A New Copper Electrodeposition Scheme to Reduce Void Defects after Chemical Mechanical Polishing

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ABSTRACT

In this article, pulse current (PC) was applied to deposit copper onto copper seed layer. In addition, chloride ions (Cl^-), polyethylene glycol (PEG), bis(3-sulfopropyl)disulfide (SPS) and Janus Green B (JGB) were used as additives and compared with baths without additives. Pulse frequency was varied to investigate its influence on the resistivity and the crystal orientation. When PC frequency is equal to 100Hz, the maximal (111)/(200) with low resistivity is achieved in the presence of additives. Furthermore, the highly (111) crystal orientation belonging to close-packed arrangement is beneficial for reducing void defects during chemical mechanical polishing (CMP). Hence, we proposed a modified filling approach which is beneficial to the polishing in CMP based on the above optimal condition. We used direct current (DC) to fill the features in the first step, and then PC was applied to complete the whole deposition. As a result, the copper deposit shows improved properties after CMP process.

Keywords: electrodeposition, CMP, orientation, pulse current, resistivity

1 INTRODUCTION

Copper has replaced aluminum as the interconnect material in integrated circuits (ICs) due to its low electrical resistivity and superior resistance to electromigration [1-3]. In response to this change, the dry etchback process has been replaced by the dual-damascene technique, in which CMP is applied to remove the overburden copper, also called overplating, and to planarize the wafer surface [4, 5]. In addition, copper is deposited via electroplating approach. Hence, the properties of deposited copper, such as resistivity, grain size and crystal orientation, are influenced by the plating bath composition, additives, operating condition, current waveform and annealing condition [7-11]. Deposited copper with highly (111) orientation not only has better electromigration resistance and lower resistivity but also reduce void defects in the CMP process [12, 13].

Electrodeposition by PC plating has been demonstrated to be superior to DC plating because finer grain-size and lower porosity deposits could be constructed from pulse plating with suitable parameter control [14, 15]. Until now, few researches addressed to the effect of PC frequency on the properties of deposited copper. Chang et al. [7, 11] reported that the resistivity decreased with increasing PC frequency in a plating bath with some commercial additives consisting of a filling promoter and a wetting agent. However, in the plating bath including PEG, smallest resistivity can be obtained at an optimal 100 Hz frequency. This seemingly inconsistent result implies that the behavior of additives may affect the resistivity of deposit. It suggests that the effect of PC frequency on the properties of copper deposit is not well known. Moreover, information regarding a practice performed in the plating bath with chloride ions (Cl^-), polyethylene glycol (PEG), bis(3-sulfopropyl)disulfide (SPS) and Janus Green B (JGB) additives is even more lacking. In this study, we investigated the influence of additives and pulse frequency on the resistivity and crystal orientation of copper deposit in the plating with above additives. Then we developed a plating scheme to obtain copper deposit with highly (111) orientation, which is beneficial to the CMP process following copper deposition.

2 EXPERIMENTAL

Deposition experiments were performed on blanket wafers, prepared by depositing a 30 nm sputtered TaN diffusion barrier layer and a 150 nm sputtered copper conduction layer on *p*-type silicon substrate with (100) orientation. A fragment of blanket wafer (1×1 cm^2) was firstly mounted on the rotating disc electrode (RDE) adaptor, basically following the design reported by Taephaisitphongse et al. [16]. A copper foil was used as anode. The plating bath was operated at room temperature and rotated at 500 rpm.

Copper was deposited with DC or PC. The waveform of PC was controlled with a 20 mA/cm^2 cathodic peak and 0.5 duty cycle. The pulse frequency for PC was 10, 100 and 1000 Hz. The PC was generated from a potentiostat/galvanostat (EG&G PARC model 362) which was controlled by a function generator (BNC Corp. model 625). The average current density of PC and the current density of DC was 10 mA/cm^2. Each experiment had equal

total charge.

The basic composition of the plating bath was 0.2 M $CuSO_4 \cdot 5H_2O$ and 1.8 M H_2SO_4. To modify the deposit, 50 ppm Cl^-, 350 ppm PEG (4000 average molecular weight), 2 ppm SPS and 2 ppm JGB were added into the bath. All chemicals were of analytical grade.

Linear sweep voltammetry (LSV) was performed in a three-electrode cell to analyze the electrochemical behaviors of electrolytes. A copper disc 1.27 cm in diameter was used as working electrode along with a Pt counter electrode and a saturated calomel Electrode (SCE) reference. The reference electrode was placed close to the working electrode to reduce the ohmic overpotential. Prior to deposition, the working electrode was carefully polished with fine emery paper, and then rinsed with deionized water. The potentiodynamic polarization sweep of the working electrode was performed from -0.2 to -1 V at 5mV/s scan rate and 200 rpm. The resistivity of the plated samples was measured with a four-point probe (CPS-05, Cascade Microtech, USA) and an α-step instrument (P-10 Surface Profile, TENCOR, USA). The deposited copper film was characterized by field emission scanning electron microscopy (FESEM) for morphology inspection and x-ray diffraction (XRD) for crystal structure.

