Surface morphology and residual stress of electroplated and electroless copper deposits

K. G. Keong¹, W. Sha¹, Z. X. Guo² & S. Malinov¹
¹School of Civil Engineering, The Queen's University of Belfast, UK.
²Department of Materials, Queen Mary and Westfield College, UK.

Abstract

In this work, surface morphology characterisation and residual stress measurements have been carried out on electroplated and electroless copper deposits. The surfaces of the solution and substrate sides of the freestanding electroplated copper deposits from stainless steel substrates have been studied at as-deposited condition and after heat treatment at 140°C for 1 hour. Electroless copper deposits with different substrates (copper cladded and laminated polymers, and screen-printed dielectric substrate) have also been studied at the two conditions. The surface morphology has been characterised using optical microscopy and scanning electron microscopy (SEM). Residual surface stress measurements were performed using the sin²ψ technique of X-ray diffraction method. The morphology of the as-deposited electroplated copper film on the substrate side includes numerous small voids scattering across the surface of the deposit, with relatively large cracks at some portions. No voids were observed in the deposit on the solution side. These features remained after heat treatment. In the electroless copper deposits, the granular particles developed on the heat-treated deposit were the most intensive, followed by the deposits on the laminated and on the copper cladded substrates, respectively. No significant amount of residual surface stress has been detected in the as-deposited electroless copper deposits.

1 Introduction

In recent years there is a great need for lightweight and more reliable integrated circuits in the electronics industry [1,2]. For example, the plated copper deposits in the Printed Circuit Board (PCB) have to be considerably thin in order to reduce weight and size of electronic components and devices. During processing
of certain types of PCB, the mounting or exchanging of components by soldering is very critical, as the plated copper deposit is subjected to thermal stresses, which might impair the integrity of the PCB [3]. Consequently, the plated copper deposits used in the electronics industry should withstand physical deformation caused by excessive stresses. Hence, the understanding of the properties and behaviour of the copper deposits during processing and application is very important. This can be achieved by characterising the plated copper deposits, such as through surface morphology and residual stress measurements.

This paper presents the results of such analyses for both the electroplated and electroless copper deposits. Studies of the surface microstructural morphology involved both optical microscopy and scanning electron microscopy (SEM). Electron microprobe analysis was carried out to investigate the chemical compositions of the electroplated copper deposits. X-ray diffraction was used to evaluate residual stresses in the electroless copper deposits.

2 Experimental procedure

2.1 Materials and treatments

All the samples of the copper deposits used in this study were provided by Shipley Europe Limited in the UK. The electroplated copper samples were made from the same deposit, but one in the as-deposited condition and the other heat-treated at 140°C for one hour. Two electroless copper samples were in the as-deposited condition, and were produced under similar plating conditions, but on different types of substrates – one on a copper cladded substrate and the other on a laminated polymeric substrate. In addition, the surface microstructure of a heat-treated electroless copper sample plated on a screen-printed dielectric substrate was also studied. The heat treatment conditions for the electroless copper sample were 140°C and one hour. This treatment was carried out because after circuit is made, a photo resisting (green) coating is required to protect the circuit. This further coating process involves a baking or curing stage at a temperature below 140°C. Therefore, the properties of the Cu coatings after a similar (in the present case, slightly more severe) treatment need to be assessed. The catalysts used before the plating of the electroless copper deposits on copper cladded / laminated and screen-printed substrates were a Sn-Pd colloid and an organic Pd compound, respectively. Both the electroplated and electroless copper deposits were 15 μm in thicknesses. The electroplated copper deposits were in freestanding form, peeled off from their stainless steel substrates, while the electroless copper deposits were on their substrates. Table 1 shows the test matrix for the copper deposits.
Table 1: Test matrix for the electroplated and electroless copper deposits.

