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Characterization of flexible copper laminates fabricated by Cu electro-plating process

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Abstract: Flexible copper clad laminates(FCCLs) were fabricated using the electro-plating process and the combined effect of the current density and plating time on their surface morphology, texture, hardness, electrical resistivity and folding behavior was evaluated. To achieve Cu layers with similar thicknesses, the current density was varied in the range of 0.2−3 A/dm^2 and the plating time was controlled in the range of 0.5−7.5 h to compensate for the variation of the current density. The surface morphology, hardness, and folding behavior were characterized by atomic force microscopy, nanoindentation technique and Massachusett Institute of Technology folding endurance test, respectively. The X-ray diffraction patterns indicated that the Cu phase was formed without any secondary phases; however, the preferred orientation changed from (220) to (111) as the current density increased over 1 A/dm^2. In addition, it was observed that the root-mean-square and hardness values decreased when the current density increased and the plating time decreased simultaneously. The electrical resistivity was as low as approximately 21 nΩ·m and the number of cycles without failure in the folding test was over 15 000, which were comparable to those of commercial FCCLs.

Key words: electro-plating; current density; Faraday’s law; FCCL; microstructure

1 Introduction

Flexible printed circuit boards(FPCBs) have received a great deal of attention due to their flexibility, downsizing ability and movable properties which render them ideal for applications involving electronic devices. Flexible copper clad laminate(FCCL), consisting of copper(Cu) and polyimide(PI) layers, is generally employed as a base material for FPCBs. FCCL is fabricated by three methods in terms of the bonding between the Cu and PI layers, viz. casting, sputtering and laminating processes, each of which has advantages and drawbacks[1]. In addition, conductive Cu layer/plate is obtained by either rolling or electroplating process, and the rolled plate is used for the casting and laminating processes, while the electro-plated layer is used for the sputtering process.

Electro-plated Cu has superior properties compared with rolled and annealed Cu in terms of its adhesion strength, due to its rough surface, control of the thickness, ease of fabrication and, above all, cost-effectiveness[2]. However, electro-plated Cu has relatively lower flexibility because the electroplating method tends to produce a columnar grain structure parallel to the thickness direction[3].

It should be noted that the surface roughness, microstructural morphology and resultant mechanical and electrical properties of the electro-plated Cu depend on the processing variables, such as the composition of the electrolyte, current density, type of power (DC or pulse), substrate and electrode materials, bath temperature and pH[2]. Among these variables, it is known that the current density affects the thickness, surface roughness, nucleation rate, grain size and texture of the electro-plated metal. In addition, for the practical application of the FCCL, the thickness of the Cu layer has to be precisely controlled. The thickness can be easily controlled by adjusting the current density and plating time. However, the combined effect of the current density and plating time on the microstructure and properties of the FCCL has not previously been reported.

In the present study, we fabricated FCCLs and studied the combined effect of the current density and

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plating time on their surface morphology, texture, hardness, electrical resistivity and folding behavior. In the fabrication process, a seed layer of Cu was introduced by electroless plating and subsequently Cu was deposited by the electroplating method.

2 Experimental

The Cu/PI plate used for the FCCL was fabricated by the electro-Cu plating method. A polyimide film (PI, Kapton® FPC, Dupont) of the pyromellitic dianhydride-oxydianiline(PMDA-ODA) type with a size of 20 cm×20 cm×25 μm was used as the substrate. Before the electroplating, a seed layer was deposited on both sides of the PI by the electroless Cu plating method in order to serve as the electrode. The Cu seed layer had a uniform surface morphology and thickness of 0.4 μm, and the detailed explanation of the electroless Cu plating process is described in Ref.[1]. In the electroplating process, Cu was deposited by direct current on both sides of the electroless-plated Cu/PI substrate in an electrolyte at room temperature. The electrolyte consisted of $CuSO_4{\cdot}5H_2O$ (70 g/L), H_2SO_4 (200 g/L), HCl (50 mg/L) and additives (5 ml/L from MK Chem & Tech. Company). The anode consisted of a phosphorized copper ball in a titanium basket. To obtain Cu layers with a similar thickness (approximately 20 μm), the current density was varied in the range of 0.2−3 A/dm^2 and the plating time was controlled in the range of 0.5−7.5 h to compensate for the variation of the current density.

