

Thin film silver deposition by electroplating for ULSI interconnect applications

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Abstract—Ag seed layers were pretreated with 1 : 1,000 diluted nitric acid cleaning solution for 60 s to obtain a clean and oxide-free Ag surface. When an applied potential was less than -800 mV in Ag electroplating, the deposition rate was over $2,000$ Å/min and the resistivity of Ag deposit was 1.80 $\mu\Omega\cdot\text{cm}$. But the deposit film became rougher with a negative increase in the potential, and it was also observed through measuring the double layer capacitance. The resistivity of Ag film annealed at 350 °C for 30 min was decreased from 1.80 $\mu\Omega\cdot\text{cm}$ to 1.67 $\mu\Omega\cdot\text{cm}$ and the agglomeration of Ag grains was not observed on the surface of the annealed Ag films. To reduce the surface roughness, thiourea was added in the electrolyte and it was decreased below 15 nm.

Key words: ULSI Interconnection, Ag, Electroplating

INTRODUCTION

To reduce the resistance-capacitance (RC) delay times, many researches about advanced interconnect materials for ultralarge scale integration (ULSI) have been conducted [1-9]. Ag has the lowest room-temperature bulk resistivity and a high resistance against oxidation and silicide formation compared to Cu [10,11]. Furthermore, Ag self-encapsulating film is believed to act as a diffusion barrier instead of Ti and Al [12,13]. Therefore, the combination of Ag and low dielectric material may be the best metallization scheme for future integrated circuits (IC). However, it is difficult to deposit Ag by using conventional techniques in microelectronic interconnections [8,9]. In case of Cu, electroplating has shown good capabilities for Cu metallization in the electronic packaging and in ULSI interconnection because of excellent via/trench filling ability, good adhesion, low process temperature, and low cost [1-6]. In this study, electroplating was also applied for Ag deposition and the properties of Ag electrodeposit were evaluated as interconnect material. KAg(CN)₂ solution was used due to its good stability against light, high solubility of Ag, and high conductivity as a junction electrolyte [14, 15]. Our study was focused on the reduction of the resistivity of electroplated Ag film with adequate deposition potential and the control of surface roughness by adding thiourea to plating bath as brightener [16,17].

EXPERIMENTAL SECTION

Thin Ag layers (75 nm) were sputtered on TiN substrate as a seed layer for Ag electroplating, and the resistivity was measured to be 2.31 $\mu\Omega\cdot\text{cm}$. Prior to Ag electroplating, the seed surface was

pretreated with nitric acid. Then, 1 cm^2 Ag seed area was exposed to the plating electrolyte and the other part was blocked with teflon coating. All electrochemical experiments were performed in a three-electrode cell. 99.9% pure Ag wire was used as a counter electrode and the potential of Ag substrate was measured with reference to the saturated calomel electrode (SCE).

The electrolytes were composed of 184 g/l KAg(CN)₂, 71.8 g/l KCN, 0-5 g/l thiourea, and deionized water. In all cases, the pH of the electrolyte was maintained at 12 ± 0.1 . The plating baths were kept at the room temperature during electroplating.

Constant potential was served by an EG&G scanning potentiostat (model 362) for Ag deposition. All samples were rinsed carefully with deionized water and dried in N₂ stream after plating. Annealing was performed at 350 °C for 30 min in N₂ ambient condition.

Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) were applied to analyze the thickness and the surface morphology of Ag deposit. Linear sweep voltammetry (LSV) was conducted in order to verify the effect of an applied potential. EG&G Applied Research potentiostat/galvanostat (model 263A) and Lock in Amplifier (model 5210) were used for electrochemical analysis. The sheet resistance of Ag deposit was measured with 4-point probe station.

RESULTS AND DISCUSSION

To investigate the continuous formation of Ag native oxide, Ag substrates were exposed to air for 90 hrs. Sheet resistance (Rs) measurement revealed that Ag native oxide was continuously formed in 40 hrs and then acted as a passivation layer against Ag oxidation (Fig. 1). Because the metal oxide inhibits the charge transfer between Ag substrate and the electrolyte, Ag oxide should be removed to get uniform and dense electroplated Ag film.

Nitric acid solutions (1 : 100, 1 : 300, and 1 : 1,000) were used to remove the native oxide on Ag substrate. To determine the proper cleaning time and nitric acid concentration, Rs was measured. If Ag was further etched after the complete removal of the native oxide,

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†This paper is dedicated to Professor Chang Kyun Choi to celebrate his retirement from the School of Chemical and Biological Engineering of Seoul National University.

