Effect of Cr Thickness on Adhesion Strength of Cu/Cr/Polyimide Flexible Copper Clad Laminate Fabricated by Roll-to-Roll Process

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The adhesion strength of a Cu/Cr/polyimide (PI) flexible copper clad laminate (FCCL), which was manufactured by the roll-to-roll process, was evaluated according to the thickness of the Cr seed layer using the 90° peel test. The changes in the morphology, chemical bonding and adhesion properties were characterized by scanning electron microscopy, atomic force microscopy and X-ray photoelectron spectroscopy. The peel strength of the FCCL decreased with increasing Cr layer thickness. The higher FCCL peel strength was attributed to the lower proportion of C-N bonds and higher proportion of C-O or carbonyl (C=O) bonds on the PI surface compared to the FCCL with the lower adhesion strength. The FCCL with the higher peel strength had a fractured PI surface with a higher surface roughness. The adhesion strength between the metal and PI was mostly attributed to the chemical interaction between the metal layer and the functional groups of the PI.
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1. Introduction

As electronic devices become smaller and lighter, there is a growing need to replace the conventional rigid circuit substrates with flexible polymer substrates. Flexible printed circuit boards (FPCBs) based on copper (Cu) on a polyimide (PI) are used as flexible interconnections, such as the hinges of cellular phones or chip on flex (COF) packaging, and are expected to be used more in upcoming flexible IT electronics.¹⁻³⁾

A flexible copper clad laminate (FCCL) is a system that unifies an electric conductor such as Cu with an insulator such as a PI. The FCCL is generally employed as a raw material for FPCBs. There are three FCCL manufacturing methods, laminating, casting and sputtering/electroplating, which correspond to the lamination of a Cu foil on the PI using an adhesive, lamination of the PI onto a Cu foil and physical vapor deposition (PVD) of an interlayer (Cr, Ni, ITO, etc.) onto the PI films and subsequent Cu coating by electroplating, respectively.^{4,5)} The bonded laminate must withstand further processing stages, such as photolithographic etching of Cu using various chemicals and immersion in a molten solder bath or the solder reflow process. The bonded laminate must also perform satisfactorily throughout its service-life where it may be exposed to a wide range of temperature and high relative humidity. One of the major requirements for the flexible laminate to withstand these various processing and in-service conditions is that the laminate possesses an adequate resistance to delamination.⁶⁾ Flexural endurance and long-term reliability of the FCCL acting as an electrically connector fundamentally rely on the peel strength of the FCCL, which is inherently related to the adhesion between the metal (Cu) and PI.⁷⁾

Mechanical reliability of the Cu/PI films is problematic because of poor interface adhesion strength. This is because Cu does not form a strong chemical bond with the constituent

elements of the PI. Cu may also act as a catalyst to decompose polymeric bonds under oxygen or a moisture containing environment at elevated temperatures.⁸⁾ In order to improve the interface adhesion strength, an additional metal layer is generally deposited at the Cu/PI interface. Chromium (Cr) has been used as an interface metal layer because of the formation of strong Cr-C bonds.⁹⁻¹¹⁾ The use of Cr is also intended to prevent Cu diffusion into the PI and to maintain the properties of PI.¹⁰⁾ Enhancement in adhesion of metals to the PI can also be accomplished by altering the surface properties using various pre-treatments of the polymer substrates.^{12,13)} Surface pre-treatments often modify the surface physically and chemically. The adhesion of metals on polymer substrate is strongly influenced by the modified chemical and physical nature of the treated surfaces. The possible mechanisms to explain the enhanced adhesion include: increase of the surface area caused by transforming a smooth surface to a roughened topology, formation of cross-linking in the chemically altered surface layer that improves its mechanical strength, production of functional groups that facilitate bonding to the metal, or increase of the surface free energy.^{12,14)}

Many studies have been performed on the adhesion properties of various Cu/PI films with different interlayers and pre-treatments.¹⁵⁻¹⁷⁾ Nevertheless, studies on the adhesion strength of the Cu/Cr/PI system with different Cr thicknesses are still not enough to be used in practical flexible electronics. In this study, the adhesion properties of the Cu/Cr/PI films were studied according to the thickness of the Cr seed layer using the 90° peel test. The test results are discussed in connection with the fracture analysis results observed in this study.

