluorine peak in curve (a) has been shifted to higher energy for clarity. Note that curve (a) has an appreciably higher fluorine signal than curve (b). Using the same procedure used to calculate the stoichiometry of the compound for curve (b) (i.e., WF_4),¹⁰ we obtain a stoichiometry from curve (a) of $F/W = 4.9 \pm 0.5$, which suggests that the film is predominately tungsten pentafluoride.

The thermal behavior of the tungsten subfluoride films was investigated by TPD. The TPD spectrum of a purple subfluoride film is displayed in Fig. 2. The ion intensity ratio ($WF_5^+/WF_4^+ \approx 0.14$) of the tungsten fluoride species desorbing at low temperature (peaking at -21 °C) indicates that it is not WF_6 ($WF_6^+/WF_4^+ = 3.4-4.0$, measured in our system). Several factors lead us to believe that the low-temperature peak is due to desorbing tungsten pentafluoride. The published mass spectral information on tungsten pentafluoride¹⁴ indicates that the WF_4^+ ion is most abundant (consistent with our data), but a quantitative comparison cannot be made because the reported fragmentation pattern was complicated by the presence of tungsten hexafluoride. Additional information on the subfluoride can be obtained from a kinetic analysis of the leading edge of the low-temperature desorption peak. If we assume zero-order kinetics, analysis of eight low-temperature TPD peaks gives a desorption activation energy of $E_a = 19 \pm 1$ kcal/mol. This value is very close to the reported values of 22 to 23

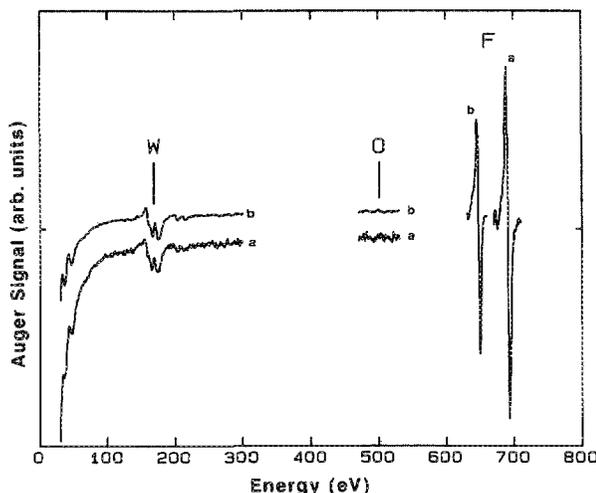


FIG. 1. AES spectra of (a) tungsten subfluoride condensed at -45 °C, see text, and (b) tungsten tetrafluoride from Ref. 10. The fluorine peak for curve (a) has been shifted $+40$ eV for clarity.

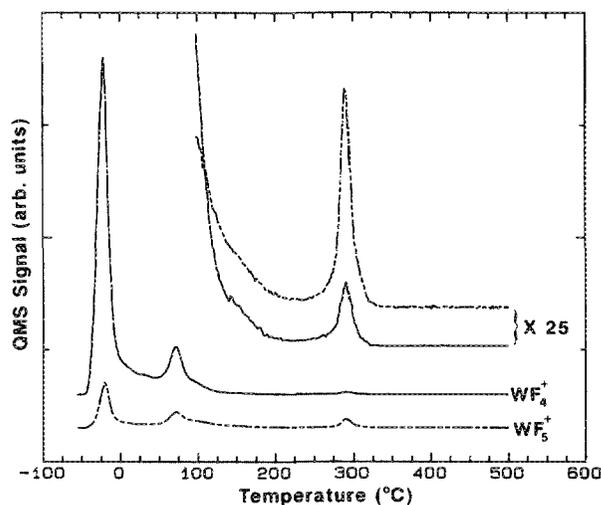


FIG. 2. TPD spectrum of tungsten subfluoride multilayer film. Solid line is for $m/e = 260$ (WF_4^+), dashed line is for $m/e = 281$ (WF_5^+)

kcal/mol for the heat of vaporization of tungsten pentafluoride.^{13,14} These Auger and TPD results indicate that WF_5 (g) is formed at the tungsten foil and then condenses on the nearby SiO_2 surface, as illustrated by reactions (1) and (2) in Sec. I.

Tungsten pentafluoride is known to disproportionate into WF_4 (s) and WF_6 (g), i.e., reaction (3) in Sec. I, near room temperature^{13,14} so we expected to see a tungsten hexafluoride TPD peak between 0 and 100 °C. However, the peak at 70 °C has a WF_5^+/WF_4^+ ratio that is different from the low-temperature WF_5 peak at -21 °C and the high temperature WF_6 peak at 290 °C (described in following paragraph). We have also detected a considerable amount of $WO_xF_y^+$ ions in the desorbing product(s) in the temperature range from 50 to 100 °C, which may indicate a reaction of the subfluoride film with the SiO_2 surface. Our initial efforts to assign the peak at 70 °C to a single desorbing product have been unsuccessful, and presently we believe the peak is due to a combination of tungsten fluorides (e.g., WF_6) and tungsten oxyfluorides (e.g., WOF_4). Further experiments are needed to resolve the complexities of the chemistry in this temperature range.

