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Conformal and Low Tempereature W-CVD by SiH_2F_2 Reduction

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New blanket W-CVD using difluoro-silane (SiH_2F_2) as a reducing gas of WF_6 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 $SiHF_3$ 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, H_2 reduction of WF_6 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 H_2 reduction of WF_6 under high pressure (≥10Torr) provides a higher deposition rate and smoother film surface[2]. 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 H_2 reduction process[3]. 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 WF_6 with Si. Although SiH_4 reduction of WF_6 offers a low deposition temperature and a smooth film surface without any encroachment, the step-coverage of SiH_4 reduced W film is poor[4]. Thus, SiH_4 reduction of WF_6 has not been used for blanket CVD.

This paper proposes a new blanket W-CVD technique using difluoro-silane (SiH_2F_2) as a reducing gas of WF_6, which is very promising for deep submicron ULSI metallization as an alternative to the conventional H_2 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 SiH_2F_2 flow and deposition temperature were varied from 50 to 400 sccm and from 270 to 395°C, respectively. The WF_6 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 H_2 and SiH_4 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-CVD[5].

Results and Discussion

The temperature dependence of the deposition rate is shown in Fig. 1, along with the results for H_2 [6] and SiH_4 reduction of WF_6. The activation energy of the SiH_2F_2 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 H_2 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 H_2 and SiH_4 reduction of WF_6 are shown in Figs. 2 (b) and 2 (c). The step-coverage of SiH_2F_2

reduced W film was as good as that of H_2 reduced W and was much better than that of SiH_4 reduced W. Moreover, the surface of SiH_2F_2 reduced W was smoother than that of H_2 reduced W.

Figure 3 shows the bottom of a Si contact after removal of W and SiO_2. A little encroachment on Si is observed in this SEM micrograph. Low deposition temperature prevents the reaction between WF_6 and Si.

The SiH_2F_2 flow dependence of film resistivity is shown in Fig. 4. Resistivity was 10.4-15.8 μΩcm, and increased with SiH_2F_2 flow. These values are lower than the resistivity of SiH_4 reduced W, and are slightly higher than that of H_2 reduced W.

Impurity concentration of the SiH_2F_2 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 SiH_4 reduction case where the Si concentration is high and strongly affected by CVD conditions, especially by the SiH_4/WF_6 flow ratio[7]. A low Si concentration of SiH_2F_2 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 SiH_2F_2 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 SiH_2F_2 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 (WF_6 and SiH_2F_2), $SiHF_3$ and SiF_4 were observed as by-products in this spectrum, and SiH_3F and HF were not detected. The amount of $SiHF_3$ was larger than that of SiF_4. Thus, the main by-product of the SiH_2F_2 reduction process was $SiHF_3$. The $SiHF_3$ formation is similar to SiH_4 reduction[5]. This implies that the surface reaction mechanism for $SiHF_3$ formation is the same in both processes.

Conclusion

New blanket W-CVD using SiH_2F_2 and WF_6 was proposed. This technique is a promising alternative to the H_2 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 μΩcm was obtained. $SiHF_3$ is the main by-product of this CVD.

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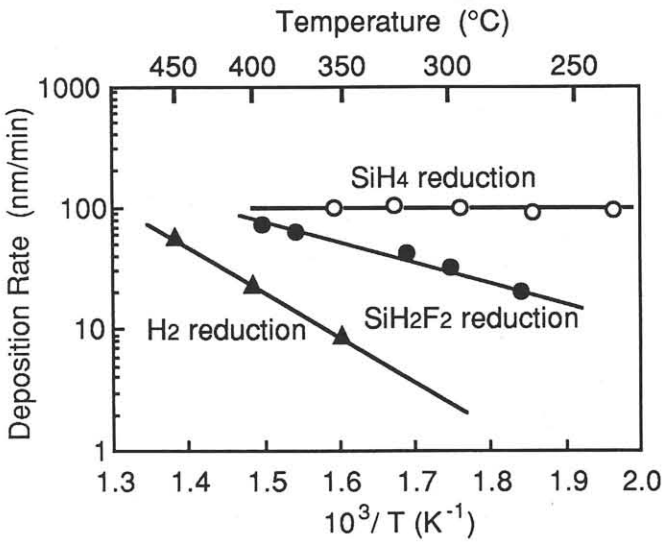
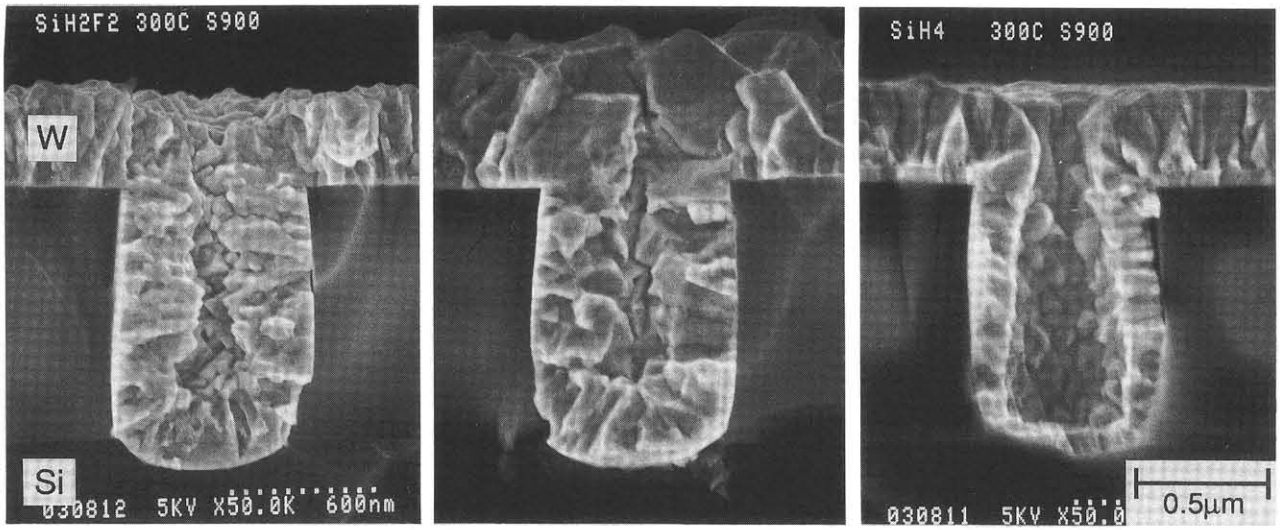


