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Effects of deposition rate on the encroachment in tungsten films reduced by H_2

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The deposition rate of tungsten selectively prepared by hydrogen reduction of WF_6 was measured, and the encroachment produced by inherent silicon reduction even in the presence of H_2 gas was examined by cross-sectional TEM and SEM. In the WF_6–H_2 system, the degree of encroachment is not explained by the Si reduction reaction alone, but is rather related to the Si reduction time decreasing with increasing deposition rate of H_2-reduced tungsten film, because a blocking layer is formed above the Si-reduced tungsten. This results in a lesser degree of encroachment. Consequently a high deposition rate of H_2-reduced tungsten can decrease the degree of encroachment. By calculation, a thickness of 6.8–13.3 nm is necessary for H_2-reduced tungsten to prevent WF_6 gas from reacting with Si.

1. Introduction

In recent years, the selective deposition of tungsten films has been extensively studied because it provides a relatively low specific contact resistance, enhances step coverage, and can eliminate the etching process [1–3]. It has been known that tungsten films are selectively deposited by silicon reduction [4, 5] and/or other reducing agents such as hydrogen [2, 6, 7] and silane [8].

Tungsten film reduced by silicon has a self-limiting thickness [4] and the Si-reduced reaction produces encroachment and wormholes [5] in the silicon substrate. These defects such as encroachment and wormholes exert a bad effect on the performance and reliability of the device. Therefore the Si-reduced reaction should be suppressed to minimize the encroachment and wormholes. Tungsten films reduced by H_2 gas can be selectively deposited up to several micrometres [9], but H_2 reduction of WF_6 is inevitably followed by the Si reduction reaction which is thermodynamically preferable to the H_2 reduction reaction. Therefore tungsten films reduced by H_2 also have interfacial defects due to the Si reduction of WF_6.

In this study, tungsten films have been deposited on contact holes by hydrogen reduction of WF_6 at various deposition temperatures and H_2 flow rates, in an effort to investigate the effects of deposition rate on the encroachment.

2. Experimental procedure

The configuration of the reactor system used in this study has been described previously [10]. 600 nm patterned SiO_2 on p-Si(1 0 0) wafers which had a resistivity of 10 Ω cm was used as substrate for selective tungsten deposition. Substrates were heated by tungsten halogen lamps from 300 to 500 °C. The flow rate of WF_6 gas (99.5%) was fixed at 10 sccm and that of H_2 gas (99.999%) was varied from 0 to 1000 sccm. The total pressure of the reactor was maintained at 1 torr throughout the deposition process. The substrates were cleaned in 10:1 H_2O:HF solution, rinsed with deionized water and dried out under N_2 gas to remove the native oxide.

The blanket tungsten was deposited by flowing WF_6 gas over the Si substrate without H_2, and the thickness was measured by profilometry and/or β-backscattering. The thickness of selective tungsten films was determined from the cross-section of as-deposited samples in a transmission electron microscope (TEM) and a scanning electron microscope (SEM).

The microstructure and encroachment were investigated by cross-sectional TEM and SEM. The cross-sectional TEM specimens were prepared with metallographic sectioning followed by Ar^+ beam milling to a thickness of less than 200 nm. TEM micrographs were taken with a Jeol JEM 2000-EX transmission electron microscope at an acceleration voltage of 200 kV.

3. Results and discussion

Fig. 1 shows the variations of the selective loss time, and the thickness measured at the selective loss time, as a function of the deposition temperature. The selective loss time tends to decrease with the deposition temperature. However, the thickness of the film deposited at a given selective loss time increases with increasing deposition temperature. Chow *et al.* [11] also observed similar results. The deposition rate calculated from the deposition thickness and selective loss time was found to increase from 0.7 to 7.1 nm s^{-1} as the deposition temperature changed from 340 to 480 °C. An activation energy of 0.51 eV was calculated.

