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Design and Achievement of Superfilling Electroless Silver Deposition for Micrometer Trenches

Xu Wang[a], *, Weiwu Ma[a], and Carlos Fernandez[b]

[a] *College of Ecology, Lishui University, Lishui, 323000 China*

[b] *School of Pharmacy and Life Sciences, Robert Gordon University, Aberdeen, AB107GJ UK*

**e-mail: lsxywx@lsu.edu.cn*

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Abstract—Electroless silver bottom-up filling has been designed and investigated by linear sweep voltammetry. It was found that the addition of polyethylene glycol 4000 (PEG 4000) had a good inhibitory effect on the electrode reaction. Experiments showed that PEG 4000 had a strong depressing action in electroless silver deposition. Specifically, when the PEG 4000 concentration was 1.0 mg/L, the plating rate of electroless silver decreased from 5.7 to 2.3 μm/h. The bottom-up silver fillings for different-sized trenches were achieved in an electroless plating bath with the addition of PEG 4000. The trenches analysis showed that all microtrenches with different widths were completely filled by electroless silver plating.

Keywords: silver deposition, bottom-up filling, microtrenches

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INTRODUCTION

Copper has been employed extensively for metal interconnections via damascene electroplating in ultra-large-scale integration (ULSI) owing to its low resistivity and high reliability against electro-migration [1, 2]. Silver is the second material of choice for metal interconnections in a ULSI, again, owing to its high electromigration resistance and low resistivity. At present, copper is one of the main choices of material for this goal. The super-filling of copper by electroless plating has been validated by using a plating bath containing a deposition accelerator or depressor [3–5]. Copper can scatter into silicon substrates at high temperatures. Due to its high thermal conductivity and electrical conductivity and better electromigration immunity than copper, silver is an attractive interconnect material [6, 7]. It was reported elsewhere that super-filling of electroplating can be obtained with the addition of thiourea as a suppressor and benzotriazole as an accelerator in cyanide-based Ag electroplating [8]. It has also been stated that the addition of $SeCN^-$ as a single catalytic additive in cyanide-based Ag electroplating improves the electrochemical characteristics and filling properties of silver [9, 10]. Besides, others managed to perform void-free electroless Ag(W) deposition in micro-trenches with PEG as the inhibitor, but the aspect ratio of microtrenches was low [11, 12]. To the best of the authors' knowledge, that was the first time that electroless silver superfilling has been reported to design and investigate superfilling of electroless silver deposition. Compared with electroplating, electroless plating requires simple equipment, the operation is simple, and the process is easy to control.

In this paper, superfilling of electroless silver in a plating bath with the addition of PEG 4000 and a high ratio of microtrenches was completed. Linear sweep voltammetry (LSV) with PEG was carried out to clarify the effects of PEG on the electroless silver deposition. The deposition rates of silver were inhibited at the substrate surface. The effect of PEG 4000 on the superfilling of trenches by electroless silver deposition was investigated by deposition rate measurements and by cross-sectional scanning electron microscopy (SEM) observations. The changes in the superfilling phenomenon at various time intervals were also investigated.

EXPERIMENTAL

SiO_2/Si substrates with trench arrays were used to investigate the superfilling processes. A diffusion barrier layer was deposited on the trench surface of the SiO_2/Si substrates by physical vapor deposition, and then a 5 nm layer of copper was deposited on the sur- face of the diffusion barrier layer. Before the experiment, the substrates were pretreated with 1 M H_2SO_4 for 2 min to remove the native cupric oxide layer, washed in pure water, and then immersed into a plating bath. A field-emission-scanning electron microscope (JSM-6700 F) was employed to investigate the

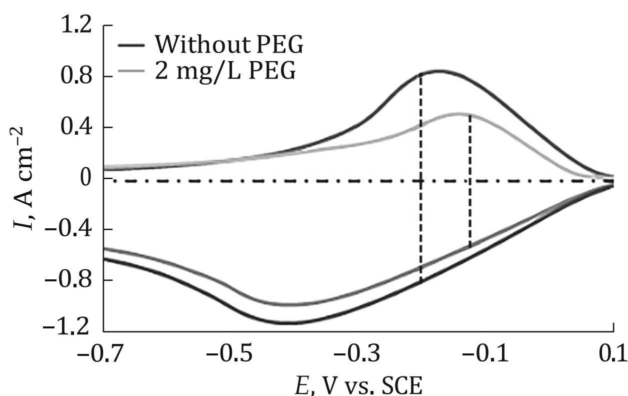

Fig. 1. Effect of PEG concentration on the polarization behavior of electroless silver plating bath.

