Investigation of Bis-(3-sodiumsulfopropyl disulfide) (SPS) Decomposition in a Copper-Electroplating Bath Using Mass Spectroscopy

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In sub-130 nm semiconductor-device manufacturing, electroplating is a promising method to form copper (Cu) interconnections in dual-damascene structures due to its excellent gap-filling capacity and high throughput. In order to achieve a defect-free gap filling, a mixture of external organic additives, such as accelerators, levelers, and suppressors, is used to control plating kinetics. In a typical bath chemistry, bis-(3-sulfopropyl)-disulfide Na salt (SPS: $NAO_3S(CH_2)_3SS(CH_2)_3SO_3Na$) acts as the accelerator. Accelerators are believed to adsorb on the growing Cu surface and to participate in charge transfer; accelerators coadsorbed with suppressors would thus offer growth sites on the cathode surface, otherwise occupied by other additives exhibiting inhibiting action. However, the gap-filling capability of Cu electroplating and the defect performance after Cu chemical-mechanical-polishing (CMP) processes are impacted as the SPS molecules are decomposed or oxidized during the aging of the plating bath. Hence, the decomposition effect of SPS is worth investigating. The most prevalent current technology for automated in-line control of bath chemistry employs cyclic voltametric stripping (CVS). Use of these methods to accurately control process chemistry is difficult at best and ignores direct measurement of breakdown products. Breakdown products which occur during processing and bath aging are expected to be a major factor in the quality of the deposited film and are a process variable in need of direct process control.

Because Cu metal is used as an anode during Cu electroplating, in this study, the decomposition effect of SPS with various surface areas of Cu metals was investigated using mass spectroscopy. The mass spectrum shows that 1,3-propanedisulfonic acid (PDS) was the most stable species among SPS by-products. The equivalent circuit of Cu electroplating was developed and then examined using electrochemical impedance spectroscopy (EIS) to characterize the properties of the aged bath with the decomposition of SPS. Defect elimination is still an arduous task in the Cu-metallization process. Hence, efficiently controlling the decomposition of SPS and the generation of PDS is very important to reduce Cu-defect formation after the Cu-CMP process.

In this study, an additive-free solution consisting of 0.25 mol/L $CuSO_4 \cdot 5H_2O$, 1.0 mol/L sulfuric acid, and 50 ppm chloride ions was used. 7.5 mL/L SPS was added to the additive-free solution as the standard electrolyte because a concentration of 5−15 mL/L SPS is used in semiconductor Cu electroplating processes. All SPS species were defined and quantized using mass spectroscopy based on the Metara Sentry CCM tool. The equivalent circuit was built and simulated using ZSimpWin version 3.1 with EIS data. The overall experiment flow is shown in Fig. 1.
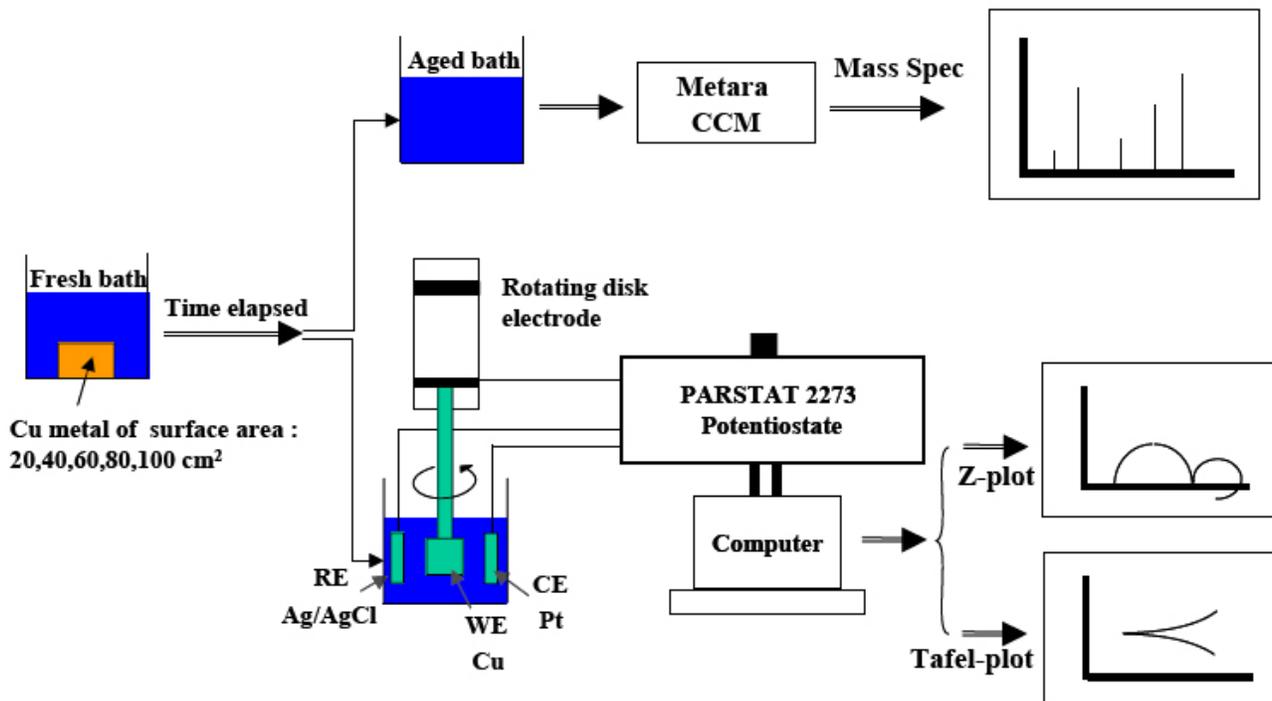
Figure 1: Scheme of the overall experiment on the decomposition of SPS with Cu metals.

