Electroless Deposited Thin Silver Film and Its Properties

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To minimize the RC delay in the integrated circuits, low resistive metals such as silver and copper were required as interconnection materials. In the deposition methods of a thin metal film, electroless deposition has been focused for its various merits such as the capability of uniform deposition on large surface area, and no requirement for seed layer [1]. In Ag electroless plating, some researches were performed with cobalt (II) ion as a reducing agent [2], and it was proved that the addition of ethylenediamine accelerated the reducing ability of cobalt (II) ion [3]. But such studies were focused for thick silver film with fast deposition rate due to the difficulties in obtaining a thin continuous Ag film below 100 nm thick, and there were few researches about electroless thin silver film deposition for the low resistivity interconnection material used as a seed layer for electroplating, or as a conducting layer itself.

Used substrate was TiN (CVD, 10 nm) / Ti (PVD, 15 nm) / Si (p-type, (100)) structure, and was treated in diluted HF solution and Pd activation solution to remove native Ti oxide and to generate catalytic Pd particles, respectively. Silver thin film with a thickness below 100 nm was electrolessly deposited on Pd-activated TiN surface with cobalt (II) ion as a reducing agent and ammonia as a complexing agent of silver. EDTA was added as a stabilizing agent of cobalt ion to prevent the oxidation, and ethylenediamine was added to accelerate the reaction. All experiments were performed at room temperature.

The addition of ethylenediamine improved the film qualities, but it also accelerated the homogeneous phase silver reduction in the electrolyte, and large clusters were observed on the film surface after the deposition as shown in Fig. 1 (a). The addition of EDTA was considered to keep cobalt (II) ions from oxidation, but was not able to prevent the homogeneous phase reaction. To avoid homogeneous reaction, BTA which had been used as a corrosion inhibitor was added as a stabilizing agent. By the addition of BTA, stability of the electrolyte was significantly improved, and no particle formed in homogeneous phase was observed as shown in Fig. 1 (b). However, added BTA strongly adsorbed on the silver surface, and wetting property of silver was changed from hydrophilic to hydrophobic. The resistivity of silver film with the addition of BTA was over 100 $\mu\Omega$㎝, which was much higher value than the bulk resistivity of silver. Self-annealing effect resulting in about 60% decrease of sheet resistance was also observed as shown in Fig. 2. By annealing of silver film in nitrogen ambient at 300℃ for 30 minutes, the resistivity were decreased to 3.5 $\mu\Omega$㎝ in 70 nm thin films, which were similar phenomena that reported in silver-tungsten thin film electroless deposition with hydrazine as a reducing agent [4]. Compared to Ag bulk film, the high resistivity of deposited film may be due to the incorporation of BTA molecules among the grain boundaries. Deposited film had pure silver, and no contaminant below the detection limit of AES was observed as shown in Fig. 3.

The following results were obtained: A very thin and continuous silver film below the thickness of 100 nm could be electrolessly deposited with high conductivity and good surface morphology. The addition of BTA could stabilize the electrolyte, but electrical resistivity also increased slightly.

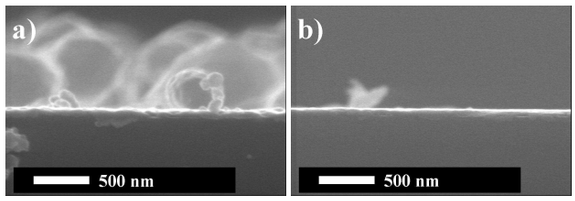

Fig. 1. FESEM image of the electroless deposited silver film (a) without the addition of BTA and (b) with the addition of 0.067 g/L BTA.

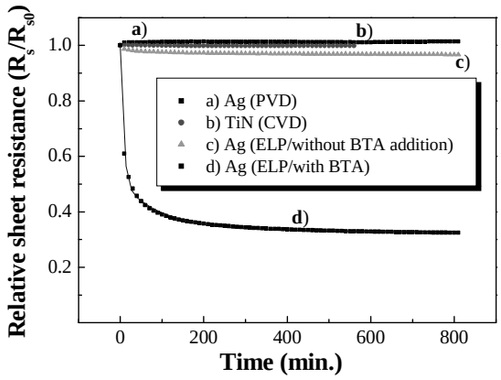

Fig. 2. Sheet resistance changes in room temperature after the deposition; (a) PVD Ag film (70 nm), (b) CVD TiN film (15 nm), electroless deposited Ag film (c) without the addition of BTA, (d) with the addition of 0.067 g/L BTA.

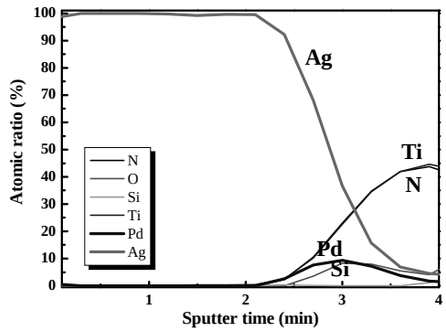

Fig. 3. AES depth profile of 70 nm thickness electroless deposited silver film with the addition of 0.067 g/L BTA.

References

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