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Self-Aligned Passivation Technology for Copper Interconnection Using Copper-Aluminum Alloy

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Self-aligned passivation procedure for copper interconnection has been developed using Al-Cu alloy formation. After annealing at 350 C, very thin aluminum on the exposed copper wire reacts with copper to form an Al-Cu intermetallic compound, whereas the under-lying copper was remains as pure metal. Using the difference of the electrode potential between pure Al and the intermetallic compound, the unreacted aluminum on SiO_2 is selectively removed by a acid treatment. Additional annealingi in the gaseous mixture of H_2 and O_2 improves the resistance of the passivation alloy to oxidation.

1. INTRODUCTION

Copper interconnection is expected to significantly improve the circuit performance and the reliability of 0.2 um scale ULSIs. However, some drawbacks have to be overcome before copper wiring can be put to practical use. The main issue is how to protect the exposed copper surface, which corrodes easily in oxygen atmosphere. Effective surface passivation technology, therefore, is indispensable for improving the reliability of wiring. Aluminum alloy formation on a copper surface is attractive for surface passivation because of its low processing temperature and its high resistance to oxidation. Conventional methods , however, have not satisfied requirements for, for instance, such as self-alignment[1-3] or reduced influence on electrical resistivity[4]. This paper presents a newly developed self-alignment procedure that protects the surface of the exposed copper wiring by means of an Al-Cu intermetallic compound film with high oxidation resistance. This technique has been applied to the damascene copper wiring process.

2. PRCESS SEQUENCE

The process sequence of the self-aligned passivation technology is as follows and is illustrated in Fig. 1.

1. Copper interconnection patterns are formed using the damascene process.
2. Very thin aluminum film (about 10 nm) is deposited on the sample.
3. The sample is annealed at 350 C. An intermetallic compound is formed on exposed copper surface.
4. Non-reacted aluminum on SiO_2 is selectively removed with phosphoric acid.
5. The sample is heated to 350 C in a gaseous mixture of hydrogen and oxygen. Aluminum oxide forms on the copper surface.

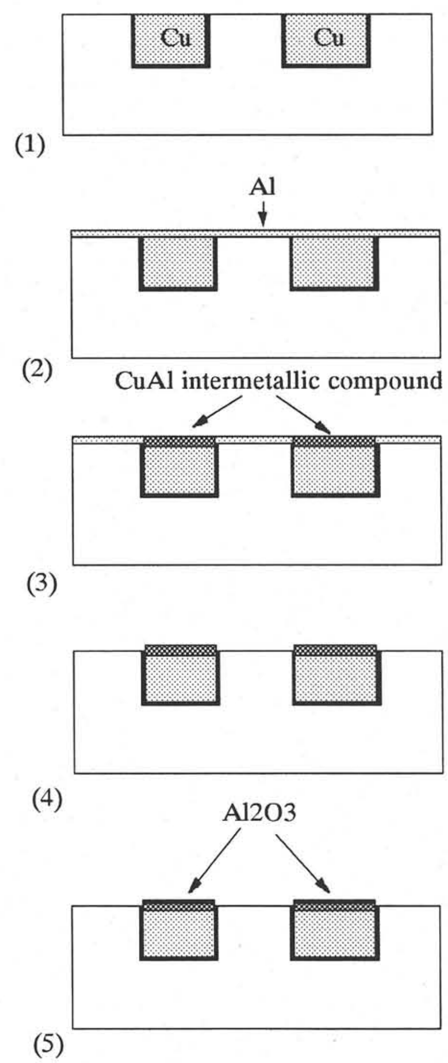


Fig. 1 Process sequence of self aligned passivation

3. ELECTRICAL RESISTIVITY OF THE FILM

Figure 2 shows the sheet resistance of Cu(600 nm)/Al(10 nm) film. The sheet resistance saturated after an increase of about 5% after the first 5 min. The increase in the resistance of the 0.6- micron-wide, 1 mm -long wire pattern was also about 5%.

