Extended Abstracts of the 22nd (1990 International) Conference on Solid State Devices and Materials, Sendai, 1990, pp. 215-218

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High Rate Reactive Ion Etching of Copper Films in $SiCl_4$, N_2, Cl_2 and NH_3 Mixture

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The high rate and highly directional reactive ion etching of copper films is examined by adding Cl_2 and NH_3 to the $SiCl_4$ and N_2 mixture. The etching rate of copper increases with an increase in Cl_2 flow rate at temperatures higher than 280°C. However, the addition of Cl_2 causes the side-etching of Cu patterns. Adding NH_3 forms a SiN-like protection film that prevents side-etching. Fine Cu patterns can be obtained by RIE with a $SiCl_4$, N_2, Cl_2 and NH_3 mixture, where the etching rate is about five times higher than that with a $SiCl_4$ and N_2 mixture.

1. Introduction

Copper films are attractive materials for interconnection lines in LSIs because of their low resistivity and high migration resistance. The dry etching of copper is a key technology in realizing fine copper patterns and it has been the subject of several reports.[1)-4)] We previously examined the anisotropic etching of copper films by RIE with a $SiCl_4$ and N_2 mixture at 250°C. However, the etching rate (about 200 Å/min.) was too low for process technology.[2)]

The object of this work was to achieve a high rate and highly directional reactive ion etching of copper films by adding Cl_2 and NH_3 to the $SiCl_4$ and N_2 mixture.

2. Experiments

A schematic of the planar diode-type single wafer reactor used in this study is shown in Fig. 1. The sample wafer was set on the cathode to which a 13.56 MHz RF generator is attached. The sample wafer temperature was controlled by the heaters which are set up in both the anode and cathode. The wafer temperature was measured using Luxtron Flluoropic™ thermometry. The etching rate of copper films was calculated from the weight loss of the samples after fixed-time etching. A $SiCl_4$ and N_2 mixture, whose flow rate was fixed at 20 and 80 SCCM respectively, was used for the base gas. Cl_2 and NH_3 were added to this base gas. The total pressure was fixed at 2 Pa.

Copper films were deposited on thermally oxidized silicon wafers using magnetron DC sputtering. A photoresist-TiN bilayer and plasma CVD SiN were used for the etching mask when copper patterns were performed. The photoresist patterns were UV-cured, and

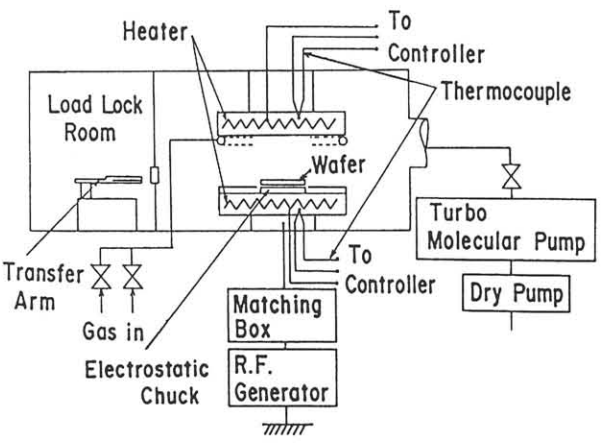

Fig. 1 Schematic diagram of the experimental apparatus

hard-baked at 260°C.

Auger Electron Spectroscopy (AES) was used to investigate the surface composition during etching.

3. Result and Discussion

3.1 The relationship between Cl_2 flow rate and etching rate

Cl_2 was added to a $SiCl_4$ and N_2 mixture to increase the etching rate of copper films. Figure 2 shows the etching rate, as well as the optical emission intensity of Cl (837.5nm) as a function of the Cl_2 flow rate. At 250°C copper could be etched in the $SiCl_4$ and N_2 mixture, but it became difficult at a Cl_2 flow rate of more than 20 SCCM because the CuCl could not volatilize. It is thought that the CuCl generation rate increases beyond volatilizing rate by adding Cl_2, and that CuCl remains on the wafer. On the other hand, at 280 and 300°C, the etching rate increased with an increase in Cl_2 flow rate. It is considered that the CuCl volatilizing rate is higher than the generation rate at a Cl_2 flow rate of more than 20 SCCM at these temperatures.