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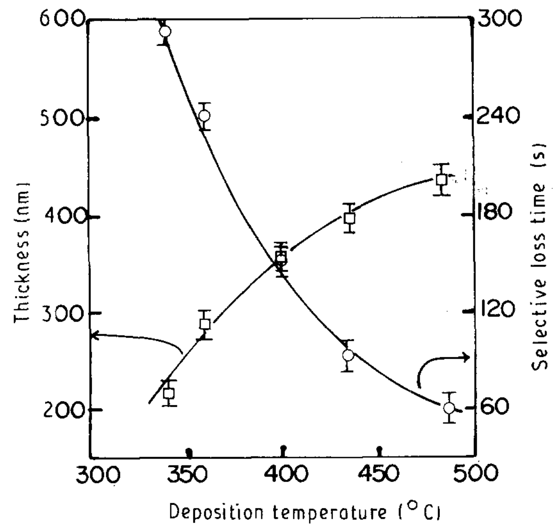

Figure 1 (☐) Thickness of selective tungsten and (○) selective loss time as a function of deposition temperature. WF_6 flow rate = 10 sccm, H_2 flow rate = 100 sccm, P_{total} = 1 torr.

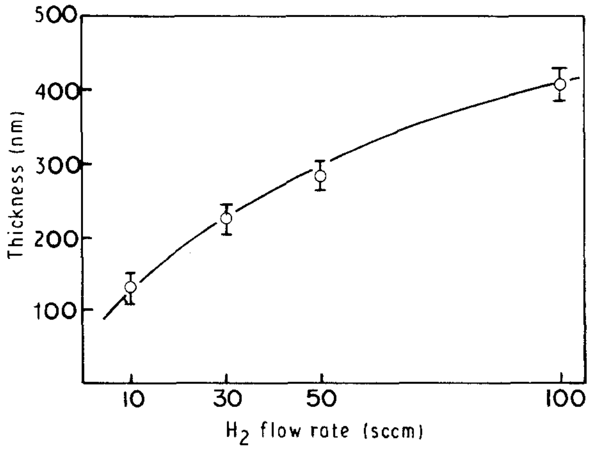

Figure 2 Thickness of selective tungsten as a function of H_2 flow rate. WF_6 flow rate = 10 sccm, deposition temperature = 440 °C, deposition time = 90 s.

The thickness (deposition rate) of the selective tungsten films had a square-root dependence on the flow rate of H_2 gas expressed as Equation 1 below (Fig. 2). In Fig. 2, the deposition temperature, deposition time and WF_6 flow rate were fixed at 440 °C, 90 s and 10 sccm, respectively.

$$R = C[F(H_2)]^{1/2} \qquad (1)$$

where $F(H_2) = H_2$ flow rate (sccm), R = deposition rate ($nm\,s^{-1}$) and C = constant.

When tungsten is deposited on a contact hole via H_2 reduction reaction of WF_6, the silicon substrate acts as a predominant reducing agent even in the presence of H_2 [5], because silicon is a thermodynamically a much more favourable reducing agent for WF_6 than H_2, as shown below:

$$2WF_6 + 3Si = 2W + 3SiF_4 \qquad G_f = -185\ \text{kcal mol}^{-1}\ (775\ \text{kJ mol}^{-1})\ \text{at 600 K}$$

$$WF_6 + 3H_2 = W + 6HF \qquad G_f = -33.6\ \text{kcal mol}^{-1}\ (141\ \text{kJ mol}^{-1})\ \text{at 600 K}$$

As a result, encroachments and/or wormholes are produced by this undesirable silicon reduction reaction of WF_6 which results in silicon consumption.

