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Surface activated bonding of LCP/Cu for electronic packaging

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A lamination technique for liquid crystal polymer (LCP)/Cu was developed for high speed and high performance printed circuit boards (PCB). This approach was accomplished by using a modified surface activated bonding (SAB) process to achieve enhanced adhesion and a smooth interface. Systematic investigation of peel strength of four categories of samples, namely "as bonded", "annealed", "Cu-deposited", and "Cu-deposited and annealed" showed highest peel strength in the "Cu-deposited and annealed" sample. Significant improvements in adhesion were observed in the samples cleaned with argon-radio frequency (Ar-rf) plasma ("as bonded" samples) followed by Cu deposition on LCP, which were heated after bonding in low vacuum pressure at 240°C (about 70–75 times higher than that of "as bonded"). XPS analyses on peeled surfaces of the "Cu-deposited and annealed" sample reveal bulk fracture in the LCP. Threefold lower loss in conduction of SAB processed laminate than that of conventional heat laminate was most likely due to smooth interface of the SAB processed laminate (surface roughness was ninefold lower than that of conventional heat laminate). A plausible adhesion mechanism of Cu/LCP might be due to bonding of Cu adhesion sites to plasma induced dangling sites of LCP surface, and thermal reconstruction of Cu deposited layers.

1. Introduction

High-speed transmission requires ultra-fine pitch interconnection of chip wiring and of packaging, and multilayer fabrication. The roadmap design for interconnections both of on-chip and of packaging showed a technological fabrication gap between 1 to10 μm pitch [1]. Therefore, a high precision fabrication technology is indispensable to maintain the signal integrity for high-speed printed circuit boards (PCB). Besides this, a little change like thermo-mechanical stress in the material results in fracture in the structure. Consequently materials having high dimensional stability are required. Furthermore, low dielectric constant and low dielectric tangent materials associated with smooth interfaces are necessary for high-speed transmission. A smooth interface can reduce the skin effect, and is convenient for fine patterning. In the skin effect, conduction takes place through the near surface resulting in high resistance against the flow of current if the surfaces are rough.

Although polyimide is widely used as laminate for high-speed electronic circuit boards in the range of GHz, liquid crystal polymer (LCP) has advantages over polyimide such as higher moisture barrier and controllable coefficient of thermal expansion (CTE). LCP films absorb 50 to 100 times lower moisture than that of polyimide film, indicating greater stable electrical and mechanical properties of LCP in the normal and humid environment [2]. Due to controllable CTE of LCP, fabrication of LCP-metal/Si laminates with greater reliability than that of polyimide is possible for PCB. And Cu is still attractive as a low resistive conductor in the microelectronic industry.

However, the poor adhesion of LCP to Cu limits its application for electronic packaging. The adhesion behavior of joining mates depends on the morphological, chemical, and physical nature of their interface [3]. Therefore, a variety of approaches has been employed based on these fundamental properties to enhance adhesion of polyimide to metal using laser treatment [4], plasma cleaning and modification [5, 6], and metal deposition and metallization with [7–9] and without [7–9] plasma cleaning. In general, polymers do not chemically react to bond with Cu unless they are cleaned or ablated by plasma. Furthermore, the electrical performance of polyimide to metal interface at high frequency was rarely investigated. To the best of our knowledge, no work has been reported on the adhesion enhancement of LCP to Cu. We approached a direct bonding between Cu foil and LCP film without adhesive to obtain strong bonding and a smooth interface. The lamination of LCP/Cu was accomplished with the modified surface activated bonding (SAB) method

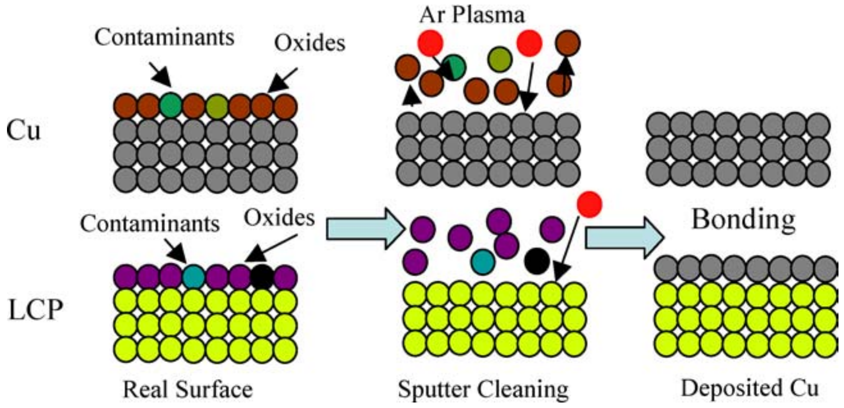


Figure 1 Schematic diagram for the modified surface activated bonding (SAB) process.

(Fig. 1). In this process, Cu and LCP surfaces were sputter cleaned with argon radio frequency (Ar-rf) plasma etching in a vacuum (to remove the inactive layers of native oxide and contaminants on the surfaces), Cu was then deposited on the LCP, and the two were bonded directly at room temperature. The bonding strength of LCP/Cu at room temperature, however, was not so strong as that of metal-metal bonding. Therefore the bonded samples were heated up to 300°C (below the glass transition point). This article reports on the lamination process of LCP/Cu for high-speed PCB associated with interface analysis in order to evaluate adhesion enhancement and low loss interfacial behavior. A comparative study of the SAB processed, and conventional laminates along with optimization of bonding parameters were accomplished.

