REFERENCES

1. T. B. Massaliki, J. L. Murray, L. H. Bermett, and H. Baker, "Binary Alloy Phase Diagrams," American Society for Metals, Metals Park, OH (1986).
2. J. C. Bean, T. T. Sheng, L. C. Feldman, A. T. Fiory, and R. T. Lynch, *Appl. Phys. Lett.*, **44,** 102 (1984).
3. C-Y Ting, S. S. Iyer, C. M. Osburn, G-J Hu, and A. M. Schweighart, in "VLSI Science and Technology/1982," C. J. Dell'Oca and W. M. Bullis, Editors, p. 224, The Electrochemical Society Softbound Proceedings Series, PV 82-7, Pennington, NJ (1982).
4. S. S. Iyer, S. L. Delage, R. D. Thompson, and B. A. Ek, To be published.
5. K. N. Tu, E. I. Alessandrini, W. K. Chu, H. Hrantle, and J. W. Mayer, *Jpn. J. Appl. Phys.*, Suppl. 2, Part 1, 669 (1974).
6. K. N. Tu, W. K. Chu, and J. W. Mayer, *Thin Solid Films,* **25,** 403 (1975).
7. M. Wittmer, M-A. Nicolet, and J. W. Mayer, *ibid.*, **42,** 51 (1977).
8. E. D. Marshall, C. S. Wu, C. S. Pai, D. M. Scott, and S. S. Lau, Mat. Res. Soc. Symp. Proc. Vol. 47 on "Thin Films: The Relationship of Structure to Properties," C. R. Aita and K. S. Srieharsha, Editors, p. 161, Pittsburgh, PA (1987).

Tungsten Deposition on Quartz by the Reaction of WF_6 and Hydrogen

E. Kato and K. Itsumi[1]

Department of Materials Science and Engineering, Waseda University, Shijyuku-ku, Tokyo 160, Japan

The rate of deposition of tungsten on quartz was determined with the aim of clarifying the mechanism of losing the selectivity of tungsten deposition on Si/SiO_2 substrates. The gaseous species above a quartz substrate proceeding during the deposition reaction were identified by the use of a mass spectrometer.

Experimental

Deposition rate determination.—A quartz furnace tube 38 cm long with an inner diameter of 42 mm was positioned within a furnace and served as the reaction chamber. The temperature in the chamber was monitored by a thermocouple placed in close proximity to the sample, and the temperature was kept at 400°C. Gases used in the experiments were tungsten hexafluoride (99.8% WF_6), hydrogen (99.99999% H_2), and argon (99.9998% Ar). Gas flows of H_2 and Ar were controlled by the use of valves and automatic flow controllers. The flow rate of WF_6 was determined by a gas flow meter. Quartz plates 10 mm × 10 mm × 3 mm were used as substrates. The surface of substrates was polished with silicon carbide powders (Caborundum no. 1500). The deposition rate of tungsten was determined by a thermobalance (Shimazu RMV-50V).

Two kinds of experiments were performed. First, the flow rate of WF_6 was kept at 0.2 sccm, and the flow rate of H_2 was changed. Second, the flow rate of H_2 was kept at 0.2 sccm and the flow rate of WF_6 was changed. The total flow rate of the gas was kept at 2.2 sccm throughout the experiments, and the pressure in the chamber was 140 Pa. Under these experimental conditions, mass transport limitation is considered to be absent (1).

Mass spectrometric identification of gaseous species.—The schematic view of the gas analysis apparatus is shown

[1] Present address: Toshiba Research and Development Center, Kawasaki 210, Japan.

