ToF-SIMS Analysis of the Effect of Bath Modulation on Impurity Incorporation into Damascene Copper

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ABSTRACT

Impurity pinning during self-annealing of damascene copper is often cited as a key inhibitor to the growth of grains. In this study, we examine the connection between the incorporation of bath additives into electrochemically deposited (ECD) copper and microstructural evolution using time of flight secondary ion mass spectrometry (ToF-SIMS), Focused Ion Beam (FIB) imaging, and Transmission Electron Microscopy (TEM).

In the first set of experiments, 450 nm-wide trenches in SiO_2 were prepared for ECD with 3 nm PVD TaN, 3 nm PVD Ta and 30 nm PVD Cu seed (nominal field values). A 3-component plating bath with an ATMI/Enthone Viaform additive package was used for beaker plating with a 2-stage current density profile: 5 mA/cm^2 for seed reinforcement and 10mA/cm^2 for trench fill and overburden deposition. TEM images comparing as-plated and self-annealed samples showed significant grain growth, but grains as small as 30 nm could still be observed (Fig. 1a). Sputter depth-profiling of 450 nm lines by ToF-SIMS revealed the concentration of impurities in the overburden was ~4 x 10^{18} atoms/cm^3 for sulfur and chlorine, while the trenches contained 4-10 times more (Fig. 1b).

The second set of experiments sought to determine the effect of changing the bath composition during plating as a means for reducing impurity incorporation. Finer lines (70 and 100 nm) were plated with the ATMI/Enthone Viaform additives using a 33 mA/cm^2 trench fill and overburden step. This initial study focused on tracing fragments containing sulfur. Two separate solutions were prepared, a standard 3-component and a 2-component bath lacking accelerator. Samples were then plated either by a manual transfer between the two beakers after trench fill or by swapping solutions during plating using a sealed microfluidic plating cell with individually programmable syringes of plating solution. FIB imaging confirmed superconformal, void-free filling of the trenches used for measurement. The ToF-SIMS sputter depth profiles were taken over 70nm or100nm lines. Results indicated a factor of 5 decrease in the average sulfur content relative to the control (single bath), from ~10^{19} to 2x10^{18}, with a gradient of increasing sulfur with depth. These observations will be discussed in light of earlier results on blanket films showing impurity segregation through a quasi-zone refrining process during recrytallization, and the transition from volumetric to 2D growth in films.

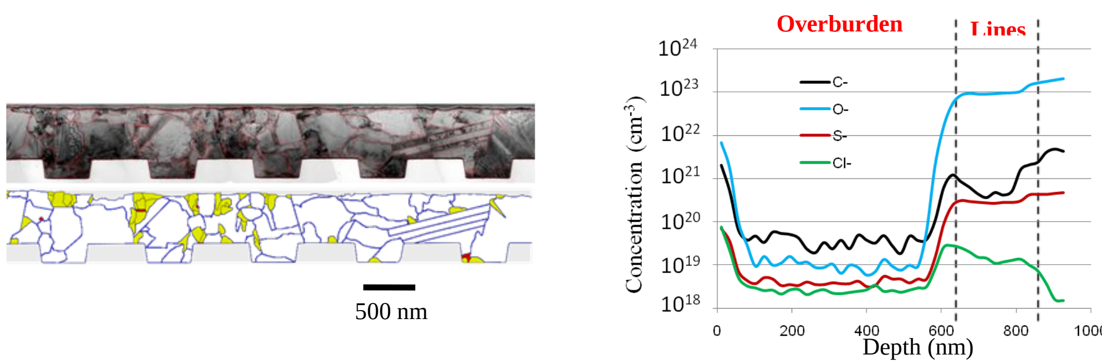

Figure 1. (a) TEM montage with grain tracing (upper) and extracted grain boundary map (lower). Yellow grains are less than 100 nm equivalent diameter, and red grains less than 30 nm. (b) SIMS depth profile showing impurity content from trenches shown in (a). The C, O, S and Cl are low and stable throughout the overburden. The oxygen content increases dramatically as the depth profile encounters the SiO_2 pattern. The carbon, sulfur, and chlorine content is 4-10 x greater in the trenches than the overburden.

Keywords: Damascene, grain growth, impurities

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