TABLE I Default parameters used in the experiment.

RF plasma irradiation		Default value
Cu-side	RF power	720 W
	Irradiation time	30 min
LCP-side	RF power	20 W
	Irradiation time	8 min
Cu-deposition on LCP		Default value
Cu-side	RF power	720 W
	Irradiation time	15 min
Bonding pressure		806 MPa
Annealing condition		Default value
Time		1 hr
Temperature		240°C
Atmosphere		Air, low vacuum

2. Experimental procedure

Samples of 35 μm-thick C1100 rolled copper foil and 50 μm-thick Vecstar CTX100 (Kuraray) LCP film were used. The sheet samples of (175 × 300) mm^2 size were wiped down with acetone, and placed on a stainless plate. Fig. 2 shows the schematic diagram of the SAB tool. It consists of process and bonding chambers separated by a gate valve. LCP film and Cu foil were placed underneath the upper plate and above the lower plate, respectively and cleaned in the process chamber using two argon (Ar) rf plasma sources at a background pressure of 3.0×10^{-3} Pa. During plasma cleaning, a shutter was inserted between the specimens to separate plasma sources. The shutter was opened as soon as the sample surfaces were cleaned. Further plasma processing continued using the bottom source yielded Cu deposition on the cleaned LCP surface. Finally the samples were passed between two rollers under a load in the bonding chamber. Table I shows the default experimental conditions used for the bonding experiments of Cu/LCP.

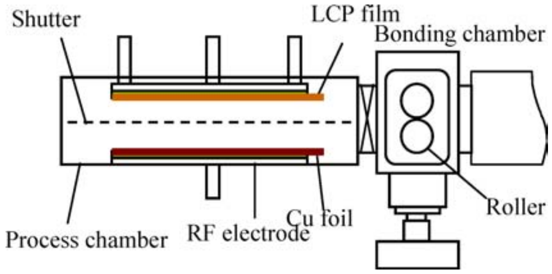


Figure 2 Schematic diagram for a SAB tool.

Bonded samples were annealed outside the chamber at a temperature below the glass transition point for 1 h. The specimens were cut into an oblong of 10 mm wide in order measure the bonding strength by the T peel test (the value measured by T peel tests is about half as much as one measured by 90° peel tests). The peeled surfaces were analyzed with an X-ray photoelectron spectroscope (XPS) from Perkin Elmer with a Mg Ka X-ray radiation source at 15 kV and 400 kW.

3. Results and discussion

3.1. Adhesion enhancement investigation

The influence of rf plasma cleaning including the effect of additional treatments on the bonding strength was investigated using the parameters shown in Table I. The rf plasma power and time used to sputter clean the LCP specimen were much lower than those of the Cu specimen.

Four categories of the specimens were used, specified as "as bonded", "annealed", "Cu-deposited", and "Cu-deposited and annealed" specimens. Table II shows the peel strength for all categories of specimens used in the bonding experiments. The "as bonded" specimen is defined as the Ar-rf plasma cleaned sample bonded

TABLE II Brief results of peel strength of Cu/LCP interface. Four categories of specimens are the "as bonded", "annealed", "Cu-deposited", and "Cu-deposited and annealed" specimens

Specimens index	RF plasma	Deposition	Bonding	Annealing	Peel strength (g/cm)
As bonded	#		#		0–10
Annealed	#		#	#	100–150
Cu-deposited	#	#	#		250–350
Cu-deposited and annealed	#	#	#	#	500–600

by the typical SAB process, which exhibited weak peel strength typically less than 10 g/cm. Therefore additional treatments were indispensable to achieve strong bonding. The "annealed" specimen is defined the "as bonded" specimen heated at 240°C for 1 h, that exhibited a higher peel strength of 100–150 g/cm than that of the "as bonded" sample. However, the adhesion strength was too weak for PCB application.

Even after heating the bonded specimen, inadequate adhesion between LCP and Cu was observed. Therefore additional adhesion layers were fabricated on LCP using Cu deposition after rf plasma treatment. The "Cu-deposited" specimen is defined as the sample for which Cu was deposited on LCP after rf plasma cleaning, and then bonded by the SAB process, that exhibited strong peel strength typically in the ranges of 250–350 g/cm. The peel strength was as strong as the specimen laminated by conventional heat press. The "Cu-deposited and annealed" specimen is defined as the "Cu-deposited" specimen heated at 240°C for 1 h, that exhibited a maximum peel strength of 500–550 g/cm. Therefore strong bonding strength by the extended SAB process was achieved, which was enough for fine pattern fabrication by chemical etching.

