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Characteristics of the Oxidation Barrier Layers for Copper Metallization

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The characteristics of oxidation barrier layers (Cr, TiN and Al) for copper were investigated. It was found that aluminum could prevent the oxidation of copper up to the highest oxygen ambient temperature among the barriers layers tested in this study. The topographical feature of the copper film in Al/Cu was better than that in other systems after an oxidation annealing. Oxygen did not diffused into copper because of ultra-thin aluminum oxide layer formed on the copper surface, and consequently ultra-thin (50Å) aluminum film was found to be a good oxidation barrier layer for copper.

1. INTRODUCTION

With scaling down of the integrated circuit devices, reliability and RC delay time are considered to be important factors in selecting the interconnection materials.[1] Since copper has lower electrical resistivity and better EM (electromigration) resistance than aluminum it has been proposed to be a promising interconnection material for ULSI in the future.[1,2] However, the low dry etching rate, fast diffusion into Si/SiO_2 and low oxidation resistance, have retarded the versatile application of copper in metallization.[3,4,5] The encapsulation of copper for the prevention of diffusion and oxidation using tungsten or refractory metal-nitride such as TiN has been widely considered.[6,7]

In the present study, characteristics of various oxidation barrier layers for copper were investigated and ultra-thin aluminum film was proposed as an oxidation barrier layer for copper.

2. EXEPERIMENTAL

Thermally oxidized (1000Å) P^-(100) silicon wafers were used as substrates. Cr (200Å), Cu (3000Å) and barrier layers (50~500Å) were deposited sequentially in a single pump down with a 3-gun RF magnetron sputtering system. Cr, TiN and Al films were used as oxidation barrier layers for copper. Bottom Cr (200Å) layer was used to enhance the adhesion of copper to the SiO_2 substrate. Experimental procedures and structure of the multilayered films are shown schematically in Fig. 1. The sputtering conditions for the films are listed in Table 1. The films were annealed in an oxidizing atmosphere controlled in a manner as illustrated in Fig. 2, which simulates the exposing condition of copper to oxygen during SiO_2 deposition. To evaluate the degree of copper oxidation, variation of the sheet resistances of the films was monitored by the four point probe technique after annealing.

Table 1. Films sputtering conditions

Material	Cu	Cr	TiN	Al
Power(W)	100	75	70	70
Sputter Gas	Ar	←	$Ar/N_2=4:1$	Ar
Dep. Rate(Å/s)	4.0	1.2	0.2	1.6
Sp. Press.(mT)	5	←	←	←

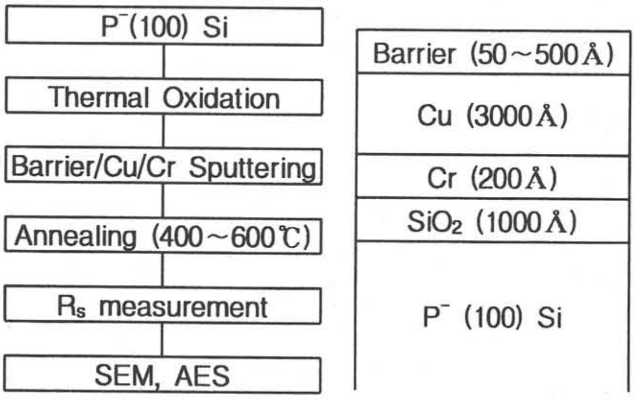

Fig. 1. Experimental procedure and the film structure.

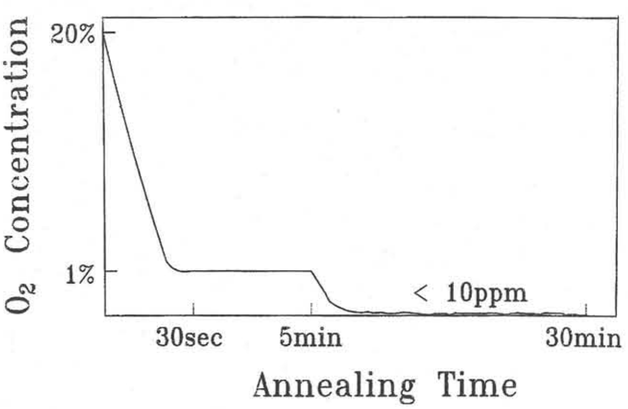

Fig. 2. Variation of oxygen concentration during annealing.

