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Adherent Electroless Copper Deposition Using Inexpensive Sn/Ag Catalyst on Non-roughened Epoxy Laminate Substrates

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The electroless deposition of copper is often used for interconnect in microelectronics. The electroless copper layer can be used as a seed layer of electroplating, or can be deposited to full metal thickness. The major challenges facing electroless deposition for interconnect include cost, deposition time, reliability, and electrical conductivity. The insulating surface onto which the deposit is made is first catalytically activated prior to electroless copper deposition. The conventional Pd-based catalyst is expensive, due to the high cost of Pd, which poses an economic constraint on the electroless deposition process. Another concern is the reliability of deposit if there is poor adhesion between the deposited electroless copper layer and the insulator. In addition, the electrical performance of copper interconnect is adversely affected by surface roughness which results in surface scattering of electrons, especially at high frequency. At high frequency, the conductivity can be compromised because the conventional swell & etch process is based on an increase in the surface roughness in order to achieve acceptable adhesion through mechanical anchoring of the catalyst and the deposited metal [1-2]. Thus, there is a clear need for improved catalysts which can lower the cost (i.e. non-palladium catalysts), and avoid adding surface roughness (i.e. elimination of the swell & etch process).

The goal of this study is to improve the electroless copper deposition process on epoxy laminate substrates using a non-palladium catalyst without the use of the swell & etch process. A Sn/Ag catalyst on non-roughened laminate substrates was investigated. It was found that a hot sulfuric acid treatment of the epoxy surface was critical in achieving adherent copper deposits. In this process, the cost was lowered by replacing the Sn/Pd co-catalyst with a less expensive, but equally effective, sequential Sn/Ag catalyst. Unclad laminates (ISOLA 185 HR) were used as substrates. A non-roughening surface modification was employed using hot sulfuric acid treatment. The deposition procedure consisted of four steps with deionized H_2O rinsing between each step: (i) hot H_2SO_4 treatment, (ii) Sn sensitization in a $SnCl_2$ bath, (iii) Ag activation in a $AgNO_3$ bath, and (iv) electroless copper deposition in an alkaline $CuSO_4$ bath containing formaldehyde as the reducing agent. The surface roughness was measured using atomic force microscopy (AFM), the chemical characterization of the surface was performed using X-ray photoelectron spectroscopy (XPS), and the adhesion strength of the electrolessly deposited film was measured using a 90° peel test. It was observed that the H_2SO_4 treatment was an essential step for electroless copper deposition because no deposition occurred without the H_2SO_4 treatment. The sulfuric acid treatment likely could have produced charge reversal on the substrate through adsorbed sulfate. It is particularly interesting that this occurred without increasing the surface roughness (see Table I). The surface coverage at different stages of treatment was investigated by X-ray photoelectron spectroscopy (XPS) analysis. Surface modification using other acids such as HCl and H_3PO_4 did not enable electroless copper deposition after catalysis, or resulted in non-uniform copper deposition, respectively. Previously, a developed Sn/Ag catalyst process was shown to deposit uniform colloidal Sn/Ag catalyst on the sample [3]. The lower cost and higher catalytic activity of Ag, compared to Pd for formaldehyde oxidation makes Ag a rational material choice as the catalyst in electroless deposition [4]. Electroless copper deposition using formaldehyde as the reducing agent in an alkaline bath produced continuous, uniform, and adherent copper on the substrate. The surface roughness did not change appreciably, compared to the untreated substrates prior to deposition. The adhesion strength of the electroless copper layer measured after copper electroplating was found to be about 0.3 N/mm, which was consistent and repeatable over a range of measurements.

Overall, a new electroless copper deposition process was studied in order to achieve adherent electroless copper deposition using a Sn/Ag catalyst on non-roughened epoxy laminate substrates. The major findings in this study can be summarized as follows: (i) H_2SO_4 enables increased Sn/Ag catalysis with good adhesion, (ii) there was little change in surface roughness, (iii) Sn/Ag can be used as an inexpensive catalyst for electroless deposition of adherent copper layers on epoxy laminates.

Table I. Surface roughness comparison

Surface Roughness	Plain sample	H_2SO_4 treated sample	Swell & etch sample
R_a	621 nm	685 nm	819 nm
R_q	767 nm	840 nm	997 nm

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