3.2. XPS analyses of peeled surfaces

In order to investigate the adhesion mechanism and fracture location (that measures interface adhesion strength) of the peeled specimens, we analyzed the peeled surfaces by XPS. Fig. 3 comparatively illustrates the spectra of "as bonded", "Cu as received" and "LCP as received" specimens. Two peaks were observed on peeled Cu of the "as bonded" specimen around O1s peak which are not similar to "Cu as received" peaks, but similar to "LCP as received" peaks (Fig. 10b before plasma cleaning). Characteristically the two Cu O1s peaks represent two oxidation states of Cu (Cu_2O: 932.8, and CuO: 934 eV). A Cu 2p peak was detected on the peeled LCP surface, as shown in (b), possibly due to the plasma glow consisting of residual Cu, and to the contact between Cu/LCP under high bonding load. If Cu was fractured from bulk Cu, the bonding strength should be very high. In fact, the weak peel strength (only a few gm/cm) of the "as bonded" sample is indicative of weak bonding between the bulk Cu and LCP due to the absence of adhesion layers.

The XPS spectra of the "annealed" specimen compared with those of the "as bonded" specimen are shown in Fig. 4. The Cu-side O1s peak of the "annealed"

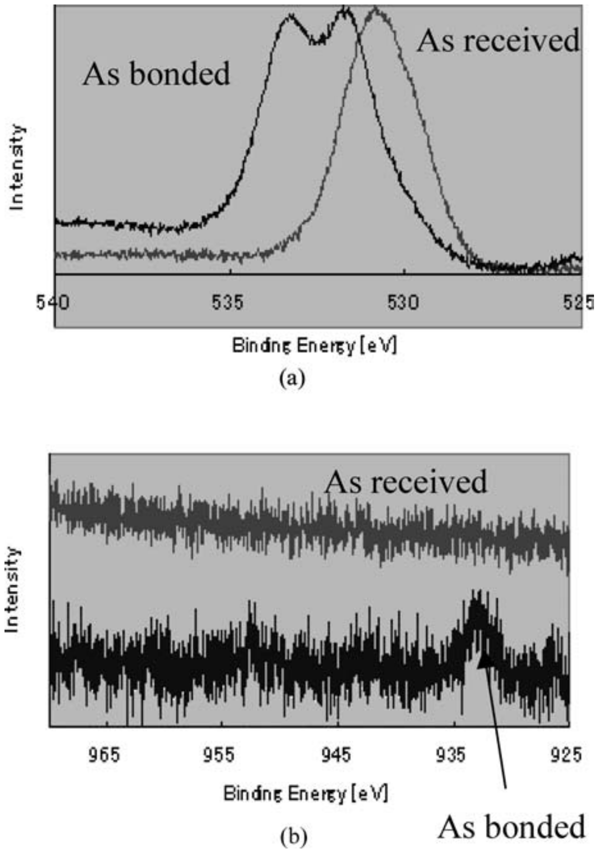


Figure 3 XPS spectra of the "as bonded" peeled surfaces for (a) Cu-side O1s peak, and (b) LCP-side Cu2P peak compared with the as received Cu and LCP surfaces.

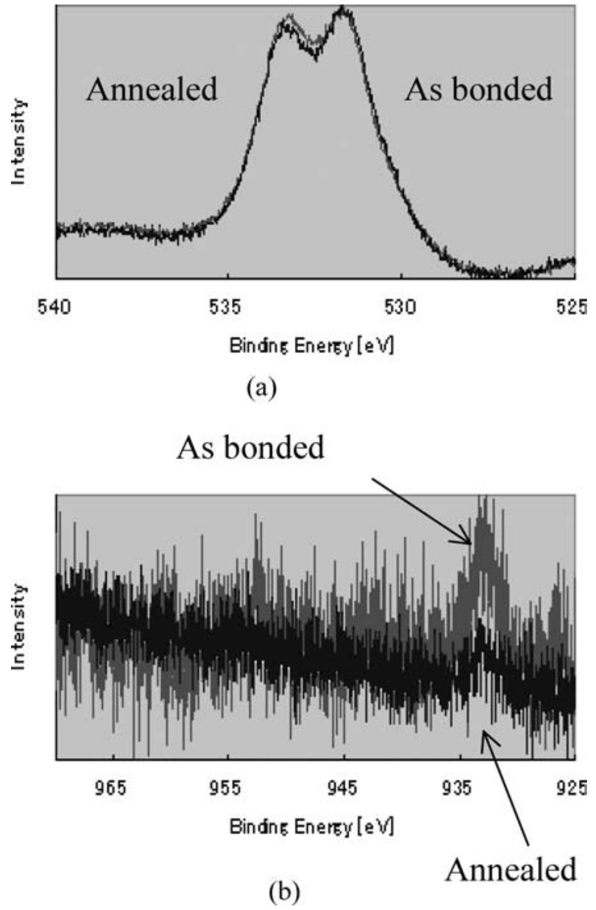
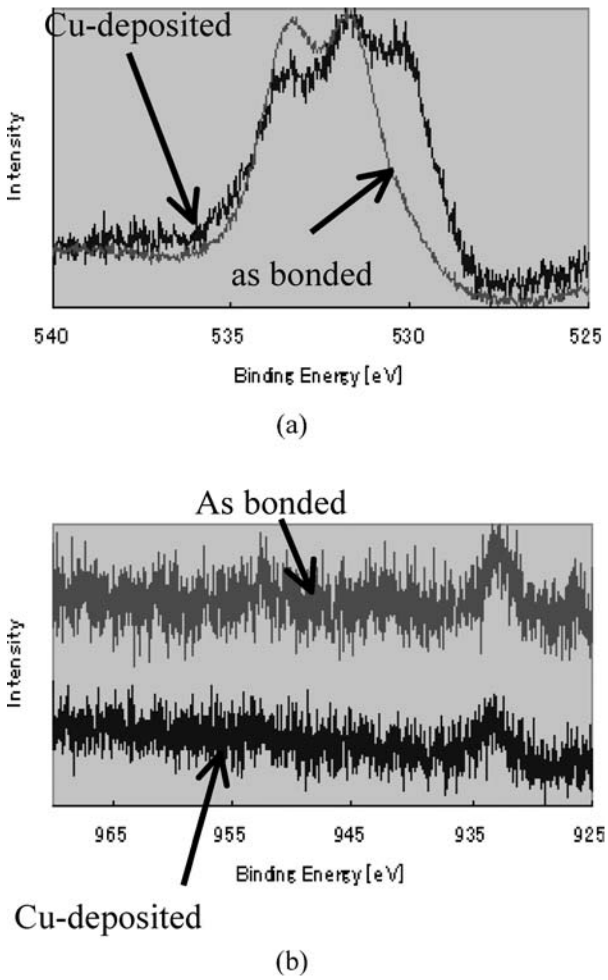


