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Role of Aluminum Chloride on Copper Chloride Vaporization in AlCu Alloy Reactive Ion Etching

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1. INTRODUCTION

Aluminum alloy films containing copper are widely used to overcome the reliability degradation of LSI interconnections. However, a problem arises in AlCu alloy reactive ion etching (RIE) when the residue containing copper remains after etching without substrate heating. This occurs because copper chloride is difficult to vaporize at lower than 200°C.[1]

In this paper, we examine the mechanism of copper chloride vaporization in AlCu alloy films and find that aluminum chloride has a role in the enhancement of copper chloride vaporization.

2. EXPERIMENTAL

RIE equipment with a wafer heating system was used. The etching electrode was heated by an oil circulator. The wafer temperature was controlled using a ceramic electrostatic chuck with backside He flow. Figure 1 shows the wafer temperature after 3 min etching as a function of oil bath temperature. At oil bath temperatures of 40°C - 230°C, wafer temperature was constant within 20 degrees. Wafers of 10 cm in diameter were used in this experiment.

The samples were 500-nm-thick Al-2%Cu films (deposited at 300°C) and Ti/Al-1%Si-0.5%Cu/TiN/Ti laminated films on SiO_2. Etching was performed using a $SiCl_4$ (20 SCCM) and Cl_2 (30 SCCM) mixture at 0.6 Pa, with and without an aluminum ring plate (about 36 cm^2) around the wafer. The surface after 100% overetching was observed using Secondary Electron Microscopy (SEM), Xray diffraction (XD) and Auger Electron Spectroscopy (AES).

3. RESULTS AND DISCUSSION

With an aluminum ring, the etching residue does not remain on the sample after etching at 80°C, whereas wafer temperature must be increased to 230°C to remove residue without an aluminum ring. In the AES analysis (Fig. 2), Cu peaks were not observed for samples etched at $\geq$ 80°C, and Cl peaks were not observed for those etched at $\geq$ 120°C with an aluminum ring (Fig. 2 (a)). However, wafers without an aluminum ring must be heated to 230°C to eliminate Cu and Cl peaks (Fig. 2 (b)). Because the residue was identified as $CuCl_2 \cdot 2H_2O$ using XD (Fig. 3), the residue composition just after etching is probably $CuCl_2$.

These results indicate that aluminum chloride generated by aluminum etching affects the vaporization of copper chloride. This reaction is thought to occur as follows. First, copper reacts with chlorine to form CuCl. Then, CuCl reacts with $AlCl_3$ to form tetrachloroaluminate copper ($CuAlCl_4$ or $AlCl_4^- \cdot Cu^+$).[2] This mixed salt contains tetrahedral tetrachloroaluminate ions, and the $CuAlCl_4$ melting point of 233°C is lower than that of CuCl (m.p. 422°C). Accordingly, $CuAlCl_4$ is vaporized at a relatively low temperature and the residue is removed.

Figure 4 shows an SEM photograph of Ti/AlSiCu/TiN/Ti multilayer interconnections etched with and without an aluminum ring at an oil bath temperature of 120°C. Fine resolution submicron patterns without residue were obtained with an aluminum ring.

When fusing the chlorides of other metals, aluminum chloride forms chloroaluminates.[3] These mixed salts have relatively lower melting points (140°C-300°C) than the original chlorides. Accordingly, it is possible to etch these metals or their compounds with the existence of aluminum chloride.

4. CONCLUSION

Copper chloride can be vaporized at a relatively low temperature through a reaction with aluminum chloride. This is likely to form tetrachloroaluminate copper. Also there is the possibility of low temperature etching of other metals or compounds whose chlorides cannot be vaporized at ordinary temperatures.

REFERENCES

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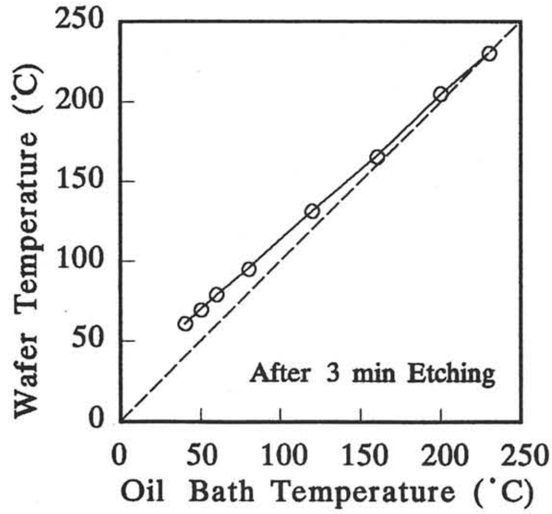

Fig. 1. Wafer temperature after 3 min etching as a function of oil bath temperature.

