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Elimination of Oxidized Mo by Self-Cleaning Reaction with WF₆ in the Initial Stages of Selective W Chemical-Vapor Deposition on Mo Interconnections

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ABSTRACT

Selective W chemical vapor deposition (CVD) on Mo interconnections is studied to elucidate the surface cleaning mechanism in the initial stages of W CVD in a WF₆-H₂ gas system using ellipsometry, x-ray photoelectron spectroscopy, and Auger electron spectroscopy. Molybdenum oxide formed on the Mo interconnections during LSI fabrication processes is automatically removed by the reaction with WF₆ to form intermediates such as volatile molybdenumoxyfluorides, MoO_xF_y , following the chemical reaction: $MoO_3 + 1/2WF_6 \rightarrow MoO_2F_2 + 1/2WO_2F_2$. This reaction exposes a Mo clean surface, and W deposition begins as soon as the oxide has been removed. From a contact-string test of two-layer interconnections, the cortext preinting to the function of the photoe on Mo interconnections is found to be lower theory $3.2 \times 10^{-10} O_{-} cm^2$. This the contact resistivity with W-filled via holes on Mo interconnections is found to be lower than $3.3 \times 10^{-10} \Omega$ -cm². This excellent contact characteristic is attributable to the surface cleaning effect on Mo by the reaction with WF₆.

Selective chemical-vapor deposition (CVD) of W for filling via and contact holes has attracted interest in the fabrication of multilayer interconnections in large-scale integrated (LSI) circuits. Several studies on selective CVD of W have been reported showing good electrical characteristics such as low contact resistivity.¹⁻³ Recently, multilayer interconnection fabrication processes using 0.5-µm Mo lines for the first layer and 0.8-µm Al lines for the second layer interconnections have been developed.⁴ In these fabrication processes, via hole filling by selective W CVD on the Mo first layer interconnection has been introduced successfully.

A key issue in W selective deposition is how to form a clean interface between the deposited W and the surface of the metal for the interconnection to obtain excellent contact characteristics. In our via hole-opening processes on Mo interconnections such as SiO₂ etching and resist ashing, about a 10-nm thick Mo oxide layer is formed. At least a 2to 5-nm layer is retained even after dipping in NH₄OH and a diluted HF solution. Nevertheless, we have obtained excellent contact characteristics between deposited W and Mo interconnections with no adverse side effects such as high contact resistivity. These results probably can be attributed to a self-cleaning mechanism that operates on Mo interconnection surfaces, *i.e.*, a reaction in the initial stages of selective W CVD that automatically removes the Mo oxide layer.

In this work, the self-cleaning mechanism of the Mo oxide on the Mo interconnection in the initial stages of W CVD in a WF_6 -H₂ gas system is investigated to clarify how the good contact characteristics in our multilayer-interconnection fabrication processes are obtained. Employing ellipsometry, x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES), we found that the removal of the Mo oxide occurs through a reaction with WF₆.

The electrical properties obtained from contact-string tests for two-layer interconnections with via hole filling by selective W CVD on Mo interconnections are also described.

Experimental

For the selective W deposition, the CVD apparatus used was a cold-wall lamp-heated-type low-pressure one with a loadlock system. The base pressure of 1.0×10^{-7} Torr was achieved by turbomolecular-pump evacuation. The evacuation during W deposition was performed by a mechanicalbooster pump and a rotary pump. A WF₆-H₂ gas system was employed to deposit W. Substrates used were prepared as follows: a 100- or 500-nm-thick layer of Mo was deposited on thermally oxidized SiO₂ by a conventional sputtering technique at 340°C. Then, a 10-nm-thick layer of Mo oxide was formed by exposing the substrate to oxygen plasma which was our resist ashing process. The former substrates were used to confirm the existence of incubation period in the initial stages of W CVD on Mo oxide, and the latter ones to investigate the interaction between WF₆ and Mo oxide. The thickness of deposited W on Mo oxide was obtained in the following way: the deposited W, Mo oxide, and Mo were partly etched in a NH₄OH-H₂O₂ solution, the total thickness (W + Mo oxide + Mo) was measured and then the thickness of the Mo oxide and Mo was subtracted. The error for W thickness was estimated roughly within ± 10 nm. The Mo oxide film thickness before and after treatment with WF₆ was measured by ellipsometry at a wavelength of 632.82 nm. The analysis to derive the Mo oxide thickness from $\Psi\text{-}\Delta$ plot data was performed according to the method described in Ref. 5. Surface analysis of the Mo oxide after WF_6 gas treatment was performed by XPS with a MgK α line (1253.6 eV). AES was used to measure the depth profile to confirm the formation of a clean interface between deposited W and Mo interconnection surfaces. A clear cross-



Fig. 1. Deposition time dependence on thickness for W deposited on 10-nm-thick oxidized Mo.

sectional view of the via holes filled with W was obtained using a scanning electron microscope (SEM) equipped with a focused ion beam (FIB). Electrical characteristics of selective W CVD on Mo interconnections were evaluated by a contact-string test.