Figure 4 XPS spectra of the "annealed" peeled surfaces compared with those of "as bonded" peeled surfaces for (a) Cu-side O1s peak, and (b) LCP-side Cu2P peak.



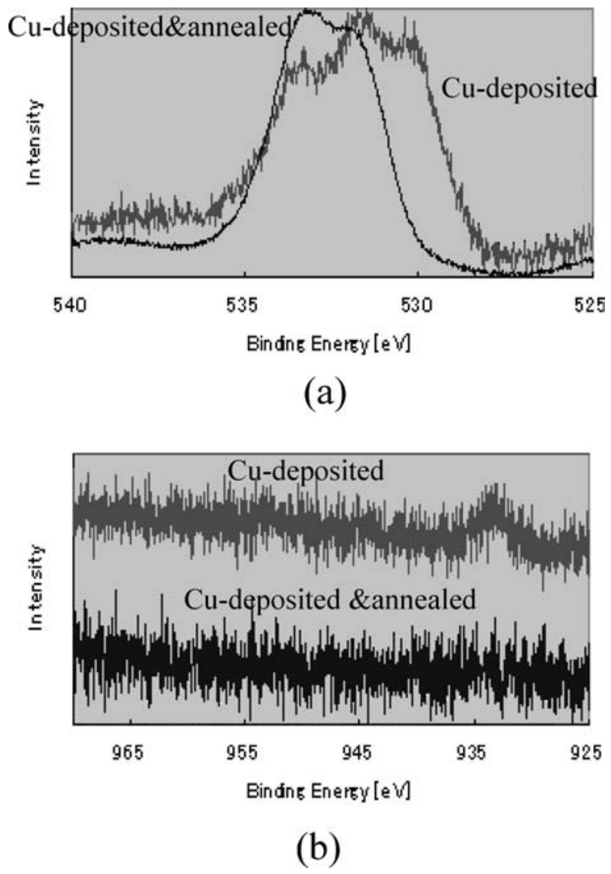
(a)

(b)

Figure 5 XPS spectra of the "Cu-deposited" peeled surfaces comparing with those of "as bonded" peeled surfaces for (a) Cu-side O1s peak, and (b) LCP-side Cu2P peak.

specimen, as shown in (a), was almost similar to that of the "as bonded" specimen. A weak Cu2p peak was detected on the peeled LCP, perhaps for the reasons mentioned for the "as bonded" specimen. The results of the weaker Cu2p peak on the peeled LCP of the "annealed" specimen compared to the "as bonded" may suggest that the "annealed" specimen was fractured over a large contact area of LCP after the peeling test and the Cu side was covered with the fractured LCP.

As mentioned previously, the deposition of Cu on LCP after cleaning by rf plasma produced adhesion layers. Fig. 5 shows the XPS spectra of the "Cu-deposited" specimen comparing with those of the "as bonded" specimen. Although the specimen should have 10–20 nm thick deposited Cu layers on LCP, a weak Cu 2p peak was detected, that is similar to that of the "as bonded" specimen. The Cu2p peak on peeled LCP of the "Cu-deposited" sample indicates that almost all of the deposited Cu on the LCP peels to the Cu-side, and few deposited copper layers remain on the peeled LCP. Therefore, microscopic interaction between the deposited copper and LCP was considered to be weaker than that between the deposited Cu and bulk Cu. Also the adhesion between the bulk Cu and LCP without deposited Cu was weak and the deposited copper can transfer more freely than the bulk copper. Consequently, the bonding site between the deposited copper and LCP is much higher than that of the bulk copper and LCP, resulting in an enhanced adhesion in the bonding of the Cu-deposited LCP and bulk Cu.



(a)

(b)

Figure 6 XPS spectra of the "Cu-deposited and annealed" peeled surfaces comparing with those of "Cu-deposited" peeled surfaces for (a) Cu-side O1s peak, and (b) LCP-side Cu2P peak.