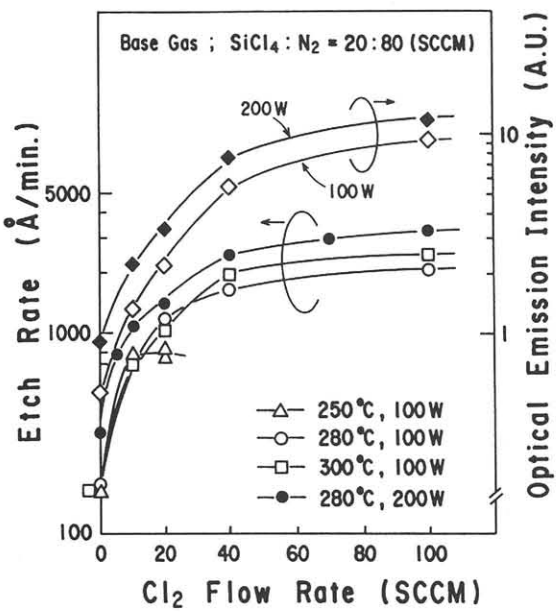

Fig. 2 Etching rate of copper films and optical emission intensity of Cl(837.5nm) as a function of a Cl_2 flow rate. Optical emission intensity measured at 280°C.

The optical emission intensity of Cl increased by increasing Cl_2 flow rate. This change in intensity represents a change in the concentration of Cl radicals. According this result, the etching of copper is dominated by Cl radicals at high temperature. Also, the optical emission intensity of Cl, as well as the etching rate of copper films increased with an increase from 100 W to 200 W in RF power. These findings indicate that the etching rate of copper films can be increased both by addition of Cl_2 and by increasing RF power to as high as 280°C.

High rate etching of copper patterns in the $SiCl_4$, N_2, and Cl_2 mixture was tried with the Cl_2 flow rate of 20 SCCM. A SEM overview photograph of the copper patterns taken after etching with a photoresist-TiN bilayer mask is shown in Fig. 3. A rough sidewall resulted from the partial side-etching, because the protection film formed on the sidewall was weak. Therefore, to obtain high rate copper etching with fine patterns, it is necessary to form a firmer protection film on the sidewalls.

3.2 NH_3 addition to the $SiCl_4$, N_2, and Cl_2 mixture

NH_3 was added to the $SiCl_4$, N_2, and Cl_2 mixture in an attempt to form a SiN-like protection film on the sidewall. Figure 4 shows etching rates of the copper film, SiO_2 and organic photoresist, as well as the optical emission intensity of Cl(837.5nm), as a function of NH_3 flow rate. The etching rate of Cu and SiO_2 decreased monotonically while

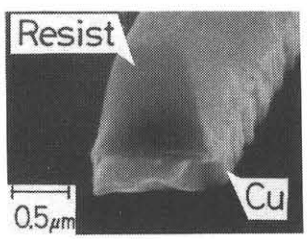

Fig. 3 SEM overview photograph of Cu pattern after etching. Cl_2 flow rate : 20 SCCM at 2Pa. RF power : 200W. Temperature : 280°C.

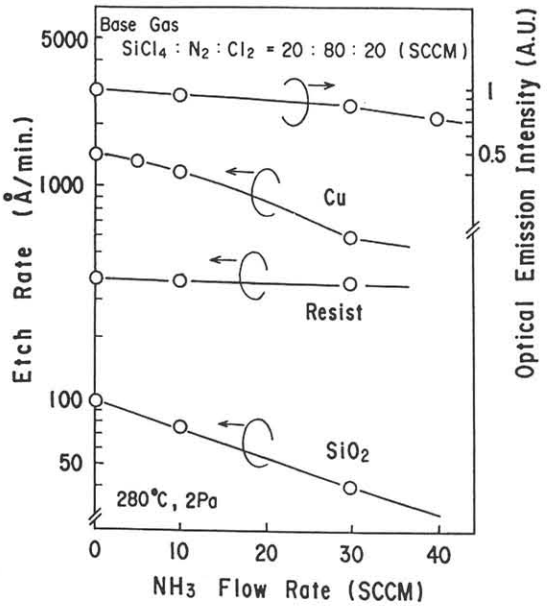

Fig. 4 Etching rates of copper film, photoresist and SiO_2, as well as the optical emission intensity of Cl(837.5nm) as a function of a NH_3 flow rate.

