

Mechanistic Study of Autocatalysis during Electroless Copper Deposition

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Electroless deposition of copper (Cu) is attractive for a variety of applications. One application is in dual-damascene fabrication of Cu interconnects, where a Cu seed layer is pre-deposited inside narrow features before subsequent trench filling by Cu electrodeposition. With device miniaturization, the conventionally sputtered Cu seed layer poses challenges such as non-conformality within sub-10nm features. Electroless Cu deposition has been considered as a promising pathway to replace the sputtering process and provide conformal seed layers.

For electroless Cu deposition, formaldehyde reducing agent has been extensively studied. However, due to its toxicity and volatility, a number of alternative reducing agents have been proposed. One candidate is glyoxylic acid due to its eco-friendliness and good reducing power.

In spite of intrinsic complexities in electroless processes, simplistic models such as the mixed potential theory have been widely applied. The mixed potential theory assumes that the partial reactions, i.e., cathodic (metal reduction) reaction and anodic (reducing agent oxidation) reaction, proceed independently. Therefore, the mixed potential theory may be applied to the two partial reactions to predict the overall reaction rate and mixed potential. However, numerous studies have shown that this simplistic application of the mixed potential theory may lead to erroneous predictions, especially in electroless systems in which the partial reactions are coupled. This is supported by a number of studies in formaldehyde-based [1, 2] and glyoxylic-based electroless Cu systems [3].

In this study, we report on the interdependence of the cathodic and anodic half reactions in a glyoxylic acid-based electroless Cu system. Polarization curves (Figure 1) demonstrate that simplistic application of the mixed potential theory to this system leads to erroneous predictions of the surface mixed potential and the electroless deposition rate. The deposition rate predicted from mixed potential analysis of the partial polarization curves is 1/6th of the value obtained by deposit weight measurement in a complete electroless bath. This suggests an interdependence between the cathodic and anodic half reactions. Chronoamperometry under various conditions was employed, which further confirmed this interdependence and suggested an autocatalytic mechanism shown schematically in Figure 2. Specifically, fresh deposited electroless Cu catalyzes glyoxylic acid oxidation on the electrode surface, and glyoxylic acid accelerates Cu reduction possibly through adsorbed intermediates generated during electroless deposition. Electrochemical measurements using rotating disc and ring disc electrodes further elucidates the nature and behavior of these adsorbed intermediates.

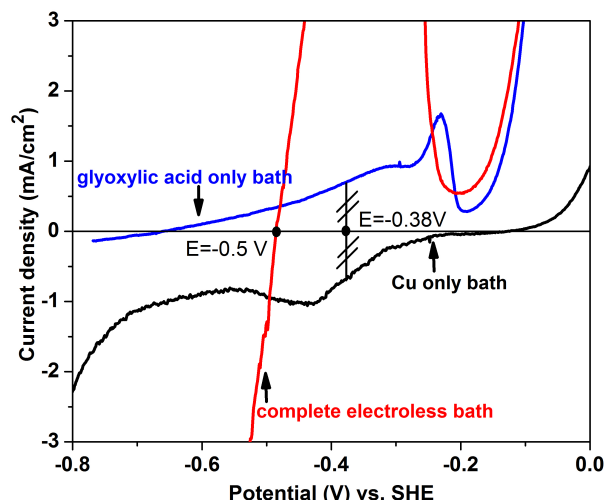


Figure 1. Polarization curves obtained on a Cu foil from a 'glyoxylic acid only' bath (blue curve), a 'Cu only' bath (black curve) and a 'complete electroless' bath. The graph clearly shows the predicted mixed potential (-0.38V) is ~120 mV more anodic than the experimentally measured mixed potential (-0.5 V).

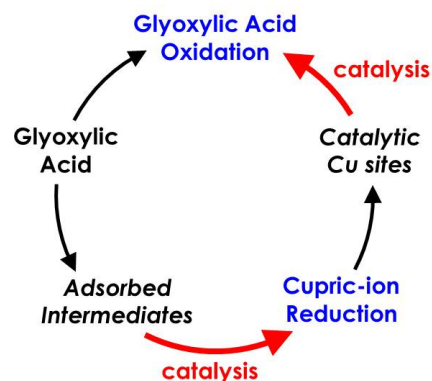


Figure 2. Proposed autocatalytic mechanism in glyoxylic acid-based electroless Cu deposition.

References

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