The XPS spectra of the "Cu-deposited and annealed" specimen compared with those of the "Cu-deposited" specimen are shown in Fig. 6. In Cu O1s, two peaks corresponded to the oxide form of Cu due to the formation of CuO and Cu_2O, and were identical to those of the "as bonded" Cu specimen. Moreover, no Cu2p peak was detected at all in the peeled LCP of the "Cu-deposited and annealed" sample. The results indicate deeper fracture the in "Cu-deposited and annealed" specimen than that of other specimens, and are consistent with the peel strength.

3.3. Optimization of bonding parameters
3.3.1. Bonding pressure

We optimized the adhesion strength as a function of bonding pressure, rf plasma and time, amount of Cu deposition on LCP after sputtering of surface, annealing temperature, and atmosphere. Generally the SAB process is based on the atomic adhesion of smooth bonding mate surfaces. Therefore significant load is not necessary in the SAB process. However, when the bonding pairs have rough surfaces, bonding load needs to be applied to get intimate contact of bonding mates that improves the adhesion. Excess bonding load can rupture LCP. Fig. 7 shows the peel strength dependence on the bonding pressure from 500 to 1700 MPa with and

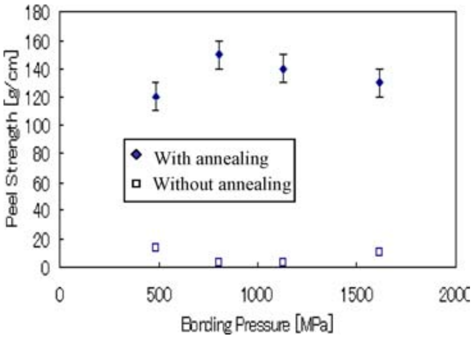


Figure 7 Dependence of peel strength on the bonding pressure of the annealing and non-annealing specimens. The annealing temperature is 240°C.

without annealing conditions. Peel strength remained constant throughout the pressure range without annealing. Nevertheless the peel strength slightly increased to a maximum value of 160 g/cm at 800 MPa for the annealing samples.

3.3.2. RF plasma power and time

The SAB process produces surface adhesion of bonding pairs by removing surface contamination by rf plasma cleaning. Therefore the plasma parameters must be controlled with care and moderate plasma power to protect surfaces especially LCP from excess radiation damage. The influence of Ar-rf plasma irradiation power and time on the peel strength of LCP/Cu is shown in Fig. 8a and b, respectively. The peel strength without heat treatment was remarkably low, whereas the peel strength was increased by more than 100 times in the annealed sample. The peel strength increased as a function of rf plasma cleaning time up to 20 min, and then remained constant except at 80 min irradiation. On the other hand, the peel strength appeared to be increased and then decreased with plasma power except at 800 W. Based on the results, the optimal irradiation time and power were 15 min and 240 W, respectively. Laurens *et al.* observed adhesion enhancement of thermally evaporated Al on PET cleaned with a excimer laser or a low pressure O_2 plasma treatment due to surface ablation of ploy ethylene terephthalate (PET) [4]. In our study, plasma power was found to have more influence on the adhesion of LCP/Cu than that of plasma cleaning time. Degradation of adhesion strength at high plasma power is consistent with that of crystal bond to poly tetra fluoroethylene (PTFE) surface at high ion dose [8].

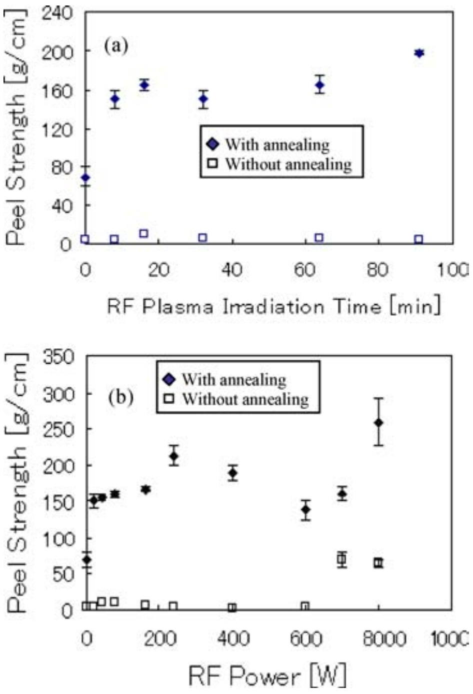


Figure 8 Dependence of peel strength on the rf plasma power and time of the annealing and non-annealing specimens. The annealing temperature is 240°C.

