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Electroless Copper Seed Activated by 1nm ICB-Pd Catalytic Layer for Fine Cu Interconnections

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1.Introduction

Copper (Cu) is used widely for interconnection metal in ULSIs due to its lower resistivity and superior resistance against electromigration compared to conventional aluminum alloys [1]. The present damascene copper interconnections are fabricated by electroplating on a sputtered Cu seed layer. However, with a shrink in dimensions of interconnections, it is getting more and more difficult to form a continuous sputtered Cu film at side walls of fine via holes because the sputtering suffers from poor step coverage, which results in a void in electroplating [2]. Copper electroless plating is an efficient means of realizing conformal deposition profile [3-4], however, the adhesion between the Cu and the substrate is poor with the conventional wet chemical Pd catalysis adsorption pretreatment. We investigated Pd catalysis layer formation by the Ion Cluster Beam (ICB) method which is affords highly directional deposition suitable for high aspect holes, and found a high adhesion between electroless plated Cu layer and barrier metal layer after annealing [5], while electrical resistivity of Cu damascene interconnection was rather large around 2.5 – 3.0 μΩcm due to Pd diffusion in Cu. In this study, we investigated Pd thickness dependence on the properties of electroless deposited Cu films. Further we tried to use electroless plated Cu film activated by thin ICB-Pd layer for seed layer of Cu electro-deposition.

2. Experiment

Various thicknesses of ICB-Pd ranging from 1 to 20 nm were deposited on the surface of $TaN/SiO_2/Si$ substrates. Prior to electroless copper plating, all substrates were cleaned by ultrasonication in acetone at room temperature for 10 min. The main composition of the electroless copper plating solution were; $CuSO_4 \cdot 5H_2O$, $C_{10}H_{16}N_2O_8$ (EDTA), glyoxylic acid as a reducing agent, and additional agents such as 2,2'-dipyridine and polyethylene glycol. The pH of the plating solution was adjusted to about 12.5 with tetramethylammonium hydroxide (TMAH).

3. Results and discussions

Cu film deposited by electroless plating on thin ICB-Pd catalytic layer showed a good adhesion against substrate barrier metals such as TaN and TiN, which is strong enough to pass CMP of damascene process. The damascene Cu interconnections were fabricated by Cu electroless plating only. Pd thickness dependence of the resistivity of Cu damascene interconnection is shown in Fig.1. It is found that the resistivity of Cu interconnect decreased with thinness of ICB-Pd layer. The resistivity of interconnect reached 2.3 μΩ·cm when ICB-Pd thickness was thinner than 2nm. It is noticed that the resistivity increases about 0.2 μΩ·cm after anneal treatment at 400 ^{o}C, which is in agreement with SIMS analysis results that showed Pd diffusion into Cu films.

In order to realize Cu filling in a fine via holes with a high aspect ratio, the best method is to use electroless Cu seed layer displacing sputtered Cu seed layer for electrodeposition. For this purpose, we succeeded in establishing a condition to form 10nm continuous Cu film by electroless deposition.

Fig. 2-a and 2-b are cross-sectional SEM image and cross-sectional TEM image of via holes deposited with electroless plated Cu film using ICB-Pd. We confirmed that an uniform and continuous 10 nm Cu seed layer was formed at side wall and bottom. The formation of a very thin continuous Cu film is ascribed to a very high Pd nanoparticle densities even at the side wall of the via hole.

Then we accomplished hole filling by combination of 10nm electrolessplated Cu seed and Cu electro-plating. Figure 3 shows cross-sectional TEM micrograph of Cu filled via hole formed by this method. There is no void , and Cu grain size is between 200 to 600 nm. The resistivity of the Cu interconnects formed by the combination of electroless and electroplating is smaller than that formed by electroless plating only. This may be due to the difference in the grain size; electroless plated Cu has smaller grains compared to electroplated Cu films. Adhesion strength of Cu films measured by peel strength method is shown in Table.1. When thickness of ICB-Pd was 20nm, adhesion between electroless plated Cu film and TaN barrier

layer was 0.72 Kg/cm after anneal process. This value is larger than that obtained for sputtered Cu seed layers.