Fig. 3 shows (in Fig. 3a) the selected-area diffraction pattern from area A of the bright-field image of the film deposited at a temperature of 360 °C (Fig. 3b); Fig. 3c shows the film deposited at 400 °C. From Fig. 3, the Si-reduced tungsten in area A has a porous structure, which is identical with other workers' results [6, 10], while the H_2-reduced tungsten formed above the porous tungsten shows a dense structure. Voids exist near the contact edge and the thickness of a tungsten film reduced by Si is thicker at the contact edge and thinner at the centre of the contact. Several workers [12, 13] have reported that the residual stress of a patterned SiO_2–Si substrate mainly concentrates at the tip of the Si–SiO_2 interface. Si reduction reaction of WF_6 could occur at stress-concentrated regions during the initial stage of the deposition. Therefore Si beneath the tip of the Si–SiO_2 interface might be consumed more than Si at the centre of contacts as shown in Fig. 3b and c.

Fig. 4 shows the encroachment occurring at various deposition temperatures. In this work, "encroachment length" is defined as the length of tungsten films which are laterally grown from the contact edge as indicated by $E(L)$ in Fig. 6 below. The encroachment lengths of deposited film at 300 and 340 °C were found to be about 0.8 and 0.6 μm, respectively, and these lengths were shortened remarkably at deposition temperatures above 340 °C. According to Green *et al.* [4], a maximum self-limiting thickness was obtained at 340 °C for silicon reduction of WF_6. In other words, silicon consumption is maximized at 340 °C. Therefore, if the encroachment phenomenon occurred only by silicon consumption in the WF_6–H_2 system, the encroachment length would reach a maximum at a deposition temperature of 340 °C. However, Fig. 4 shows that the encroachment length is almost the same at 300 and 340 °C. Therefore these results indicate that the degree of encroachment cannot be explained by the silicon reduction reaction alone, when the tungsten is selectively deposited by a two-step process of silicon and H_2 reduction.

The dependence of the encroachment length on H_2 flow rate is shown in Fig. 5. The encroachment length produced by silicon reduction without H_2 gas was 2.5 μm (Fig. 5a), whereas the presence of H_2 gas with a flow rate of 10 sccm reduced the encroachment length to 0.8 μm (Fig. 5b). The encroachment length decreased with increase of the H_2 flow rate.

In Fig. 6, the encroachment length (Fig. 5) and the deposition rate at 340 °C for a corresponding H_2 flow rate are superimposed to investigate the effects of deposition rate on encroachment length. The encroachment length decreases rapidly with increasing H_2 flow rate until 100 sccm, and decreases rather slowly above 100 sccm. As shown in Fig. 6, increasing H_2 flow rate increases the deposition rate. As the deposition rate increases, the time needed for the formation of the blocking H_2-reduced layer which prevents WF_6 gas from flowing to the Si surface might be shortened, which results in a decrease of Si-reduction reaction time. As a result, the short Si-reduction time decreases the encroachment length. Because the