2. Experimental Procedures

The FCCL structure investigated in this study was Cu/Cr/PI. The manufacturing process of the FCCL used in this study is shown in Fig. 1. The substrate was a 25 µm-thick PI film

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Fig. 1 Manufacturing process of the FCCL used in this study.

Fig. 2 Schematic of the vacuum chamber using the roll-to-roll process.

(Kaneka, Japan) that had not undergone any plasma or chemical surface treatment. The ion beam treatment and two sputtering steps were performed in the same vacuum chamber using the roll-to-roll process (Fig. 2). The base pressure and roll speed of the sputtering system were 10^{-4} – 10^{-6} Pa and 0.6 m/min, respectively, for both the ion beam treatment and sputtering process. First, the ion beam treatment was performed on the PI under argon (Ar) and oxygen (O_2) gas conditions. The constant current and flow rate of Ar and O_2 were 3.5 A and 5 standard cubic centimeters per minute (sccm) and 20 sccm, respectively. Second, a Cr seed layer was sputtered on the PI under Ar and O_2 gas conditions. Three Cr thicknesses were 10 nm, 20 nm,

Table 1 Power and flow rate used in the Cr sputtering process.

Thickness of Cr layer, nm	Power, kW	Flow rate, sccm
10	0.65	Ar 10/ O_2 45
20	0.96	Ar 10/ O_2 50
30	1.32	Ar 15/ O_2 60

Fig. 3 Schematics of (a) the top view of the FCCL and (b) the 90° peel test.

and 30 nm. The power and gas flow rate for the three samples are listed in Table 1. Finally, a 0.2 μ m-thick Cu layer was sputtered on the PI. After the sputtering of Cu, the samples were subsequently electroplated with pure Cu to a thickness of 8 μ m. The current density and roll speed for the Cu electroplating were 1.3 A/dm² (ASD) and 320 mm/min, respectively.

The dimensions of the PI and Cu layers for the peel test were 100 mm $\times$ 10 mm and 100 mm $\times$ 3 mm, respectively. Figure 3(a) shows a schematic of the FCCL manufactured for the peel test. The samples underwent 90° peel testing conducted at 4 mm/min with 10 specimens at each condition. Figure 3(b) shows the schematic of the 90° peel test. After the peel test, the fracture surface and composition on the Cu and PI surfaces were identified with scanning electron microscopy (SEM, S-3000H, Hitachi, Japan) and energy dispersive X-ray spectroscopy (EDS). The morphologies of the fracture surfaces were also studied by atomic force microscopy (AFM, Thermo-Microscopes, CP Research, USA). In each case, an area of 10 μ m $\times$ 10 μ m was scanned using the tapping mode. The AFM observation was carried out at atmosphere pressure and room temperature. The root-mean-square (RMS) roughness was calculated from the roughness profile determined by AFM. X-ray photoelectron spectroscopy (XPS, ESCA 2000 LAB MK-II spectrometer, VG Microtech, England) analysis with an MgK α X-ray source was performed on the peeled PI surface to elucidate the chemical bonding state at the interface. The base pressure in the sample chamber was controlled in the range of 1.3×10^{-6} to 1.3×10^{-7} Pa.