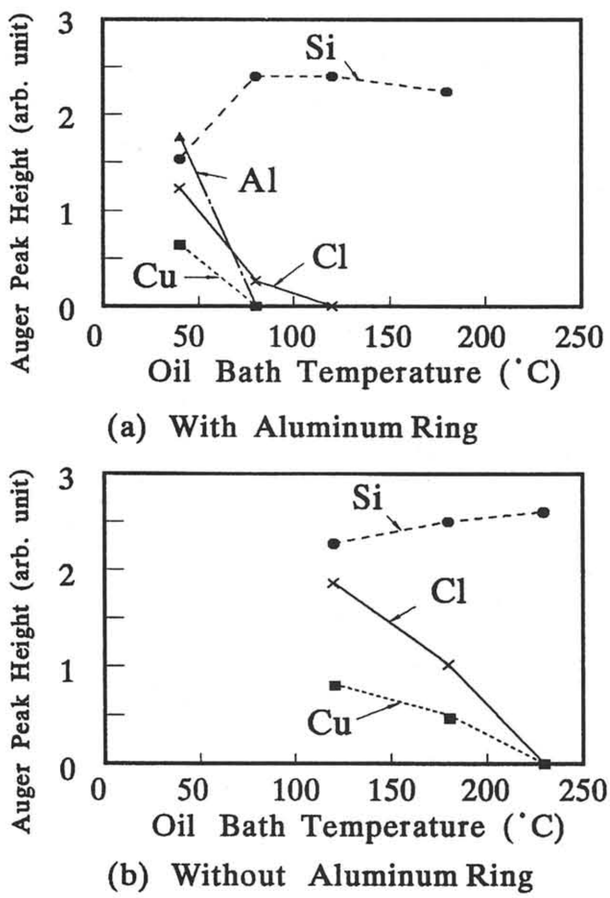

Fig. 2. Auger Peak Height of Cu, Cl, Al, and Si as a function of oil bath temperature for the surface after etching (a) with an aluminum ring, and (b) without an aluminum ring.

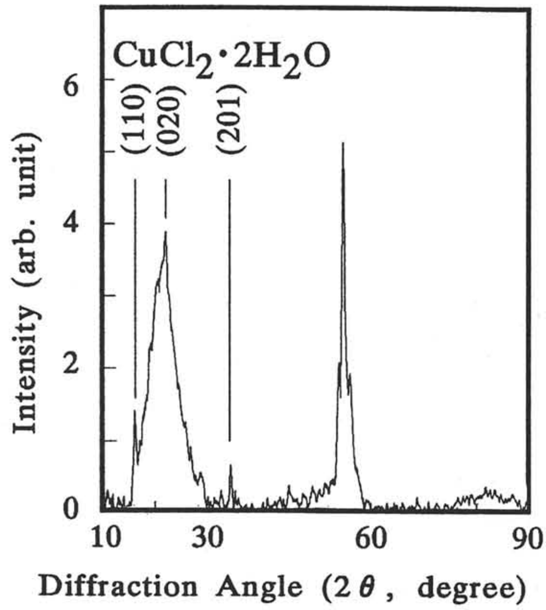

Fig. 3. Xray diffraction spectra of the surface after etching at 180°C without an aluminum ring.

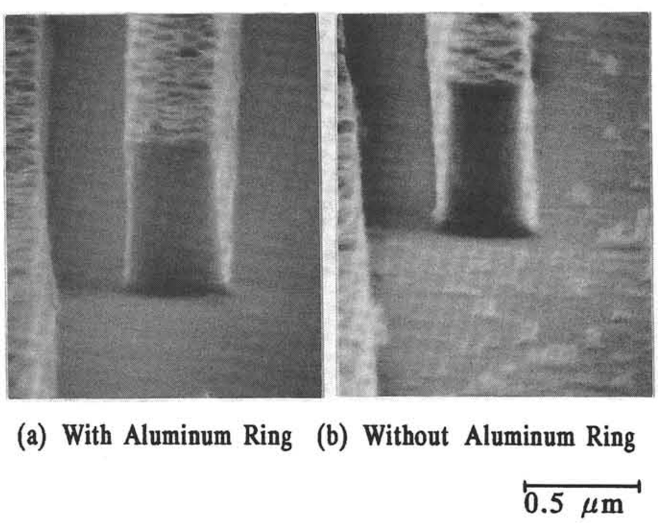

Fig. 4. An SEM photogrough of Ti/AlSiCu /TiN/Ti multilayer interconnections etched (a) with an aluminum ring, and (b) without an aluminum ring.