Abstract #2087, 224th ECS Meeting, © 2013 The Electrochemical Society

Screening Techniques for Selecting Improved Additives for Bottom-up Copper Metallization

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Semiconductor interconnect metallization is achieved by copper electrodeposition from acidified copper sulfate electrolyte in the presence of a special additives mixture. A combination of common additives, polyethylene glycol (PEG) as slow diffusing, fast adsorbing inhibitor, bis(3-sulfopropyl) disulfide (SPS) as fast diffusing, slower adsorbing anti-suppressor, and chloride are effective for bottom-up fill of sub-micron features. However, as geometries become more challenging, with decreasing feature sizes and with increasing aspect ratios, more effective additives are required. In particular, suppressors exhibiting stronger inhibition, which can, however, still be displaced by the anti-suppressor are sought. Since, fundamental theory relating the chemical structure of the additives to their electrochemical properties is still lacking, identification of effective additives is mostly empirical, involving screening of numerous species.

The common additive screening method is by injection test[1]. This test is commonly performed by injecting a given amount of additive into a solution from which a non-patterned copper substrate is being plated at a constant current, typically, 10 mA/cm^2. The overpotential shift from pure copper deposition to that with the suppressor is measured (Figure 1). It is commonly accepted that the larger this shift, the more effective the suppressor will be. The rationale for this supposition is that the pre-injection current density represents the non-inhibited features bottom, while the post-injection more negative overpotential, corresponds to the suppressed via rim and sidewalls. Visualizing the common injection method on typical polarization curves will correspond to comparing the overpotentials η_B to η_{sw} in Figure 2.

The main issue with this methodology is that it does not represent the actual wafer plating scenario. While the wafer is plated at an overall constant current, the actual current density between the non–inhibited propagating features bottom and the inhibited flat regions varies considerably, and therefore a constant current injection test may lead to the wrong conclusions. A condition that simulates the actual wafer plating would be a constant overpotential experiment, where the overpotential is selected such that it corresponds to that of the plated wafer. Accordingly, injection studies should be performed at a constant overpotential and the current ratio i_B to i_{SW} (Figure 2) compared. Unfortunately, performing injection studies at a constant voltage is challenging since we do not know a-priory the value of the potential to be selected, since the latter depends on the degree of inhibition provided by the tested inhibitor.

To overcome this issue, we propose a new screening technique that more accurately identifies potential effective suppressors. The approach is based on recognizing that under practical wafer metallization conditions, the suppressed region exhibits very low current densities, in the range of 1 mA/cm^2. Performing a steady-state polarization experiment at this low current density in the presence of a suppressor, voltage response can be directly compared: the larger the overpotential at this very low current density, the more effective the suppressor is.

To validate this statement, further analysis is conducted. A plot of i_B/i_{SW} vs. $i_{average}$, where i_B, i_{SW} and $i_{average}$ correspond to the current density at the feature bottom, sidewall, and the average, respectively, indicates which suppressors should perform best and the size of feature they are expected to fill (Figure 3). The larger this ratio, the smaller the plated feature can be.

Acknowledgements

We acknowledge support from Atotech and helpful discussions with Robert Preisser.

References:

1. R. Akolkar and U. Landau, J. Electrochem. Soc., 151, C702 (2004).

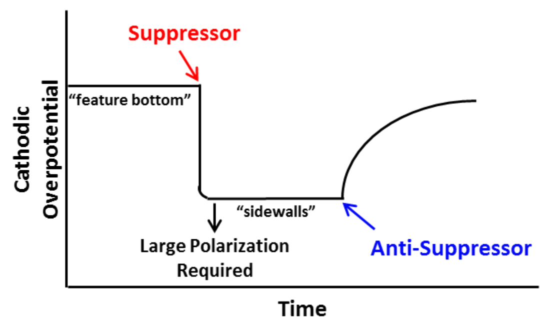

Figure 1: Schematic of conventional injection study at constant current. The cathodic overpotential increases with the injection of suppressor, and decreases with subsequent injection of anti-suppressor.

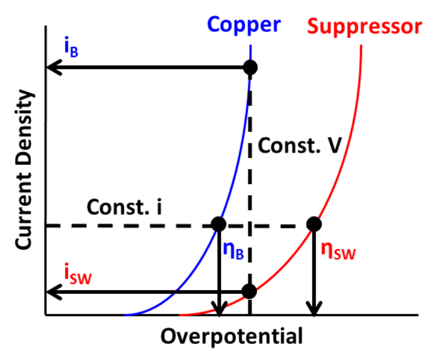

Figure 2: Schematic of polarization curves for pure copper and copper in the presence of suppressor. The potential difference corresponding to the conventional injection study is given by η_B - η_{sw}. In reality the wafer is held at a constant voltage, and the current ratio between pure copper (i_B, bottom of feature) and suppressor (i_{SW}, sidewalls of feature) must be larger than the aspect ratio of the feature for bottom-up fill to occur.

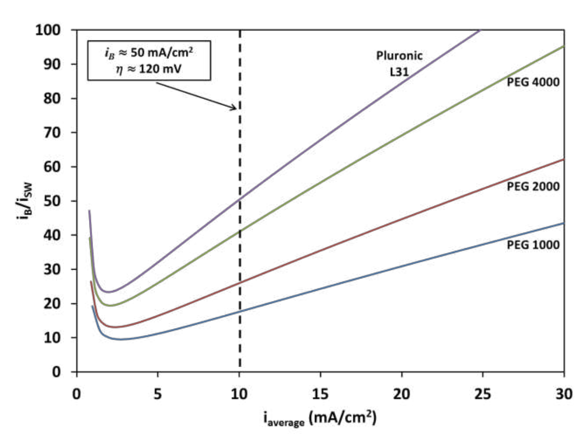

Figure 3: Bottom-up fill ratio simulated for PEG1000, 2000, 4000 and Pluronic L31. At $i_{average}$ of 10mA/cm^2 the i_B/i_{SW} ratio is largest for Pluronic L31 (about 50), indicating that it is expected to fill features with aspect ratios as high as 50.