Enhanced Cu/LCP Adhesion by Pre-Sputter Cleaning Prior to Cu Deposition

M. M. R. Howlader, M. Iwashita, K. Nanbu, K. Saijo, and T. Suga

Abstract—Liquid crystal polymer (LCP) and Cu thin film cleaned with radio frequency (RF) plasma in a vacuum pressure of 3.0×10^{-3} Pa followed by Cu deposition on LCP were bonded at room temperature. Immediately after bonding, the samples were unloaded, heated in air, argon, nitrogen, hydrogen, and oxygen gases, and subjected to peel strength measurements before and after heating to investigate the adhesion enhancement and the bonding mechanism of Cu/LCP. The interfacial adhesion was evaluated in terms of peel strength (180°) measured by a peel tester (AGS—1 kNG, Shimadzu Corporation). The adhesion strength after the heat treatment depended on the heating environment and increased in the order of oxygen, air, nitrogen, and argon gas environments, respectively, but significantly declined in further heating in O_2 gas, approximating the level prior to heating. Visual and optical inspections on the delaminated samples showed bulk fractures or partial bulk fractures in LCP heated in all gas environments except in O_2 and its sequential treatments. X-ray photoelectron spectroscopy (XPS) analyses showed a carbon-rich LCP surface with a reduced amount of oxygen after sputter cleaning with RF plasma, which favorably reacted with the deposited Cu. Heating of bonded samples in various environments might enhance or suppress the interfacial reaction resulting in strong adhesion or poor adhesion depending on the heating environments. Depth profile on peeled LCP sample (which was heated first in Ar and then in oxygen prior to delamination) revealed thicker Cu oxide layers on delaminated LCP than natural Cu oxide layers. The new oxidized Cu layers produced across the interface were likely a result of the reaction of diffused oxygen in LCP with deposited Cu layers.

Index Terms—Adhesion, deposition, diffusion, interfacial reaction, liquid crystal polymer (LCP), peel strength, radio frequency (RF) plasma.

I. INTRODUCTION

ADHESION of Cu to polyimide, which is a polymer, has persistently attracted attention due to the prevalence of polymers in the electronic industry [1]. Liquid crystal polymer (LCP) combined with Cu has been considered a potential candidate for the flexible lamination in high-speed and highly portable miniaturized devices because of lowest electrical conductivity of Cu, and lower dielectric constant and higher moisture barrier of LCP [2] than that of polyimide. However, the weak adhesion between LCP and Cu is the critical barrier to its wide spread application in microelectronics packaging.

Three technical papers have been published on the interfacial adhesion enhancement of polymers to Cu among the procedures discussed were insertion of metallic layers prior to bonding [2], morphological modification of polymer surface [3], and cleaning the Cu and polymer surfaces and depositing Cu on cleaned polymer surface by low-damage radio frequency (RF) plasma [4]. Recently, a bonding process was developed in which LCP and Cu thin films were cleaned with RF plasma in a vacuum. Cu was then deposited on LCP, and then the Cu-deposited LCP was bonded with Cu film at room temperature. Subsequently, the Cu/LCP samples were heated, resulting in higher interface adhesion than that of the conventional heat-laminated process. Additional characterization of the interfacial strength of LCP/Cu heated in atmospheric air and low vacuum pressure has been accomplished in terms of peel strength, skin effect, and plasma parameter optimization. Recently, a significant improvement in the interface smoothness and an adhesion strength enhancement compared to other integration processes were observed [4].

Although our early work in the improvement of the interfacial adhesion strength of Cu/LCP after heating at a below-glass transition temperature in low vacuum pressure was successful, the bonding mechanism of Cu/LCP was not clarified. To gain greater insights into the adhesion enhancement mechanism of Cu/LCP, heating of the bonded samples in various gaseous environments would be advantageous. In addition, Cu-laminated LCP in packaged devices must perform satisfactorily under exposure to different environments. A large reduction in adhesion could lead to failures in microelectronic packaging applications. The adhesion mechanism of Cu/LCP might be due to the interfacial reaction of deposited Cu and constituents of LCP (most likely C and O). On the other hand, diffusion in polymer [5] is generally accepted; therefore, heating of Cu/LCP in different environments below glass-transition temperature might influence the bonding strength. Since both films used for the adhesion experiments were too thick to allow investigating the interfacial reaction directly by surface spectroscopy, the interfaces after heating them in different environments were delaminated and the delaminated surfaces were investigated to clarify the interaction across the interface by X-ray photoelectron spectroscopy (XPS). The article reports on the investigation of the adhesion enhancement mechanism and the environmental (gaseous) influence on the adhesion strength of Cu/LCP by XPS analysis.