3. Results and Discussion

Peel tests have been widely used to measure the adhesion strength of various materials with thin films. Figure 4 shows the results of the peel strength test of the three FCCLs according to the thickness of the Cr seed layer. Although a significant difference in the peel strength was not observed, the peel strength of the FCCLs decreased with increasing thickness of the Cr seed layer, and the Cr thickness with the highest peel strength was 10 nm. The peel strengths for the 10 nm-thick, 20 nm-thick and 30 nm-thick Cr seed layers were about 560 gf/cm, 555 gf/cm and 540 gf/cm, respectively. Recently, the peel strength of the FCCL with a Ni-Cr

Fig. 4 Peel strength of the FCCLs according to the thickness of the Cr seed layer.

seed layer was investigated. The results of the study showed that the peel strength of the Cu/Ni-Cr/PI FCCL increased with increasing Cr content and Cu electroplating layer thickness, and that the Cr content had a greater effect on the peel strength than the Cu electroplating layer thickness.^{16,17)} Generally, the good adhesion between the metal layer and polymer was attributed not only to the mechanical interlocking but also to the interfacial chemical bonds. It is especially known that the adhesion strength is significantly affected by the chemical interaction between the metal layer and functional groups of the polymer.^{9,18)} It was reported that some metals can interact with oxygen-containing groups on polymer surfaces, thereby creating metal-oxygen-carbon type bonding.¹⁸⁾ It is also known that the ion bombardment of a polymer induces scission of the chains, due to their collision with the incident ions, causing them to undergo further reactions such as cross-linking, carbonization and chemical reactions. These reactions lead to changes in the polymer surface, resulting in increased chemical bonding, physical interaction, and mechanical interlocking between the PI and metal layer. From these results, an inference was made that the change in adhesion was due to the resulting changes in the characteristics of the PI surface.

Figure 5 shows the SEM images and EDS analysis results of 10 nm-thick Cr seed layer FCCL, before and after the peel test. Figures 5(a) and (b) revealed that the adhesion interface of the manufactured FCCL was very uniform and that the fracturing observed after the peel test occurred between the PI and metal layer. Figures 5(c) and (d) show that the oxygen, copper and chromium elements were detected on the

Fig. 5 SEM images and EDS analysis results of the FCCL with the 10 nm-thick Cr seed layer: (a) cross-section of the FCCL before peel testing, (b) cross-section of the FCCL after peel testing, (c) Cu side of the FCCL after peel testing and (d) PI side of the FCCL after peel testing.

Fig. 6 AFM images of the fracture surfaces (PI sides) for the three samples after the peel test: (a) 10 nm, (b) 20 nm and (c) 30 nm. The scale of the vertical range is different for each image.

Cu side of the FCCL after the peel test, whereas only carbon and oxygen were the only elements detected on the PI side. These results indicated that the failure occurred at the interface between the Ni-Cr layer and PI. In this study, the failure sites for the 20 nm-thick and 30 nm-thick Cr seed layer FCCL samples were similar to the results shown in Fig. 5.

Figure 6 shows the AFM images of the fracture surfaces (PI sides) for the three samples after the peel test. The RMS roughnesses of the fracture surfaces for the 10 nm-thick, 20 nm-thick and 30 nm-thick Cr seed layer FCCL samples were 34.6 nm, 23.4 nm and 22.0 nm, respectively. From these results, the fracture surface of the FCCL with the 10 nm-thick Cr seed layer had the highest RMS roughness. Previous studies have shown that the surface roughness is an important factor in enhancing the adhesion properties.^{18–22} In fact, the surface roughness of the fractured PI surface increased with

Fig. 7 XPS results for the C_{1s} spectra of the fracture surfaces (PI side) for the three samples: (a) 10 nm, (b) 20 nm and (c) 30 nm.

increasing adhesion strength for the FCCL. This observation was attributed to the higher bond ratio between the Cr seed layer and the functional groups on the PI surface, as described in the next paragraphs.