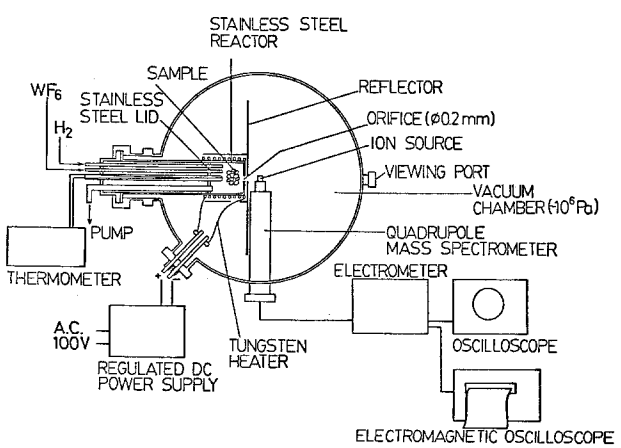


Fig. 1. Schematic view of gas analysis apparatus

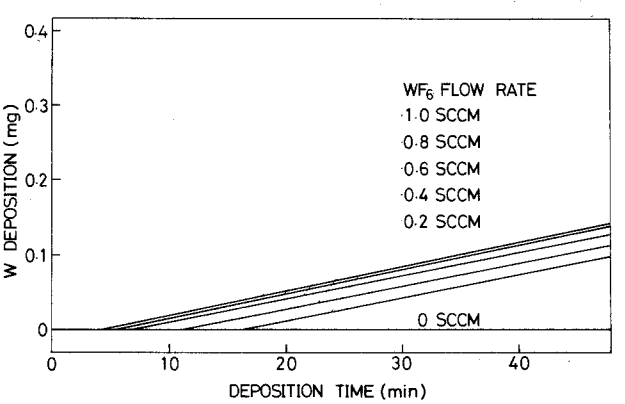


Fig. 2. Dependence of tungsten deposition on the flow rate of WF_6

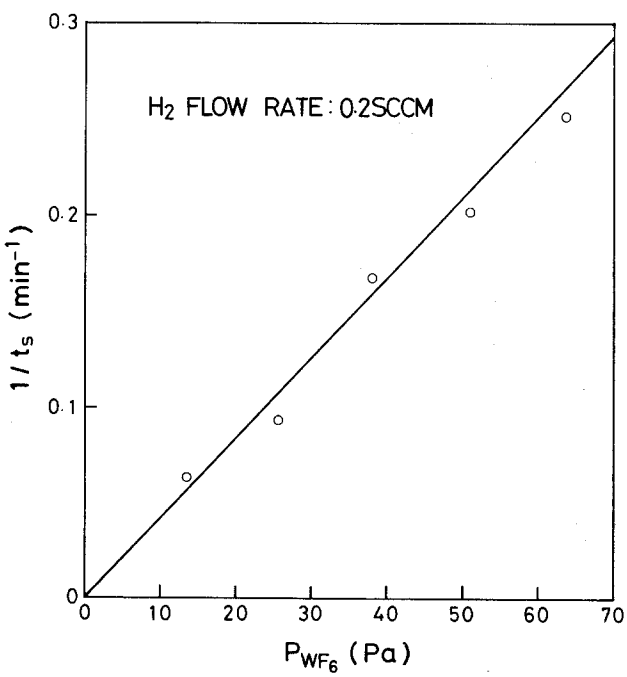


Fig. 3. Dependence of the incubation period of tungsten deposition (t_s) on the partial pressure of WF_6.