The mass spectrometry (MS) spectrums of fresh and aged baths are shown in Fig. 2a and b, respectively. Except for SPS and $Cu(SO4)2^{2-}$, the MS spectrums reveal many peaks, including $[O_3S(C_2H_4)CHO]^-$, $[O_3(C_3H_5)]^-$, and $[O_3S(C_3H_6)SH]^-$ [mercaptopropanesulfonic acid](MPS), and PDS, all of which were by-products decomposed from SPS. In order to quantize the SPS concentration, bis(2-sulfethyl) disulfide and bis(1-sulfopropyl-1-sulfobutyl) disulfide peaks were used as spikes. Furthermore, the peaks such as $[O_3(C_3H_5)]^-$ changed less and the concentration was not stable for the comparison with PDS because it was the intermedium of SPS decomposition. The PDS peaks in Fig. 2a and b changed more than other peaks of the SPS by-products because PDS was the most stable species among them.
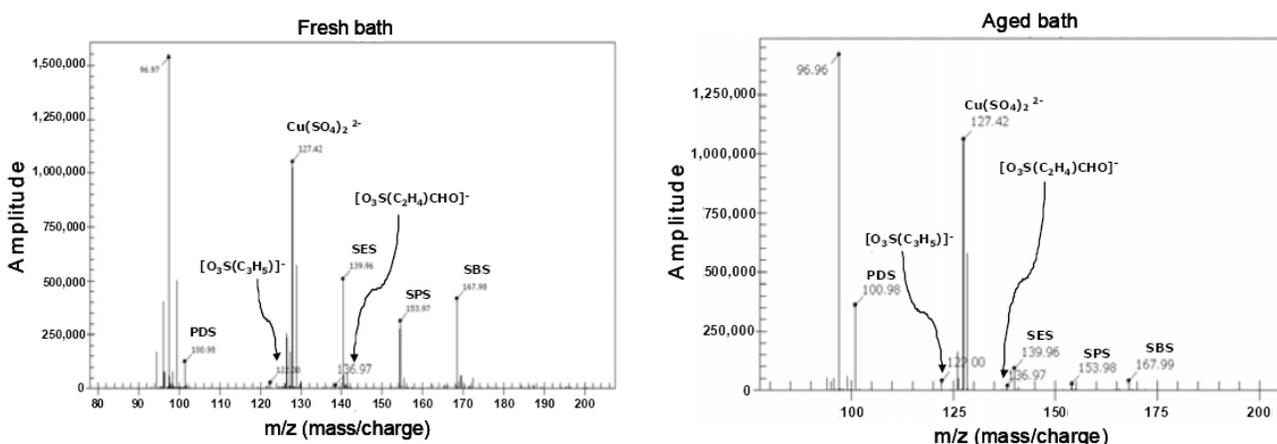

Figure 2: Mass spectrum of SPS species and its byproducts in (a) the fresh bath and (b) the aged bath.