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II. EXPERIMENTAL

Samples of 35-μm-thick C1100 rolled copper foil and 50-μm-thick Vecstar CTX100 (Kuraray) LCP film were used.
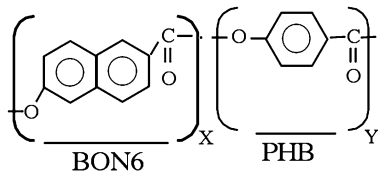
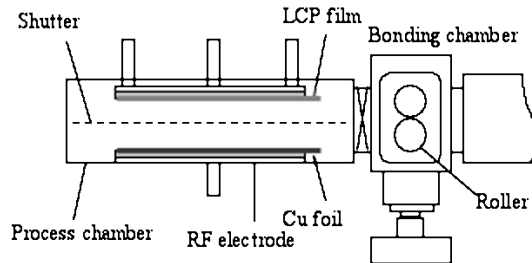Fig. 1.   Schematic diagram of chemical structure for Vecstar CTX100.

Fig. 2.   Schematic diagram of the SAB tool with the process flow used for the bonding experiment of Cu and LCP.

Fig. 1 shows the chemical structure of Vecstar CTX100, which consists of a chain of para–hydroxyl Benzoic acid and bi–oxide 6–Naptholine acids. Vecstar is a high-performance polymer having high glass transition temperature, low dielectric constant, and low thermal expansion coefficient properties.

The sheet samples of 175×300 mm^2 size were cleaned and wiped down with acetone and placed on two stainless plates before being loaded into the process chamber of the bonding tool (Fig. 2). 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 was continued using the bottom source yielded Cu deposition on the cleaned LCP surface. Finally, the samples were passed between two rollers under a load (cold rolling) in the bonding chamber. Table I shows the default experimental conditions used for the bonding experiments of Cu/LCP. The default parameters were chosen from experimental experiences of Cu/LCP bonding to improve peel strength [4], [6]. For instance, the RF plasma cleaning time to remove natural oxides and contaminants for Cu surface was higher than that of LCP surface. The Cu deposition time required to cover all over the LCP surface was found to be 15 min. Excess bonding pressure was avoided to protect LCP from rupturing.

After bonding, the samples were unloaded and heated in an Ar and N$_2$ gas media in a quartz box $25 \times 25 \times 25$ cm^3 (outside the bonding chamber) to increase interface strength at a temperature below the glass-transition point (at 240 °C) for 1 h. Additional sequential heating of Ar and N$_2$ treated and/or untreated samples was performed in air and O$_2$ gas. Table II shows the brief names and heating environments of bonded samples used for peel test and XPS analysis. The specimen was cut into a rectangular shape of 10 mm wide to measure the bonding strength of Cu/LCP by 180° peel test. The schematic diagram of 180° peel test is shown in Fig. 3. Due to inhomogeneous fractures in LCP

TABLE I
DEFAULT EXPERIMENTAL CONDITIONS USED FOR THE BONDING
EXPERIMENTS OF Cu/LCP

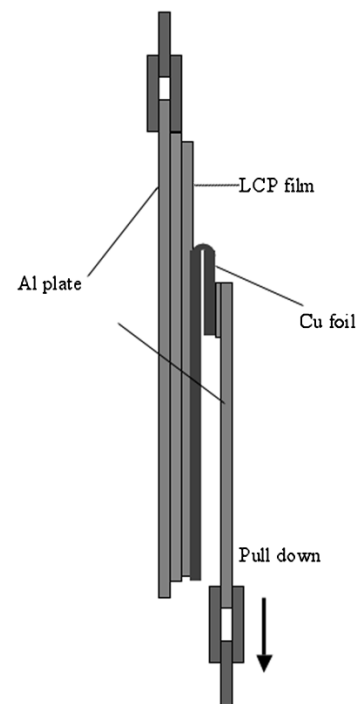| RF Plasma Irradiation		Default Value
Cu-side	RF Power	700 W
	Irradiation Time	30 min
LCP-side	RF Power	600 W
	Irradiation Time	8 min
Cu Deposition		Default Value
Cu-side	RF Power	700 W
	Irradiation Time	15 min
Bonding Pressure		Optimum Value
		322 MPa
Heating Condition		Optimum Value
Time		1 hour
Temperature		240 ℃
Atmosphere		Air, Ar, O$_2$, N$_2$

Fig. 3.   Schematic diagram for 180° peel test.