3.3.3. Cu deposited thickness

LCP has an ordered atomic structure very different to that of metals, and bulk copper atoms remain near their perfect lattice sites. So bulk Cu atoms are rarely bonded to LCP molecules, resulting in a weak adhesion between bulk Cu and LCP (see "as bonded" specimen). On the other hand, since sputtered Cu atoms are free to rearrange themselves on the surface as the deposition proceeds, Cu deposition on LCP increases bonding sites. Fig. 9 shows the dependence of peel strength on the thickness of the deposited Cu layer. Peel strength increased up to 20 nm thicknesses and then changed more slowly with increasing Cu layers. The results can be explained by the findings of Chopra *et al.* [10]. They have investigated the growth process of islands, and found that the required thickness of the deposited layers to make connection between the islands is 10–20 nm. So if a thickness of 10–20 nm Cu deposited layers was required to cover the LCP surface, and this value agrees with the result shown in Fig. 9. Moreover the peel strength of the specimens without annealing increased about 100 g/cm by the deposition of 7 nm until 21 nm thick. In other word, the peel strength was linearly increased with increasing deposited Cu coverage. Therefore we suggest that the main effect of the Cu-deposition overlayer was to increase the number of Cu bonding sites. Oxygen plasma treatment is found to increase the number of single and double bonds be-

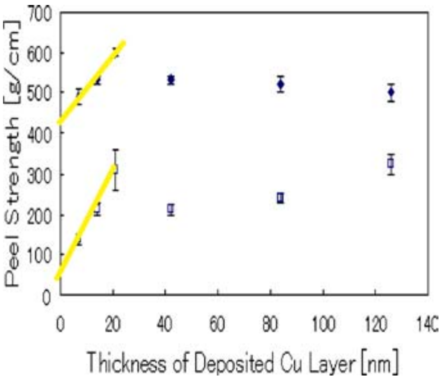


Figure 9 Dependence of peel strength on the thickness of Cu deposited layer on the LCP after rf plasma cleaning. Annealing and non-annealing results are included.

tween the polymer C and the oxygen supplied by oxygen plasma [6, 11]. These bonds could be modified by the presence of a deposited metal overlayer, generating a complex of carbon-oxygen-metal. However, Ar-rf plasma decreased the amount of single and double bonded oxygen at the LCP surface. So there were no available oxygen sites to react with the deposited Cu overlayer, which is in contrast to Refs. [6] and [11], and indicates a reaction between the dangling sites of LCP carbon, produced by the plasma treatment, and the deposited Cu overlayer.

3.3.4. Annealing effect

Since LCP has an extremely compact molecular structure, LCP hardly transforms plastically at room temperature. On the other hand, Cu is highly ductile. So enormous shear stress can arise in the bonding interface between Cu and LCP under cold rolling. The bonded specimen before annealing curled due to the difference in the amount of expansion. In contrast, after annealing it became flat, resulting from creep, indicating stress relaxation was one of the main effects of annealing. Fig. 10 shows the peel strength dependence on annealing temperature in air and vacuum. The vacuum pressure was 10^{-2} Pa. In both cases, the peel strength appeared to be constant from 200 to 260°C, then lowered from 270°C, and was finally worst at 300°C. The peel strength for LCP/Cu was estimated to be 700–750 g/cm, which is 2 to 3 times higher than that of heat laminate. The reasons for declining peel strength at higher temperatures could be due to the thermal contraction, and effect of oxidation. However, a similar trend in the decrease of peel strength of the sample annealed in vacuum indicated that the oxidation effect might not responsible for the decrease of peel strength. So thermal contraction seems the most likely reason for the declining peel strength at the glass transition temperature.

Generally movement of molecular chains in polymer is activated at the glass transition point. Therefore annealing at this temperature might promote the restructuring and strengthening of binding between the molecular chains damaged by rf plasma and the deposited Cu overlayer. More peeled LCP was detected in the “annealed” specimen than in the “as bonded” specimen. This shows the evidence of strong LCP/Cu bonding strengthened by annealing.

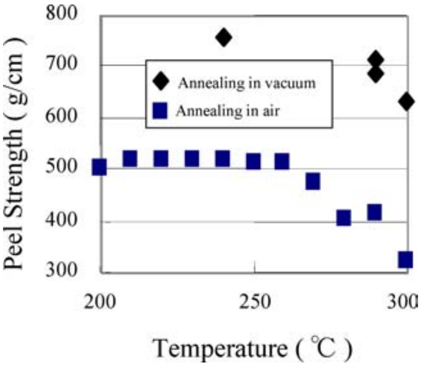


Figure 10 Peel strength of the specimens as a function of annealing temperature in vacuum and air.

3.4. Ar-rf plasma influence on LCP

Surface cleaning with rf plasma significantly removes contaminants and oxide layers on Cu. On the other hand, as previously mentioned, LCP is a set of molecular chains, so physical bombardment cuts the molecular chains and exposes active radicals. Fig. 11 shows the effect of rf plasma source power on the shape of C1s and O1s peaks of LCP. An rf plasma source of power ranges from 0 to 800 W (8 min) was used. The C1s spectra of virgin LCP surface has three components which are C-C/C-H peak (main peak), C—O peak 1–2 eV above the main peak (hidden at the left shoulder of main peak), and C=O peak near the second peak. The C=O peak began changing from 20 W, then disappeared with increasing plasma power, and finally disappeared completely at 800 W. Shifting of C1s peak positions toward higher energy with increasing plasma power is not understood yet. On the other hand, in the case of O1s peaks (Fig. 11b), the C—O and C=O peaks were disappeared from cleaning the LCP surface with 20 W and so on. In other words, the Ar-rf plasma cleaning greatly reduced C—O and C=O species of the LCP. The arrow in Fig. 11a shows C—O peak and the arrows in Fig. 11b show C—O and C=O peaks. Both C1s and