According to Bailey et al., there are two pathways for the SPS decomposition to PDS, as shown in Fig. 3. In addition, MPS converted into SPS with time, which suggested that SPS decomposition to PDS formation is mainly processed through $[(SPS)O_x]$ oxidation. By going through complex redox or hydrolysis reactions, it is thought that two PDS molecules will be generated from the consumption of one

SPS molecule.

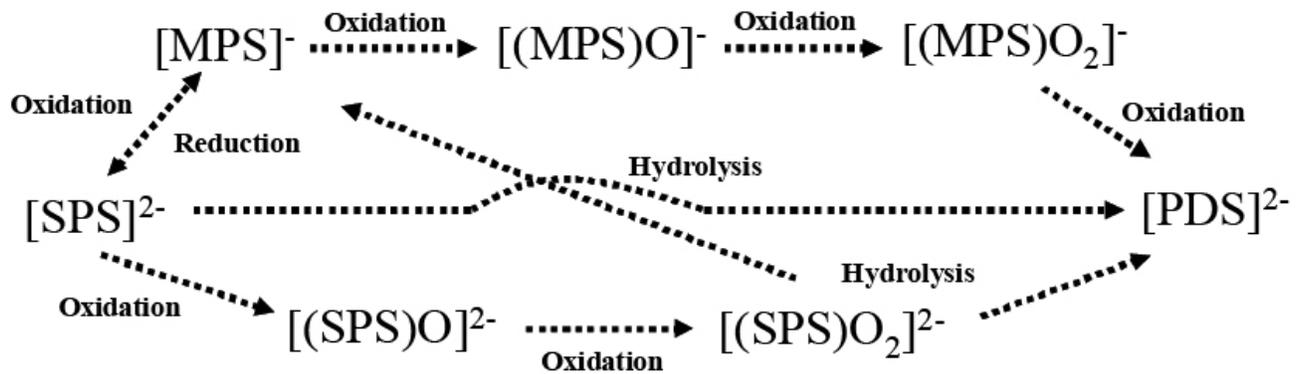$$[MPS]^- \xrightarrow{\text{Oxidation}} [(MPS)O]^- \xrightarrow{\text{Oxidation}} [(MPS)O_2]^-$$

Figure 3: Major decomposition pathways of SPS to MPS and PDS.

