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# The use of electroless copper seed in electrochemical deposited copper interconnect

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**Abstract**

Copper (Cu) electroplating (EP) process requires a Cu seed to conduct the current. Conventional physical vapor deposition (PVD) seed suffers from poor step coverage while chemical vapor deposition (CVD) seed is cost-ineffective. We therefore propose the use of electroless (EL) technique as a Cu seed deposition method and demonstrate its integration with conventional Cu EP. The EL seed has excellent step coverage which when combined with the bottom-up fill capability of additives-based EP process, produces void-free fill. The EL seed-EP Cu film stack has good resistivity, roughness and acceptable (111) texture. However, some adhesion issues remain to be solved for this integration scheme.

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*Keywords:* Electroless; Electroplating; Copper; Interconnect

## 1. Introduction

The deployment of copper (Cu) in future generation integrated circuit devices has been called for in the Semiconductor Industry Association (SIA) roadmap. Damascene (inlaid) technique has become the choice of integration technique for Cu metallizations because it eliminates the need for Cu etch, reduces the number of process steps, and offers significant cost reduction. The formation of planarized inlaid Cu interconnects requires sequential deposition of a continuous diffusion barrier followed by Cu seeding/fill. Cu electroplating (EP) or electrochemical deposition (ECD) is the preferred method of fill for such damascene structure. However, the EP technique necessitates a Cu seed layer for conducting the currents during plating operation due to the use of highly resistive barrier materials. This Cu seed layer is usually deposited by chemical vapor deposition (CVD) or physical vapor deposition (PVD) technique.

CVD seed generally provides good step coverage but suffers from poor adhesion and high cost. PVD or ionized PVD (IPVD) such as the ionized metal plasma (IMP) or hollow cathode magnetron (HCM) technique can deposit the Cu seed with good adhesion but has the disadvantage of non-conformal step coverage. Since the EP process relies entirely on the seed layer to carry current from the top of the trench to the bottom, non-continuous PVD Cu seed tends to produce void in the feature. Besides, the thick PVD Cu seed (100–200 nm) at the field level will not be viable for more aggressive features such as those of 0.13 μm and beyond. The upper portion of the feature may be closed-off by the PVD seed prior to the EP process. However, this may lead to the formation of center and/or bottom voids in the feature [1].

In this paper, the electroless (EL) Cu deposition technique is used to deposit a thin conformal seed layer for the subsequent EP process. The deposition scheme is of low-cost due to the wet process involved. Details of the EL seed deposition process had been reported in our earlier work [2]. Our focus here is on the properties of the integrated EL seed-electrolytic Cu film, since there have been limited reported works on the integrated Cu film [3,4].

## 2. Experimental procedures

Oxidized silicon (Si) substrate coated concurrently with 30 nm of titanium (Ti) and 30 nm of titanium nitride (TiN) were employed in our studies. Both the TiN and Ti films were deposited in-situ without breaking the vacuum using the direct current (DC) sputtering method. These layers

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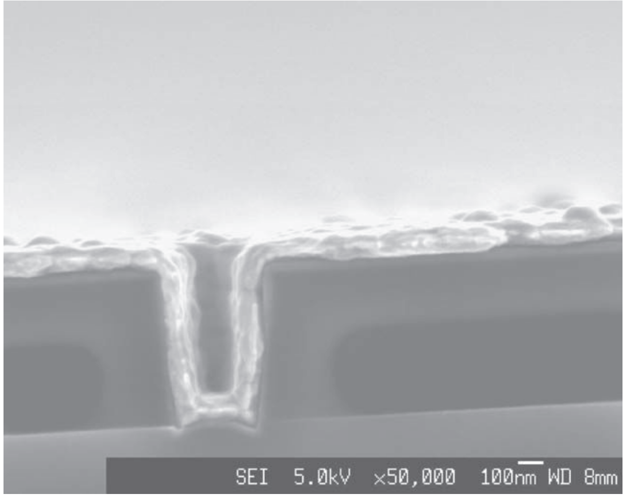

Fig. 1. Conformal step coverage of EL Cu (~ 80 nm thick) seed in 0.32-μm via, with AR = 1.8.