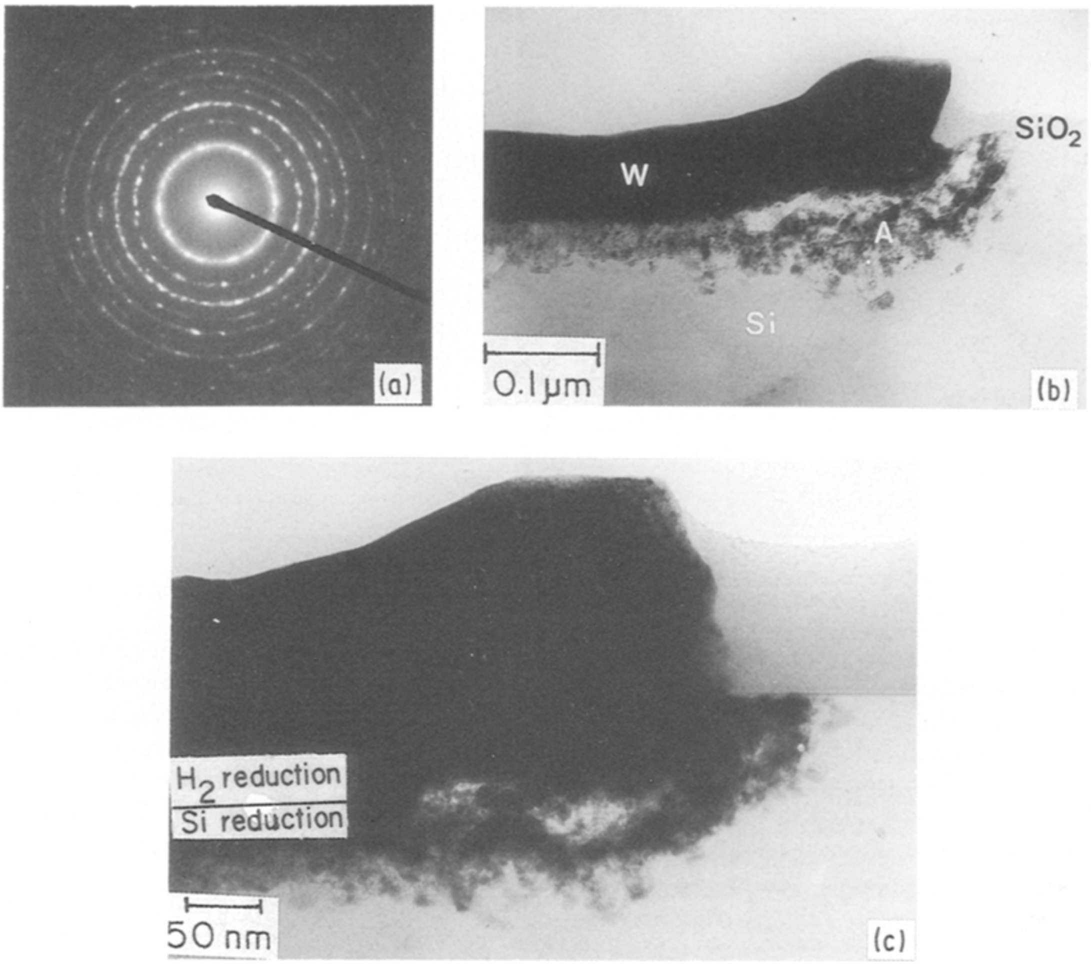

Figure 3 Cross-sectional TEM of tungsten films selectively deposited on contact hole: (a) selected-area diffraction patterns of area A in (b), (b) bright-field image at 360 °C, (c) bright-field image at 400 °C.

Si-reduction time in the WF_6–H_2 system plays a major role in determining the degree of encroachment, it is important to determine the Si-reduction time.

In order to find the Si-reduction time, changes in the thickness of Si-reduced tungsten without H_2 gas were investigated as a function of time, and these results are illustrated in Fig. 7. This shows that the thickness of the Si-reduced tungsten film increases with a square-root dependence on deposition time up to 120 s, and above 120 s it increases with a power of 1.64 expressed by the following equations:

$$T(\mathrm{Si}) = k_1 t^{0.51} \qquad t < 120 \tag{2}$$

$$T(\mathrm{Si}) = k_2 t^{1.64} \qquad t > 120 \tag{3}$$

where t = deposition time (s), $T(\mathrm{Si})$ = Si-reduced tungsten thickness and k_1, k_2 are constants.

The deposition rate of Si-reduced tungsten is thought to decrease with the thickness below 120 s because the reduction of the area which is needed for diffusion of WF_6 to Si has a square-root dependence on the thickness. However, the growth rate of encroachment cannot be affected by the thickness of a laterally grown layer because voids are formed beneath the SiO_2–Si interface.

