Conformal and Low Temperature W-CVD by SiH₂F₂ Reduction

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New blanket W-CVD using difluoro-silane (SiH₂F₂) as a reducing gas of WF₆ is developed for deep submicron ULSI metallization. Conformal W films are obtained because of surface reaction limited deposition at temperatures from 270 to 395°C. Low temperature deposition is favorable to prevent an encroachment on Si. Little Si is incorporated into the W films and a low film resistivity of 10.4 μΩcm is obtained. Infrared spectroscopy shows that SiHF₃ is the main by-product of this CVD.

Introduction
Blanket W-CVD is a key technique for filling contacts with high aspect ratios, because sputtering of aluminum cannot provide conformal films in the contacts. Conventionally, H₂ reduction of WF₆ has been used for blanket CVD because it provides conformal W films. However, it has some problems, such as low deposition rate, a rough film surface and high deposition temperature (>450°C)₁. Recently, it has been reported that H₂ reduction of WF₆ under high pressure (≥10 Torr) provides a higher deposition rate and smoother film surface². However, it is difficult to obtain the CVD conditions for good step-coverage and smooth surface at the same time, so two-step CVD has been used practically in the high pressure H₂ reduction process³. Moreover, high deposition temperature is still unfavorable in preventing an encroachment at the bottom of deep contacts, where the sputter-deposited adhesion layer is too thin to prevent the reaction of WF₆ with Si. Although SiH₄ reduction of WF₆ offers a low deposition temperature and a smooth film surface without any encroachment, the step-coverage of SiH₄ reduced W film is poor⁴. Thus, SiH₄ reduction of WF₆ has not been used for blanket CVD.

This paper proposes a new blanket W-CVD technique using difluoro-silane (SiH₂F₂) as a reducing gas of WF₆, which is very promising for deep submicron ULSI metallization as an alternative to the conventional H₂ reduction process.

Experiment
W-CVD was performed using a cold-wall type reactor. The W films were deposited on sputter-deposited W films on a thermally oxidized wafer. The CVD conditions were as follows: the SiH₂F₂ flow and deposition temperature were varied from 50 to 400 sccm and from 270 to 395°C, respectively. The WF₆ flow was 100 sccm, the Ar flow was 300 sccm and the total pressure was 500 mTorr. The deposition rate, resistivity, impurity concentration and step-coverage of the W films were investigated and compared with those of conventional H₂ and SiH₄ reduced W. W films were deposited on patterned wafers with submicron Si contacts using sputter-deposited W films as adhesion layers to evaluate the step-coverage. Impurity concentration of the W films was measured by Auger Electron Spectroscopy (AES). Chemical reaction was quantitatively investigated using in-situ infrared (IR) spectroscopy during the W-CVD⁵.

Results and Discussion
The temperature dependence of the deposition rate is shown in Fig. 1, along with the results for H₂ ⁶ and SiH₄ reduction of WF₆. The activation energy of the SiH₂F₂ reduction process is 0.3 eV. This means the W deposition is limited by the surface reaction at temperatures from 270 to 395°C. It is similar to the H₂ reduction process. Therefore, conformal W film deposition was obtained in 0.8 μm contacts and is shown in Fig. 2 (a). W films deposited in 0.8 μm contacts by H₂ and SiH₄ reduction of WF₆ are shown in Figs. 2 (b) and 2 (c). The step-coverage of SiH₂F₂
reduced W film was as good as that of H₂ reduced W and was much better than that of SiH₄ reduced W. Moreover, the surface of SiH₂F₂ reduced W was smoother than that of H₂ reduced W.

Figure 3 shows the bottom of a Si contact after removal of W and SiO₂. A little encroachment on Si is observed in this SEM micrograph. Low deposition temperature prevents the reaction between WF₆ and Si.

The SiH₂F₂ flow dependence of film resistivity is shown in Fig. 4. Resistivity was 10.4-15.8 Ωcm, and increased with SiH₂F₂ flow. These values are lower than the resistivity of SiH₄ reduced W, and are slightly higher than that of H₂ reduced W.

Impurity concentration of the SiH₂F₂ reduced W films was measured by AES, and Si concentration was found to be less than the detection limit of AES (≤0.2 at%) for all samples. This is extremely different from the SiH₄ reduction case where the Si concentration is high and strongly affected by CVD conditions, especially by the SiH₄/WF₆ flow ratio. A low Si concentration of SiH₂F₂ reduced W resulted in the low film resistivity. It is necessary for Si incorporation in the W film that the Si-F chemical bond in the SiH₂F₂ molecule is broken by the CVD reaction. However, this is unfavorable because of the large binding energy of the Si-F chemical bond. This might be the reason why Si is hardly incorporated in the W film.

The CVD reaction of the SiH₂F₂ reduction process was analyzed using IR spectroscopy during W film deposition. Figure 5 shows an IR spectrum of reaction gases. In addition to the source gases (WF₆ and SiH₂F₂), SiHF₃ and SiF₄ were observed as by-products in this spectrum, as SiH₃F and HF were not detected. The amount of SiHF₃ was larger than that of SiF₄. Thus, the main by-product of the SiH₂F₂ reduction process was SiHF₃. The SiHF₃ formation is similar to SiH₄ reduction. This implies that the surface reaction mechanism for SiHF₃ formation is the same in both processes.

Conclusion

New blanket W-CVD using SiH₂F₂ and WF₆ was proposed. This technique is a promising alternative to the H₂ reduction process, because it provides a conformal W film in submicron contacts with a smooth surface, and a little encroachment on Si because of low deposition temperature (≥270°C). Si was not detected in the W film, and a low film resistivity of 10.4 Ωcm was obtained. SiHF₃ is the main by-product of this CVD.

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References

6) M. Saitoh, private communication.
Fig. 2. Cross-sectional SEM micrographs of W films deposited in 0.8μm contacts

Fig. 3 SEM micrograph of the bottom of 0.8 μm contact after removal of W and SiO₂

Fig. 4 SiH₂F₂ flow dependence of film resistivity

Fig. 5 IR spectrum of reaction gases.

WF₆ / SiH₂F₂ / N₂ = 20 / 31 / 720 sccm
300°C, 0.5Torr