A novel bottom up fill mechanism for the metallization of advanced node copper interconnects

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Abstract— **A new alkaline copper plating bath enabling a unique and innovative bottom up effect for advanced damascene and dual damascene interconnect metallization is described. The formation of an ultra-stable polynuclear copper(I) complex during the early stage of the deposition process inhibits copper reduction, leading to a very strong suppressing effect. Bottom up growth is then achieved by means of selective breakdown of the suppressing layer from the bottom to the top of the features without any accelerator additive.**

Keywords—alkaline, copper, bottom up, mechanism, damascene, metallization, interconnect

I. INTRODUCTION

Copper electrodeposition for on-chip interconnection has been widely described in the semiconductor industry. Most copper plating chemistries currently used for copper interconnects are acidic, involving special additives that provide bottom up fill of the narrow structures[1]. However, as copper interconnects continue to be scaled down in order to improve device performance within a minimum area, conventional acidic bath chemistries have shown limitations, due to the non-uniform coverage of the copper seed layer obtained with physical vapor deposition (PVD). In fact, acidic copper plating baths require a perfectly continuous copper seed layer in order to achieve void-free filling, which is mainly due to poor nucleation density of the acidic bath on resistive under layers (e.g., the barrier layer). Several years ago, cobalt liner was widely studied as an additional layer to promote copper seed layer coverage onto barrier layer by improving copper wetting[2,3]. It resulted in a thin, continuous and conformal copper layer that facilitates the repair of discontinuities and the formation of a robust seed layer favorable to void-free copper filling. Also, geometry shrinking created high line resistance and trend to copper line failure. Interface quality between copper and dielectric barrier then appeared to be vital justifying again the introduction of cobalt layer to insure chip reliability, especially electromigration. Nevertheless, next generation interconnects will tend to adopt new integration schemes with increased copper volume inside the features in order to decrease RC delay. Additionally, aggressive critical dimensions (CD) will require a greater suppressing effect of

the plating copper chemistries to avoid premature closure of the trenches / vias. In order to achieve void-free filling of advanced node interconnects, novel and innovative plating chemistries have to be developed. The conventional acidic three-component bath (accelerator, suppressor, and leveler) used for decades must be reinvented in order to improve the suppressing effect and bottom up efficiency, and to prevent any pinch-off during the gap fill of very aggressive and narrow trenches (<20 nm CD). Those new plating chemistries should be efficient enough to allow void-free gap fill, perfect nucleation, and ideally, enable the removal of the cobalt liner in order to improve line resistance and reduce cost. In this paper is presented a novel alkaline copper plating chemistry that addresses all of the above requirements for advanced node metallization, thanks to a new and innovative bottom up mechanism.

II. BOTTOM UP MECHANISM OF ALKALINE COPPER CHEMISTRY

A. Polynuclear copper(I) suppressing layer

Many studies have been carried out to understand the bottom up effect induced by conventional acidic copper plating chemistries. Diffusion adsorption theory[4], Curvature Enhanced Accelerator Coverage (CEAC)[5]., and catalytic activity of the accelerator[6]. were highlighted as part of the copper bottom up growth in damascene structures. Another very interesting paper describes the bottom up effect as a result of the breakdown of the suppressing layer poly-ethylene glycol-chloride from the bottom to the top of the feature [7].
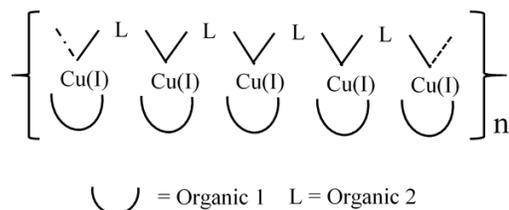
Fig. 1. Suppressing layer formed during the early stage of the plating process
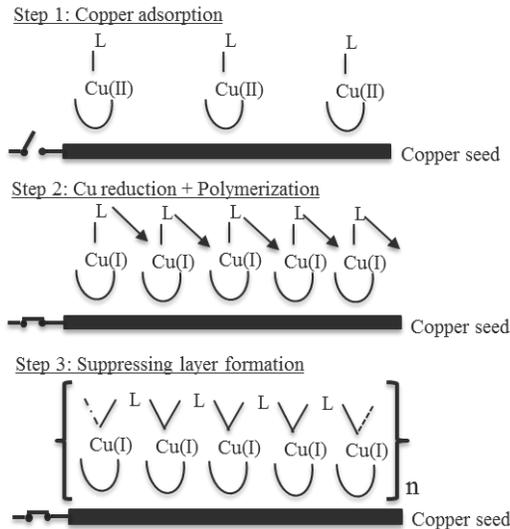
Fig. 2. Polynuclear Cu(I) suppressing layer formation mechanism