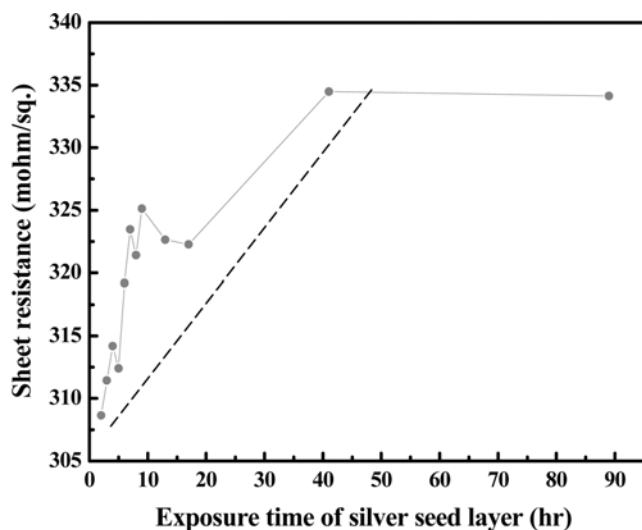


Fig. 1. Sheet resistance vs exposure time of a Ag seed layer for 90 hrs.

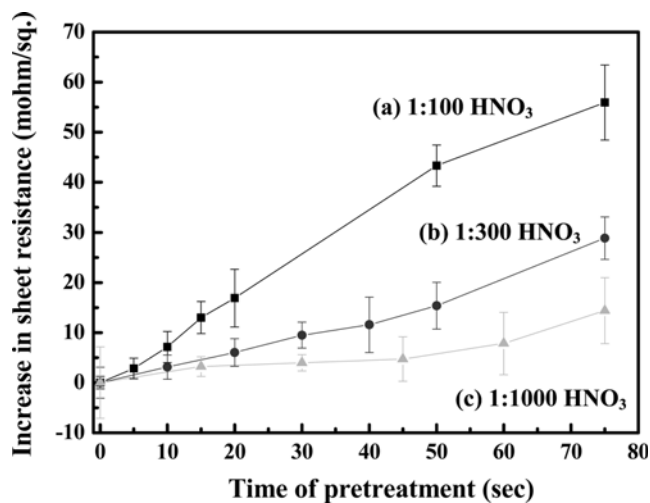


Fig. 2. Sheet resistance change after Ag oxide cleaning according to cleaning time with various concentrations of HNO₃ solution ((a) 1 : 100, (b) 1 : 300, and (c) 1 : 1,000).

Rs would increase because of the decrease in the thickness of Ag layer. Fig. 2 shows the change in Rs with the cleaning time according to the nitric acid concentration. Only when the 1 : 1,000 nitric acid solution was used, a precise transition in the change of Rs detected at 60 s. At higher concentration, the removal rate of Ag oxide was so fast that transition was not found in the graph. AFM analyses were performed on the Ag substrate pretreated with the 1 : 1,000 solution for 60 s and with the 1 : 300 solution for 30 s, respectively. Two cleaning conditions made the reduction of 7 mΩ/sq. in Rs. Root mean square (RMS) roughness values were 1.45 nm for the 1 : 1,000 solution and 1.62 nm for the 1 : 300 solution. These results showed that the pretreatment with the 1 : 1,000 nitric acid solution was more adequate for electroplating. We therefore used the 1 : 1,000 nitric acid solution for 60 s as a pretreatment process.

In linear sweep voltammetry (LSV) analysis, the equilibrium potential (E_0) of the electrolyte was -634 mV (vs. SCE) (Fig. 3). Potentials less than E_0 were applied for Ag electroplating. In order to investigate the effect of an applied potential on Ag electrodeposition, -700 , -800 , -900 , $-1,000$, $-1,100$, and $-1,200$ mV (vs. SCE) were applied on the pretreated Ag substrate for 240 s. As the applied potential increased negatively, the deposition rate increased from 550 Å/min to 9,200 Å/min. It was comparable to that of Cu electroplating (500–1,000 Å/min) [5]. Fig. 4 shows the resistivity of Ag films electroplated with different applied potentials. As the potential became negative over -800 mV (vs. SCE), the resistivities converged on 1.80 μΩ·cm. Its value was superior to that of CVD Ag film [9].