by T peel test, we used 180° peel method for measuring peel strength of Cu/LCP. Bonded LCP and Cu films were forcibly opened about one cm from the bonding edge. The LCP was then fixed on the LCP side on an aluminum plate and tightly held together with a peel tester (AGS—1 kNG) made by Shimadzu Corporation. The delaminated Cu side was fixed on an Al plate after bending and fixed with the bottom side of the pull tester clamp. Peel test was performed at a speed of 100 mm/min. The total numbers of samples used for peel strength measurements were 20. To investigate the bonding mechanism of Cu and LCP, the peeled surfaces were analyzed using Mg-α X-ray
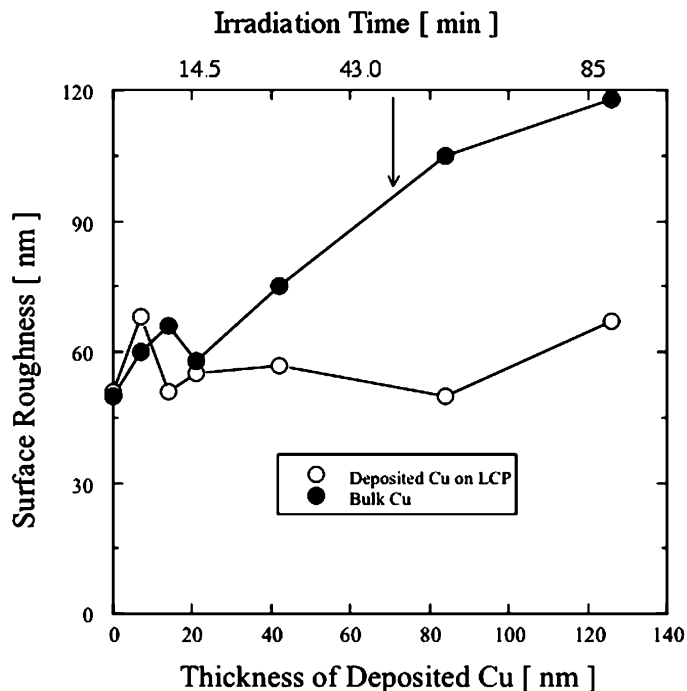
Fig. 4. Surface roughness (root mean square) of LCP as a function of Cu deposition on cleaned LCP surface with an RF plasma source of 600 W for 8 min. Cu surface roughness is also included as a function of sputter cleaning with an RF source of 700 W. The sputter deposition rate was 1.4 nm/min.
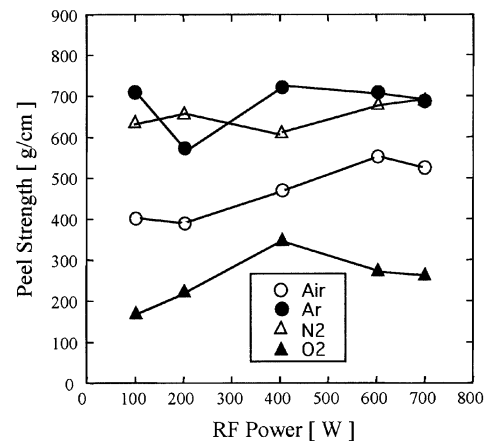

Fig. 5. Peel strength expressing adhesion of Cu/Cu-deposited LCP as a function of RF power used for pre-sputter cleaning of LCP. The samples were bonded at room temperature followed by heating in air, O_2, Ar, and N_2 gas flow at the rate of 2 mL/min in a quartz box at 240 $^\circ$C.

radiation source XPS at 10 keV and 10 mA (JEOL JPS 9200 T). The take-off angle used in the XPS was 0°.

III. RESULTS AND DISCUSSION

A. Surface Roughness by AFM

Since the RF plasma was used to clean and activate the LCP and Cu surfaces prior to and followed by Cu deposition on LCP, the surface roughness of mating surfaces can be a critical factor affecting bonding strength and, therefore, must be evaluated. Surface smoothness during bonding allows intimate contact and ultimately controls interface adhesion. Measurements of surface roughness were carried out over an area of 3×3 μm^2 with an atomic force microscope (AFM) from Seiko Instruments. Fig. 4 shows the surface roughness (root mean square value) dependence of LCP sputtered for 8 min before Cu deposition with an Ar RF plasma source on deposited Cu thickness. Surface roughness of LCP was not significantly dependent on the surface roughness of deposited Cu on LCP up to 120 nm thickness, indicating smooth LCP surfaces consistent with that of the bare LCP (typical value of LCP before sputter cleaning was 50 nm). On the other hand, the surface roughness of bulk Cu increased greatly with increasing the Cu deposition thickness on LCP. Doubling the RF plasma exposures to remove Cu oxides and contaminants and to deposit Cu from bulk Cu on LCP might cause an increase in the surface roughness of Cu.