Scanning electron microscopy was applied to reveal the topographical feature and Auger Electron Spectroscopy to evaluate the oxygen profile in depth.

3. RESULTS AND DISCUSSIONS

The advantages of copper interconnection over aluminum line are not only better EM resistance but higher electrical conductivity. It is, therefore, desirable that the resultant electrical resistance of a barrier/copper line is low enough when compared with that of an aluminum line. When the copper is encapsulated by diffusion and oxygen barrier layer whose resistivities are much higher than that of copper, the resistance of the encapsulated copper line increases. The relative resistances of encapsulated copper and aluminum were calculated as functions of the resistivity and thickness of a copper barrier layer. As shown in Fig. 3, it can be easily found that the encapsulation layer should be thinner than copper by tenth to twentith, which means the thickness of the barrier layers are important as well as barrier properties. In the case of quarter micron wide interconnection line, copper line has a merit over aluminum line in electrical resistance when the thickness of the barrier layer such as TiN is less than 200Å.

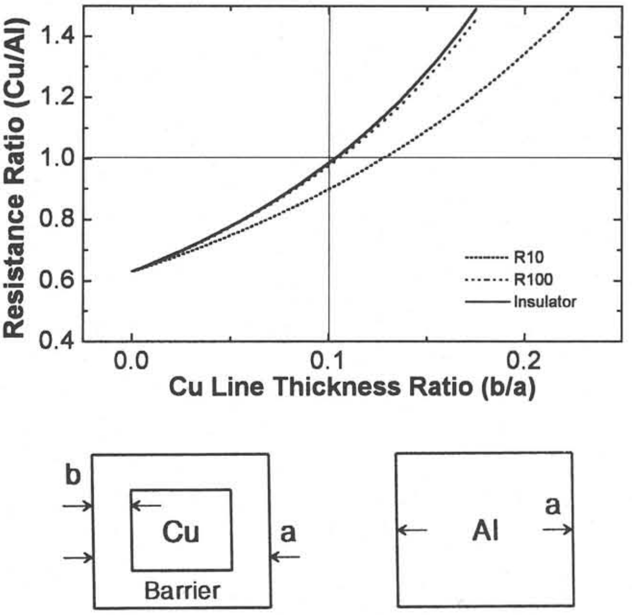

Fig. 3. Relative Al to Cu line electrical resistance with copper barrier thickness. Line cross sections are square. (R : resistivity of barrier layer, μΩ · cm)

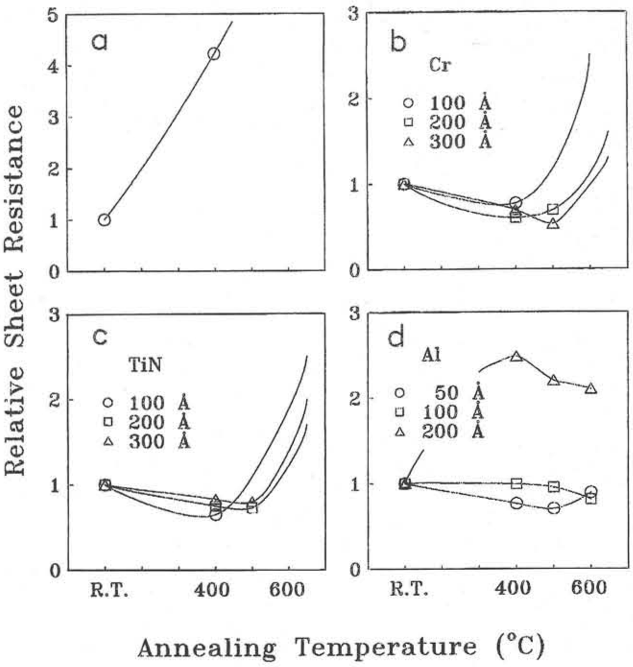

Fig. 4. Variation of sheet resistance with annealing temperature. Barrier layers were (a) None, (b) Cr, (c) TiN, (d) Al.

Fig. 4. shows the variation of sheet resistance of the multilayered films with annealing temperature. When there was no oxidation barrier layer, the sheet resistance of the copper film increased four times higher than that of the as-deposited film after 400℃ annealing. Cr(>300Å) and TiN(300Å) and Al (50~500Å) films prevented the oxidation of copper up to 500℃ annealing. However, when the annealing temperature was 600℃, only copper covered with aluminum was not oxidized. The ultra-thin aluminum film (50Å) prevented the oxidation of copper while the 500Å TiN film, known as one of the best oxidation prevention barrier layer, did not.