Only a few papers report the bottom up mechanism of alkaline copper plating baths. As an example, Joi *et al.* [8]. describe the bottom up mechanism of an alkaline copper plating bath to be non-CEAC. In this paper, we present a new and innovative example of the bottom up mechanism in an alkaline plating bath, based on the *in situ* formation of a highly stable suppressing layer made of a polynuclear copper(I) (Figure 1). The use of organic complexing molecules in the copper plating bath provides many advantages during the plating process; in particular, to improve copper nucleation density and reduce terminal effect. In this new formulation, we also use an organic complexing agent (**L**) as a reactant to initiate polymerization of the intermediate Cu(I) complex formed during the early stage of the cathodic reduction (Figure 2).

Then, the resulting suppressing layer formed at the copper seed surface avoids the reduction of Cu(II) to Cu(I) (1st reduction), and consequently, the reduction of Cu(I) to Cu(0) (2nd reduction). The consequence is that very few nanometers (< 2nm) of copper are deposited on the flat surfaces over a period of several minutes or even hours. The suppressing layer forms on the entire surface of the substrate to be plated, including sidewalls and bottom of the trenches / vias. The bottom up fill of damascene and dual damascene structure is then achieved through selective degradation of the suppressing layer from the bottom to the top of the feature without the use of any accelerator additive.

B. Bottom up mechanism by breakdown of polynuclear Cu(I) suppressing layer

Free Cu(I) is necessary to the formation of metallic copper and the launching of bottom-up fill. In that purpose, suppressing layer needs to be preferentially destabilized at the bottom of trenches and locally broken to allow copper reduction.
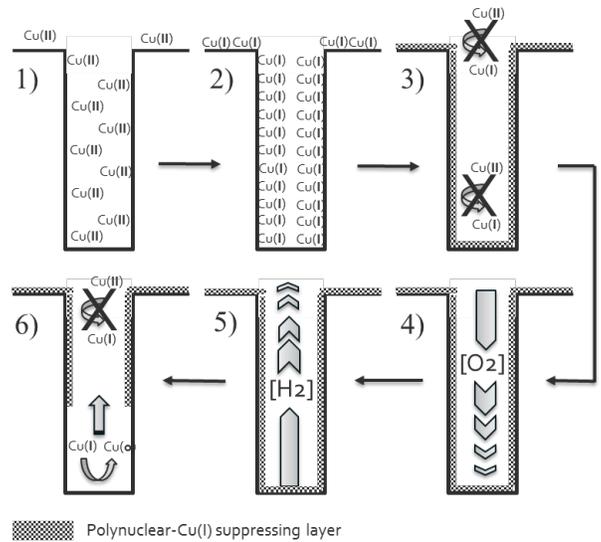
Fig. 3. Bottom up mechanism induced by selective breakdown of the polynuclear Cu(I) suppressing layer.

The entire bottom up mechanism is summarized in Figure 3. After reduction of Cu(II) to Cu(I) (Figures 3.1 and 3.2), the suppressing layer is formed, and copper reduction can no longer occur at the copper surface due to steric inhibition induced by the polynuclear Cu(I) complex (Figure 3.3). Nevertheless, small molecules such as oxygen (O_2) and water (H_2O) can pass through the suppressing layer, and undergo reduction at the copper seed / electrolyte interface. H2O reduction potential being more negative than O_2 reduction potential, O_2 is firstly reduced and enters a diffusional mode in the trenches. Gradually, O_2 concentration will decrease at the bottom of the trenches (Figure 3.4), leading then to the H_2O reduction. Consequently, hydrogen (H_2) will accumulate on the bottom of the trenches (Figure 3.5). The polynuclear Cu(I) complex being unstable under hydrogen atmosphere (hydrogen cleavage of the organic to metal bond), the breakdown of the suppressing layer occurs first at the bottom of the trenches, releasing un-suppressed Cu(I) that can then be reduced to Cu(0) (Figure 3.6). The trenches and vias are then completely filled until the top of the features.