3 RESULTS AND DISCUSSION

The steady-state i-E characteristics of plating with and without additives are shown in Figure 1, which is in agreement with previous studies [6]. The addition of a package of commercial additives inhibits the deposition of copper compared to the additive-free electrolyte. This is reasonable since the overpotential in the plating bath with additives is larger than that in the additive-free electrolyte at the same current density.

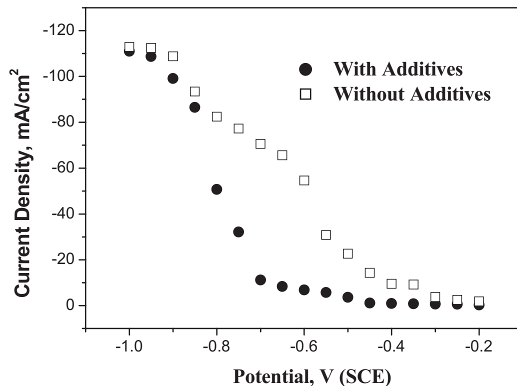

Figure 1: Linear Sweep Voltammetry in the plating baths with and without additives. The plating bath was operated at room temperature and was rotated at 200 rpm. The scan rate is 5 mV/ sec.

Based on the kinetics of crystallization, the nucleation rate, ν, is given by the following equation.

$$\nu = B\exp\left\{-K/\eta^2\right\} \tag{1}$$

where the constants B and K are specified for a given metal and temperature and η is overpotential. According to Eqn.1, the nucleation rate increases exponentially with increasing overpotential. In principle, a balance is established between the two crystallization modes, building up existing crystals or formation of new nuclei. In presence of additives, the formation of new nuclei is favored. Therefore, a decrease of grain size is expected. Since the properties of deposited copper may be dependent on the change of surface morphology, we expect the properties of copper deposit could be different between plating baths with additives and without additives.

The effect of pulse frequency on the resistivity of copper deposit in baths with and without additives is shown in Figure 2, which shows that the resistivity becomes smaller as the frequency is increased from 10 to 100 Hz. However, the resistivity increases and approaches the DC process when frequency increases over 100 Hz. In addition, in the presence of additives, the resistivity is generally reduced, consistent with the result of Moffat et al. [6] with DC plating.

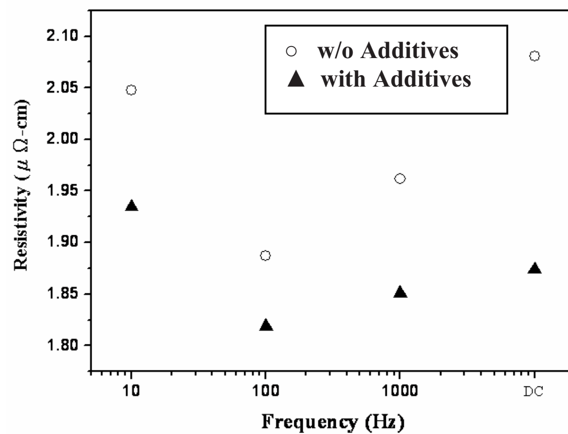

Figure 2: Effects of PC frequency on the resistivity in the baths with and without additives. Here, all Cu films are thermal annealed at 200℃ with 1 min after electroplating.

Moreover, the effect of pulse frequency on the crystal orientations of copper deposit in baths with and without additives is shown in Figure 3. Apparently, (111) is the dominant crystal orientation in any case. Without additives, the influence of pulse frequency on crystal orientation is not significant. However, in the present of additives (111)/(200) is greatly influenced by the frequency and reaches a maximum at 100 Hz. Hara et al. [12] reported that the (111) orientation has low resistivity and better electromigration resistance. Our results show that PC at 100Hz frequency

has the maximum (111)/(200) ratio and the lowest resistivity, which is also consistent with that reported by Hara et al. [12]. However, Chang et al. [7] observed that the resistivity decreased with increasing frequency in a bath containing a filling promoter and a wetting agent. Their results are inconsistent with ours, implying that the use of different additives may affect the properties of copper deposit.

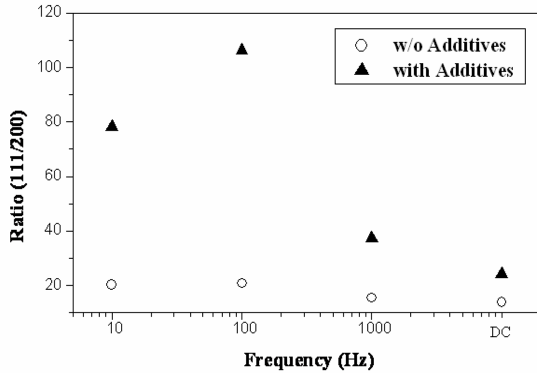

Figure 3: Effects of PC frequency on the crystal orientation in the baths with and without additives. Here, all Cu films are thermal annealed at 200 ℃ with 1 min after electroplating.