The surface morphology was characterized by atomic force microscopy (AFM, SPA−300HV, SII Nano Technology Inc.) in tapping mode over an area of 20 μm ×20 μm. The phase identification of the FCCL was performed by X-ray diffractometer (BRUKER-AXS, D8 discover) with Cu K_α radiation. The hardness of the Cu layer was measured with a nanoindenter (Nano Indenter XP, MTS). The electrical resistivity of Cu was determined by the conventional 4-point probe method. Approximately ten specimens were tested per condition for the hardness measurements, while two specimens were used for the resistivity measurement. The folding endurance was evaluated by the Massachusett Institute of Technology (MIT) folding endurance test. For the test, the specimen was cut to dimensions of 15 mm×15 mm and patterned, i.e., additive patterns were introduced to the PI through a conventional photolithography process. The photo masking, exposure and development procedure were used in this process. The patterned specimen was then tensioned with a force of 5 N and the specimen holder was moved repeatedly right and left with a fixed angle of (135±5)°, in a manner similar to the motion of a pendulum.

3 Results and discussion

In order to evaluate the efficiency of the plating process as a function of the current density, the variations of the calculated and measured thickness of the electro-plated Cu with the current density for 30 min are shown in Fig.1. The measured thickness of the Cu layer increased almost linearly from 4.3 to 13.2 μm as the current density increased from 1 to 3 A/dm^2 and then the thickness slightly increased to 14.6 μm as the current density was further increased to 5 A/dm^2. On the other hand, the calculated thickness, according to Faraday's law, increased linearly as the current density increased, as shown in Fig.1. The thicknesses were calculated to be 6.7, 13.3, 20.0, 26.6 and 33.3 μm for current densities of 1, 2, 3, 4 and 5 A/dm^2, respectively.

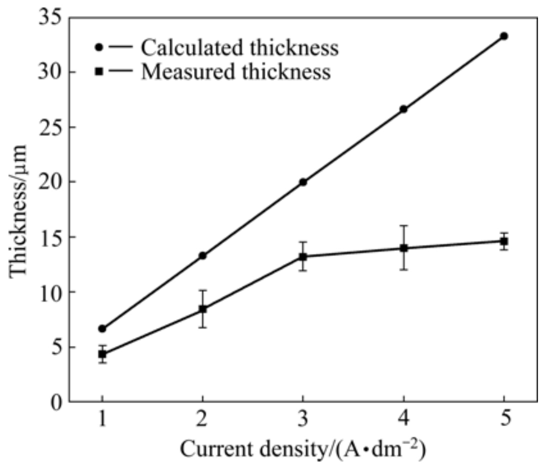

Fig.1 Variation in thickness of Cu layer with current density

The calculated thicknesses were higher than the measured values and the difference between them became larger as the current density increased, indicating that the efficiency of deposition decreases as the current density increases. This can be explained as follows. For the Cu electroplating process, the Cu layer is deposited in two steps according to the following reactions:

$$Cu^{2+}+e=Cu^{+}(ad) \quad (1)$$

$$Cu^{+}(ad)+e=Cu \quad (2)$$

It is known that the rate of reaction (1) is lower than that of reaction (2); thus, reaction (1) will control the overall reaction rate, because the two reactions occur in sequence. In reaction (1), as the current density increases, the concentration of electrons produced from the cathode increases; on the other hand, the concentration of Cu ions (Cu^{2+}) does not change, resulting in a decrease of the reaction rate and consequent decrease in the efficiency of plating.

To evaluate the combined effect of the current density and plating time on the microstructural evolution and resultant properties of the FCCLs having Cu layers with similar thicknesses, we varied the current density and plating time in the ranges of 0.2−3 A/dm^2 and 0.5−7.5 h, respectively, based on Faraday's law:

$$m=It\alpha/nF \tag{3}$$

where m is the reacted mass; I is the current; t is the time; α is the atomic mass; n is the number of exchanged equivalents and F is Faraday's constant. To obtain a thickness of 20 μm in each case, Cu plating was performed at current densities of 0.2 A/dm^2 for 7.5 h, 1 A/dm^2 for 1.5 h and 3 A/dm^2 for 0.5 h according to Eq.(3) and the corresponding specimens are hereafter denoted as the 0.2−7.5, 1−1.5 and 3−0.5 specimens, respectively. The thicknesses of all three samples were measured to be approximately 18 μm.

The surface morphology of the specimens was observed by the AFM profiles, as shown in Fig.2. The surface morphology of the electroless-plated Cu on the PI substrate is also presented for comparison. The surface of the electroless-plated Cu/PI was relatively smooth, wavy with a uniform pattern and dense and its root-mean-square(RMS) value was estimated to be 13.4 nm. On the other hand, different surface morphologies were observed and a granular-type microstructure formed for the electro-plated Cu, as shown in Figs.2(b) and (c). The RMS value was 29.8 nm for the 1−1.5 specimen and 18.5 nm for the 3−0.5 specimen, revealing that its value decreased as the current density increased and the plating time decreased simultaneously. In addition, it should be noted that the decrease of the RMS values became smaller with increasing current density.