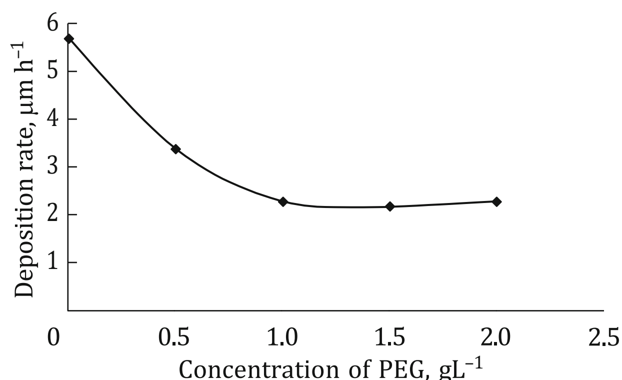

Fig. 2. The effect of PEG concentration on the deposition rate.

superfilling feature in cross-sectioned trenches after the deposition.

Electroless silver plating on para-aramid fibers using Seignette Salt as a reducing agent has been described previously [13] for which the authors obtained good results. Based on those results, we have optimized and improved the electroless plating bath. The electroless silver plating solution was formed by 0.03 mol/L $AgNO_3$, 0.6 mol/L $NH_3 \cdot H_2O$, and 0.04 mol/L Seignette Salt as a reducing agent. The concentration of PEG 4000 changed from 0 to 2.0 mg/L, and the bath temperature was maintained at 40°C. The bath could be stabilized for more than 30 days at 40°C.

A pure silver electrode with a 3.0 mm diameter was employed as the working electrode for LSV, a 4.0 cm^2 platinum sheet was utilized as the counter electrode, and Hg/Hg_2Cl_2 saturated with KCl was used as the reference electrode. The experiments were carried out at 25°C at a scan rate of 15 mV/s. The anodic polarization curves were gauged in the plating bath without Seignette Salt.

RESULTS AND DISCUSSION

An inhibitor should have a low diffusion velocity and a long chain molecule to create the concentration gradient in microtrenches. PEG 4000 was selected as an inhibitor for the present experiments to investigate its effects on the polarization curves of the electroless silver solution by LSV measurements.

The silver oxidation potential did not vary when additives were applied to the anodic reaction. However, the silver oxidation peak current associated with Seignette Salt changed with the addition of PEG 4000 (see Fig. 1). The oxidation peak current of silver was found to be 0.838 mA/cm^2 without any additive,

which then decreased to a value of 0.504 mA/cm^2 upon the addition of PEG 4000. In the cathodic reaction (see Fig. 2), the silver reduction potential was not modified by the additives. However, the silver reduction peak current observed for Seignette Salt varied with the PEG 4000 addition. The reduction peak current for the cathodic reaction of silver was found to be 1.134 mA/cm^2 without the additive, but it decreased to 0.991 mA/cm^2 with the addition of PEG 4000. As mentioned above, the change in the reduction and oxidation peak currents of silver when PEG 4000 was added was noticeable. This suggested that the silver reduction reaction was restrained by the addition of PEG 4000.

The electrochemical mechanism of electroless plating is based on the mixed potential theory. It is considered that any redox reaction can be decom

posed into a reduction reaction (the cathode reaction) and an oxidation reaction (the anode reaction). The reduction reaction and the oxygenation reaction are relatively independent; the reaction process of electroless plating anodes and cathodes can be explained by i–E curves.

When PEG 4000 was added, both the peak potential and current changed, resulting in the mixed potential of the electroless silver solution shifting from –0.103 to –0.204 V. In addition, the mixed current also shifted from 0.810 to 0.453 mA/cm^2, which caused the inhibition of the electroless silver deposition rate.