B. Influence of Plasma Power and Deposition Time

Fig. 5 shows the peel strength of Cu and Cu-deposited LCP interface heated in air, Ar, N_2, O_2 environments as a function

of RF plasma power (see Table II). The flow rate of air and different gases was 2 mL/min. The peel strength was found to be independent of RF plasma power at all heating environments. However, if the RF plasma power is too low, the sputtering time to clean LCP needs to be prolonged, which can modify LCP surface due to plasma-induced over heating. The optimum value of RF plasma power was observed to be 600 W. The highest peel strength of the samples heated in Ar and N_2 appeared to vary. Absolute peel strength declined in the sequence of heating in air and oxygen gas. Without Cu deposition on LCP after pre-sputter cleaning and without heating the bonded samples, the Cu/LCP adhesion was weak, with a value below 10 g/cm. After heating the sample, the Cu/LCP adhesion improved by 10–15 times [4]. A comparison of the fact of increasing the peel strength of Cu/Cu-deposited LCP heated in various gas environments, as shown in Fig. 5, indicates the enhancement of the interfacial adhesion.

The Cu deposited time (deposition rate was 1.4 nm/min) on LCP as a function of peel strength of Cu/Cu-deposited LCP interface with and without annealing in various environments is shown in Fig. 6. An enhancement of peel strength of heated Cu/LCP is evident when compared to that of the sample that was not heated. The lowest peel strength was found in the nonheated samples having typical values from 200 to 300 g/cm. Without heating, the peel strength increased up to 15 min, then changed in a constant manner with increased Cu deposition time. The increase of peel strength in the first 15 min can be explained by the increase in the number of bonded Cu sites on the LCP. Once the bonding sites are sufficient to cover the surface area, no significant increase in the adhesion strength was found. Heating in air and O_2 showed identical increase of peel strength up to a certain time, followed by environment dependent monotonous change with Cu deposition time. Nevertheless, the peel strength increases with different activation processes until saturation. In the case of N_2 heating, the peel strength is almost constant up to 60 min, then peaks at 800 g/cm at 105 min, and finally lowers at 140 min. The standard deviation (SD) of peel strength of the samples without annealing was 12.8%. The SD for the samples annealed in Ar, N_2, air, and O_2 was 12.1%, 12.2%, 18.6%, and

TABLE II
BRIEF NAMES AND HEATING CONDITIONS OF BONDED SAMPLES USED FOR PEEL TEST AND XPS ANALYSIS

| Brief Names of Samples	Plasma Cleaning	Cu Deposition	Heating Environment (at 240 °C)	Observed Surface
Unirr	No	No	No heating	Virgin
Asrolled	Yes	Yes	No heating	Delaminated
Ar	Yes	Yes	1 hr in Ar gas	Delaminated
Ar →H$_2$	Yes	Yes	1 hr in Ar gas and 1 hr in H$_2$ gas	Delaminated
N$_2$	Yes	Yes	1 hr in N$_2$	Delaminated
N$_2$→H$_2$	Yes	Yes	1 hr in N$_2$ and then 1 hr in H$_2$	Delaminated
Air	Yes	Yes	1 hr in air	Delaminated
O$_2$	Yes	Yes	1 hr in O$_2$	Delaminated
Ar→O$_2$	Yes	Yes	1 hr in Ar and then 1 hr in O$_2$	Delaminated
Ar→O$_2$→O$_2$	Yes	Yes	1 hr in Ar, then 1 hr in O$_2$ and finally 1 hr in O$_2$	Delaminated
N$_2$→O$_2$	Yes	Yes	1 hr in N$_2$ and then 1 hr in O$_2$	Delaminated
N$_2$→O$_2$→O$_2$	Yes	Yes	1 hr in N$_2$, then 1 hr in O$_2$, and finally 1 hr in O$_2$	Delaminated
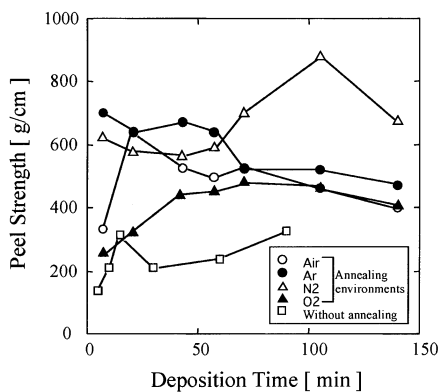
Fig. 6. Peel strength of Cu/Cu-deposited LCP with respect to Cu deposition time without heating in atmospheric air and with heating in air, O$_2$, Ar, and N$_2$ flow at the rate of 2 mL/min in a quartz box at 240 °C.

Fig. 7. Mean peel strength dependence on the sequential heating in air, O$_2$, Ar, and N$_2$. Peel strength increases in the heating sequence of O$_2$, air, N$_2$ and Ar media. Second and third heating in O$_2$ gas degrade the interface adhesion between Cu/LCP. Heating media change was indicated by the arrows.