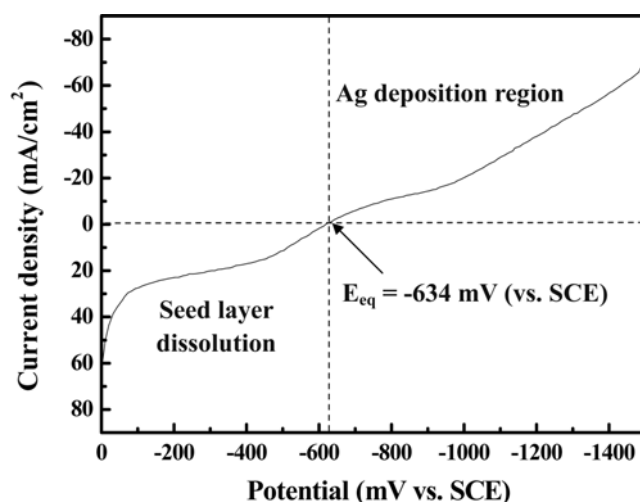


Fig. 3. Linear potential sweep in the range from 0 to 1.5 V (vs. SCE) with 10 mV/s scan rate.

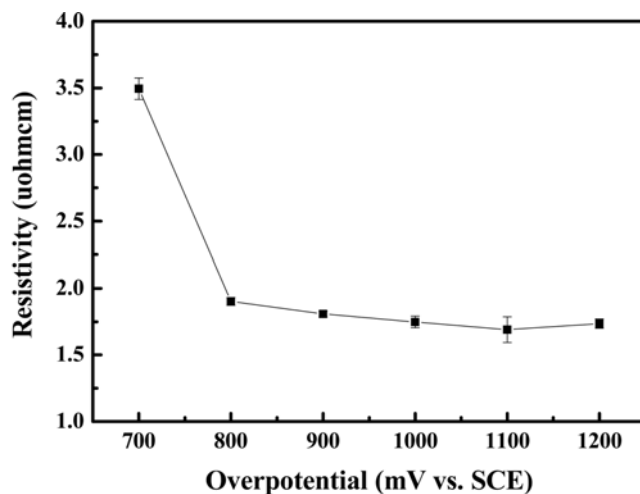


Fig. 4. The resistivities of Ag films according to a cathodic potentials.

Fig. 5 shows the planar and three-dimensional AFM images of Ag electrodeposit with different applied potentials. In all deposits, RMS roughnesses were higher than 20 nm, and those increased with the negative increase of the potential. The roughness of Ag films should be reduced by adding organic additives in the electrolyte for microelectronics applications. The surface roughness also can be monitored by measuring the double layer capacitance (C_{dl}) at the electrode surface.

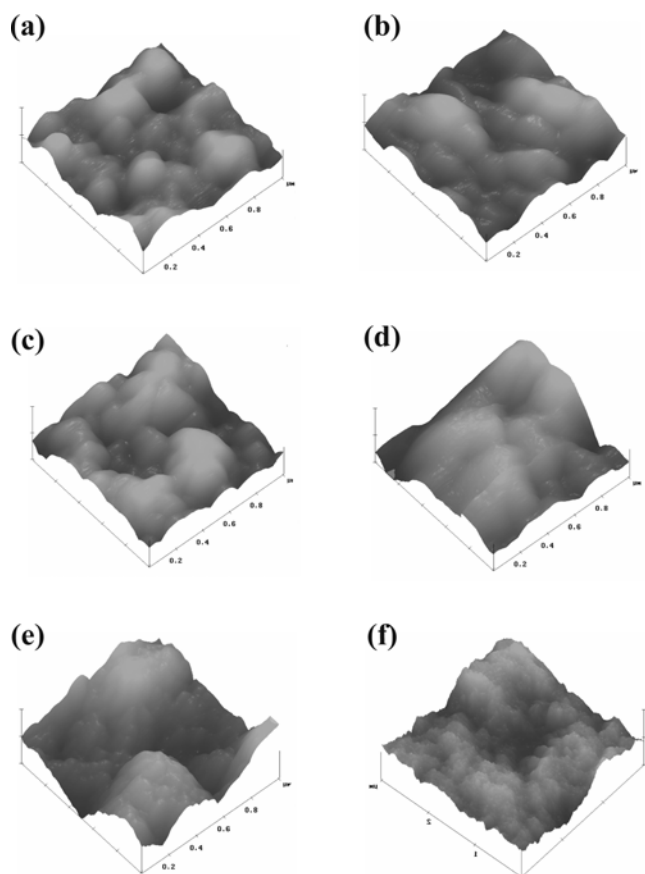


Fig. 5. AFM images of Ag films electroplated at (a) -700, (b) -800, (c) -900, (d) -1,000, (e) -1,100, and (f) -1,200 mV (vs. SCE). Each RMS roughness value was (a) 20.9, (b) 21.3, (c) 23.8, (d) 32.2, (e) 41.4, and (f) 62.3 nm, respectively.