<table>
<thead>
<tr>
<th>Plating</th>
<th>Electroplating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Electroless</td>
</tr>
<tr>
<td>Condition</td>
<td>140°C, 1 hr.</td>
</tr>
<tr>
<td>Side</td>
<td>Substrate</td>
</tr>
<tr>
<td>Microscopy</td>
<td>✓</td>
</tr>
<tr>
<td>Microprobe</td>
<td>✓</td>
</tr>
<tr>
<td>Stress analysis</td>
<td>✓</td>
</tr>
</tbody>
</table>

2.2 Etching

The electroplated copper deposits for the surface morphology analysis on the substrate sides were not etched, whereas those on the solution sides were etched before analysing. All the electroless copper deposits were etched before analysing. It was found that without etching, for some samples it was difficult to achieve clear imaging. Comparing results between etched and un-etched samples, however, indicated that the etching process did not modify significantly surface morphology but enhanced the image quality.

The solution for etching contains 33% of NH₂OH (sp. gr. 0.90) and 1% of H₂O₂ in water [4,5]. The specimens were immersed and swabbed in the solution for 1 minute at ambient temperature.

2.3 Surface morphology analysis

Optical microscopy and scanning electron microscopy (SEM) techniques were used for surface morphology. Electron microprobe and X-ray diffraction (XRD) techniques were employed to identify the chemical compositions and phase structure of the deposits.

As indicated in Table 1, two electroplated samples were analysed for both the substrate and solution sides, whereas three electroless samples were analysed for only the solution side.

2.4 X-ray stress analysis

In the work reported here, only the electroless copper deposits have been analysed for residual surface stress, a stress distribution only in the plane parallel to the surface. No stress is assumed perpendicular to the surface of the deposit [6].
For this purpose, the multi-exposure or sin$^2$ψ technique of X-ray diffraction method [6,7,8,9] was deployed.

The X-ray stress analysis was performed with a scanning step of 0.02° using a Siemens D5000 x-ray diffractometer and Cu K$_{α1-α2}$ radiation. The X-ray sin$^2$ψ technique of residual surface stress analysis is based on the change in the lattice spacing (strain) of the deposit. According to Bragg’s Law, X-ray diffraction occurs at an angle 2θ defined by $nλ = 2d\sinθ$, where $n$ is an integer defining the order of diffraction, $λ$ is the wavelength of x-ray beam, $d$ is the lattice spacing between the deflecting planes, and $θ$ is the angle between incident beam and the deflecting planes. Any increase or decrease in magnitudes in the lattice spacing ($d$) will be followed by the corresponding shift in the diffraction angle (2θ). Since the presence of residual surface stresses can alter the magnitude of lattice spacing, the corresponding diffraction angle can be used to calculate the related stress in the deposit. For example, the presence of residual tensile stress in the deposit can reduce the lattice spacing for lattice planes parallel to the surface and increases the diffraction angle (2θ) of the deposit [6].

A standard procedure using the X-ray sin$^2$ψ technique for the reported residual surface stress measurements in this work is as follows (Fig. 1):

1. Choose and locate the 2θ$_{o}$ angle of a known Cu {hkl} line from the normal-scan ($ψ = 0$) X-ray intensity profile of the deposit.
2. Determine the new positions (2θ$_{ψ}$) of the known Cu {hkl} line from the specimen scanned over several tilted orientations ($ψ > 0$).
3. Plot 2θ$_{ψ}$ versus the corresponding sin$^2$ψ values.
4. Calculate the slope of the best-fit line from the plot.
5. Determine the residual stress using the equation (1) below [7]:

$$
\sigma = - \frac{E}{2(1 + \nu)} \cot θ_{o} \left( \frac{\pi}{180} \right) \left[ \frac{\delta (2θ)}{\delta \sin^2 ψ} \right]
$$

where:

$E$ = Young’s Modulus of the deposit
$\nu$ = Poisson’s ratio
$θ_{o}$ = Bragg’s angle of the known Cu {hkl} diffraction peak at $ψ = 0$
$θ_{ψ}$ = Bragg’s angle of the known Cu {hkl} diffraction peak at $ψ > 0$
$ψ$ = Angle between the diffracting lattice planes and the specimen surface
$\delta 2θ_{ψ} / \delta \sin^2 ψ$ = Slope of the plot 2θ$_{ψ}$ versus sin$^2$ψ.
Figure 1: Schematic diagrams showing the positions of specimen at (a) \( \psi = 0 \), and (b) \( \psi > 0 \).