36.2%, respectively. Island-like growth of Au was reported, and a thickness of 10–20 nm was required to complete Au coverage on the substrate [7]. Therefore, the general trend in the decrease of peel strength at high Cu coverage before heating can be attributed to the weak deposited thick films. Even after heating, the peel strength was not improved (except heating in N$_2$ gas due to unknown reason) because of insufficient thermal restructuring of Cu thick films at low temperature (240 °C is too low for restructuring of Cu films).

C. Adhesion Dependence on Heating Environments

A comparative study of the peel strength of Cu/Cu-deposited LCP interface on heating environments in N$_2$, Ar, air, and O$_2$ is shown in Fig. 7 (see Table II). It also includes peel results of the samples heating in Ar and N$_2$ first and after that, additionally in H$_2$ and O$_2$. Mean peel strength ($\pm 10\%$) is plotted against environments. Peel strength of the samples heated in Ar and N$_2$ was found to be much higher than that of samples heated in air and O$_2$ gases. As previously seen, peel strength in O$_2$ gas
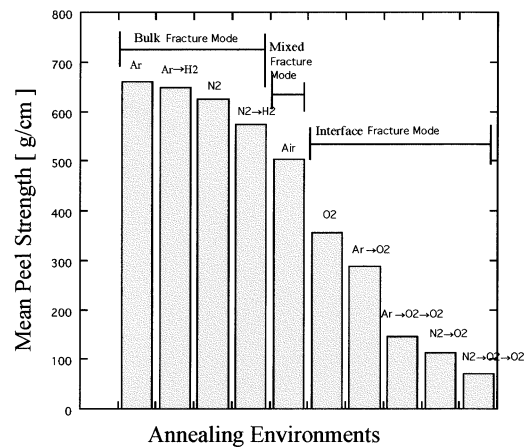
medium was the lowest compared with other environments. Due to the high peel strength of the samples heated in Ar and N$_2$ gases, we performed sequential treatments of those samples in O$_2$ and H$_2$ for second and third heating to measure the influence on the adhesion strength of Cu and LCP. Subsequent heating of Ar and N$_2$-treated samples in H$_2$ environment had no significant effect on the peel strength. However, subsequent heating of Ar and N$_2$–treated samples in O$_2$ drastically degraded the peel strength. Further heating in O$_2$ for the samples heated in Ar or N$_2$ and then in O$_2$ resulted in degradation of peel strength. Three fracture modes, namely bulk fracture, partial bulk fracture, and interface fracture were observed from visual observation of delaminated LCP and Cu surfaces. The SD of peel strength was <12.2, 18.6, and $>36.2\%$, respectively, for the bulk, partial bulk, and interface fractured samples after delamination. Second and third heating only in O$_2$ gas severely increased the SD. For example, the SD for the samples heated
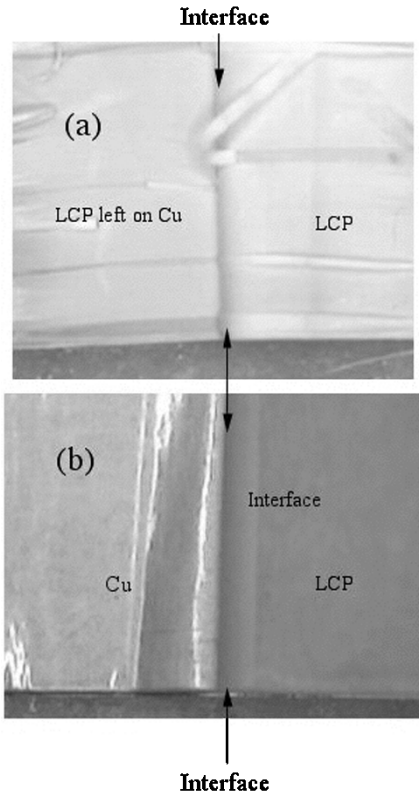
Fig. 8. Typical delaminated images of Cu/LCP heated in Ar and O$_2$ gases. Diffusion caused O$_2$ reaction with deposited Cu generates brittle Cu oxide, resulting in week adhesion in O$_2$ heating.