III. CHARACTERIZATION OF THE POLYNUCLEAR CU(I) SUPPRESSING LAYER

A. Current-Voltage (CV) analysis

The suppressing layer formation was highlighted using current-voltage analysis with a rotating disk electrode (RDE). A three-electrode single-compartment electrochemical cell was used. The working electrode (WE) is a polished copper disk in an epoxy resin (d = 5 mm). The counter electrode (CE) is a polished platinum disk, and a saturated calomel electrode (SCE) was used as reference. The experiment was carried out in alkaline chemistry with 0.05 M K2SO4 as a supporting electrolyte
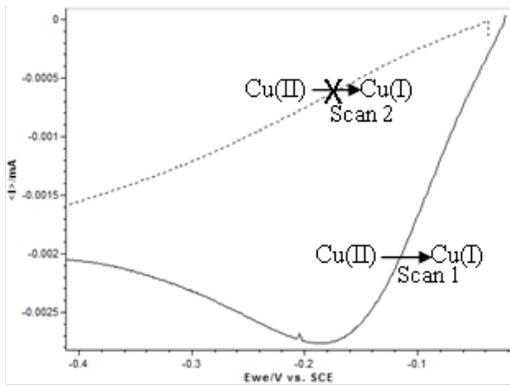
Fig. 4. Two successive cathodic polarizations at 20 mV/s from OCP to -0.41 V/SCE in N₂ environment.

The electrolyte solution was carefully degassed with dry nitrogen. Successive cathodic polarizations were performed at 20 mV/s from open circuit potential to -0.41 V/SCE (Figure 4).The reduction of Cu(II) to Cu(I) is responsible for the cathodic peak with a peak potential of -0.19 V/SCE. A second scan was performed 2 seconds after the first scan. The peak reduction of Cu(II) to Cu(I) disappeared during the second scan, showing the suppression of copper reduction after formation of the polynuclear Cu(I) layer.

B. Overpotential measurement analysis

Figure 5 shows overpotential measurement at -0.5 mA/cm² of the described alkaline chemistry, and overpotential variation when 200 ppm of polyethylene glycol (PEG) is added to a conventional acidic copper chemistry containing chloride anion (Cl). Copper concentration is equivalent in both cases. After PEG addition in the acidic bath, overpotential increases from -0.08 to -0.24 V/SCE characterizing the PEG-Cl suppressing effect. However, with the same current density, overpotential observed for the described alkaline bath is higher than -1.2 V/SCE without any additive in the bath. Therefore, it is expected that the suppressing effect induced by the polynuclear Cu(I) layer is considerably higher than conventional PEG-Cl suppression observed with acidic chemistries.
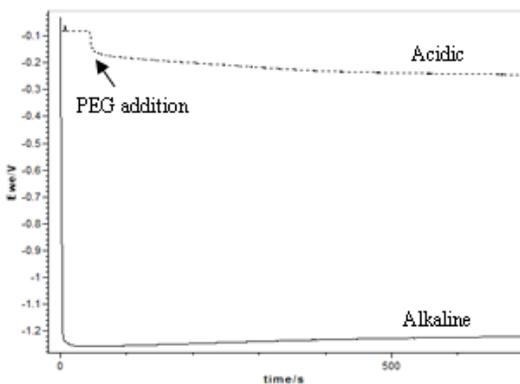
Fig. 5. Overpotential measurement at -0.5 mA/cm² for alkaline and acidic chemistries

C. Bottom up fill observation through Scanning Electron Microscopy (SEM) analyses

The bottom up fill mechanism described in this paper leads to void-free filling of narrow trenches without the use of any additive in the bath. Figure 6 shows SEM cross sections performed at two different process charge values during the filling process in order to enhance the copper bottom up growth. Field and sidewall suppression can be easily observed on the SEM cross section. Only 2 nm of copper was deposited on the top surface during the complete filling of the trenches.
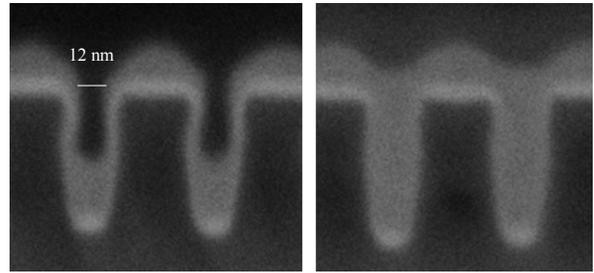
Fig. 6. SEM micrograph of trenches at two different process charges.

IV. CONCLUSION

We described a novel and innovative bottom up mechanism in this paper involving an alkaline copper plating bath without the use of any additional additives, such as accelerator or suppressor. The formation of a stable suppressing layer made of polynuclear Cu(I) complexes during the early stage of the plating process was proposed, and verified by current-voltage analysis. Bottom up filling of narrow trenches was observed by SEM cross section and was explained as the selective breakdown of the suppressing layer from the bottom to the top of the trenches due to hydrogen accumulation.

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