Results and Discussion

Relationship between Mo oxide etching rate and WF_6 treatment.—The relationship between Mo oxide etching rates and WF_6 treatment time, temperature, and WF_6 partial pressures are described in this section.

Figure 1 shows the dependence of the deposited thickness of W on deposition time with WF₆ of 10 sccm and H₂ of 1.8 slm at 420°C at a total pressure of 0.17 Torr. The deposited thickness of W is proportional to deposition time after 5 min. There is about a 5-min incubation period in the initial stages of W CVD during which no W is deposited. The Mo surface may be undergoing some sort of self-cleaning process during this time; that is, this incubation period probably corresponds to the Mo oxide removal reaction period. This hypothesis is confirmed later by XPS and AES analyses. Before these discussions, however, we first show the factors affecting the etching of the oxide layer.

Figure 2 shows the dependence of the reduction in Mo oxide thickness on the gas treatment time at 420°C at a total pressure of 0.17 Torr. The gas flow rate for WF₆ was 10 sccm and that for H₂ and Ar was 1.8 slm. The figure shows that the rate at which thickness decreases with WF₆ + Ar treatment is some three times faster than when H₂ or Ar treatment is enhanced by the presence of WF₆ and that removal with WF₆ proceeds by a different reaction path from H₂ or Ar treatment. Incidentally, in the figure, the decrease with H₂ is almost the same as that with Ar after a 210-s treatment, implying that the reduction in Mo oxide thickness with H₂ is caused by evaporation. This is supported further in the following discussion of the activation



Fig. 2. Dependence of the reduction in Mo oxide thickness on gas treatment time.

energy for etching rates with various gas treatments and in the XPS surface analysis.

Figure 3 shows the dependence of Mo oxide etching rates on the gas treatment temperature. The total pressure was maintained at 0.17 Torr for each gas (WF₆ + H₂, H₂, and Ar) introduction into the chamber. The flow rate for H₂ and Ar was 1.8 slm and that for WF₆ was varied between 5 and 60 sccm. When introducing WF₆ + H₂, flow rates for H₂ were changed slightly from 1.8 slm as the flow rates for WF₆ were varied to maintain the total pressure at 0.17 Torr; however, their changes were very small and negligible within experimental error. In the figure, etching rates for the gas treatment with WF₆ are obtained by subtracting the etching



Fig. 3. Dependence of the Mo oxide etching rate on temperature.



Fig. 4. Dependence of the Mo oxide etching rate on WF_6 partial pressure.

rates with H_2 from those with $WF_6 + H_2$. Thus the figure represents net etching rates for WF_6 to show the cleaning effect of WF_6 on the Mo oxide more clearly. Hereafter, we refer to the etching rate for WF_6 , as the net etching rate. The etching rate with H_2 is almost the same as the rate with the inert gas Ar. And the activation energies for both gases are 1.07 eV. Therefore, the reduction in the Mo oxide thickness with H_2 is probably due only to evaporation. In contrast, the activation energy for WF_6 is 0.531 eV, which is much smaller than for H_2 and Ar. This difference must be due to a reaction involving WF_6 that removes the Mo oxide. Moreover, this lower activation energy for the etching rates with WF_6 compared to that with H_2 treatment significantly enhances the Mo oxide removal reaction with WF_6 .

Figure 4 indicates the dependence of the etching rate on WF₆ partial pressure, P_{WF_6} . The slope of the Mo oxide etching rates with P_{WF_6} is close to unity at 460°C. At this temperature, the etching rate is proportional to P_{WF_6} . This means that at 460°C, the etching rate is determined by the supply of WF₆. At temperatures below 420°C, the slope with P_{WF_6} is less than unity, indicating that the etching rate is controlled by the surface reaction. Moreover, at temperatures of 370 and 320°C, the slope is 1/2; that is, etching rate is proportional to P_{WF_6} .

From the results presented, the activation energy of the oxide etching rate for WF_6 treatment is 0.531 eV, and the etching reaction order for WF_6 is 1/2 at temperatures of 370 and 320°C, the etching rate (*ER*) in the surface reaction region can be given by

$$ER = A \times \exp(-0.531 \text{ eV}/kT) \times P_{WF_6}^{1/2}$$

where k is the Boltzmann constant, T is absolute temperature, and A is a constant.