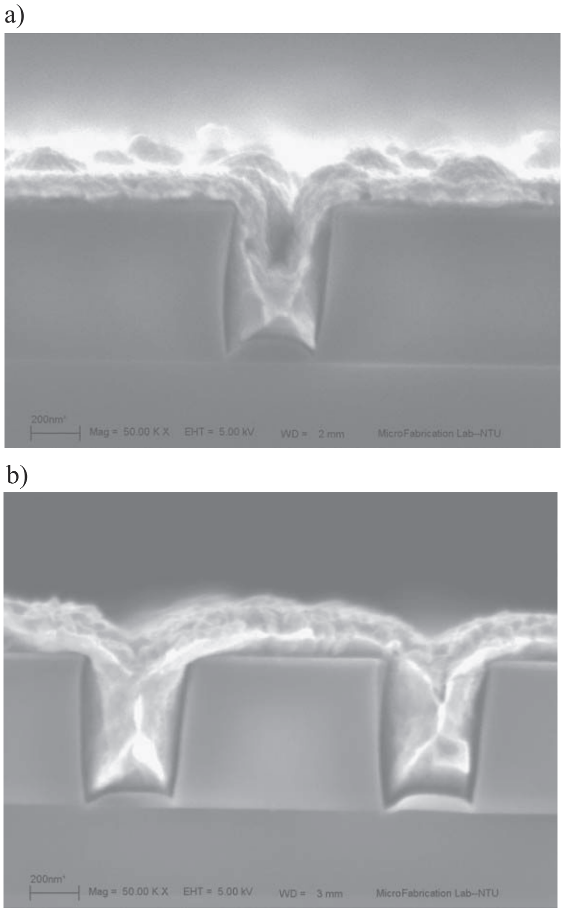

Fig. 2. Illustrations of bottom-up fills using electrolytic bulk-fill technique in 0.38-μm trenches (AR = 1.6): (a) after 20 s of Cu EP and (b) after 40 s of Cu EP.

served as a diffusion barrier as well as an adhesion promoter.

The deposition of EL Cu seed requires catalyzation of the TiN surface. This was achieved by immersing the TiN/Ti in a mixture of HF/$PdCl_2$ activating solution for 1 to 3 min. The EL Cu deposition involving chemicals such as copper sulfate ($CuSO_4$), ethylenediamine-tetraacetic acid tetrasodium salt (EDTA), formaldehyde (HCHO), and tetramethylammonium hydroxide (TMAH), was carried out at 65 °C for 3 to 5 min. The pH level was maintained at 13. More details on this technique could be found in our earlier work [2].

After the EL seed formation, Cu EP was carried out using a DC power supply and at a current density of 15 mA/cm$^2$. Commercial EP bath, i.e., Cubath-SC from Enthone-Omi was used for the evaluation study. The phosphorized Cu anode was employed, and no rotation was involved for both the EL and EP processes. The resistivity of the as-deposited film was measured using the ResMap™ four-point probe, while the surface roughness and morphology were determined using the Atomic Force Microscopy (AFM) technique (contact mode). Scanning Electron Microscope (SEM) was employed to examine the step coverage and the microstructure of the film. The thickness of the deposited film was obtained from the KLA-Tencor™ Alpha-Step profilometer. The crystallinity and texture of the deposited film were determined using the conventional $\theta$–$2\theta$ Bragg diffraction method, i.e., the Shimadzu™ XRD 6000 diffractometer. The standard scotch-tape test was used to assess the adhesive strength of the EL Cu film. Secondary Ion Mass Spectroscopy (SIMS) and Rutherford Backscattering Spec-

Table 1
Properties of EL seed

| Sample | Electroless (EL) Cu seed |
|---|---|
| Thickness (nm) | 50–80 |
| Roughness (nm) | ~ 9–10 |
| Resistivity (μΩ-cm) | 7–7.5 |
| Texture ($I_{111/200}$) | 6–7 × |
| Grain size (μm) (microstructure) | 0.1–0.2 |
| Adhesion test (scotch-tape test) | Passed |