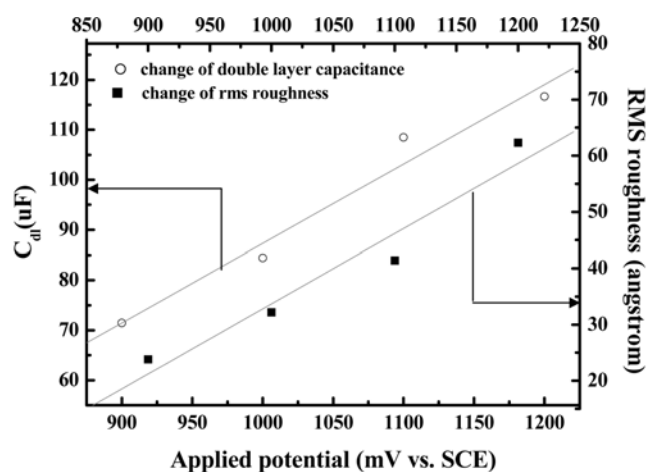


Fig. 6. Double layer capacitance from AC impedance analysis and RMS roughness of Ag films according to an electrode potential.

$$C_{dl} = \frac{\epsilon A}{d} \quad (1)$$

where C_{dl} represents the double layer capacitance, ϵ the dielectric constant, A the area of the electrode, and d the thickness of the elec-

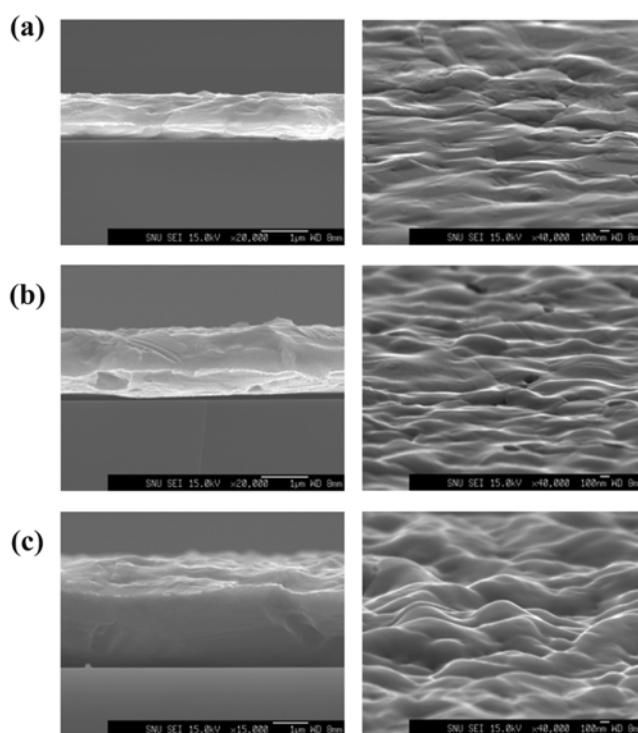


Fig. 7. FESEM images of Ag films annealed at 350 °C for 30 min. Ag films were electroplated at (a) -800, (b) -900, and (c) -1,100 mV (vs. SCE). The resistivities of the annealed Ag films were (a) 1.67, (b) 1.73, and (c) 1.75 $\mu\Omega\cdot\text{cm}$.