If the encroachment length is proportional to the square of Si-reduced tungsten thickness below 120 s deposition time and the same is true for the WF_6–H_2 system (Equation 4 below), the Si-reduction time (Equation 5) in the H_2 reduction reaction can be calculated from Equations 2 and 4, tabulated in Table I.

$$E(L) = k_3[T(\mathrm{Si})]^2 \tag{4}$$

where $E(L)$ = encroachment length and k_3 = constant;

$$\begin{aligned} t &= K'[E(L)]^{1/1.02} \\ &\approx K[E(L)] \qquad t < 120 \end{aligned} \tag{5}$$

where $K' \approx K = 1/(k_1^2 k_3)$.

In addition, the thickness of the tungsten produced by H_2 reduction for various Si-reduction times (Equation 6) can be calculated from Equations 5 and 6, and is tabulated in Table I.

$$T(H_2) = Rt \tag{6}$$

where $T(H_2)$ = H_2-reduced tungsten thickness, R = deposition rate from Equation 1 and t = time of Si reduction from Equation 5.

From Table I, it is calculated that a thin layer of 6.8–13.3 nm H_2-reduced tungsten film can prevent WF_6 from diffusing to the Si substrate, while a thick layer of 70 nm self-limiting thickness is needed to block the WF_6 gas for a porous Si-reduced tungsten film.