Fig. 1 Arrhenius plot of deposition rate
WF_6 / SiH_2F_2 = 100 / 400 sccm, 0.5Torr
WF_6 / H_2 = 40 / 2000 sccm, 0.65Torr [6]
WF_6 / SiH_4 = 80 / 80 sccm, 0.65Torr



(a) SiH_2F_2 reduction (b) H_2 reduction (c) SiH_4 reduction

Fig. 2. Cross-sectional SEM micrographs of W films deposited in 0.8μm contacts

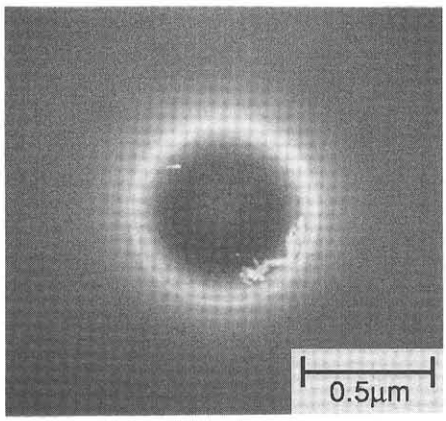


Fig. 3 SEM micrograph of the bottom of 0.8 μm contact after removal of W and SiO_2

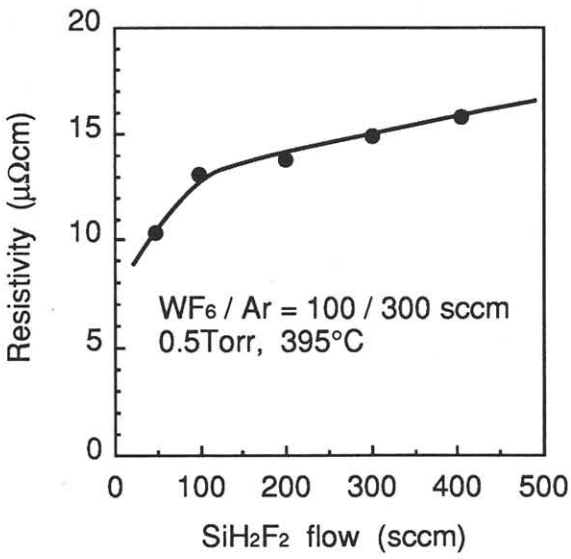


Fig. 4 SiH_2F_2 flow dependence of film resistivity

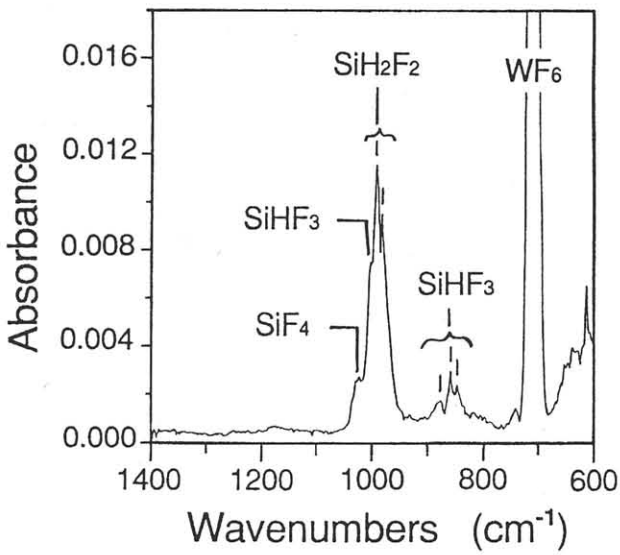


Fig. 5 IR spectrum of reaction gases.
WF_6 / SiH_2F_2 / N_2 = 20 / 31 / 720 sccm
300°C, 0.5Torr