the optical emission intensity of Cl slightly decreased. The decrease in the concentration of Cl radicals and/or the formation of protection film on the surface appears to cause the decrease in etching rate. On the other hand, the etching rate of the photoresist is almost constant.

The copper surface after etching was examined by AES. The Auger spectra without NH_3 and at 10-SCCM NH_3 flow rate are shown in Fig. 5(a) and (b) respectively. The Si spectra were observed at the 10-SCCM NH_3 flow rate (Fig. 5(b)), but not without it (Fig. 5(a)). The Si spectra were broad at peak energy between 74 and 90(eV) (Fig. 5(b)). The Si LVV peak shifts from 91(eV) in elemental silion to 78(eV) in SiO_2 and to 83 or 87(eV) in Si_3N_4.[5)-7)] This suggests that both Si-O and Si-N bonds exist on the surface. It is thought that the formation of the Si-O bond occurs in the air when a sample is taken out from reactor. On the other hand, the spectra of N became clear by adding of NH_3. Figure 6 shows the peak height of Si and N as a function of NH_3 flow rate. The peak height of both Si and N increased with an increase in

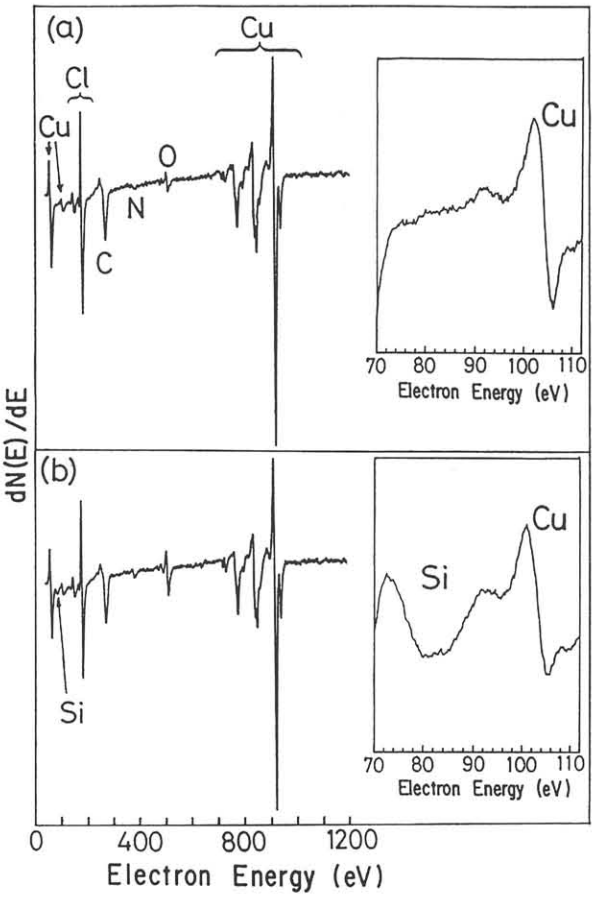

Fig. 5 AES spectra of the Cu surface after etching. Cl_2 flow rate : 20 SCCM. (a) without NH_3, (b) with 10 SCCM of NH_3. Insets show enlarged spectra between 70 and 110 eV.