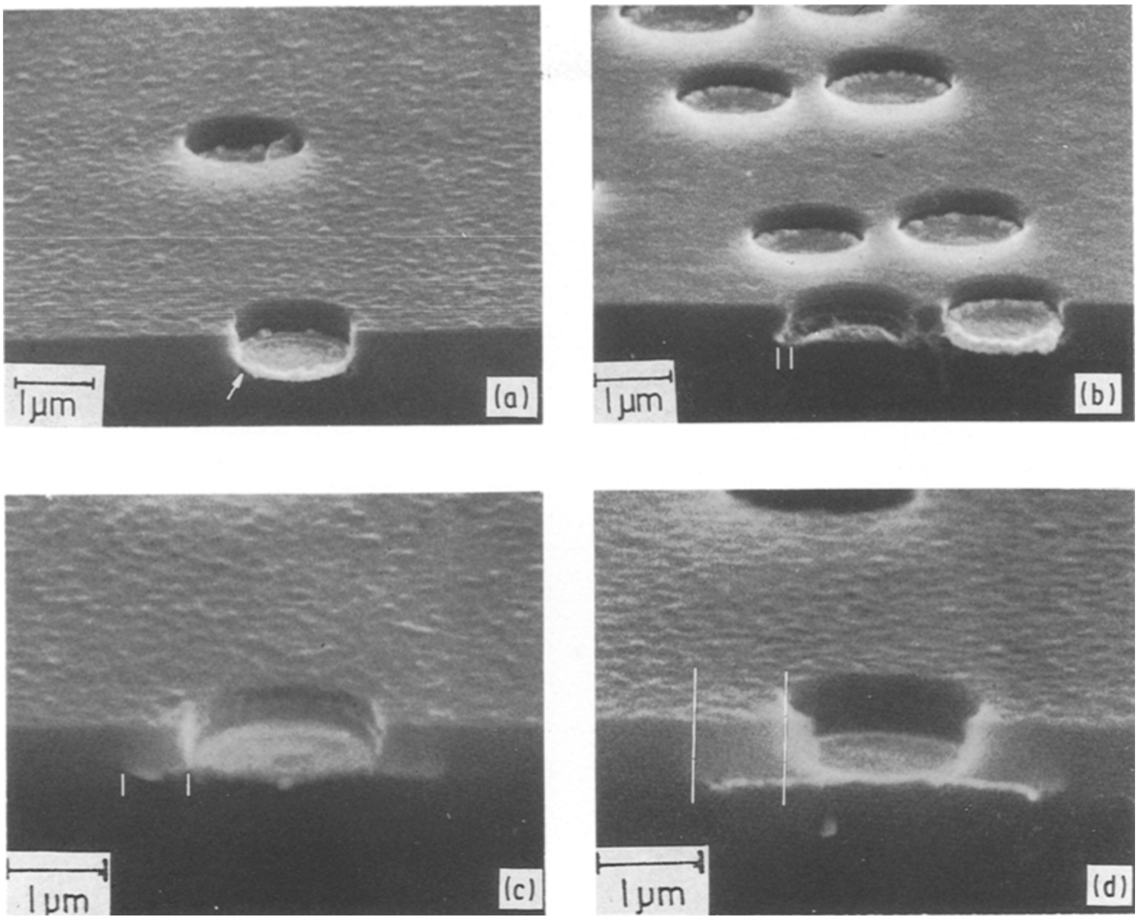

Figure 4 Scanning electron micrographs of encroachment as a function of deposition temperature: (a) 420 °C, (b) 380°C, (c) 340 °C, (d) 300 °C.

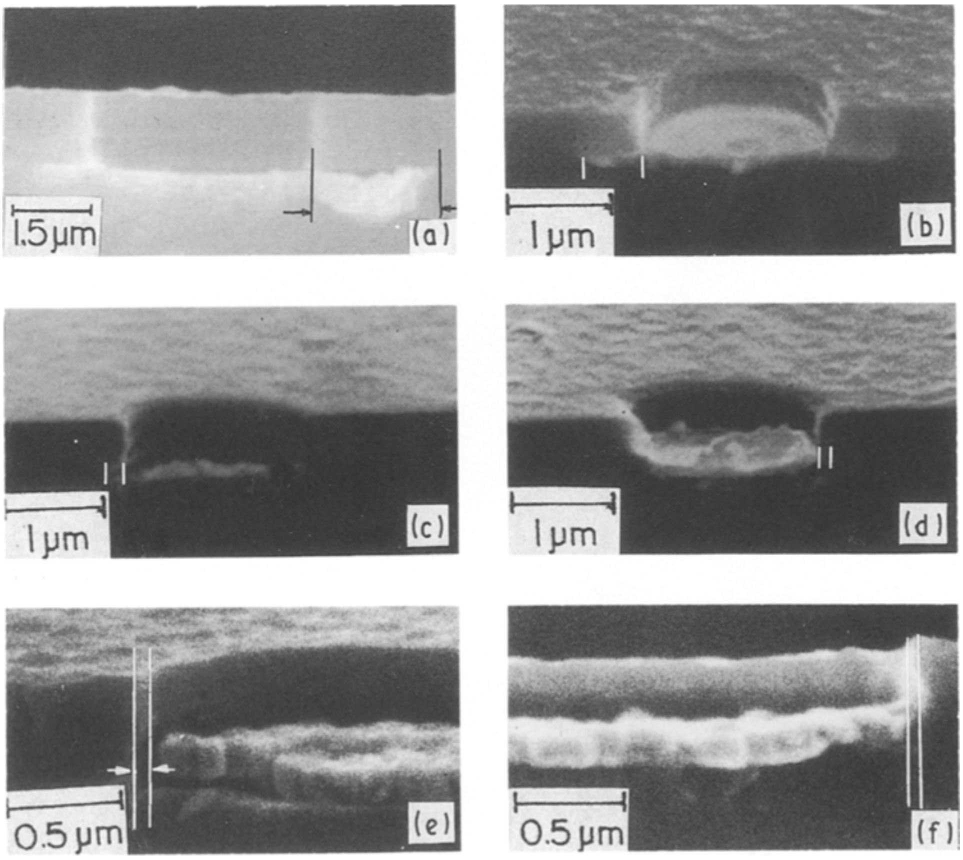

Figure 5 SEM of encroachment at various H_2 flow rates. Deposition temperature = 340 °C; H_2 flow rate (sccm) = (a) 0, (b) 10, (c) 50, (d) 100, (e) 500, (f) 1000.

