

Fabrication of two-layer flexible copper clad laminate by electroless-Cu plating on surface modified polyimide

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Abstract: A flexible copper clad laminate (FCCL) was fabricated using electroless- and electro-Cu plating processes and the effects of pre-treatment time on the adhesion strength of the FCCL were evaluated based on interfacial morphology. The neutralization and catalyst time were varied in the range of 0–20 min and 0.1–10 min, respectively, and the interfacial condition of the FCCL was characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). It is observed that the peel strength increases significantly as the neutralization and catalyst time increase. Peel strength as high as 7.2–7.3 N/cm is obtained as the neutralization and catalyst time increase up to 20 min and 10 min, respectively, which is comparable to the strength achieved by the conventional laminating and sputtering processes. These improvements are probably due to an increase in the surface roughness of polyimide (PI), the activated surface condition, and the adsorption of palladium ions/atoms (Pd) on the PI surface which act as nucleation sites for Cu.

Key words: adhesion strength; electroless-Cu plating; flexible clad laminate; X-ray photoelectron spectroscopy

1 Introduction

The recent demand for flexible printed circuits (FPC) is rising due to their employment not only in portable electronics and smart cards, which require flexibility and durability, but also in displays and micro-electromechanical system (MEMS) devices. Accordingly, there has been substantial research and development regarding the manufacturing process and improvement in performance of flexible copper clad laminate (FCCL), i.e. base materials used for FPC. The FCCL generally consists of copper and polyimide (PI) layers, and thin and homogeneous structures with good interlayer bonding strength are desirable to satisfy the trend of downsized microelectronics and a longer service life.

There are three processes used to create bond between the layers of FCCLs: casting, sputtering, and laminating [1]. Although the former two processes are cost effective and have merits of high flexibility and adhesion strength between Cu and PI, it is difficult to make a double-sided FCCL covered with Cu on both sides of PI in the casting process and to make thin FCCL due to the three-layer structure (Cu-adhesive-PI layer)

created by the laminating process. In the sputtering process, the seed layer, typically Cr, Ti, Co, or Ni [2–3], is sputtered on PI modified by a dry or wet process [4–5] and afterwards a thicker Cu layer is deposited by Cu-electroplating. This method has the potential to improve the adhesion between Cu and PI, but it is expensive due to the requirement for a vacuum apparatus and it requires the removal of the seed layer during the etching process to make the pattern of the FPC.

Therefore, it is necessary to develop a new synthetic method which allows a thin, two-layer structure, and double-sided FCCL and is also cost-effective. Our approach introduced Cu as a seed layer via electroless-plating to ensure sufficient adhesion to PI, and then subsequently deposited a Cu layer by an electroplating method. Electroless-Cu plating is cost-effective and is a widely used electrochemical process for the deposition of Cu films. In this study, we fabricated a two-layer FCCL by electroless- and electro-Cu plating processes. To achieve high adhesion strength between Cu and PI, which is essential to ensure the reliability of the FPC, the neutralization and catalyst process time varied during pre-treatment on PI. Then, the effect of the process time on the peel strength of the FCCL was evaluated based on

the interface morphology.

2 Experimental

A two-layer FCCL was fabricated using electroless- and electro-Cu plating methods. A 25 μm -thick polyimide (PI, Kapton® FPC, Dupont) film of the pyromellitic dianhydride-oxydianiline (PMDA-ODA) type was used as the substrate with a size of 20 cm \times 20 cm. The pre-treatment and plating of Cu on the PI substrate were successively processed, as listed in Table 1. Water rinsing was also carried out between steps. Cu layers were then formed by electroless- and electroplating on both sides of the PI substrate and the layers of approximately 0.4 μm and 20 μm in thickness were obtained, respectively. To obtain an FCCL of high adhesion strength, neutralization and catalyst processes were performed for 0–20 min and 0.1–10 min, respectively. The FCCLs were fabricated with a neutralization time of 0, 0.5, 2, 5, and 20 min and are hereafter denoted as the N-0, N-0.5, N-2, N-5, and N-20 specimens, respectively. The FCCLs with a catalyst time of 0.1, 5, and 10 min are denoted as the C-0.1, C-5, and C-10 specimens, respectively.