The variation of the surface roughness with the current density for the electro-plated Cu layer has been studied by several researchers[4−7] and their results were not consistent with one another. CHEN et al[4] reported that the RMS values decreased with increasing current density from 1 to 6 A/dm^2, whereas, in contrast, BUND and ISPAS[6] reported that the RMS values increased with increasing current density from 0.05 to 5 A/dm^2, in which the plating time was fixed. The tendency of our results is partly in accordance with that of CHEN et al[4].

Fig.3 shows the XRD patterns of the electro-plated specimens. In all of the specimens, the Cu phase was formed without any secondary phases; however, there was a distinct change in the preferred orientation with increasing current density. For the 0.2−7.5 specimen, the Cu (220) plane was formed parallel to the surface without any other planes. On the other hand, the 1−1.5 and 3−0.5 specimens consisted of (111) as the major peak

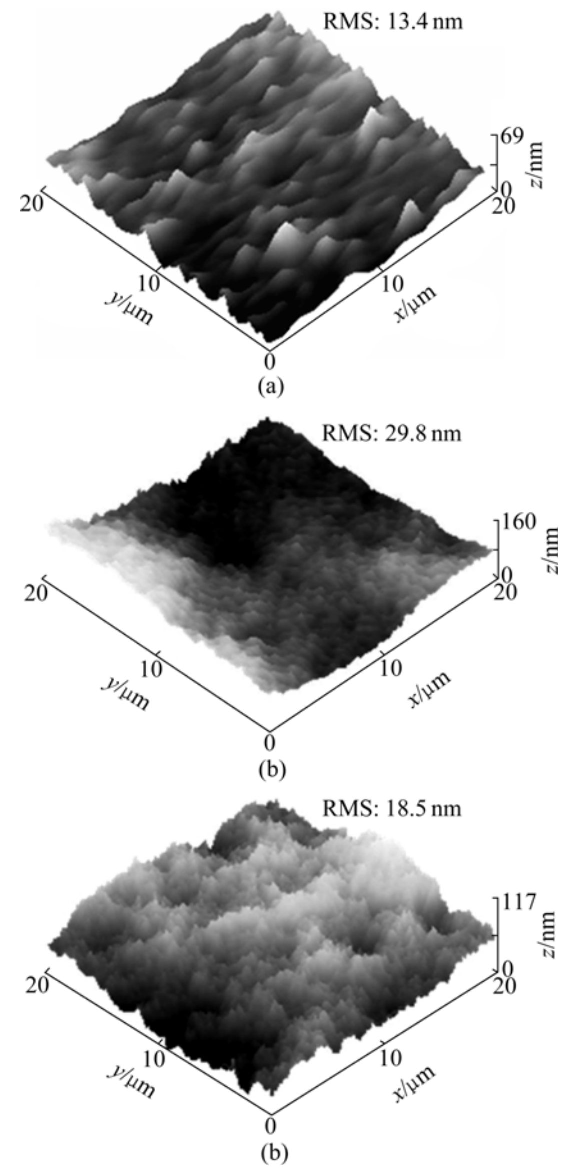

Fig.2 AFM profiles (20 μm × 20 μm) of surfaces: (a) Electroless-plated Cu/PI; (b) 1−1.5 specimen; (c) 3−0.5 specimen

and (200), (220) and (311) as minor peaks.

The full width at half maximum (FWHM) values were measured from the XRD patterns. The FWHM values decreased with increasing current density. The values obtained from the (220) peaks were measured to be 0.54°, 0.44° and 0.37° for the 0.2−7.5, 1−1.5 and 3−0.5 specimens, while those from the (111) peaks were 0.31° and 0.30° for the 1−1.5 and 3−0.5 specimens, respectively. It is known that the grain size can be calculated using the following equation:

$$d=0.9\lambda/B\cos\theta \tag{4}$$

where d is the grain size; λ is the wavelength of Cu K_α; B is the FWHM value and θ is the angle of diffraction, and FWHM value is inversely proportional to the grain size.