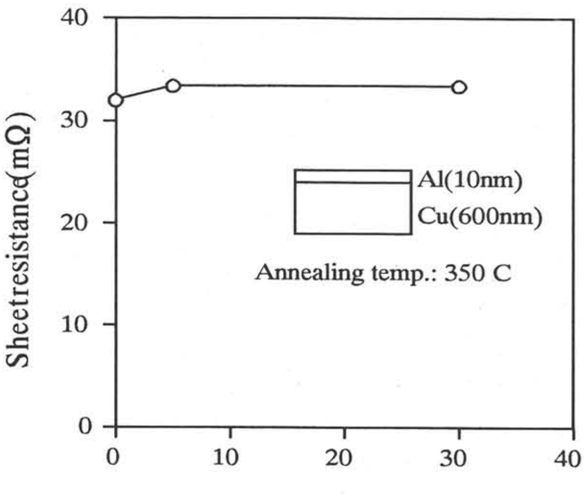


Fig.2 Sheet resistance vs. annealing time

4. STRUCTURAL ANALYSIS

The surface passivated copper film was analyzed by transmission electron microscopy (TEM). A cross-sectional bright field TEM image is shown in Fig. 3. The different layers are separated by well-defined interfaces. Figures 4 show the local atomic composition measured by energy dispersion spectroscopy (EDS). In surface area **a**, oxigen, aluminum and copper were detected. The copper signal is presumably attributed to the copper in the under layers because area **a** is thinner than the EDS resolution. We, therefore, assume that surface area **a** is an aluminum oxide layer that protect the film against oxidation.

The results of a electron diffraction and EDS analysis indicate that an, intermetallic compound comprising copper and aluminum was formed in area **b**. From X-ray diffraction, the crystal structure of intermetallic compound was found to correspond to that of Al_4Cu_9. The EDS results for area **c** clearly show that the internal area of this film is pure copper metal. The electron diffraction pattern also corresponded to the lattice constant of pure copper. The aluminum concentration in this pure copper is about 100 ppm, as determined from additional SIMS measurement. These results explain the low electrical resistance of the passivated copper film in Fig. 2.

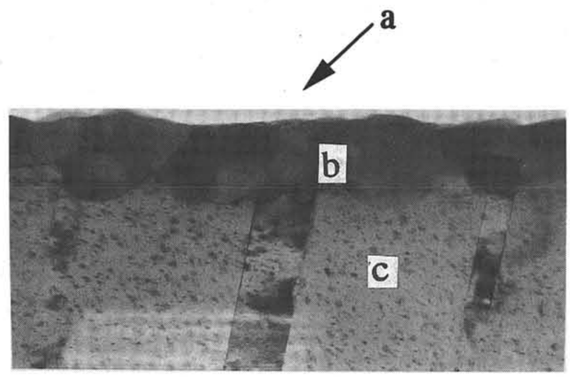
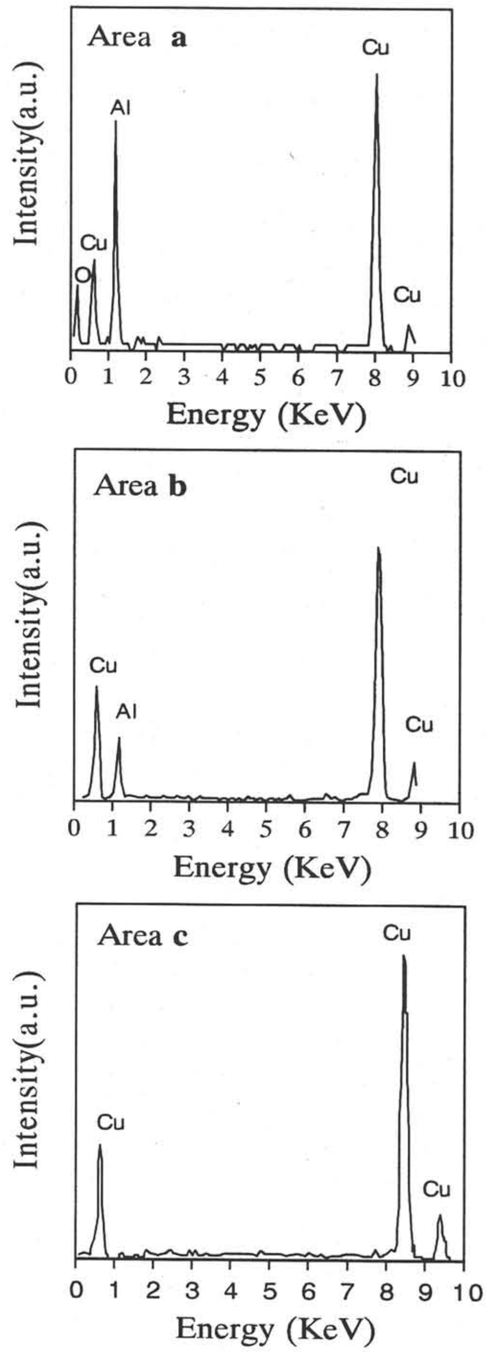