3 Results and discussion

3.1 Surface morphology

The surface morphology of deposits has been identified as one of the very important microstructural factors in dictating their property and behaviour in various applications [10]. A series of micrographs showing the surface morphologies of both the electroplated and electroless copper deposits have been taken from the optical microscopy and SEM analysis. Grain structures of the as-deposited electroplated copper deposit on the substrate side are shown in the optical micrograph in Fig. 2. There seem relatively large cracks (see arrow on Fig. 2), appearing as dark irregular lines of varying width, probably caused by peeling. The SEM micrograph in Fig. 3 shows the small grains from Fig. 2. Many grain boundaries of these grains are populated with the relatively large cracks. There are series of lamella lines observed inside the small grains grown into different directions. These lamella appearances might simply be caused by the effect from lamella pearlite [11] in the stainless-steel substrate, rather than from real Cu grains in the deposits. Small voids that are probably caused by the hydrogen bubbles during plating process are also observed in the deposit [12,13], distributed unevenly across the surface.

SEM micrograph in Fig. 4 shows that the surface microstructure of the solution-side of the as-deposited electroplated copper is very different from that of the substrate-side. The fine structure of the solution-side does not show any voids. The overall appearance of the surface structure suggests that the grains are of fine lamella structure. The white spots on the surface of the deposit are likely contaminants, which are attached to the deposit.

For the heat-treated electroplated copper deposit, the microstructural features of the deposit on the substrate and solution sides (Figs. 5 & 6) are similar to that in the as-deposited condition. However, the small voids on the substrate side are slightly more than those in the as-deposited condition. The effects of the heat-treatment temperature on the microstructural features of the electroplated copper
Figure 2: Optical micrograph of electroplated copper deposit at substrate side in as-deposited condition. Numerous large cracks exist in film surface; one example is indicated by the arrow.

Figure 3: Scanning electron micrograph of electroplated copper deposit at substrate side in as-deposited condition.
Figure 4: Scanning electron micrograph of electroplated copper deposit at solution side in as-deposited condition.

Figure 5: Scanning electron micrograph of heat-treated electroplated copper deposit at substrate side.
Electron microprobe analyses on both the as-deposited and heat-treated electroplated copper deposits have shown that copper was the only element present in the deposits.

In Fig. 7, the SEM micrograph shows the surface morphology of the solution-side of electroless copper deposit plated on the copper cladded substrate. Compared to the morphology of the electroplated copper deposit on the solution side, the electroless copper deposit has a relatively rough surface structure, large granular particles, and rather faceted grains. The faceted grains are more clearly shown at a large magnification (Fig. 8). Small voids that were found in the electroplated copper are not observed in the electroless copper. However, transmission electron microscopy (TEM) analysis in a previous study has shown that small voids were present both within grains and at grain boundaries, and that the electroless deposit contained a significant amount of hydrogen [14]. Furthermore, chemical attack could enlarge the voids and form cracks at grain boundaries, which were populated with relatively large voids [15]. Overall, the surface structure of the electroless copper plated on the copper cladded substrate is homogeneous with a small number of relatively large particles scattered randomly on fine faceted grains.

For the solution-side electroless copper deposit plated on the laminated substrate (Fig. 9), the surface morphology is very similar to that in the electroless copper deposit plated on the copper cladded substrate (see Figs. 7 & 8). The dif-
ference between these two samples in the SEM micrographs is the larger number of granular particles in the copper deposit plated on the laminated substrate.

Fig. 10 shows the solution side of the heat-treated electroless copper deposit plated on the dielectric substrate. Apparently, the heat treatment process at temperature 140°C for 1 hour had intensified the large granular particles. The surface area of the deposit was almost totally covered by these large particles. The large granular particles have well-defined boundaries and valleys are created between the particles. The fine faceted grains in the as-deposited electroless copper disappeared. However, this intensified growing might be the effects of different catalyst and substrate used in the plating process.