Initial surface reaction in a WF_{6} -H₂ gas system.—Next, we consider the mechanism of Mo oxide removal reaction with WF_{6} based on the surface analysis of XPS and the results obtained in the previous section.

Figure 5 shows the Mo3d area XPS analysis for an as-deposited Mo (Fig. 5a) and Mo oxide surface with (Fig. 5c) and without (Fig. 5b) gas treatment with WF₆ (10 sccm) + H₂ (1.8 slm) at 420°C for 2 min at a pressure of 0.17 Torr. Without the gas treatment shown by spectrum in Fig. 5b, the Mo3d doublet peaks shifted by 4.2 eV toward a higher binding energy compared with the as-deposited Mo shown by spectrum in Fig. 5a. This shows that Mo has a valence of 6 in the oxidized state and MoO₃ is formed. Since MoO₃ is volatile, these results confirm that etching with H₂ or Ar is due to the evaporation of MoO₃.



Fig. 5. Mo3d area XPS spectra: (a) as-deposited Mo, (b) Mo oxide without the WF₆ + H₂ gas treatment, and (c) Mo oxide with the gas treatment at 420° C for 2 min.



Fig. 6. XPS survey spectra of Mo oxide. (a) before and (b) after gas treatment with WF₆ + H_2 at 420°C for 2 min; (c) spectrum for W deposited by CVD.

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Fig. 7. AES depth profile measurements; (a, left) measurement for oxidized Mo and (b, right) measurement for deposited W on the oxidized Mo.

Meanwhile, gas treatment with $WF_6 + H_2$ at 420°C for 2 min yields the spectrum in Fig. 5c. A shoulder peak (indicated by the arrow) appears near 230 eV and the peak resolution between $Mo3d_{3/2}$ and $Mo3d_{5/2}$ is blurred, which characterize the oxidized Mo with a lower valence. That is, after the $WF_6 + H_2$ treatment, the surface changes from MoO_3 to a mixture of MoO_3 and oxidized Mo with a lower valence such as MoO_2 , which is nonvolatile.⁶ This means that the Mo oxide removal reaction proceeds via the generation of some intermediates with the $WF_6 + H_2$ treatment, although this XPS information does not reflect necessarily direct surface reactions because the samples were exposed to air during transfer from the CVD chamber to the XPS instrument.

The XPS survey spectrum is shown in Fig. 6. The spectrum in Fig. 6b shows that fluorine is adsorbed on the Mo oxide surface treated with WF₆ (10 sccm) + H₂ (1.8 slm) at 420°C for 2 min at a pressure of 0.17 Torr. Since the surface of the oxide changes from MoO₃ to a mixture of MoO₃ and oxidized Mo with a lower valence, and since fluorine adsorbs to the surface after treatment with WF₆ + H₂, we conclude that the enhanced reduction in Mo oxide thickness with the gas treatment is caused by the reaction between WF₆ and MoO₃ to form volatile MoO₂ F_y.⁷ Incorporating this result and our earlier finding that the etching rate is proportional to $P_{WF_6}^{1/2}$ in the surface reaction region, one stoichiometrically possible reaction equation is proposed as follows

$$MoO_3(s) + 1/2WF_6(g) \rightarrow a MoF_6(g) + b MoOF_4(g)$$
$$+ c MoO_2F_2(g) + d WOF_4(g) + e WO_2F_2(g) + f MoO_x(s)$$

where *a*, *b*, *c*, *d*, *e*, and *f* are reaction coefficients, (s) and (g) represent the solid state and gas phase, respectively. This reaction equation means that the reaction of MOO_3 with WF₆ can generate some volatile Mo fluorides, Mo oxyfluorides, W oxyfluorides, and Mo oxide with a lower valence which could remain. This reaction equation should be solved under the conditions where *a*, *b*, *c*, *d*, *e*, and $f \ge 0$ and $0 \le x < 3$. The equation is satisfied only when a = 0, b = 0, c = 1, d = 0, e = 1/2, and f = 0 (see Appendix). Therefore, the Mo oxide etching reaction with WF₆ can most tentatively be given as

$$MoO_3(s) + 1/2WF_6(g) \rightarrow MoO_2F_2(g) + 1/2WO_2F_2(g)$$

in which the change in Gibbs free energy, ΔG is roughly estimated as -100 kJ/mol at 420°C .^{7,8} To prove this reaction equation, however, further work such as mass analysis or thermal desorption is necessary.

Comparing the spectra in Fig. 6b and c which is for W deposited by CVD, no W peaks are observed in the XPS spectrum in Fig. 6b, meaning that during the Mo oxide etching reaction, no deposition of W occurs. Therefore, this etching period is indeed the incubation period which was hypothesized earlier.