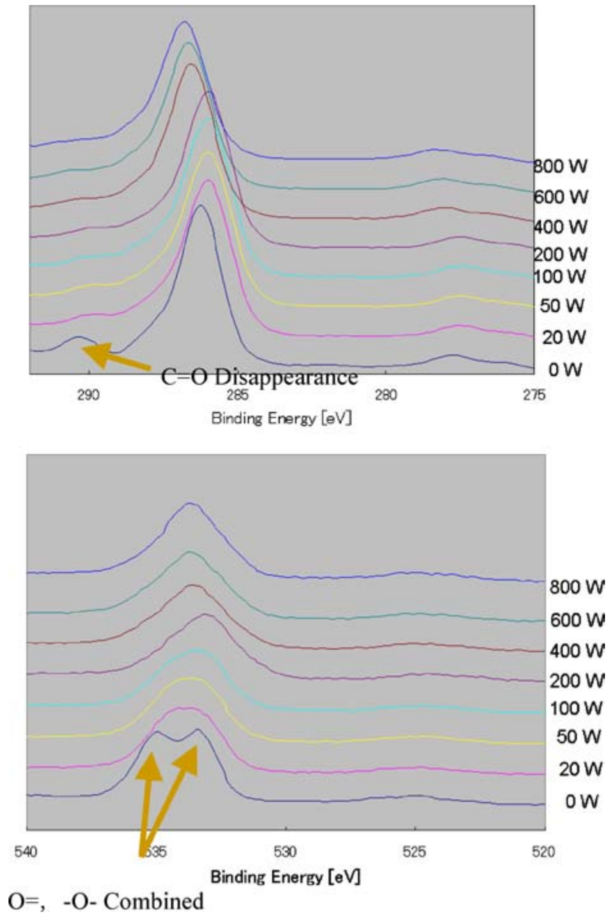


Figure 11 XPS spectra (a) C1s, and (b) O1s for LCP showing the influence of rf plasma cleaning on the virgin LCP surface. The arrow in Fig. (a) shows the C—O peak. The arrows in Fig. (b) show C—O and C=O peaks.

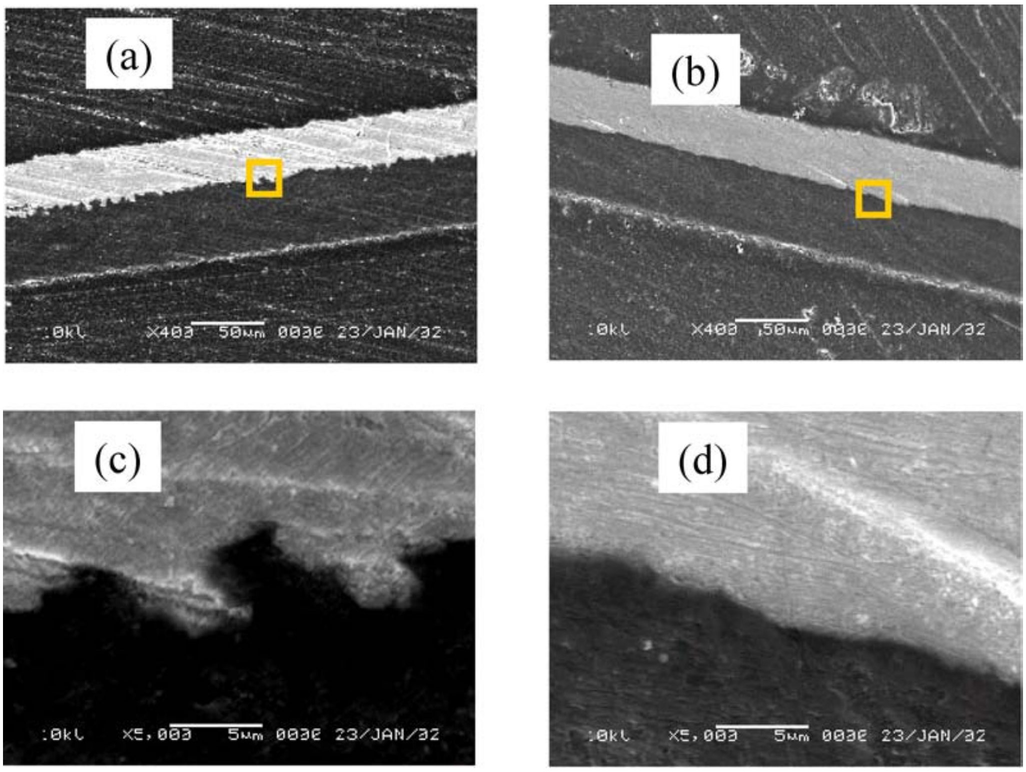


Figure 12 SEM images of the interface of LCP/Cu laminate fabricated by (a) the heat laminated, and (b) the SAB process. Fig. (c) and (d) show magnified images for them, respectively.