Fig.3 Cross-sectional TEM image of the surface passivated copper film



Figs.4 Local atomic composition of the passivated film

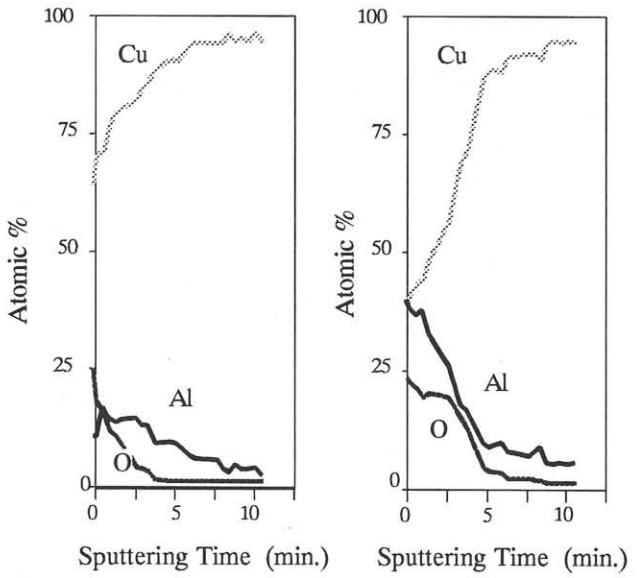
5. ELECTROCHEMICAL PROPERTY OF THE INTER-METALLIC COMPOUND

The electrode potential of the copper, the aluminum and the metallic compound were measured in buffered phosphoric acid (see Table 1) to determine the electrochemical property of the films. The electrode potential of the metallic compound was very close to that of pure copper. This inert electrochemical property of the intermetallic compound indicated the feasibility of selective wet removal of non-reacted aluminum Accordingly, the non-reacted aluminum on the insulating layer was selectively removed by dipping in concentrated phosphoric acid or dilute fluoric acid.

Table 1 Electrode potential in buffered phosphoric acid

	Electrode Potential (V)
Cu	-0.05
Cu-Al compound	-0.05
Al	-1.44

Reference electrode: calomel
Test solution: Na2HPO4-12H2O, pH 9.8



Figs. 5 AES depth profile before and after annealing in mixed gas

6. OXIDATION PROPERTY

After selective wet removal of the aluminum, the oxidation resistance deteriorated somewhat due to the disappearance of the surface Al2O3. To form the surface Al2O3, the sample was annealed at 350 C in a gaseous mixture of hydrogen and oxygen. In this gas system, aluminum is selectively oxidized because copper oxidation is prevented by hydrogen reduction. The AES profiles before and after this treatment (Figs 5) clearly show the passivation layer formed by this annealing. Sheet resistance vs. oxidation time (Fig. 6) shows that complete passivation was achieved in this process.

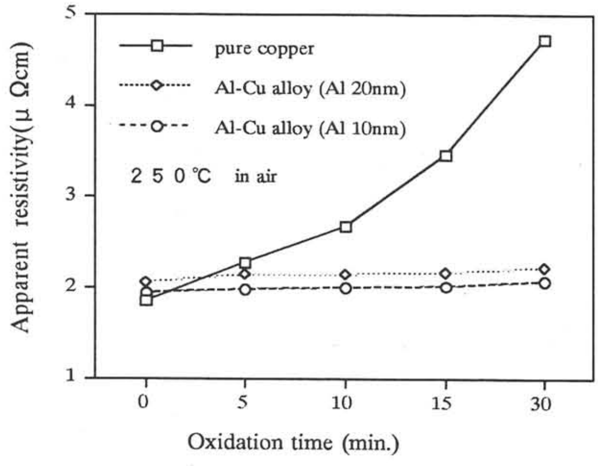


Fig. 6 Oxidation time vs. Apparent resistivity

7. SiO2 ADHESION ON THE PASSIVATED COPPER

SiO2 adhesion on the passivated copper was evaluated by a scotch tape peeling test. The adhesion strength of plasma CVD SiO2 was stronger on the passivated copper film, than that on the pure copper sample.

8. CONCLUSION

In summary, self-aligned Al-Cu alloy formation on exposed copper is very promissing passivation technology for copper interconnections due to its high oxidation resitance, low processing temperature and improvement of adhesion.

Acknowledgment

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References

(1) K.I. Lee, et al. , *Extended abstracts of the SSDM*, Yokohama, (1994), 940.
(2) K. Ueno, et al., *Extended Abstract of the 55th fall meeting of the Jpn. Soc. of Appl. Phys.*, 21P-ZD-7, 1994
(3) K. Ueno, et al., *Extended Abstract of 1995 Symp. VLSI Technol.*Kyoto, p.27
(4)W.A. Lanford, et al., Thin Solid Films, **262**, (1995),.234.