Potential Oscillations in Galvanostatic Cu Electrodeposition: Antagonistic and Synergistic Effects Among SPS, Chloride and Suppressor Additives

1Nguyen T.M. Hai, 1Jan Odermatt, 1Valentine Grimaudo, 1Karl W. Krämer, 2Alexander Fluegel, 2Marco Arnold, 2Dieter Mayer, and 1,2Peter Broekmann*

1Department of Chemistry and Biochemistry, University of Bern, Freiestr. 3, 3012 Bern, Switzerland

2BASF SE, Global Business Unit Electronic Materials, 67056 Ludwigshafen, Germany
**Supplemental Fig. 1:**

Diagram indicating the current density regime (y-axis), in which potential oscillations occur during galvanostatic plating, as function of the Cu(II) ion concentration (x-axis). Periods of the observed potential oscillations are indicated next to the bars. Grey bars: regime of regular periodic oscillations of high amplitude; dark bars: regime of non-periodic, damped oscillations of small amplitude.

All plating experiments were performed with electrolytes containing 10 g/L H₂SO₄ + 51.42 mg/L HCl + 21.8 mg/L SPS + 109 mg/L Imep and various concentrations of copper ions.
Supplemental Fig. 2:

a) Chronoamperometric measurements indicating the absence of temporal instabilities in the current transients representative for the potential regime where the HN-NDR is observed in the linear sweep experiment (Fig. 4). Equivalents of 20 ppm SPS were dosed to bath 2 at $t = 250$ s followed by the dosage of 100 ppm Imep at $t = 300$ s. The observed steps in the current transients upon Imep dosage are indicative for the strong suppressing action of the additive.

b) Chronoamperometric measurements indicating the presence of temporal instabilities in the current transients when a finite ohmic resistance is present in the external circuit. Note that the intrinsic ohmic resistances of wafer-coupons are sufficiently high to induce such a temporal instability in the current transient without the need to insert an extra resistance into the external circuit.
Supplemental Fig. 3:
SIMS depth profiling of copper films deposited at $j = -5$ mA/cm$^2$ under a) oscillatory conditions (bath2 + 50ppm SPS and 100 ppm Imep) and b) non-oscillatory conditions (bath 2 + 50ppm SPS + 20ppm JGB). Janus Green B is described in literature as a prototypical, monomeric leveler that is used for 3D-TSV plating (see ref. 46; Luehn et al.). The overall contamination level is higher for the JGB.
Supplemental Fig. 4:

SEM images after FIB cut of both copper films characterized in Figs. 6a-b. a corresponds to the 4.2 µm copper film plated under high-frequent conditions. b corresponds to the 25.6 µm thick copper film plated under low-frequent conditions.
**Supplemental Fig. 5:**

The presented UV-VIS spectra correspond to solutions shown in Fig. 8 a), b), d). and e). UV-VIS spectra prove the disappearance of the characteristic peak in the absorbance at $A_{\text{max}} = 805.5$ nm as a characteristic fingerprint for Cu(II) in aqueous solution (a, b). This observation points to a quantitative Cu(II) $\rightarrow$ Cu(I) transition for the given experimental conditions. The Cu(II) $\rightarrow$ Cu(I) transition goes along with the appearance of a strong absorbance below 480 nm thus explaining the yellow appearance of the Cu(I) containing solution (b). Note the pure MPS and SPS solutions do not show this characteristic absorbance in the absence of Cu(I).

UV-VIS spectra further indicate no contribution from Cu(II) when the precipitate was dissolved by chloride or MPS, respectively (d, e).
Supplemental Fig. 6:

The presented linear sweep experiments correspond to solutions shown in Fig. 8 a), b) and c). Working electrode: glassy carbon; dE/dt = 10 mV/s.

The presence of Cu(I) in the yellow-colored solution (Fig. 8b) can be proven by means of electrochemical analytics. Linear sweep experiments on glassy carbon in an RDE configuration clearly indicate the Cu(I) → Cu(II) transition at working potentials above $E_{\text{work}} = +0.2$ V vs Ag/AgCl (b) while the respective linear sweep of the Cu(II) solution remains featureless (a). Extra measurements using copper-free but MPS or SPS containing solutions do not indicate any MPS or SPS related oxidation processes that might interfere with the Cu(I) → Cu(II) transition within the potential window of interest (data not shown here).

The filtered solution in Fig. 8c does show no contribution from the from Cu(I) → Cu(II) transition in the linear sweep voltammetry indicating that the precipitation of the Imep-Cu(I)-MPS removed quantitatively the Cu(I) from the solution.
Supplemental Fig. 7:

a) Part of the reaction scheme of Fig. 10 demonstrating the surface reaction of the SPS as figured out by our STM studies.

b) STM images of Cu(100) in 10 mM HCl + 1 mM SPS imaged with alternating soft (I_t = 1 nA; U_b = 120 mV) and more drastic tunneling conditions (I_t = 12 nA; U_b = 22 mV). The mobile physisorbed SPS is imaged with diffuse and noisy appearance while the c(2x2)-Cl matrix is clearly resolved at smaller tip-surface separations.

c) Partial dissociation of the SPS in the c(2x2)-Cl matrix on Cu(100).

d) MPS/Cl co-adsorption layer on Cu(100). The apparent p(2x2) symmetry in the STM picture corresponds to the imaged layer of sulfonic head-groups of the MPS. Dark lines represent chloride-rich domain walls in the MPS/Cl co-adsorption layer.