Numerical simulation of the effect of additives on copper electro-deposition

Litao Yin[a], Ying Jin[a,*], Lei Wen[a], Xiuli Zhang[b]
a. National Center for Materials Service Safety (NCMS), University of Science and Technology Beijing (USTB) Beijng, china
b. North China Electric Power Research Institute Co. Ltd Beijing, China

PEG and SPS are one set of the promising additives in via-filling and copper foil manufacture. There have been several hypotheses to explain the effect mechanism of these additives in copper deposition. Among them, the most widely accepted theory is curvature enhanced accelerator coverage (CEAC) model [1, 2] for damascene plating, in which competitive adsorption of additives influenced by interface curvature was proposed to be the key factor of super-filling. Other models suggest the different diffusivity between large inhibitor and small accelerator plays an important role [3]. Also, some researchers believe the formation, consumption and distribution of the intermediate are not neglectable [4-6]. So far, it is still too early to reach a consensus on the effect mechanism of PEG and SPS upon copper deposition. Further investigations are necessary.

In the present study, the separate impacts of PEG, SPS, and their synergistic effects, as well as the influence of convection were investigated, respectively, by combining the experiments, modeling, and numerical simulation.

Linear sweep voltammetry were performed with rotating disk electrode (RDE) to examine the influences of forced convection on copper electro-deposition for the Cu-PEG-SPS-Cl^- system under various scanning rate. The results indicated that, under strong convection condition, the inhibiting effect of PEG enhanced, while the accelerating effect of SPS became unobvious or even acted as a weak inhibitor. This phenomenon is consistent with the reported results.

Experimental results suggested this electro-deposition a complex process involving a balance between mass transfer and interface electrochemical reaction. In which process, the surface adsorption of additives and intermediate should also be taken into account. In our modeling work, the diffusion and surface adsorption of reactive ions, the electrochemical reaction on the electrode surface and their coupling effects were considered. Unlike some existing kinetic models in the literature, the competition among the different routes of copper reduction, and the intermediate consumption through desorption and diffusion were taken into account, for Cu^+, Cu^+-SPS, or Cu^+-Cl^--PEG certainly take important role in copper reduction process.

Basing on the above model, potential scanning process of the electrode was simulated by Matlab® programming. By fitting the simulation results with the experimental curves, the proposed kinetic model was verified and some parameters in it were estimated. Fig. 1 showed example of results measured in the electrolyte without any additives under rotating speed of 100, 500, 1000, and 2000rpm/min, and with a scanning rate of 10mV/s and 50mV/s, respectively. The results for different additive conditions will be illustrated in the full article.

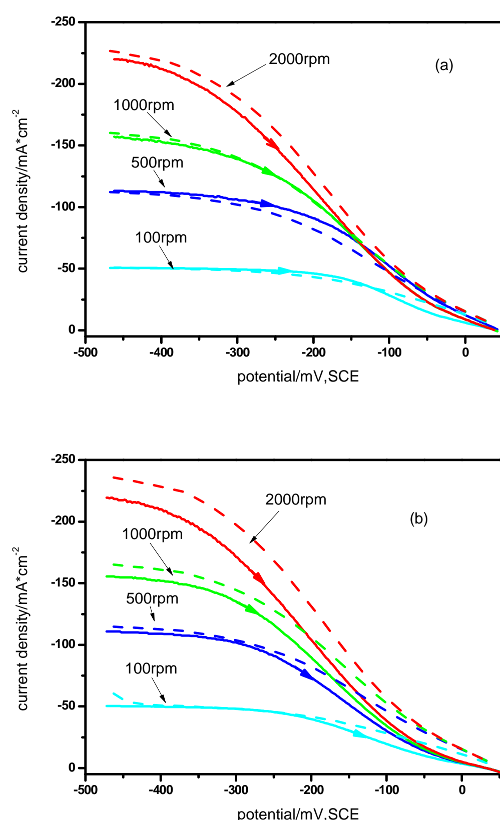

Fig.1

Fig.1 Influence of rotating speed on the voltammograms obtained in $CuSO_4$ 0.2M+H_2SO_4 1.85M+Cl^- 100ppm solution. Solid line is the experimental data, dash line is the simulation result. Scan rate: (a) 10mV/s. (b) 50mV/s.

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