Table 1 Process flow and conditions for FCCL fabrication

Process	Constituents	Condition
Cleaning/ etching	NaOH, Na ₂ SO ₃	45 °C, 2 min
Conditioning	3Na(NO ₂) ₃ ·(CH ₃ COCH ₃) ₃ , C ₁₂ H ₂₅ N(CH ₃) ₃ Cl, C12TMA, (CH ₂ CH ₂ OH) ₃ N	60°C, 5 min
Neutralization	H ₂ SO ₄ , Na ₂ S ₂ O ₈	Room temperature; 0, 0.5, 2, 5, 20 min
Catalyst	HCl, SnCl ₂ , PdCl ₂	Room temperature; 0.1, 5, 10 min
Accelerator	HBF ₄ , HF	30 °C, 7 min
Electroless- Cu plating	CuSO ₄ , KNaC ₄ H ₄ O ₆ ·4H ₂ O, HCHO, NaOH, NiSO ₄ ·6H ₂ O	30 °C, 15 min, pH 12.3
Electro- Cu plating	CuSO ₄ ·5H ₂ O, H ₂ SO ₄ , HCl, additive	Room temperature; 0.5 A/dm ² , 3 h

The adhesion strength of FCCL was measured using a 90° peel test at a peeling rate of 10 mm/min. The peel strength was determined using an average value of five FCCL strips (10 mm in width). After the neutralization process, the morphology of the PI surfaces was characterized by atomic force microscopy (AFM, SPA-300HV, SII Nano Technology Inc., tapping mode) over an area of 10 μm \times 10 μm . The peeled PI surface

and PI after pre-treatment process were investigated by X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech) to determine the delamination behavior of FCCL. All spectra obtained by a non-monochromatic Al K α (1 486.6 eV) source were referenced to the C 1s peak (285.0 eV) for neutral carbon.

3 Results and discussion

Fig.1 shows the variation of peel strength of the FCCLs as a function of neutralization process time. The catalyst process for all samples was carried out for 5 min. The peel strength of the N-0 specimen (untreated specimen) was measured to be (0.3 \pm 0.1) N/cm. The strength increased significantly to (6.1 \pm 0.3) N/cm as the processing time increased to 5 min and then it increased more slowly to (7.3 \pm 0.3) N/cm with further increase in process time up to 20 min. The peeling strengths of the N-5 and N-20 specimens were comparable to those of the FCCLs made by laminating or sputtering processes[6–7].

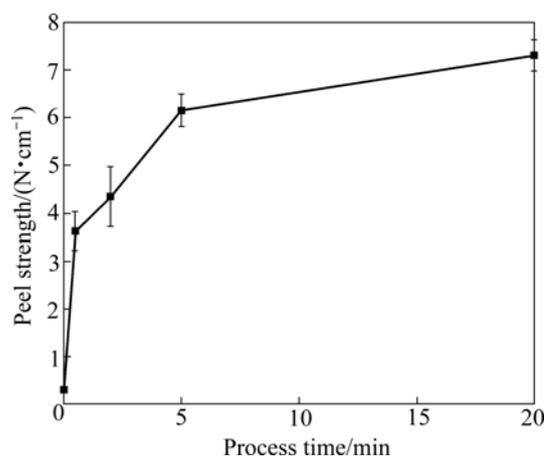


Fig.1 Peel strength of FCCLs as function of neutralization time

Atomic force microscopy (AFM) profiles of the surface morphology of the pristine, N-0, and N-5 PIs after neutralization are presented in Fig.2. The pristine PI surface had large protrusions which probably originated during PI fabrication[8]. The arithmetic mean roughness (R_a) of the pristine PI surface was 1.79 nm. The R_a of the N-0 PI was estimated to be 2.09 nm, indicating no outstanding change of the arithmetic mean roughness in comparison with that of the pristine. In contrast, the different surface morphology was observed, as shown in Fig.2(b). It is likely that the cleaning/etching process based on a NaOH constituent resulted in the removal of the previous protrusions and consequently modified the PI surface[8]. Regardless of surface morphology, the N-0 specimen had a low peel strength of approximately 0.3 N/cm. This was thought to be due to alkali constituents that were not completely removed and remained on the PI surface during the cleaning/etching and conditioning