1 h in N$_2$ gas was 11.7%, whereas the SD for the samples heated, first 1 h in N$_2$, then 1 h in O$_2$, and finally 1 h in O$_2$ gas environments (N$_2$ $\rightarrow$ O$_2$ $\rightarrow$ O$_2$, see Table II) was 80%, indicating unstable fracture locations at the interfaces after second and third heating in O$_2$. Typical fracture images of peeled Cu and LCP surfaces after being heated in Ar and O$_2$ environments are shown in Fig. 8. Left and right sides of each image show the optical images of delaminated Cu and LCP surfaces, respectively. Bulk fracture of LCP was evident for the samples annealed in Ar environment, where LCP was left on Cu side, indicating higher interfacial adhesion strength than that of bulk LCP material. Chuo and Tang [8] showed that the deposited Cu on polyimide was not oxidized throughout the deposition process in high vacuum. The adhesion strength of Cu/LCP heated in Ar gas was very high presumably due to the reaction of deposited Cu with vacant sites of oxygen in polymer chains on LCP surface and good vacuum level during bonding. On the other hand, oxygen-heated peel surfaces showed clean fracture across the interface. This might correspond to the oxidation of deposited Cu due to the reaction of diffused oxygen from LCP, which is brittle in nature, resulting in degradation of interface strength. It is interesting to note here that the significant adhesion increment of poly tetrafluoro ethylene with Cu was demonstrated by increasing surface roughness of mating surfaces irradiated with 1 keV Ar ions [9]. However, from the point of skin effect, our study showed good smooth interface [4] and surface associated with considerable improvement of adhesion strength of Cu/LCP heated in Ar, which might be useful for microelectronics packaging.
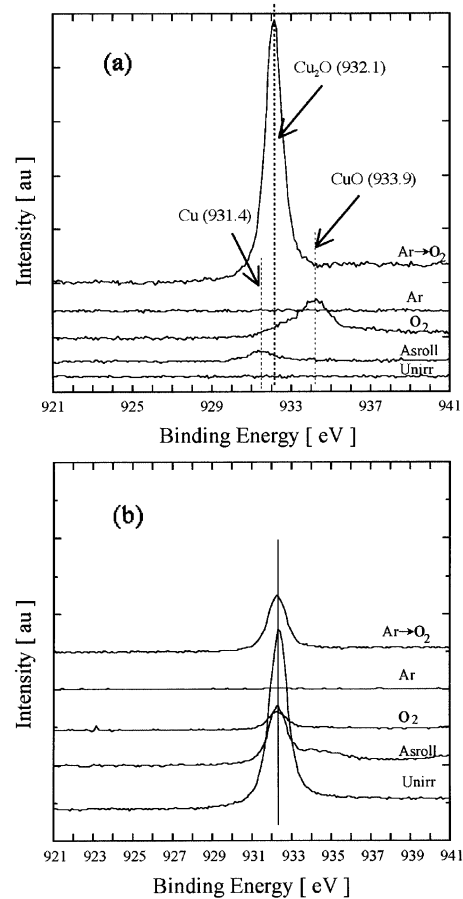

Fig. 9. Cu2p3/2 XPS spectra for nonsputtered and as-rolled delaminated (a) LCP and (b) Cu surfaces compared with that of the LCP delaminated surfaces heated in various gas environments. "Unirr" represents virgin surfaces before irradiation. Asroll, O$_2$, Ar, and Ar $\rightarrow$ O$_2$ represent delaminated surfaces cleaned with plasma having deposited Cu on LCP without heating, after heating in O$_2$ gas, after heating in Ar gas, and after heating in Ar and then in O$_2$ gas, respectively.

D. Interfacial Chemistry by XPS

For XPS measurements, the samples were first heated in various environments except nonsputtered and as-rolled samples. Peel tests were performed and C1s, O1s, and Cu2p3/2 spectra for the delaminated surfaces were investigated.