3. Conclusions

We succeeded in formation of 10 nm thick continuous Cu layer by electroless deposition using a thin ICB-Pd catalysis layer. The electroless plated Cu has a high adhesion strength to endure against CMP. Thus we formed Cu filled via and interconnections by combination of electroless seed deposition and electrodeposition of Cu, without sputtering. The resistivity of Cu interconnections is kept low value around 2.2-2.3 μΩcm when Pd layer thickness at the surface is smaller than 2 nm. Thus Electroless plating of Cu using ICB-Pd catalysis is promising method for sub-100nm Cu multilevel interconnection technology.

Reference

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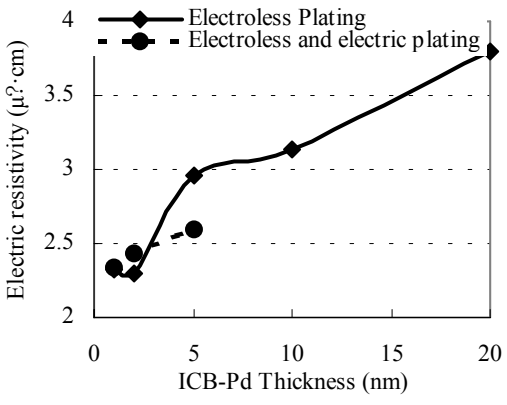

Fig. 1 . The resistivity of Cu damascene interconnect dependence of ICB-Pd thickness

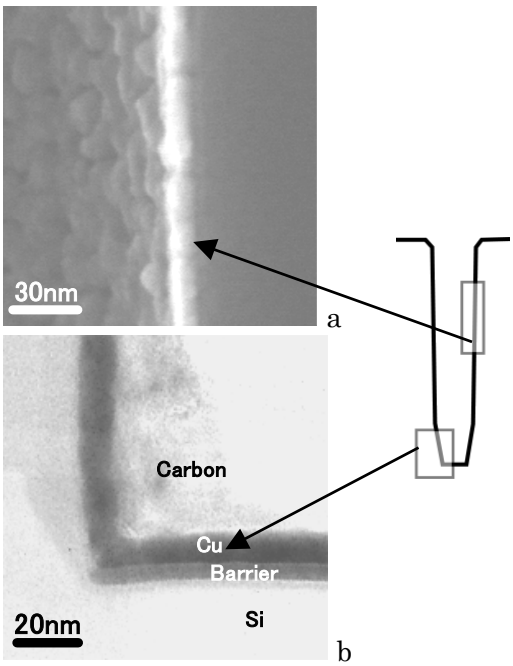

Fig. 2 Cross- sectional SEM and TEM images of the electroless copper plating for filling via-hole
a. SEM image, b TEM image

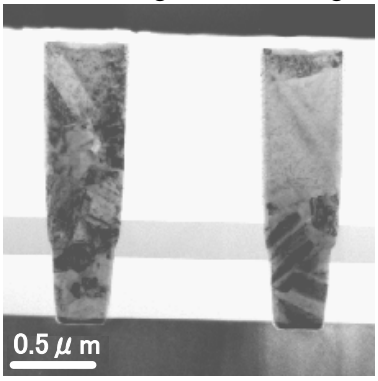

Fig.3 Cross-sectional TEM image of electroplated copper with electroless plated Cu seed

Table1 Adhesion of electroless plated copper

Treatment condition	ICB-Pd／ELP-Cu/EPCu anneal 400℃, 30min	TaN/ELP-Cu/EPCu anneal 400℃, 30min	TaN/sputter-Cu/ EP-Cu withou anneal	TaN/sputter-Cu/EP-Cu anneal 400℃, 30min
Adhesion (Kgf/cm)	0.72	0.11	0.25	0.35
Peeled surface	Cu/Pd /TaN	Cu/ TaN	TaN/ SiO_2	TaN/ SiO_2