XPS analysis was conducted to investigate the chemical bonding state at the peeled interface of Cr/PI. Figure 7 shows the XPS results of the C_{1s} spectra for the fractured PI surfaces after the peel test. The 10 nm-thick Cr seed layer FCCL had a C-N ratio of 36.6%, C-O ratio of 22.6% and carbonyl (C=O) ratio of 40.8%. On the other hand, the 20 nm-thick Cr seed layer FCCL had a C-N ratio of 38.9%, C-O ratio of 18.8% and carbonyl (C=O) ratio of 42.3%. Also, the 30 nm-thick Cr seed layer FCCL had a C-N ratio of 41.2%, C-O ratio of 22.8% and carbonyl (C=O) ratio of 36.0%. The ratio of C-N bonds increased with increasing Cr thickness from 10 nm to 30 nm. On the other hand, the ratios of the C-O or carbonyl (C=O) bonds decreased with increasing thickness of the Cr

Fig. 8 Relationship between the peel strength and the chemical bonding ratio according to the thickness of the Cr seed layer.

seed layer. These results indicated that the 10 nm-thick Cr seed layer FCCL had a lower C-N ratio, but higher C-O or carbonyl (C=O) ratios, than the 20 nm-thick and 30 nm-thick Cr seed layer FCCLs. In other words, the thickness of the Cr seed layer in the Cu/Cr/PI FCCL slightly affected the chemical bonding states on the PI surface, due to the different bombardment caused by the different power levels used in the Cr sputtering process, as shown in Table 1.

Previous studies reported that suitable functional groups, such as hydroxyl (–OH), carbonyl (C=O) and carboxyl (COOH) species, promotes the adhesion strength at the metal/polymer interface.^{1,18} It was also reported that the adhesion of Cr to PI occurs through the formation of Cr-O complexes or Cr oxides at the interface through the reaction of Cr with the pendent oxygen atoms in the PI¹¹ or through the reaction of Cr with the oxygen functionality, in particular carbonyl groups, in the pyromellitic dianhydride (PMDA) units of the PI.^{18,23} These results suggest that the reduction in the C-O or carbonyl (C=O) ratios decreased the adhesion strength between the Cr layer and PI. Figure 8 shows the relationship between the peel strength and chemical bonding ratio according to the thickness of the Cr seed layer in this study. The decreased formation of functional groups identified as C-O or carbonyl (C=O) bonds, as well as the increase in the C-N component ratio, may have contributed to the deteriorated chemical interactions between the Cr and PI surfaces, thereby decreasing the peel strength. As a result, the AFM and XPS results revealed that the 10 nm-thick Cr seed layer FCCL exhibited stronger chemical bonding and higher fracture surface roughness than the 20 nm-thick and 30 nm-thick Cr seed layer FCCLs.

Recently, the peel strength of the FCCL with a Ni-Cr seed layer (Cu/Ni-Cr/PI) was investigated. The peel strength of the FCCL increased with increasing Ni-Cr seed layer thickness (or sputtering power).²⁴ However, in this study, the peel strength of the Cu/Cr/PI FCCL decreased slightly with increasing Cr thickness. We speculated that the peel strength is presumably saturated at 10 nm-thick Cr layer. Although more studies on the peel strength of the Cu/Cr/PI FCCL with thinner than 10 nm-thick Cr layer are needed, it has been concluded that the selection of the thinnest Cr (10 nm-thick) layer will be very useful in the view point of energy saving.

4. Conclusions

In this study, the mechanical reliability, as measured by the adhesion strength, of FCCLs having Cr seed layers with different thickness were investigated by the 90° peel test. The 10 nm-thick Cr seed layer FCCL had a higher adhesion strength than the 20 nm or 30 nm thicknesses. The morphological observation of the fracture surface revealed that the surface roughness of the fractured PI surface increased with increasing adhesion strength for the FCCL. The 10 nm-thick Cr seed layer FCCL had a lower C-N bond ratio, but higher C-O or carbonyl (C=O) bond ratios. These results suggested that the reduction in the C-O or carbonyl (C=O) ratios decreased the adhesion strengths between the Cr seed layer and PI. Therefore, the adhesion strength between the metal and PI was mostly attributed to the chemical interaction between the metal layer and the functional groups of the PI.

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