Fig. 9 shows the Cu2p3/2 XPS spectra for nonsputtered and as-rolled delaminated LCP and Cu surfaces compared with that of LCP-delaminated surfaces heated in various environments prior to delamination (see Table II). Delaminated surfaces were exposed to atmospheric air prior to loading into the XPS chamber. As expected, there were no peaks of Cu2p3/2 on unirradiated LCP and delaminated LCP heated in Ar gas. The as-rolled delaminated LCP surface (Cu deposited on plasma-cleaned LCP, but not heated) showed a weak peak for metallic Cu (931.4 eV) consistent with trace amounts of deposited Cu only, due to the poor adhesion of the Cu to LCP prior to heating. In the case of O$_2$ heating, a stronger Cu peak (at 933.9 eV) than that of as-rolled LCP was found, indicating CuO associated with the existence of other particles because of large full-width at half-maximum (FWHM). Further heating of Ar-heated samples in O$_2$ gas generated single oxidation of
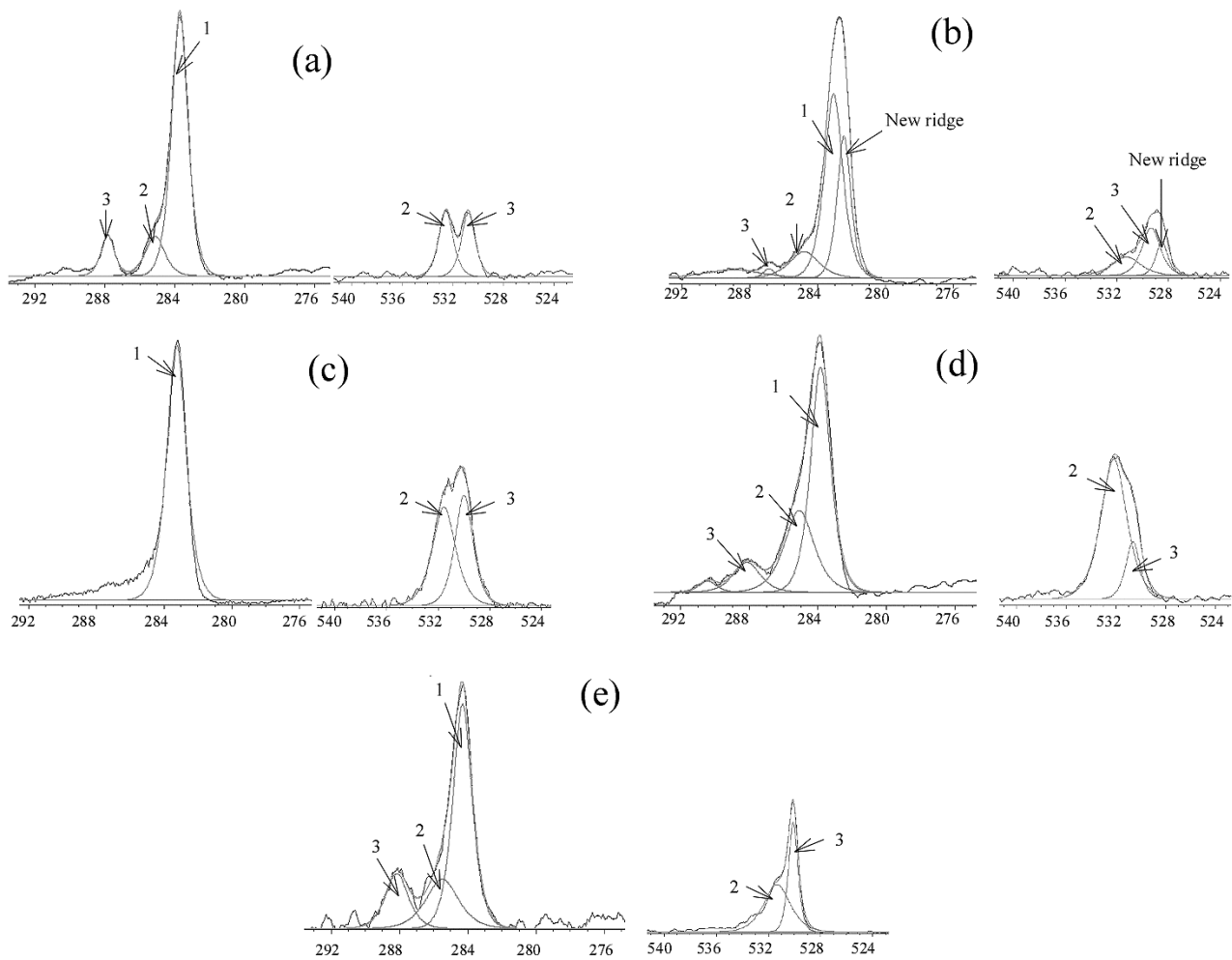
Fig. 10. C1s and O1s XPS spectra for LCP (a) before sputter cleaning, (b) after sputter cleaning with an RF plasma source of 50 W for 10 min, (c) after delamination of Cu deposited LCP bonded with Cu (without heating), (d) after delamination of Cu deposited LCP bonded with Cu and heated the Cu/LCP in O_2 prior to delamination, and (e) after delamination of Cu deposited LCP bonded with Cu and heated the Cu/LCP, first in the Ar and then in the O_2 gas prior to delamination. The peaks for C-C-/C-H, -C-O-, and O—C=O were labeled by 1, 2, and 3, respectively.

Cu (Cu_2O) peak on LCP at lower energy, which was identical to that of unirradiated Cu2p3/2 peak on Cu in terms of photo electrons counts and chemical energy position. The fact of nonexistence of Cu on peeled Cu and LCP surfaces (heated in Ar gas before delamination) can be attributed to the presence of fractured LCP on Cu side [Fig. 9(b)]. Similar behavior is also observed in the case of N_2 heating. Based on the XPS spectra, it can be concluded that the fracture occurred in the oxidized deposited Cu layers of Cu/Cu-deposited LCP heated in Ar $\rightarrow$ O_2 and O_2 gas.