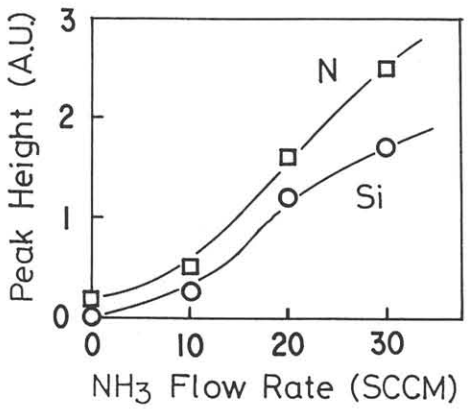

Fig. 6 Peak height of Si and N spectra as a function of NH_3 flow rate.

NH_3 flow rate. Therefore, it is considered that the formation of the SiN-like film proceeds by adding of NH_3.

Fig. 7 shows SEM overview photographs taken after etching with a SiN-TiN bilayer mask. Here, Cl_2 flow rate was 20 SCCM and NH_3 flow rate was 0, 10 and 30 SCCM. Side-etching occurred without NH_3 (Fig. 7(a)) but was prevented by adding NH_3. Copper patterns with almost vertical walls were obtained with the 10-SCCM NH_3 flow rate (Fig. 7(b)). Moreover, tapered walls were obtained with 30 SCCM of NH_3 (Fig. 7(c)). This is because a sidewall protection film is formed by adding NH_3.

In accordance with above results, adding NH_3 makes it possible to etch copper films directionally because the SiN-like protection film is formed on the sidewalls. The etching rate about 1200(Å/min.), which is five times higher than that with the $SiCl_4$ and N_2 mixture when Cl_2 and NH_3 flow rate were 20 and 10 SCCM, respectively (Fig. 4). The fine Cu patterns shown in Fig. 8 could be obtained even with the photoresist-TiN bilayer mask.

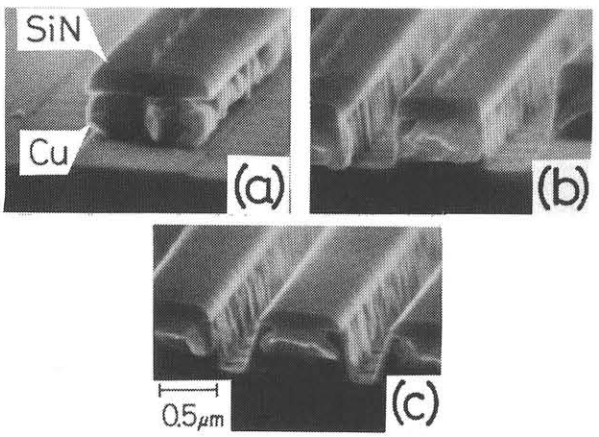

Fig. 7 SEM overview photographs of Cu pattern after etching in the $SiCl_4$, N_2, Cl_2 and NH_3 mixture at 280°C, 2Pa, 200W. Cl_2 : 20 SCCM. (a) without NH_3, (b) NH_3 : 10 SCCM, (c) NH_3 : 30 SCCM

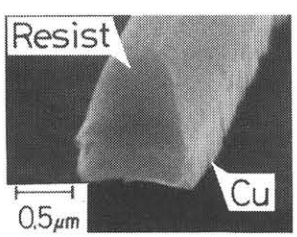

Fig. 8 SEM overview photograph of Cu pattern after etching in the $SiCl_4$, N_2, Cl_2 and NH_3 mixture at 280°C, 2Pa, 200W. Cl_2 : 20 SCCM. NH_3 : 10 SCCM

4. Summary

The high rate and highly directional etching of copper film was examined by RIE with the $SiCl_4$, N_2, Cl_2 and NH_3 mixture. The etching rate of copper films increased with the addition of Cl_2 and an increase in RF power at more than 280°C ; however, the addition of Cl_2 caused side-etching. NH_3 addition effectuated the highly directional etching of copper films through the formation of protective film on the sidewalls. Fine copper patterns could be obtained and the etching rate was about five times higher than that with the $SiCl_4$ and N_2 mixture. This method surely enhances progress toward a Cu interconnection in LSIs.

Acknowledgments

The authors thank Tetsushi Sakai for his encouragement and support throughout this study. They also wish to thank Nobuyoshi Awaya and Koichi Ikeda for their valuable discussions.

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