Figure 7 shows the AES depth profile measurements of the Mo oxide and W deposited on top at 420°C at a pressure of 0.17 Torr with a WF₆ of 10 sccm and a H₂ of 1.8 slm for 13 min which is enough to remove the Mo oxide. In Fig. 7b no oxygen is observed in the deposited W film and at the interface between W and Mo. This result also supports the reaction proposed above, showing that neither MoO_x nor WO_y remains during the course of the etching reaction unlike the case reported by Joshi *et al.* that WO₁₅ is formed and remains on Si by the reaction between WF₆ and SiO.⁹

From these results, the W deposition process on Mo in the initial stages in the WF_6 -H₂ gas system can be summarized as follows: Mo oxide removal is initiated by the reaction with WF_6 , which exposes the Mo surface. W deposition then begins after the removal of the oxide. This cleaning mechanism operates in the initial stages of W selective CVD on Mo interconnections whose surface is oxidized after fabrication processes.

Electrical characteristics of via holes filled with W.—To evaluate the influence of W-CVD via hole filling electrical characteristics on Mo interconnections, a contact-string test was performed using two-layer interconnections and via holes with aspect ratios of 1.5 (0.9 μ m deep/0.6 μ m in diameter). For this test, a Mo interconnection with 1.7- μ m feature was used as the first layer interconnection and a Ti/Al multilayered interconnection also with 1.7- μ m features was used as the second. After via-hole opening processes such as resist ashing and diluted-HF solution dipping, about 5-nm of Mo oxide was formed as described earlier. Via-hole filling with W was performed on this Mo interconnection surface. The selective W deposition condi-



Fig. 8. Cross-sectional view of via holes filled with W on Mo interconnections.

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Fig. 9. Histogram of via resistance in the two-layer interconnections obtained from the contact-string test.

tions were WF₆ and H₂ flow rates of 10 sccm and 1.8 slm, respectively, a deposition temperature of 420°C, and total pressure of 0.17 Torr. A SEM cross-sectional view of via holes filled with selective W on Mo interconnections under this deposition condition is shown in Fig. 8. It is apparent from the figure that an abrupt interface is formed between the W and Mo interconnection surfaces. A histogram of the resistance for a W-filled via hole is shown in Fig. 9. The resistance is obtained by subtracting the Mo first layer and Ti/Al second layer interconnection resistances (ca. $3.97 \times$ $10^4 \Omega$) from the total resistance of the contact strings and dividing the remainder by the number of via holes which was 259,560. The deviation is fairly small, indicating the formation of a stable contact between the first layer and the second layer interconnections via the W plug. From the histogram, maximum contact resistivity for the two interfaces, i.e., W and the lower-layer Mo interconnection and W and the upper-layer Ti/Al interconnection, is 3.3 \times $10^{-10} \Omega$ -cm². The contact resistivity between the W and Mo interconnection surface is below this value. This low contact resistivity is attributable to the Mo surface-cleaning effect by WF_6 in the initial stages of selective W CVD.

Conclusion

The oxidized Mo elimination mechanism in selective W CVD in a WF_6-H_2 gas system has been investigated. Mo oxide is removed automatically by reaction with WF₆ to form volatile ${\rm MoO}_x {\rm F}_y$ to expose clean Mo surfaces in the initial stages of selective W CVD on Mo interconnections, and the deposition of W begins to take place on the clean Mo interconnection surfaces after removal of the oxide.

The contact resistivity derived by the contact-string test is less than 3.3×10^{-10} $\check{\Omega}$ -cm². This excellent contact characteristic is due to the surface-cleaning effect on Mo. Thus, the combination of via-hole filling by selective W CVD and Mo interconnections offers a promising technique for forming LSI multilayer interconnections.

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APPENDIX

From the reaction equation, simultaneous equations for the number of each element are derived in the following expressions

$$a + b + c + f = 1$$
 [A-1]

$$b + 2c + d + 2e + xf = 3$$
 [A-2]

$$d + e = 1/2$$
 [A-3]

$$6a + 4b + 2c + 4d + 2e = 3$$
 [A-4]

The equation, 3(a + b + c) + xf = 3 is derived from Eq. 2, 3 and 4. This relation and Eq. 1 give the relation, (x - 3)f = 0. Therefore, f = 0 under the condition $0 \le x < 3$. Furthermore, using this result of f = 0, d = -1 - a + c and b = 1 - a - c are given. From the condition, $b, d \ge 0$, that is, $b + d \ge 0, a \le 0$ is given; $a \ge 0$ under the condition. Then, a is given as 0. In a similar manner, b = 0, c = 1, d = 0, and e = 1/2 are derived.

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