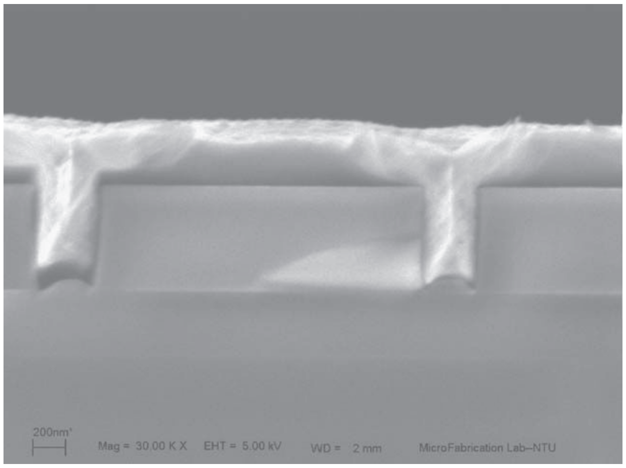

Fig. 3. Successful EL seed-EP bulk-fill Cu in 0.32-μm structure, with AR = 1.8.

Table 2
Properties of EL seed-electrolytic-filled Cu film

| Sample type | EL seed-EP Cu film |
|---|---|
| Thickness (μm) | 1 |
| Roughness (nm) | 9–10 |
| Resistivity (μΩ-cm) | 2.0–2.1 |
| Texture ($I_{111/200}$) | 5–6 × |
| Deposition rate (μm/min) | 0.15 |
| Adhesion (by scotch-tape test) | Passed, but with slight de-lamination |

troscopy (RBS) were also engaged to help determine the purity of the Cu films.

## 3. Results and discussion

The conformal step coverage achieved via the EL Cu seed is illustrated in Fig. 1, and its properties are summarized in Table 1. The data obtained agreed well with literatures [3,4]. The resistivity and roughness obtained for the EL Cu seed were higher than typical PVD seed. As for the (111) texture, the EL Cu seed was also observed to be more inferior to that of the PVD Cu seed. However, no adhesion issue was noted for the EL Cu seed.

The EL Cu seed serves as a nucleation layer as well as to conduct the current necessary for Cu electrolytic bulk-fill (through EL). The Cubath-SC contains additives (accelerators and suppressors) that are capable of accelerating the deposition rate within the feature while suppressing the deposition rate on the field, i.e., bottom-up fill. This bottom-up fill phenomenon is clearly seen in Fig. 2. The suppressor (organic macromolecules such as the polyethylene glycol ([PEG]) is usually very bulky and tends to stay at the field, deterring further deposition. The accelerators are mainly sulphur (S)-based organic molecules, and their small size allows for their rapid diffusion into the features, enhancing the deposition rate within the feature [5]. The microstructure of the EP-Cu on the EL-Cu seed (formed during the initial stage of EP) was examined using SEM. Very fine Cu grains of ~ 0.1 μm range was observed. This is attributed to the presence of accelerators (brightener) in the plating bath. These accelerators promote dense nucleation that contributed to the fine grain observed. Incidentally, the fine grain also accounted for the brightness of the plated Cu film [5]. The bottom-up deposition had led to excellent void-free fill of the damascene structures for down to 0.32 μm, with an aspect ratio (AR) of 1.8, as depicted in Fig. 3. It should be noted that the feature sizes demonstrated were actually being limited by the lithography technique used in the study rather than any inherent limitations in the EL seed or electrolytic-fill deposition process.

The properties of the integrated EL seed and electrolytic bulk-fill Cu film are presented in Table 2. The resistivity and surface roughness based on the PVD (IMP) seed were noted to be comparable to those of the EP Cu film. The high initial seed resistivity and roughness did not have any negative impact on the overall properties of the plated film. However, the (111) texture and adhesion of the EL-EP film were rather inferior when compared to the conventional PVD-EP Cu film. From the Transmission Electron Microscopy (TEM) of Fig. 4, de-lamination could be seen at the EL seed-ECD Cu interface. The EL seed (~ 50 nm) achieved excellent adhesion to the TiN barrier but upon EP the film to a thickness of 1 μm, degradation in adhesion was observed (Fig. 4). Further works have to be done to assess the effects of thermal annealing on the film's adhesion. The EL Cu seed adhered well to the substrate due to the compressive nature of the thin EL film. However, the 1-μm EP Cu film was in a tensile state of stress. Therefore, the cause of adhesion degradation between the EL seed and the plated