3.2 Residual surface stress

The basic cause of residual stresses in a coating is the remains of non-uniform plastic stress flow in the coating [8]. These internal stresses can be either tensile or compressive. In this study, it was calculated that more than 95% of the reflected X-ray beam for the Cu \{311\} diffraction peak was from within the depth of penetration at 24 μm. Since the thicknesses of the electroless copper deposits were only 15 μm, the entire coatings were subjected to the penetrated X-ray beams.

From Table 2, the angles of $2\theta_0$ that are related to the positions of the Cu \{311\} obtained at the corresponding tilted angles ($\psi_1$ to $\psi_1 = 10^\circ$, 20°, 30°, 40°) during XRD analysis do not show significant amount of shift (Figs. 11a & b). As a result, it can be concluded that the electroless copper deposits plated on the two different kinds of substrates have insignificant amount of residual surface stress.

Table 2: Values of X-ray diffraction angles.

<table>
<thead>
<tr>
<th>Description</th>
<th>Electroless copper deposit on copper cladded substrate</th>
<th>Electroless copper deposit on laminated substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu {hkl} at $\psi = 0$</td>
<td>Cu {311}, $2\theta_0 = 89.94^\circ$</td>
<td>Cu {311}, $2\theta_0 = 89.98^\circ$</td>
</tr>
<tr>
<td>Tilted Angle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\theta_0$</td>
<td>$10^\circ$</td>
<td>$20^\circ$</td>
</tr>
<tr>
<td>$90.04^\circ$</td>
<td>$90.02^\circ$</td>
<td>$90^\circ$</td>
</tr>
</tbody>
</table>
Figure 7: Low magnification scanning electron micrograph of electroless copper deposit at solution side on copper cladded substrate in as-deposited condition.

Figure 8: High magnification scanning electron micrograph of electroless copper deposit at solution side on copper cladded substrate in as-deposited condition.
Figure 9: High magnification scanning electron micrograph of electroless copper deposit at solution side on laminated substrate in as-deposited condition.

Figure 10: High magnification scanning electron micrograph of heat-treated electroless copper deposit at solution side on dielectric substrate.
Figure 11a: X-ray diffraction profiles of the Cu {311} with tilted angle $\psi = 10^\circ$, $20^\circ$, $30^\circ$ and $40^\circ$ for electroless copper deposit plated on copper cladded substrate.
Figure 11b: X-ray diffraction profiles of the Cu \{311\} with tilted angle $\psi = 10^\circ$, $20^\circ$, $30^\circ$ and $40^\circ$ for electroless copper deposit plated on laminated substrate.
4 Conclusions

The electroplated copper deposits on the substrate side and the solution side have very different surface microstructural features, likely caused by the substrates of the deposits. The deposit on the substrate side has small voids scattering across the surface of the deposit, and has relatively large cracks at some portions. In contrast, no voids were observed in the electroplated deposit on the solution side, which consists of fine grain structure. Heat treatment of the electroplated copper deposit did not change much the surface morphology of the deposit. Electron microprobe analyses have confirmed that copper was the only element present in the electroplated copper deposits both at as-deposited and heat-treated conditions. In the electroless copper deposits, the effect of the substrates on the deposits is very obvious. The number of large granular particles on the deposit plated on copper cladded substrate is smaller than that in the deposit that was plated on the laminated substrate. After heat treatment at 140°C for 1 hour, the electroless copper deposit that was plated on a screen-printed dielectric substrate had its surfaces almost fully covered with the large granular particles. However, the effect might come from the use of different catalyst and substrate during plating process, rather than from the heat treatment. Comparing to the electroplated deposits, the electroless copper deposits are relatively rough and virtually void free under observation.

Measurements of the residual surface stresses in the as-deposited electroless copper deposits did not detect any significant amount of stress in the deposits.

Acknowledgements

The authors gratefully acknowledge Dr. J. Graves at Shipley Europe Limited for supplying the samples used in the study. In addition, the authors would like to thank Dr. Z. Guo (Queen’s University) and Dr. M. Bououdina (Queen Mary College) for their technical assistance.

References