When the aluminum thickness was 500Å, the sheet resistance of the annealed films became twice of the as-deposited film while in case the thickness of aluminum was 50Å, the change of sheet resistance of the film was

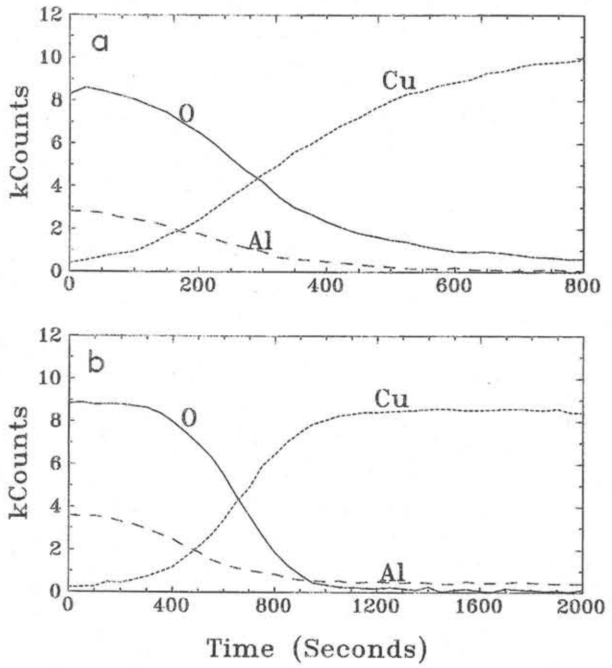

Fig. 5. AES depth profile of 600℃ annealed samples (a) Al (50Å), (b) Al (500Å).

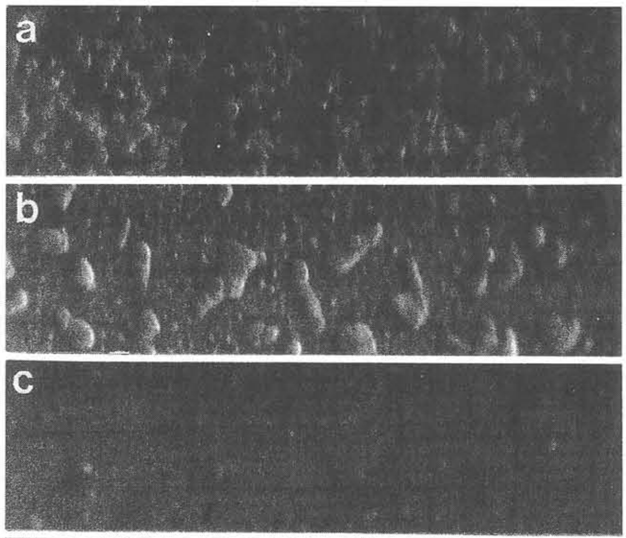

Fig. 6. Surface topography of the films after annealing (600℃, 30min). (a) (500Å)Cr/Cu, (b) (500Å)TiN/Cu, (c) (50Å)Al/Cu, (d) (100Å) Al/Cu, (e) (500Å)Al/Cu.

trivial. The depth profile by AES shown in Fig. 5, when the thickness of aluminum film was 50Å, reveals no trace of aluminum in copper and aluminum on copper surface was fully oxidized. When the thickness of aluminum was 500Å, aluminum was found to be oxidized at the surface and aluminum that was not oxidized diffused into copper so that constant concentration of aluminum was detected in the copper matrix. This means that Cu-Al alloy films were formed, which caused the increase of resistance. Aluminum becomes soluble in copper by more than 10 a/o at such a low temperature as 300℃.[8] When the aluminum films are thick enough, aluminum that was not oxidized might diffuse into copper and increase the resistivity of copper film.

The topographical features of the multi-layered films were examined with SEM after an annealing at 600℃. The surfaces of Cr/Cu and TiN/Cu films became rough while that of Al/Cu films remained relatively smooth as shown in Fig. 6. The surfaces of (50Å) Al/Cu and (100Å) Al/Cu were smoother than (500Å) Al/Cu.

4. CONCLUSION

In this study, the characteristics of oxidation barrier layers for the copper metallization were investigated. It was found that oxygen did not diffused into copper through aluminum film because of the aluminum oxide layer formed on the surface. The ultra-thin aluminum films as thin as 50Å could be a good oxidation barrier layer for copper.

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