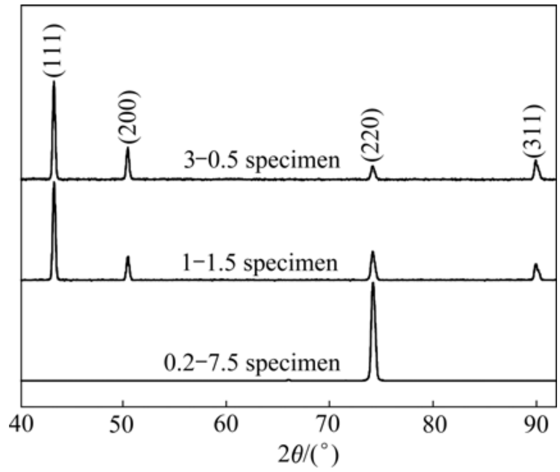

Fig.3 XRD patterns of FCCL specimens

Therefore, for all of the samples, it seemed that the grain size slightly increased when the current density increased and plating time decreased simultaneously. In general, it was reported that the grain size of electro-plated Cu decreased as the current density increased, which is thought to result from the increased nucleation rate[8−9]. In contrast, our result is consistent with EBRAHIMI et al and AHMED[3], in which the grain size increased from 11 to 17 nm as the current density increased from 1.8 to 2.5 A/dm^2. In order to measure the grain size precisely, a TEM analysis is currently underway.

Fig.4 shows the dependence of the hardness of the specimens on the current density together with the plating time. The hardness value was measured to be 938 MPa for the 0.2−7.5 specimen, which is higher than that of the 1−1.5 or 3−0.5 specimen (560−623 MPa). This is partly related to the smaller grain size in the 0.2−7.5 specimen, as noted earlier, because it is known that the hardness is generally inversely proportional to the grain size[7]. It should also be noted that the preferred orientation may have an influence on the hardness of the specimens; however, the role of the relative orientation is not clearly understood.

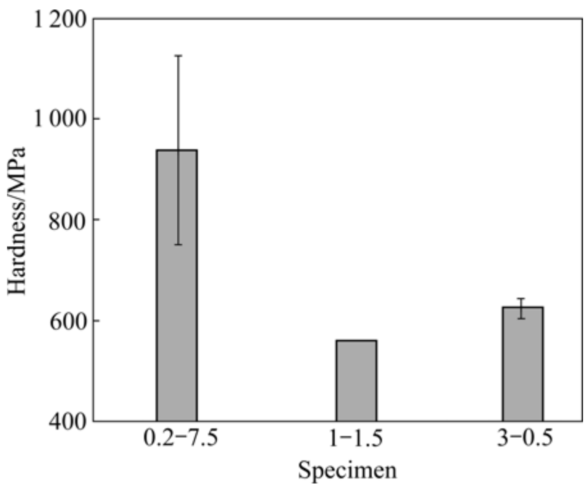

Fig.4 Dependence of hardness of Cu layer on current density

For their application to electronic packages, we measured the electrical resistivity of the specimens. The resistivities of the samples were not significantly different and were measured to be in the range of 20.6−22.1 nΩ·m, which is comparable to that of commercial FCCLs made by the casting and laminating technique (approximately 18 nΩ·m). In addition, the FCCLs were patterned to evaluate their folding endurance, as shown in Fig.5. In the MIT folding endurance test, failure did not occur after more than 15 000 cycles for any of the specimens and this result was also comparable to that of the commercial FCCLs. It is suggested that FCCLs fabricated with a current density in the range of 0.2−3 A/dm^2 in combination with a plating time in the range of 0.5−7.5 h have satisfactory resistivity and folding behavior. Furthermore, the 3−0.5 specimen is considered to have sufficient productivity and cost-effectiveness to be applied to FPCBs due to its short process time.

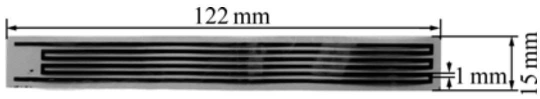

Fig.5 Patterned FCCL for MIT folding endurance test

4 Conclusions

1) It was observed that the thickness of Cu increased as the current density increased when the plating time was fixed; on the other hand, the efficiency of deposition decreased as the current density increased.

2) The RMS decreased when the current density increased and the plating time decreased simultaneously.

3) The XRD pattern showed that the Cu phase was formed without any secondary phases; however, the preferred orientation changed from (220) to (111) as the current density increased over 1 A/dm^2.

4) With increasing current density, the hardness value decreased, probably due to the increase in the grain size, based on the FWHM analyses.

5) The electrical resistance was in the range of 20.6−22.1 nΩ·m and the folding test was conducted for over 15 000 cycles without failure.

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