The small high-temperature peak at 290 °C in Fig. 2 has a WF_5^+/WF_4^+ ratio indicative of WF_6 . Based on our earlier observations¹⁰ and the WF_4 literature,^{11,15} we believe this peak represents the disproportionation of tungsten tetrafluoride, i.e., reaction (4) in Sec. I, which is known to occur ≈ 300 °C. Auger spectroscopy also indicates $\approx \frac{1}{2}$ monolayer (assuming two-dimensional growth) of tungsten remains on the surface after heating to 500 °C. This process represents the final step in the tungsten transport mechanism via the subfluorides.

IV. SUMMARY

Further details of a tungsten transport mechanism that can lead to selectivity loss during tungsten CVD have been elucidated. A tungsten subfluoride species formed by the reaction of WF_6 with a hot metallic tungsten foil may be con-

densed on a SiO_2 surface at $\approx -45^\circ\text{C}$. Multilayers of this species desorb in the temperature range from -40 to $+40^\circ\text{C}$, depending on the initial coverage. Color of the multilayer film, its stoichiometry as determined by Auger spectroscopy, and the desorption activation energy are all indicative of tungsten pentafluoride (WF_5). Heating of the WF_5 multilayers also results in desorption of an unidentified product(s) at $\approx 70^\circ\text{C}$. We have tentatively described this peak as due to a combination of WF_6 , formed from the disproportionation of $\text{WF}_6(\text{s})$, and of a tungsten oxyfluoride species formed from the reaction of WF_5 with the SiO_2 surface. A high-temperature WF_6 peak at $\approx 290^\circ\text{C}$ is apparently due to the disproportionation of a small amount of tungsten tetrafluoride, which also leaves a fractional tungsten coverage on the SiO_2 surface. This last step, $3\text{WF}_4(\text{s}) \rightarrow 2\text{WF}_6(\text{g}) + \text{W}(\text{s})$, corresponds to the completion of the tungsten transport mechanism. From the interpretation of these results, our previous work,^{10,17} and the available literature on tungsten subfluorides,¹¹⁻¹⁶ we conclude that tungsten pentafluoride is the most important gas-phase intermediate participating in the tungsten transport mechanism that leads to selectivity loss during tungsten CVD.

- ¹J. M. Shaw and J. A. Amic, *RCA Rev.* **31**, 306 (1970).
- ²E. K. Broadbent and C. L. Ramiller, *J. Electrochem. Soc.* **131**, 1427 (1984).
- ³N. E. Miller and I. Beinglass, *Solid State Technol.* **23**, 79 (1980).
- ⁴N. E. Miller and I. Beinglass *Solid State Technol.* **25**, 85 (1982).
- ⁵E. K. Broadbent and W. T. Stacy, *Solid State Technol.* **28**, 51 (1985).
- ⁶R. S. Blewer, *Solid State Technol.* **29**, 117 (1985).
- ⁷W. A. Bryant, *J. Electrochem. Soc.* **125**, 1534 (1978).
- ⁸Y. Pauleau and Ph. Lami, *J. Electrochem. Soc.* **132**, 2779 (1985).
- ⁹T. Moriya and H. Itôh, in *Proceedings of the 1985 Workshop on Tungsten and Other Refractory Metals for VLSI Applications* (MRS, Pittsburgh, PA, 1986), p. 21.
- ¹⁰J. R. Creighton, *J. Electrochem. Soc.* **136**, 271 (1989).
- ¹¹V. D. Butskii, V. S. Pervov, and V. G. Sevast'yanov, *Zh. Neorg. Khim.* **22**, 1416 (1977).
- ¹²I. P. Malkerova, A. S. Alikhanyan, V. D. Butskii, V. S. Pervov, and V. I. Gorgoraki, *Zh. Neorg. Khim.* **30**, 2761 (1985).
- ¹³J. Shroder and F. J. Grewe, *Chem. Ber.* **103**, 1536 (1970).
- ¹⁴A. V. Gusarov, V. S. Pervov, I. S. Gotkis, L. I. Klyuev, and V. D. Butskii, *Dokl. Akad. Nauk SSSR* **216**, 1296 (1974).
- ¹⁵V. D. Butskii and V. S. Pervov, *Zh. Neorg. Khim.* **22**, 14 (1977).
- ¹⁶W. E. Falconer, G. R. Jones, W. A. Sunder, I. Haigh, and R. D. Peacock, *J. Inorg. Nucl. Chem.* **35**, 751 (1973).
- ¹⁷J. R. Creighton and J. W. Rogers, Jr., in *Proceedings of the 1987 Workshop on Tungsten and Other Refractory Metals for VLSI Applications III* (MRS, Pittsburgh, PA, 1988), p. 63.