CVD-Al/Flow-Al Technology for Filling Large Aspect Ratio Contact Holes

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1. Introduction

Filling low-resistivity metal into large-aspect-ratio contact/via holes is important technology in the fabrication of Si ULSI. This paper reports the filling capability of Al using CVD-Al/Flow-Al technology, which has superior filling capabilities. The importance of Al filling technology is (1) the possibility of eliminating the W-plug process that usually requires CMP or etch-back processes, resulting in low-contact-resistivity low-cost technology, and (2) compatibility with well-established contact/via processes. The filling technology is applied to system LSI and DRAM contacts.

This paper reports the filling capability of CVD-Al/Flow-Al technology and Fourier-Transform Infrared-Spectroscopy (FT-IR) measurement and discusses the deposition mechanism of methylpyrrolidine alane (MPA).

2. Al Precursor for CVD

Figure 1 shows the molecular structure of methylpyrrolidine alane (MPA), which is used in this study. MPA is a colorless liquid at room temperature, and exhibits selectivity, low flammability and chemical stability, which is believed to be due to the larger binding strength of Al-N as compared to DMEAA [1][2].

3. Al CVD Using MPA

Commercially available cluster apparatus is used for CVD-Al/Flow-Al. The available wafer size is 8-inch. MPA is delivered by the conventional bubbling method using Ar carrier gas. Figure 2 shows a deposition rate of CVD-Al as a function of temperature. The activation energy was found to be 0.20-0.23eV. Figure 3 shows the surface morphology of as-deposited CVD-Al. As deposition temperature increases, surface morphology becomes slightly rough. The carbon incorporation is less than 0.1% from the Auger depth profile measurement. As a seed layer for the subsequent Flow-Al process, continuous and thin Al is required [3]. At the present time, CVD-Al deposition at 105°C is used for filling.

4. Contact Hole Filling

The contact hole filling sequence is as follows. TiN(60nm)/Ti(40nm) layer is deposited by long-throw

sputtering (LTS). The wafer is carried through an air environment to LTS-Al/Flow-Al or CVD-Al/Flow-Al apparatuses. The seed Al layer is deposited by LTS or CVD. Then, without exposing wafers to atmosphere, Flow-Al is deposited; thick Al is deposited by sputtering method at a relatively high temperature of 400°C. During the sputtering duration at high temperature, Al is flowed to fill contact holes. The sequence is a so-called 2-step filling process. LTS-Al is deposited at room temperature and CVD-Al is deposited at 105°C/30 Pa.

As shown in Fig. 4(a), $0.25 \mu m \phi$ contact holes with an aspect ratio of 4 cannot be filled by the LTS-Al/Flow-Al process. In the 2-step process, step coverage of the seed layer is a key issue. If the sidewalls and bottoms of contact holes are not covered by the seed layer, contact holes cannot be filled by the subsequent Flow-Al process. Because of the inferior step coverage of LTS-Al, contact holes are not filled by subsequent Flow-Al deposition. As shown in Fig. 4(b), however, the contact holes are filled by the CVD-Al/Flow-Al process. Figure 5(a) shows the filling of contact holes of 0.13µm¢ with an aspect ratio of 8. However, although the diameter of this hole is reduced at the middle of the hole, the hole is successfully filled by CVD-Al/Flow-Al. Figure 5(b) shows the mirror-like Al surface on TiN/Ti. The relative reflectivity of the Si surface is sufficiently high, being 208% at 480 nm.

5. FT-IR Analysis of Al-CVD Using MPA

The gas phase decomposition of MPA is known as shown in Fig. 6 [2]. Surface reaction of MPA on TiN/Ti/SiO₂/Si surface was investigated by Fourier-Transform Infrared-Spectroscopy (FT-IR) measurement. Figure 7 shows a schematic of the measurement system. MPA is directly injected into the chamber. No inert gas is used in this experiment. Figure 8 shows FT-IR spectrum at 50°C and a chamber pressure was 0.8 Pa. Peaks of Al-N, C-C, Al-H, C-H and N-CH bonds could be observed. Identification of peaks is as follows; (1) 770 cm⁻¹ is related to Al-N and C-C bonds, (2) 1790 cm⁻¹ is Al-H bond, and (3) 2780 cm^{-1} and 2980 cm^{-1} are both related to C-H and N-CH bonds [2]. Figure 9 shows the change in Al-H and Al-N peak areas as the substrate temperature is changed. Peak areas are defined as the integration of the peak over a baseline. Each IR spectrum was measured 10 min after MPA injection at the target temperature. The Peak area is proportional to average time of adsorption τ , where τ is

given by $\tau = \tau_0 \exp(E/kT)$ and E is the activation energy of desorption. The E of Al-H changed at 75°C as shown in Fig. 9, although the E of Al-N did not change. This result is thought to be due to the adsorbed molecules changing from MPA to alane at 75°C. The change of adsorbed molecules have shown that MPA decomposes to produce Al *at the surface* by the 2-step reaction as shown in Fig. 6.

6. Conclusions

We have investigated contact hole filling by CVD-Al/Flow-Al technology. Aluminum filling to a $0.13 \mu m \phi$ contact hole with an aspect ratio of 8 was experimentally confirmed. The Fourier-Transform Infrared-Spectroscopy (FT-IR) measurement demonstrated two-step MPA reaction.

References

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(a) LTS-Al at RT, 200nm Flow-Al at 400°C, 600nm (b) CVD-Al at 30Pa/105°C, 100nm Flow-Al at 400°C, 600nm

Fig. 4 SEM photos. Contact hole is 0.25µm¢ with an aspect ratio of 4.





(a) Contact hole
(b) Surface
(c) SEM photos of Al-CVD/Flow-Al.
(c) Contact hole is 0.13µmφ with an aspect ratio of 8.
(c) CVD-Al is deposited at 30Pa/105°C, and thickness is 80nm.
(c) 600nm-thick Flow-Al is deposited at 400



Fig. 9 The peak area as a function of substrate temperature.