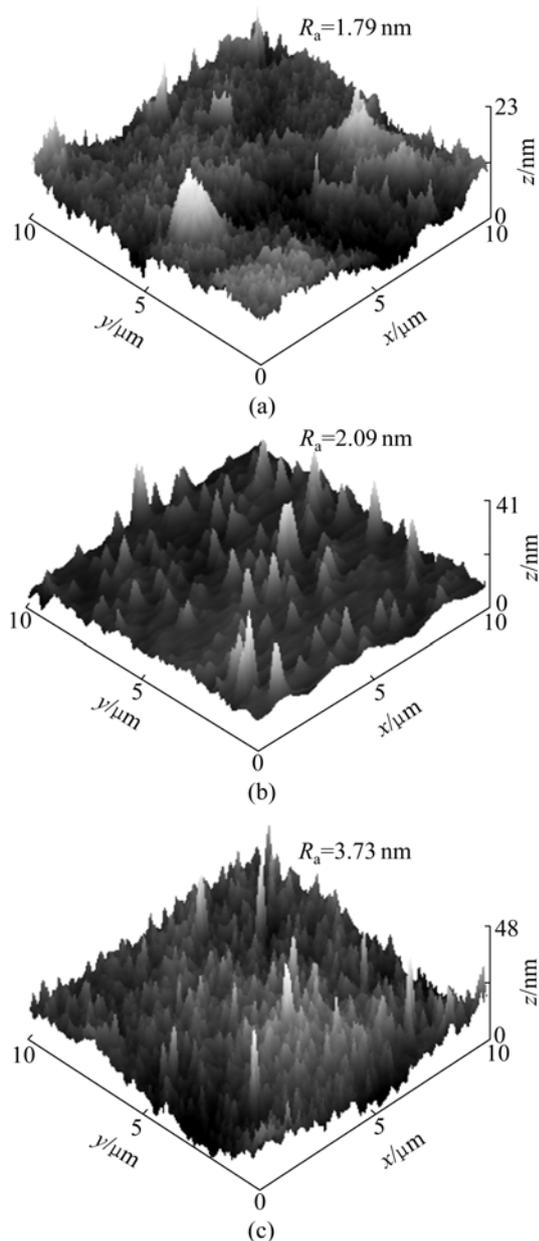


Fig.2 AFM profiles of surfaces of pristine (a), N-0 (b) and N-5 PIs (c)

processes. These alkali constituents likely obstructed the reaction between the PI and the solution constituents in the subsequent processes.

The R_a value increased as the neutralization time increased and the R_a of the N-5 PI was 3.73 nm as shown in Fig.2(c), which probably resulted from chemical attack (etching) by H_2SO_4 and $Na_2S_2O_4$ during the neutralization process. The increase in peel strength with increasing neutralization time shown in Fig.1 can be attributed to the improved adhesion between Cu and PI partly caused by mechanical interlocking because of the surface roughness of PI[9]. It is thought that the neutralization by H_2SO_4 and $Na_2(SO_4)_2$ also plays roles of removing the remaining alkali constituents, such as

OH^- , on the PI surface after the conditioning process, thereby improving adhesion between Cu and PI. In addition, the neutralization process leads to the conversion of sodium polyamate, formed by NaOH in the cleaning/etching process, to polyamic acid ($RCO_2Na+H^+ \rightarrow RCO_2H+Na^+$, where R represents the polymer backbone). It is known that the presence of polyamic acid promotes the adsorption/adhesion of Pd-Sn catalyst on PI during the subsequent catalyst process. This may also result in the improved adhesion between Cu and PI[10]. Therefore, we consider that the increase of peel strength according to increased neutralization time is likely due to the combined effects of an increase in roughness and the adsorption of the Pd-Sn catalyst used for electroless-Cu plating.

To determine the delamination behavior of FCCLs during the peel test, we investigated XPS spectra from the peeled PI surfaces of the pristine, N-0.5, and N-5 specimens as shown in Fig.3. A typical XPS spectrum of the PI was obtained from the pristine specimen for comparison. In the XPS spectrum for the N-0.5 specimen (Fig.3(b)), the peaks of metal elements such as Pd, Sn, Cu, and Na were clearly apparent. In contrast, for the N-5 specimen (Fig.3(c)), the XPS spectrum was similar to that of pristine PI, except for the presence of a small Pd peak. The amount of metal elements was related to the peak area ratio of the metal to C in PI. The peak area ratios of Pd/C, Sn/C, and Cu/C were 0.037, 0.006, and 0.013, respectively, for the N-0.5; while the ratio of Pd/C was 0.002 for the N-5, which was considerably lower than the former specimen.

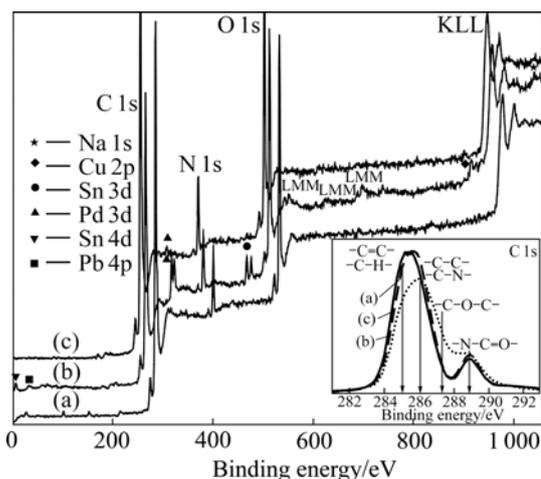


Fig.3 XPS survey spectra of pristine PI (a) and peeled surfaces of PI of N-0.5 (b) and N-5 specimens (c) (Inset: Normalized C 1s spectra of PIs)

These results enabled us to assume that delamination can occur in one mode (adhesive or cohesive mode) or in multiple modes (both adhesive and cohesive modes). The presence of metal element peaks

on the peeled surface of the N-0.5 specimen suggests that delamination occurred mainly along the interface between the PI and Cu layer (i.e., mainly in adhesive mode). It was noted that Pd was adhered/adsorbed on the PI, promoting the nucleation of Cu during electroless-Cu plating and this improved the adhesion between the Cu and PI layer[11]. On the other hand, for the N-5 specimen, delamination occurred mainly within the inner region of PI (i.e., mainly in cohesive mode). This delamination behavior is thought to result from the improved peel strength due to the enhanced adhesion between Cu and PI.

