Structural Effect of Polymers on Their Microvia Filling Performance as Suppressors During the Copper Electroplating

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Suppressors are crucial to microvia filling via Cu electrodeposition in electronic industry. In this work, two types of polymer suppressors with different structures (PEG6000 vs EPE2900) are compared in terms of their microvia filling performance during the Cu electrodeposition by using cyclic voltammetry (CV) measurements on rotating ring-disk electrode (RRDE). CV curves obtained on the disk electrode prove our previous conclusion that, compared to PEG6000, EPE2900 can more effectively inhibit Cu electrodeposition on the cathode. Importantly, the plots measured on the ring electrode provide solid evidence for the interaction between the suppressors and Cu⁺. The addition of Cl⁻ can greatly enhance the adsorption strength of suppressor-Cu⁺ complex due to the formation of suppressor-Cu⁺-Cl⁻ complex. on the cathode surface, effectively inhibiting the copper deposition. According to the mechanism of the suppressors obtained from RRDE technique, the reasons for the stronger suppression strength of EPE2900 are elucidated by molecular dynamic (MD) simulations and Gaussian 03 program based on molecular structures, the electronegativity of oxygen atoms, and the steric hindrance for these two different suppressors. In good agreement with the theoretical studies, it has been experimentally demonstrated that the plating solution using EPE2900 as the suppressor shows better microvia filling performance than PEG6000 evidenced by the corresponding optical microscope images. More hydrophilic properties of the obtained copper layer by using EPE2900 is also advantageous over the PEG6000 as the suppressor.

Keywords: Microvia filling; Copper electroplating; Polymer suppressor; Rotating ring-disk electrode.

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