To further study the effect of inhibitors on the deposition rate of electroless silver plating, the effect of PEG 4000 on the deposition rate and time of electroless silver plating was studied. When PEG 4000 was added, the deposition rate of electroless silver plating was significantly reduced from 5.7 to 2.3 μm/h, equating to a reduction of ~60% (Fig. 2). This is due to an increase in the concentration of PEG 4000 from 0 to 1 mg/L during the electroless silver plating.

According to the aforementioned results of the experiment, when the PEG 4000 concentration was 1.0 mg/L in the electroless silver solution, the superfilling performances of the electroless silver bath with different channels were investigated. Figure 3 depicts the cross-sectional SEM results. The trenches of dif-

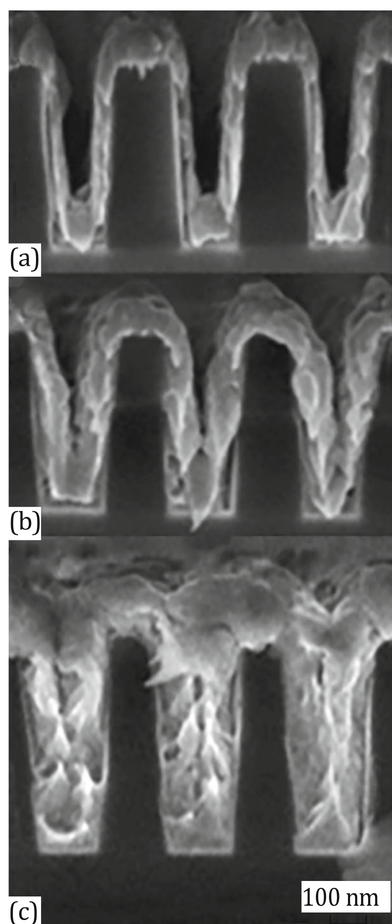

Fig. 3. Cross-sectional SEM images of trenches (width of 200 nm and depth 650 nm) at different depositing times; (a) 2 min, (b) 5 min, and (c) 15 min.

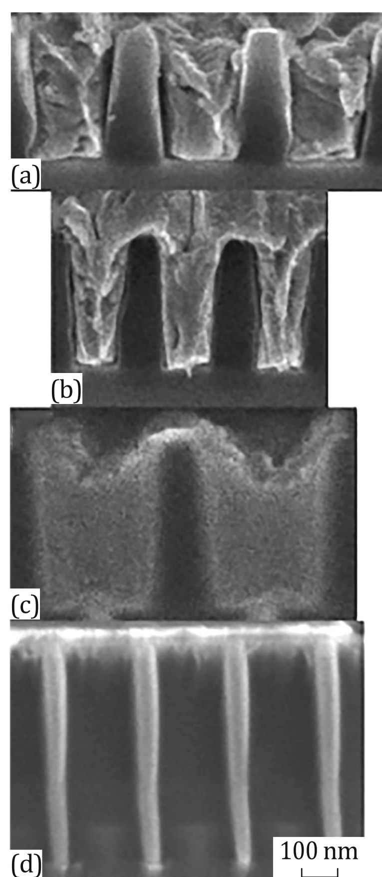

Fig. 4. Cross-sectional SEM micrographs of electroless silver profiles for various trenches: (a) trench width 270 nm, trench depth 470 nm; (b) trench width 150 nm, trench depth 490 nm; (c) trench width 360 nm, trench depth 600 nm; and (d) trench width 80 nm, trench depth 800 nm.

ferent sizes and aspect ratios (Fig. 3) were perfectly filled via electroless silver plating, and neither cracks nor gaps were found in the cross-sectional SEM images. That is, superfilling with the addition of PEG 4000 was successfully obtained.

Figure 3a illustrates the silver thickness at the sur face and the bottom of a trench. At the deposition time of 2 min, the thickness at the surface and bottom of the trench was found to be 102 and 153 nm, respectively. When the deposition time increased to 5 min, the silver thickness values increased to 111 and 271 nm, respectively (see Fig. 3b). Therefore, the Ag deposition rate was found to be high on the surface compared to that at the bottom of the trenches. Figure 3c shows that at the deposition time of 15 min, the trenches were completely filled with Ag. This is due to the addition of PEG 4000 with a low diffusion rate and a higher molecular weight in the electroless silver solution. In addition, silver prefers to be adsorbed on the surface of the substrate than to enter the sub-micrometer trenches. In the sub-micrometer trenches, a concentration gradation of PEG 4000 was also observed. At the same time, the deposition rate of electroless silver plating depended strongly on the PEG 4000 concentration in the electroless silver bath, however, the filling of electroless silver was accomplished.