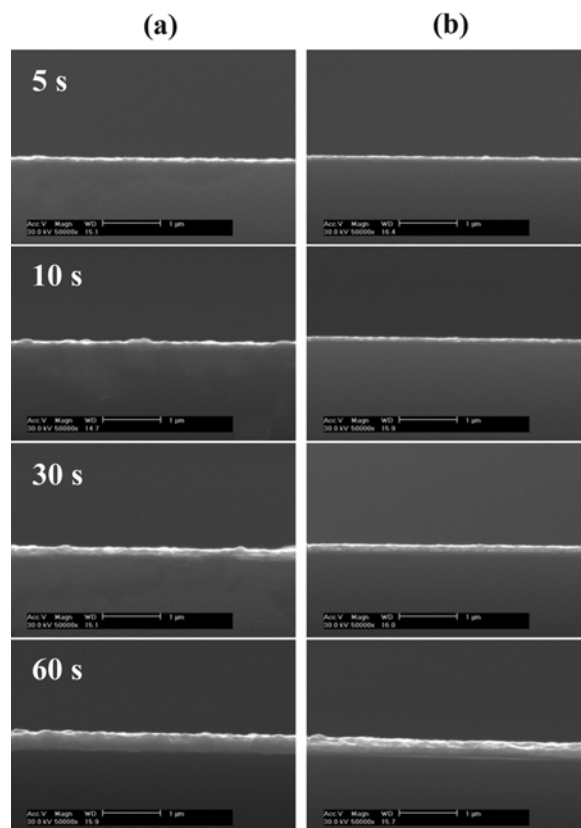


Fig. 8. Cross-sectional FESEM images of Ag films electroplated (a) without and (b) with thiourea.

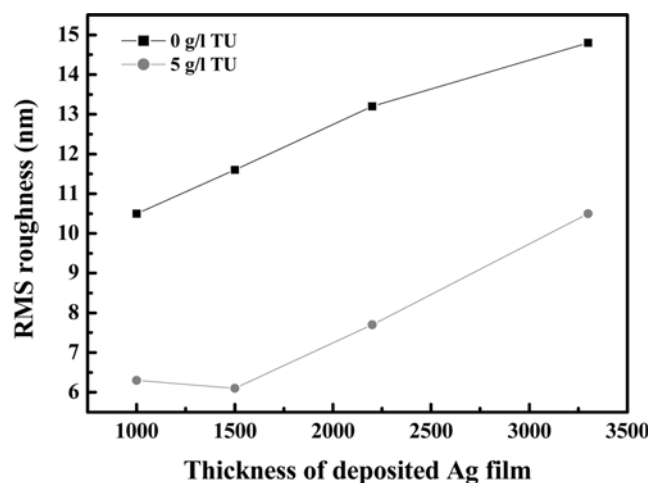


Fig. 9. RMS roughness of Ag films electroplated with and without thiourea according to the deposit thickness.

tric double layer, respectively. Fig. 6 shows the experimental C_{dl} values according to the applied potentials in the comparison with RMS roughnesses. Two values showed similar change, that is, both C_{dl} and RMS roughness increased with the negative increase of the applied potential.

Ag films were annealed at 350 °C for 30 min in N_2 ambient condition. After the annealing process, the resistivity of Ag film electroplated at -800 mV was reduced from $1.80 \mu\Omega\cdot\text{cm}$ to $1.67 \mu\Omega\cdot\text{cm}$. This value is only 5% higher than that of bulk Ag. Moreover, as shown in Fig. 7, there was no agglomeration of Ag grains during the annealing process.

In this study, thiourea was added in the electrolyte to decrease the roughness of the Ag deposit. Thiourea is a common brightener that can reduce the surface roughness below the wavelength of visible light in electroplating. Fig. 8 shows FESEM images of Ag electroplated at -800 mV (vs. SCE) without (Fig. 8(a)) and with 5 g/l thiourea (Fig. 8(b)). With the addition of thiourea, the formation of Ag cluster was completely suppressed and smooth Ag surface was observed. Thiourea could adsorb on Ag surface via S atom of it [18]. Its adsorption inhibited the surface diffusion of Ag adatom, and consequently, lateral growth of Ag grains was suppressed. The deposit film, therefore, showed a smooth and bright surface [17,18]. RMS roughness analysis also showed the brightening effect of thiourea. At the same thickness, the roughness levels of Ag electrodeposit sharply decreased by 5 nm with thiourea (Fig. 9).

CONCLUSIONS

Ag oxide was formed natively on the sputtered Ag seed layer. A clean and oxide-free Ag surface could be obtained with the 1 : 1,000 nitric acid pretreatment. In Ag electroplating, when the applied potential was less than -800 mV, the deposition rate of Ag was over 2,000 Å/min and the resistivity of Ag electrodeposit was converged on $1.80 \mu\Omega\cdot\text{cm}$. After the annealing process, the resistivity of Ag electrodeposit decreased to $1.67 \mu\Omega\cdot\text{cm}$, which was comparable to that

of bulk Ag. Ag electrodeposit, however, had a little rough surface and the RMS roughness of the Ag film was over 20 nm. To be applicable to ULSI interconnection, the reduction of surface roughness was tried by the addition of thiourea. Ag film electroplated with 5 g/l thiourea had 33% lower RMS roughness compared to that electroplated without thiourea.

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