The differences in delamination behavior were also supported by the C 1s core-level spectra shown in the inset in Fig.3. In comparison with the spectrum of the pristine PI, the spectra of the specimens subjected to the neutralization treatment shifted to high binding energies. These shifts indicate the chemical interaction between the metal elements and the PI backbone[2, 12]. For the N-0.5 specimen, the shift was more intense than that of the N-5, suggesting that more metal elements were presented on the peeled PI surface of the N-0.5 specimen compared with that of the N-5 specimen.

To evaluate the effect of catalyst process time on the adhesion strength of FCCLs, the process time was varied from 0.1 to 10 min after using a neutralization of 5 min. Fig.4 shows the dependence of peel strength of the FCCLs on the catalyst process time. The peel strength of the FCCL increased monotonically with increasing catalyst time. For the C-0.1, C-5, and C-10 specimens, the peel strength was (2.9±1.3), (5.9±0.3), and (7.2±0.3) N/cm, respectively. This improvement in peel strength is likely due to the role of Pd on the PI surface.

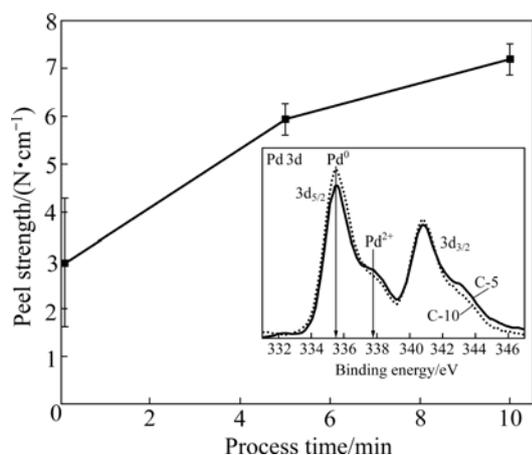


Fig.4 Peel strength of FCCLs with respect to catalyst process time (Inset: Normalized XPS Pd 3d spectra of C-5 and C-10 PI surfaces)

The XPS spectra of the PI after catalyst and accelerator processes were obtained to evaluate the presence and state of Pd on the PI. The normalized XPS

Pd 3d spectra for the C-5 and C-10 specimens are presented in the inset in Fig.4, revealing a small difference in the surface conditions. The Pd 3d_{5/2} peaks for both specimens had more Pd⁰ (~335.5 eV) components than Pd²⁺ (~337.7 eV) components. However, the ratio of peak intensity of Pd⁰ to Pd²⁺ was higher for the C-10 (1.91) than for the C-5 specimen (1.04). This implies that the Pd-Sn colloidal compound decomposed during catalyst and accelerator processes and more Pd in metallic form, Pd⁰, (i.e., less PdCl₂) adhered/adsorbed on the PI surface for the C-10 specimen, probably due to a longer process time.

It is known that Pd⁰ nuclei activated by an acceleration process act as nucleation or initiation sites during electroless-Cu plating and improve adhesion between Cu and PI[11]. Therefore, the higher peel strength of the C-10 specimen compared with the C-5 specimen was probably due to the existence of relatively more Pd⁰ on the PI surface of the former. It was noted that the formation of more active Pd⁰ metals and their uniform distribution on the PI surface, prior to immersion in an electroless plating solution, were essential to improve the adhesion between Cu and PI for FCCLs.

4 Conclusions

We fabricated double-sided and two-layer FCCLs by electroless- and electro-Cu plating processes and evaluated the effects of neutralization and catalyst time on the peeling strength of the FCCL.

1) When the neutralization time increased from 0 to 5 and 10 min, the peel strength increased from 0.3 to 6.1 and 7.3 N/cm, respectively. These improvements were probably due to the combined effects of an increase in the roughness and adsorption of the Pd-Sn catalyst for electroless-Cu plating.

2) Delamination occurred mainly on the inner region of PI (cohesive mode) rather than the interface between the Cu and PI (adhesive mode) due to the improved adhesion strength.

3) The peel strength was improved significantly as the catalyst time increased. An XPS analysis also implied that the greater amount of Pd ions/atoms adhered/adsorbed on the PI surface acted as nucleation sites during the electroless-Cu plating and improved the adhesion between the Cu and PI when the catalyst time increased.

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