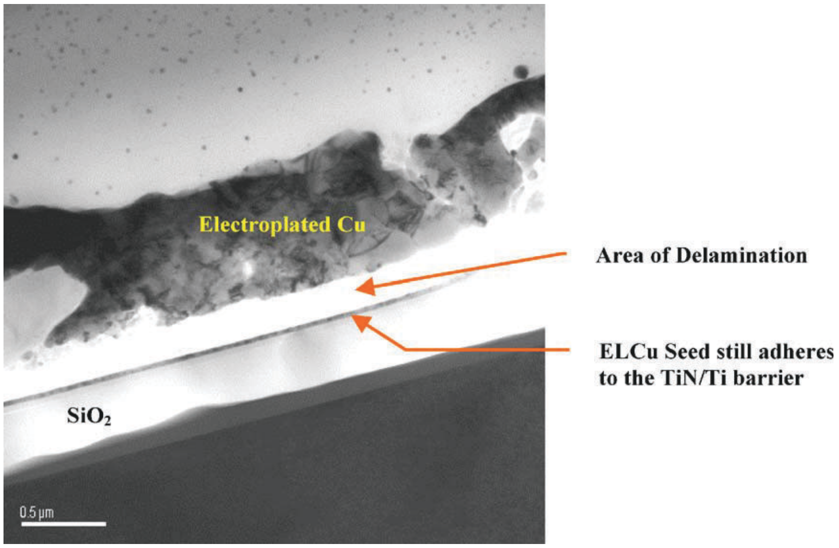

Fig. 4. TEM of EL Cu seed on EP Cu where de-lamination is noted at the EL seed-EP Cu interface.

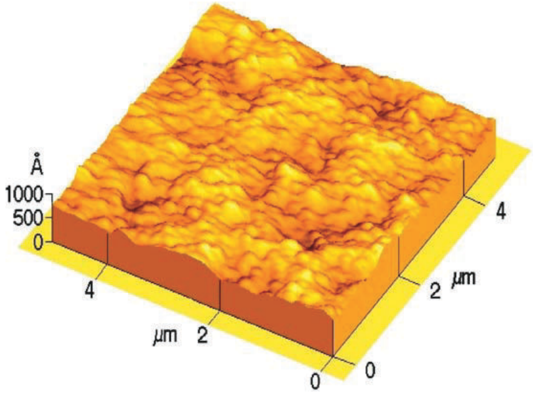

Fig. 5. Surface roughness of the EP Cu (on EL Cu seed). RMS roughness is ∼ 9 to 10 nm.

Cu was speculated to be due to the tensile nature of the plated Cu. The high density of twins observed in Fig. 4 was due to the crystallite nucleation and coalescence.

Qualitative SIMS had also been employed to determine the purity of the EL Cu seed and the plated Cu film. For the EL seed, the contaminants detected include chlorine ($Cl_2$), due to the hydrofluoric/palladium chloride ($HF/PdCl_2$) catalyzation process that was necessary for EL Cu deposition, and sulfur (S) that probably originated from the $CuSO_4$ source itself. RBS quantified the palladium (Pd) amount to be equivalent to ∼ 1 nm in an 80-nm-thick EL Cu film (calculation was based on the collected Pd atoms during RBS and the theoretical density of Pd). The EP Cu film suffered also from $Cl_2$ and S contaminations, and these were attributed to the additives used during EP. Fortunately, the carbon (C) and fluorine (F) incorporation had not been an issue in both types of films. Our SIMS results were comparable to the conventional IMP-EP film. Quantitative SIMS would be undertaken in future to further quantify the impurities.

The surface topography of the EP Cu (on EL Cu seed) shown in Fig. 5 presents a RMS roughness that range from 9 to 10 nm. This roughness is comparable to the EP Cu that is based on the conventional IPVD Cu seed.

## 4. Conclusion

For dimensions below 0.13 µm, IPVD seed may have difficulty providing a continuous surface coverage (requirement for void free Cu EP) due to sidewall thinning and overhang problem. EL Cu seed is a result of surface-initiated reaction and is highly capable of continuous surface coverage. Our studies have demonstrated the feasibility of using EL seed-electrolytic bulk fill (Cu EP) approach for Cu metallization. The advantages of following low cost, low deposition temperature and ease of integration to Cu EP, make EL Cu a viable seeding scheme. The higher resistivity and roughness of the initial EL Cu seed had not impose a negative impact on the subsequent EP Cu. Characterization of the integrated Cu film using the SIMS, AFM and TEM revealed resistivity and film roughness that were comparable to that of the PVD seed-electrolytic-filled film.

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