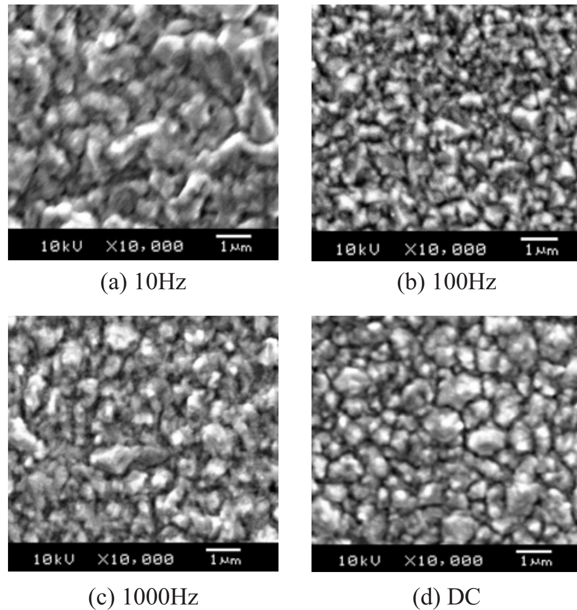

Figure 4: Surface morphology of copper deposit with PC plating at various frequencies as well as with DC at 10 mA/cm^2 in the presence of additives.

The surface morphology of copper deposit with PC at various frequencies as well as with DC at 10mA/cm^2 in plating bath with additives is shown in Figure 4. Clearly, the grain size of copper deposit becomes smaller as the frequency increases from 10 Hz to 100 Hz. When frequency increases from 100 Hz to 1000 Hz, the grain size starts to grow. It implies that the overpotential should increase as the frequency increases from 10 Hz to 100 Hz and then it should decrease as the frequency increases over 100 Hz according to Eqn.1. The overpotential caused from polarization in an electroplating process can derived from the surface, concentration, and ohmic polarization [16].

$$\eta = \eta_{conc} + \eta_{ohm} + \eta_s \tag{2}$$

where η_s , η_{conc} and η_{ohm} means surface, concentration and ohmic overpotential respectively. In particular, the ohmic overpotential could be neglected if the reference electrode is placed very close to the working electrode. When the pulse current density is low and the RDE provides sufficient agitation, the concentration overpotential can be neglected. By the Butler-Volmer equation [17], the faradic current density without additives at the electrode is then controlled by the surface overpotential. If we assume that the fraction of electrode surface blocked by additives is θ_A , the Butler-Volmer equation can be written as follows,

$$i_f = i_0(1-\theta_A)\left(\frac{C_s}{C_b}\right)^{\gamma} \times \left[\exp\left(\frac{\alpha_a nF}{RT}\eta_s\right) - \exp\left(-\frac{\alpha_c nF}{RT}\eta_s\right)\right] \tag{3}$$

From Eqn.3, the surface overpotential is related to θ_A . Moreover, the grain size was found to reach a minimal value when the pulse frequency was equal to 100 Hz. It suggests that the suppressor or leveler is most active and θ_A reaches a maximum at 100 Hz.

Furthermore, it has been reported that the void defects in CMP process decreases as the (111)/(200) ratio increases [13]. The use of pulse plating at 100 Hz pulse frequency to deposit copper film could reduce defects in CMP process. However, the use of pulse current to fill features is difficult since many parameters should be modified. Beside, the function and influence of additives during pulse plating is more perplexing [18]. Hence, we propose a revised deposition approach which can fully exploit the benefits of both DC and PC. This new scheme comprises utilizing DC to fill the features first and then PC at the end to reduce defects in the CMP operation. Prior to adopt this approach, the switch time should be determined. A series of FESEM cross-sectional images of partial fill sequence of electroplated copper in approximately 200nm wide, 400nm deep trench is shown in Figure 5(a). So the switch time can be determined. After that, the deposit will be subjected to

CMP and should be operated by PC. Once the switch time is determined, the deposition result by means of the DC/PC combination is shown in Figure 5(b). The deposit seems to exhibit a uniform and continuous texture and there is no sign of defect due to the current switch.

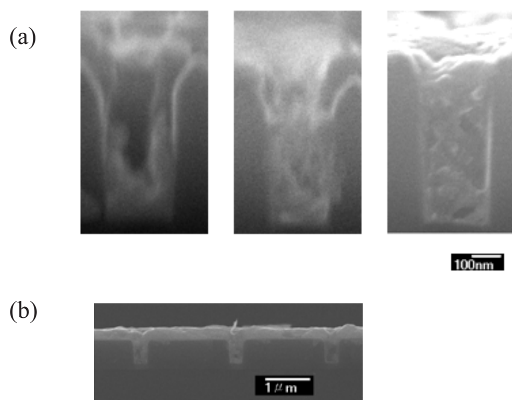

Figure 5: FESEM cross-sectional images of partial fill sequence of deposited copper by DC in approximately 200nm wide, 400nm deep trench is shown in (a). Utilizing the novel approach to complete the whole deposition is shown in (b).

4 CONCLUSION

We have found PC at 100 Hz can result in high (111)/(200) ratio and low resistivity in the presence of additives. Hence, we propose a new filling approach to reduce void defects in CMP process by utilizing DC to fill the features in the first stage, and then PC in the second stage.

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