Furthermore, the Nyquist plots of Fig. 4 reveal that there were three semicircles in the electrochemical analysis of plating baths containing SPS. An equivalent circuit simulated using the EIS data shows that the electrochemical system consisted of three resistances, two capacitances, and one inductance, as shown in Fig. 5. In this circuit, R_s is the bulk solution resistance, C_{dl} is the double-layer capacitance, R_c is the charge-transfer resistance associated with the double layer, R_{ad} is the resistance of the adsorption layer, C_p is the passivative capacitance associated with the adsorption layer, and L is the adsorption-layer inductance. In summary, the elements of the equivalent circuit in the electrochemical system reveal the properties of the aged bath with the decomposition of SPS.
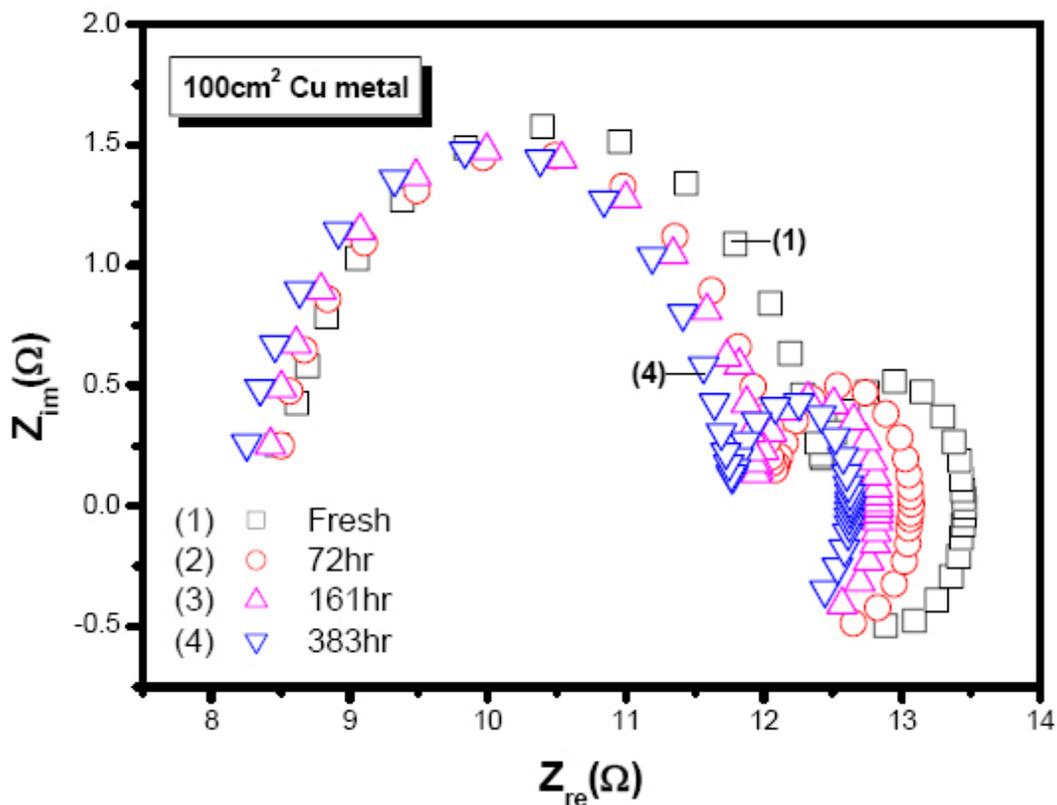
Figure 4: Nyquist plots of the bath at different hours after dipping the samples.
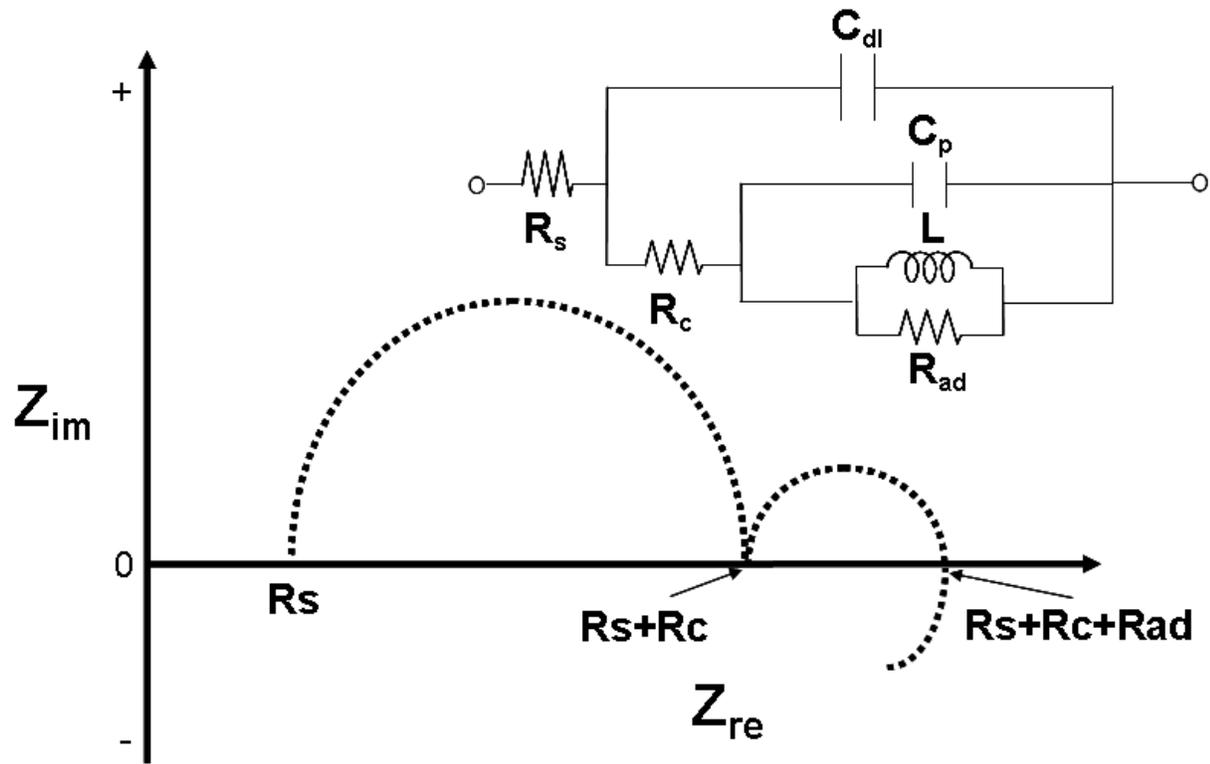
Figure 5: Proposed equivalent circuit diagram of Cu electroplating in the electrolyte with SPS.