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Characterization of Electrodeposited Copper Films with Time-of-Flight SIMS

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This paper summarizes recent experimental results that address concerns about the difficulty in achieving desired grain structure for optimal copper interconnect line resistivity and reliability. The copper electrodeposition used in the damascene process use organic additives to achieve void free filling of narrow feature. These additives are suspected to affect the copper microstructure by limiting the final grain size after recrystallization. The time-of-flight SIMS (ToF-SIMS) quantitative analysis allows the studied of the impurities incorporation into deposited copper for various electrodeposition conditions. In this work, the current density and additives composition and concentration in the electrolyte bath is analyzed by Tof-SIMS.

Figure 1 shows the effect of current density variation on impurity concentration during the electrodeposition. The chlorine and sulfur concentration are obtained by quantitative analysis with a ToF-SIMS instrument. The impurities incorporation rate depends on the overpotential, which is modified by the change of the current density. The ToF-SIMS results show a decrease of the impurities concentration when the current density increases (medium to high current). Impurity concentration increase is observed when the current density is decreased (high to medium current).

The microfluidic electroplating device allows to change the electrolyte solution during the electrodeposition in-situ without stopping the experiment. The chlorine and sulfur concentration are obtained by quantitative analysis with a ToF-SIMS instrument. The sulfur impurity is associated with the incorporation of the accelerator SPS into the electrodeposited copper. The chlorine impurity is related to the suppressor PEG.

Figure 2 shows a decrease of chlorine and sulfur impurity concentration during the electrodeposition when the accelerator SPS additive concentration is increased (10X). This result indicates that the chlorine start his decrease before the sulfur during the SPS concentration increase. Also the magnitude of the decrease is not equal for chlorine and sulfur after the SPS concentration increase possibly indicating a change in the electrodeposition process.

Figure 3 shows the effect of addition of leveler PVP additive in the electrolyte solution on impurity concentration during the electrodeposition. The chlorine and sulfur impurity concentration decrease when the PVP is added to the solution. But in this case, both impurities start their incorporation concentration decrease at the same time and the magnitude of this concentration change is similar.

Initial impurities concentration increase at the Cu seed and electrodeposited Cu interface. These results indicate the formation of a Cl-/SPS (and possibly PEG) layer at the Cu seed surface during the immersion of the sample into the electrolyte (cold entry).

References

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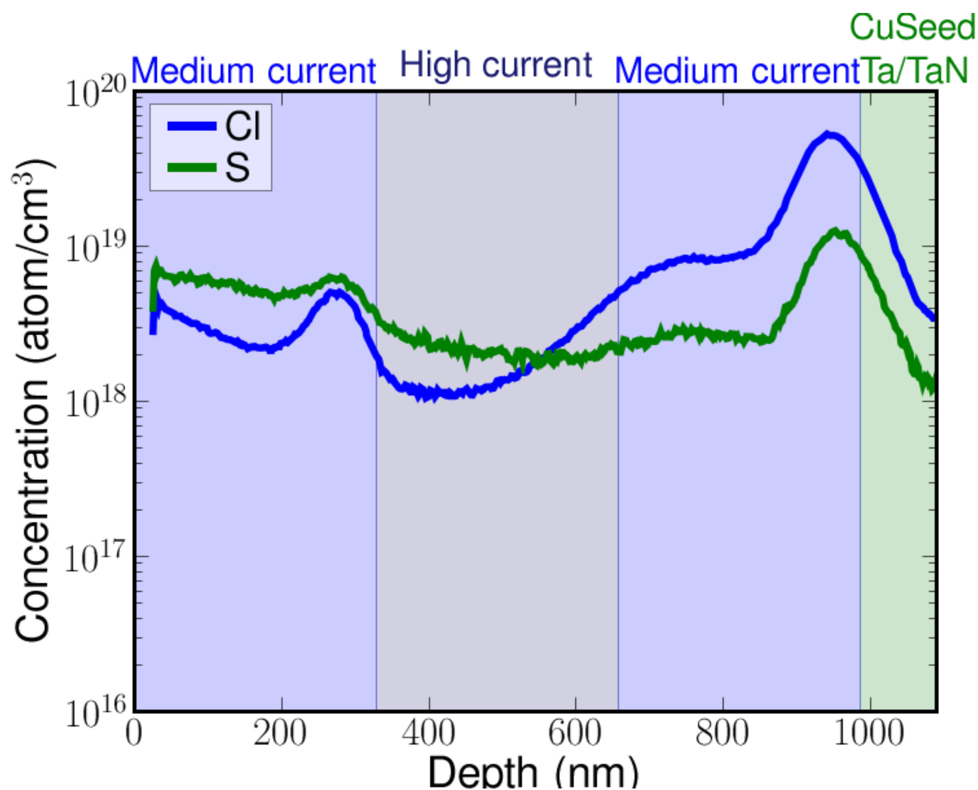

Figure 1: Time-of-Flight SIMS concentration variation of the chlorine and sulfur incorporation in electrodeposited copper film with change in the current density during the electrodeposition.

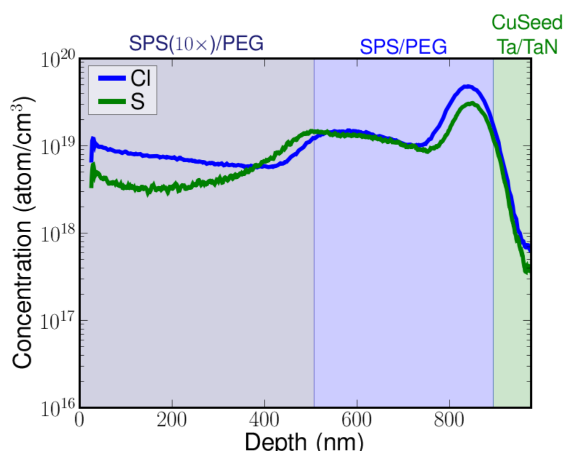

Figure 2: Time-of-Flight SIMS concentration variation of the chlorine and sulfur incorporation in electrodeposited copper film with the increase (10X) of accelerator SPS additive during the electrodeposition.

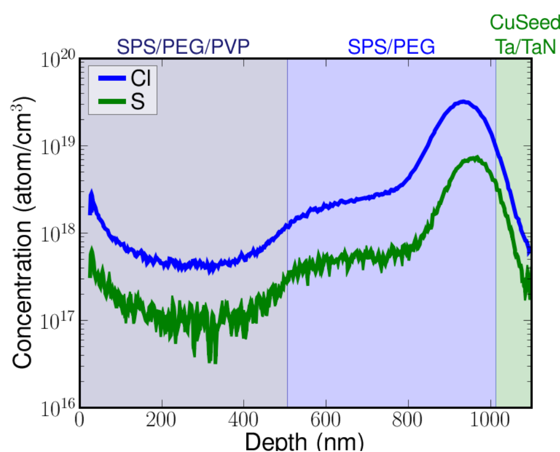

Figure 3: Time-of-Flight SIMS concentration variation of the chlorine and sulfur incorporation in electrodeposited copper film with the addition of leveler PVP additive during the electrodeposition.

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