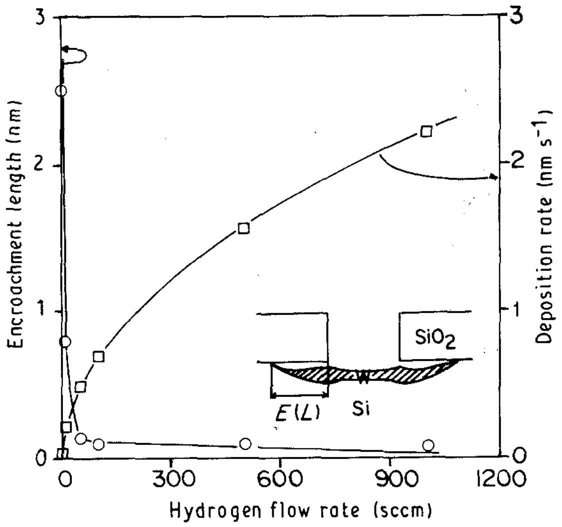

Figure 6 (○) Encroachment length $E(L)$ and (□) deposition rate as a function of H_2 flow rate. Deposition temperature = 340 °C, WF_6 flow rate = 10 sccm.

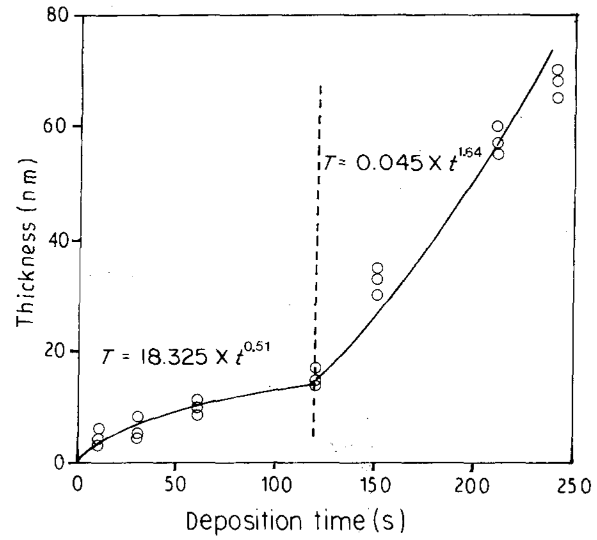

Figure 7 Thickness of tungsten reduced only by Si as a function of deposition time. WF_6 flow rate = 10 sccm, deposition temperature = 340 °C, P_{total} = 1 torr.

TABLE I Time of Si reduction and corresponding deposition thickness by H_2 reduction as a function of H_2 flow rate

H_2 flow rate (sccm)	(a) Encroachment length (μm)	(b) Time of Si reduction for (a) (s)	Deposition thickness by H_2 reduction for (b) (nm)
0	2.5	240	
10	0.6	57.6	13.3
50	0.15	13.5	6.8
100	0.11	9.9	6.9
500	0.06	5.4	8.6
1000	0.04	3.6	8.2

4. Conclusions

As the deposition temperature and the H_2 flow rate increase, the deposition rate of tungsten selectively prepared by H_2 reduction of WF_6 increases. In these experiments, the activation energy for selective deposition was found to be 0.51 eV, and the deposition rate increased with the square root of H_2 flow rate.

The distribution of residual stress existing in the Si substrate may result in non-uniformity of the encroachment. The microstructure of H_2-reduced tungsten is less porous than that of Si-reduced tungsten.

The encroachment length decreases with deposition temperature and H_2 flow rate. These experimental results show that the degree of encroachment is not explained by Si reduction alone, but is related to the time of Si reduction reaction of WF_6. From calculations, the time of Si reduction reaction of WF_6 is found to decrease with increasing deposition rate of H_2-reduced tungsten film, which results from the fast formation of a blocking layer above the Si-reduced tungsten, and thus produces a lesser degree of encroachment.

It is also calculated that the thickness of H_2-reduced tungsten needs to be 6.8–13.3 nm to prevent WF_6 gas from reacting with silicon.

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