Trenches with a width of 80 to 360 nm and a depth of 470 to 800 nm were also utilized to further investigate the superfilling of electroless silver as a function of depositing time (see Fig. 4). The plating bath, which contains 1.0 mg/L of PEG 4000, was used to examine the dependence of the depositing time on trench-filling characteristics. Figure 4 presents the sectional SEM images of trenches at different depositing times. The silver deposition rates both at the surfaces and at the bottoms of the trenches were inhibited by the PEG 4000 addition, but the level of inhibition of PEG 4000 on the surfaces and the bottoms of the trenches was different. This could be attributed to a greater inhibition on the surface compared to that on the bottom of the trenches.

The crystallography of bottom-up filling plated silver films with electroless plated from the plating

Table 1. Electroless plating solution composition

Destination	Chemical	Concentration
Source Ag	$AgNO_3$	0.03 (mol/L)
Complexing agent	NH_3H_2O	0.6 (mol/L)
Reducing agent	Seignette Salt	0.04 (mol/L)
Additives	PEG 4000	0–2.0 (mg/L)

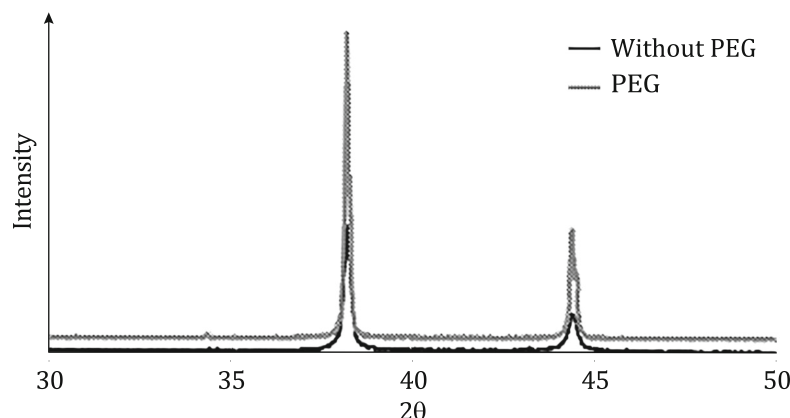

Fig. 5. XRD patterns of electroless plated silver films.

solution with and without PEG-4000 additive was characterized by X-ray diffraction (XRD) (Fig. 5). When the PEG 4000 concentration was 1 mg/L, the peak intensity ratio I(111)/I(200) was found to be 4.2, and the full-width at half-maximum (FWHM) of the (111) peak for a 1.2 mm thick silver film was found to be 0.23°. In comparison to an electroless-plated silver film without PEG 4000, the peak intensity ratio I(111)/I(200) was found to be 2.6 and the FWHM of the (111) peak for a 1.5 mm thick silver film was found to be 0.26°. The results clearly show that the crystallinity of the electroless plated silver film was inhibited by the addition of PEG 4000, however, the peak intensity ratio of I(111)/I(200) increased with the addition of PEG 4000. The electromigration resistivity performance increased by the silver film attachment to the (111) texture. This could be attributed to a low degree of anisotropy in the grain boundary transport. Put simply, the addition of PEG 4000 enhances the electroless plated silver film's performance.

CONCLUSIONS

The influences of PEG 4000 as an additive agent on the deposition rate and superfilling characteristics in an electroless silver solution were studied. It was found that PEG 4000 has a strong depressing impact on electroless silver deposition. When the PEG 4000 concentration was 1.0 mg/L, the plating rate of electroless silver decreased from 5.7 to 2.3 μm/h. The bot- tom-up silver filling for different-sized trenches was achieved in an electroless plating bath by the addition of PEG 4000, which can be attributed to the formation of a PEG 4000 concentration gradient inside the channels. Using LSV, it was established that the addition of PEG 4000 has a good inhibitory effect on both the anodic and the cathodic reactions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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