O1s spectra indicate the reduction of singly –and doubly bonded oxygen resulting in dangling sites on LCP. On the other hand, plasma induced surface modification in polymer is reported [11]. Therefore we suggest that plasma cleaned LCP surface having dangling sites bonded with the deposited Cu, which enhanced adhesion between Cu and polymer. Nevertheless, heating of bonded LCP/Cu was essential in order to thermally reconstruct deposited Cu to strengthen deposited film itself indeed.

3.5. Interface roughness

The atomic force microscope is a versatile tool for the analysis of nanometer scale surface roughness and was utilized to measure the interface roughness of LCP/Cu fabricated by the SAB and heat laminated processes. The Cu surface was etched out by dry etching before the measurement. The AFM images for the bonded interfaces of the heat laminated and "Cu-deposited and annealed" specimens were taken over the scanning area of (25 × 25) μm^2. The root mean square (rms) value of the roughness for the conventional heat-laminated surface was 970 nm, whereas for the SAB laminated surface it was 64 nm. The comparison clearly shows that the bonded interface of the specimen prepared by the SAB process is about 15 times smoother than that of the heat laminated process. Since electrical current flows only through the parts of conductors within 1 μm of the surface during high-speed signal transmission due to the skin effect, micron size roughness of the interface leads to failure of the function of the electrical circuit.

Therefore SAB can improve the circuit performance for high-speed transmission. In addition, low magnification SEM images also indicate the superiority of SAB compared to heat lamination (Fig. 12). It appears that plasma induced surface modification and chemical bonding of Cu to LCP after thermal reconstruction are likely be dominant over surface roughness of LCP for adhesion enhancement.

3.6. Conduction loss and fine pattern

The adhesion enhancement will only be useful for applications if the interfacial conduction loss can be kept low at high frequency, where the interfacial morphology controls interface current flow. Recently we have measured the conduction loss of the SAB laminated Cu/LCP compared with that of the conventional heat laminated Cu/LCP interface (Fig. 13a) [13]. Increased loss at both interfaces with increasing of frequency was observed, and it was threefold lower for the SAB laminate compared with the conventional heat laminate. The low loss of the SAB laminate can be correlated with the smooth interface, and explained in terms of the lower contact area of Cu/LCP across the interface compared to the conventional heat laminate as observed by the SEM images (Fig. 12). Also the SAB processed laminate might have influence of radiation damage induced by cleaning with the Ar-rf plasma, which can generate defects in Cu and LCP [12]. The applicability of LCP/Cu bonding as a laminate was examined. Fig. 13b gives the photograph of the patterned sample fabricated on the SAB processed samples. The line and space for the etching patterns were 50 μm. Successful patterning on the SAB processed samples indicates that the SAB lamination is strong enough to be etched and applicable to the circuit boards lamination.

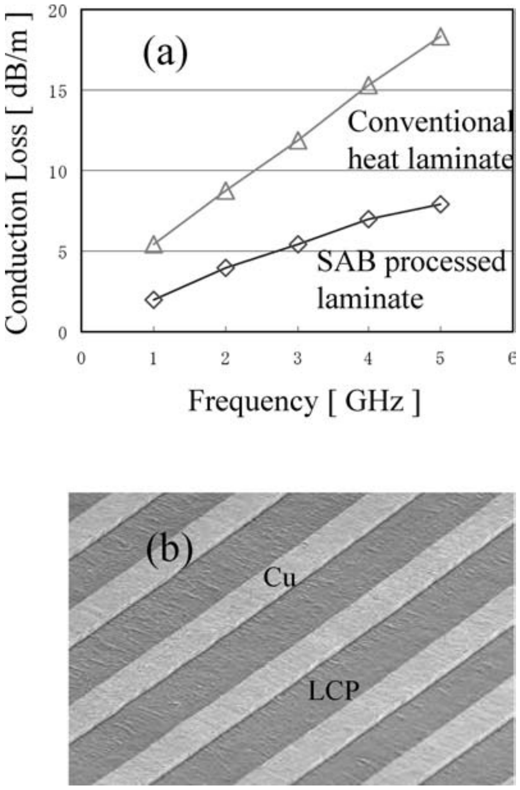


Figure 13 (a) Conduction loss of the SAB laminate and conventional heat laminate of LCP/Cu as a function of frequency. (b) Fine pattern fabricated by etching on the SAB processed LCP/Cu specimen. Both the line and space for the etching pattern was 50 μm.

4. Conclusions

This article reported on the lamination process of LCP/Cu for high-speed and high-performance printed circuit boards (PCB). This was accomplished by the use of a modified surface activated bonding (SAB) process. Analysis of peeled surfaces by XPS showed bulk fracture of the laminate produced by the bonding between Cu deposited LCP and Cu interface after annealing, indicating adhesion enhancement. Peel strength in the range 600–700 g/cm was observed in the SAB processed laminate, which is much higher than that of the heat laminate. A smooth interface of the SAB processed LCP/Cu samples resulting in lower contact area may be correlated with the threefold lower conductor loss than that of conventional heat laminate. A fine pattern with 50 μm line and space was fabricated on the SAB laminate. A plausible adhesion mechanism of Cu/LCP would be bonding of Cu adhesion sites to plasma induced dangling sites of the LCP surface, and thermal reconstruction of the deposited Cu layers.

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