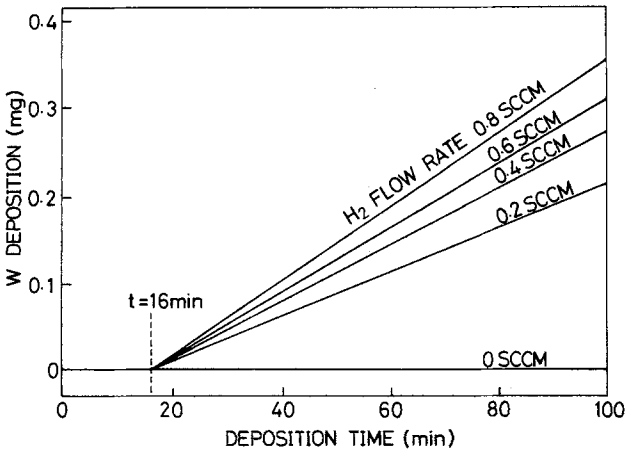


Fig. 4. Dependence of tungsten deposition on the flow rate of H_2

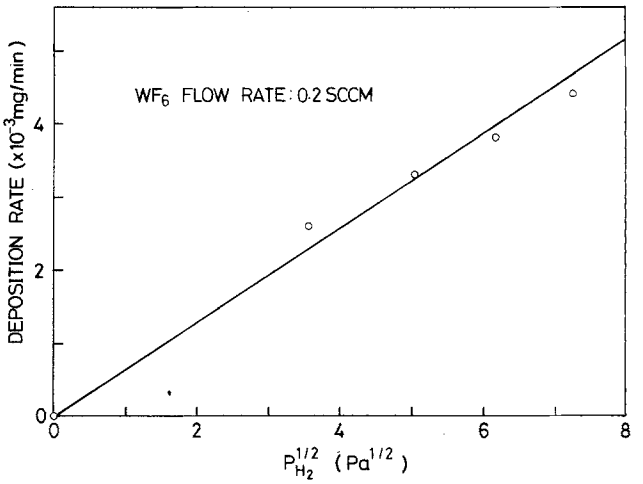
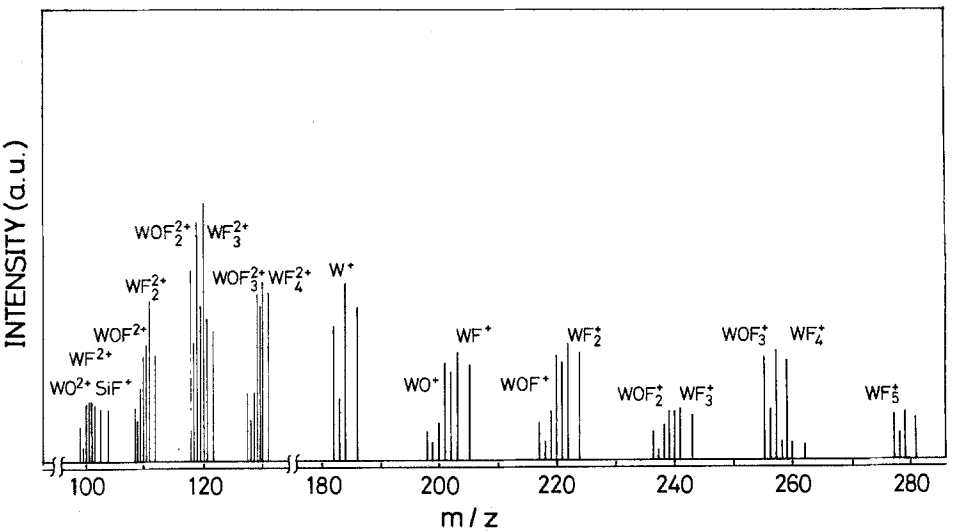


Fig. 5. Dependence of tungsten deposition rate on the partial pressure of H_2.

Fig. 6. An example of mass spectrum of gases above quartz during the deposition reaction process.



in Fig. 1. A quadrupole mass spectrometer (ANELVA AGA-360) was used. The gas in a small LPCVD apparatus was introduced to the ion source of the mass spectrometer, and the gaseous species above the substrate that proceeded during the deposition reaction were identified. The distance between the orifice of the reaction chamber and the ion source of the mass spectrometer was 10 mm.

Results and Discussion

Deposition rate determination.—The effect of the flow rate of WF_6 on the deposition of tungsten on the quartz substrates is shown in Fig. 2. The deposition rate was independent of the flow rate of WF_6, but the incubation period of the deposition was shortened by increasing the flow rate of WF_6. As shown in Fig. 3, the reciprocal of the incubation period is linearly related to the partial pressure of WF_6 which is in proportion to its flow rate. The effect of the flow rate of H_2 is shown in Fig. 4. The incubation period is independent of the flow rate of H_2, but the deposition rate is increased with increasing flow rate of H_2 as shown in Fig. 5. A linear relationship exists between the deposition rate and the square root of the partial pressure of H_2 which is computed from the flow rate of H_2. This relationship supports the consideration that these experiments were conducted under the conditions which are absent from mass transport limitation (1).

When tungsten is deposited on silicon by the reduction of WF_6 by H_2, instantaneous deposition occurs (2), and the reaction orders with respect to WF_6 and H_2 have been found to be zero and one-half, respectively, (1, 2). Therefore, for the purpose of obtaining good selective deposition of tungsten on Si/SiO_2 substrates, the partial pressure of WF_6 above the substrates should be small as possible and that of H_2 should be large as possible.

Identification of gaseous species.—Figure 6 is a typical mass spectrum obtained in this study. The temperature of the substrate was 400°C and the flow rate of H_2 was 0.2 sccm and that of WF_6 was 0.6 sccm. Various tungsten oxifluoride ions are observed in the spectrum, and the intensities of these ions decreased as the reaction between the gases and the quartz substrates proceeded. Large amount of SiF_3^+ ion was also observed, and the precursor of this ion is SiF_4 as indicated in EPA/NIH mass spectral data base. These experimental results suggest that WF_6 reacts with SiO_2 and the oxygen in SiO_2 is removed as tungsten oxifluorides, and silicon in SiO_2 is removed as SiF_4. Through such reactions, nucleation sites of tungsten on SiO_2 seem to be formed.

Conclusions

From the experimental results described above, it is concluded that in order to obtain good selective deposition of tungsten on Si/SiO_2 substrates, the partial pressure of WF_6 on substrates should be small as possible and that of H_2 should be large as possible.

Acknowledgment

Manuscript received April 19, 1988. This was Paper 1052 presented at the Honolulu, HI, Meeting of the Society, Oct. 18-23, 1987.

Waseda University assisted in meeting the publication costs of this article.

REFERENCES

1. W. A. Bryant, *This Journal*, **125,** 1534 (1978).
2. C. M. McConica, and K. Krishnamani, *ibid.*, **133,** 2542 (1986).