In order to gain insights into the adhesion mechanism of Cu/LCP, the LCP surfaces, prior to and after plasma cleaning, and the delaminated LCP surfaces with and without heating in oxygen and sequentially in Ar and oxygen were intensively investigated (see Table II). In each case, curve fitting of C1s and O1s spectra was precisely accomplished to determine the hidden peaks and their chemical shifts.

The C1s spectrum for nonsputtered LCP surfaces has three components: benzene structured C—C (283.7 eV) peak; C—O (285.1 eV) peak at higher energy by 1–2 eV near the main peak; and C=O (287.8 eV) peak near the second peak [Fig. 10(a)].

Single (C—O)- and double-bonded (C=O) peaks for C to oxygen were observed at 532.5 and 530.7 eV, respectively, for nonsputtered LCP surfaces. Fig. 10(b) shows the spectra for LCP surfaces cleaned with an RF plasma source in a load lock chamber of the XPS tool. The vacuum pressure of the load lock and analysis chambers of the XPS tool, which were separated by a gate valve were 10^{-5} and 10^{-7} Pa, respectively. The power of the RF source (13.56-MHz 500-RF generator, ULVAC RFS-1305A) used for surface cleaning of LCP for XPS investigation was 50 W. The RF source intensity (power/electrode area) used for the LCP surface cleaning in XPS tool is three times higher than that of the bonding tool. Here, the measurements were performed without breaking the vacuum after the plasma cleaning of LCP. The RF plasma cleaning greatly reduced not only the amplitudes of C—O and C=O species more than C-C/C-H species, but also the organic oxygen as shown both in the C1s and O1s spectra, which is indicative of plasma modification. Furthermore, plasma modification resulted in a new peak for C1s appearing at 282.5 eV, which might be a characteristic of a carbon-rich surface. Surface modification of Teflon (-CF_2-CF_2-)$_n$ using a sputtering source of 500 eV Ar

ions has been reported due to the preferential sputtering of fluorine atoms [1]. Reduction of oxygen from LCP surfaces due to sputter cleaning would create favorable chemical states (dangling bonds) for Cu after deposition with LCP carbon.

The C1s spectrum for as-rolled (plasma-cleaned LCP surface deposited with Cu layers and bonded with bulk Cu) delaminated LCP surfaces has an almost identical C—C peak to that of nonsputtered LCP in terms of intensity. However, the peaks for C—O and C=O were absent [Fig. 10(c)]. On the other hand, the O1s spectrum appears to be identical to that of nonsputtered LCP surface with the dominance of C=O peak over C—O peak. The O1s species appear to be relatively higher than the C-C/C-H species. Perhaps Cu deposition on RF plasma cleaned LCP surface allow Cu to occupy the vacant sites for oxygen bonded with carbon [10]. While heating the Cu/LCP samples in O_2 gas, the occupied sites for Cu are oxidized presumably due to the diffusion of O_2 through LCP surface [Fig. 10(d)]. It should be noted that the bonded Cu/LCP samples were curled after cold rolling because of remaining residual stress induced by different elastic expansion in Cu and LCP. At the temperature below 100 °C, the LCP slightly absorbs O_2 because of the nonsignificant elastic expansion. After heating at 240 °C, the curled samples become flat due to the stress relaxation. Probably O_2 diffusion in LCP during heating in O_2 is thermodynamically favorable [5] due to thermal expansion, resulting in Cu–oxide by reacting with deposited Cu at the interface. As previously shown in the peel test results, Cu/LCP samples heated in Ar gas were fractured in bulk LCP. Nonetheless, XPS observation on bulk-fractured LCP did not give any interface information. Therefore, the samples heated in Ar were further heated in O_2 gas and the delaminated LCP surface subsequently was analyzed. The result showed that the delaminated LCP has similar spectra to that of the unirradiated LCP surface in terms of O1s and C1s spectra [Fig. 10(e)]. However, the strong Cu peak of LCP, as shown in Fig. 9, associated with O1s and C1s spectra is indicative of partial oxidation of deposited Cu on LCP. The peaks for C—O and C=O reappeared, and their ratio is nonidentical with that of nonsputtered LCP surface. This fact indicates that deposited Cu on LCP (across LCP/Cu interface) is oxidized upon heating in O_2, (which was visually observed on peeled Cu surface) and contributes to the C—O peak. We can conclude that the plausible adhesion enhancement is attributable to the chemical reactions of Cu occupied to the dangling bonds for —O and =O with C and crosslink formation of chains through Cu.

Fig. 11 shows the depth profile of the peeled LCP side heated in Ar followed by heating in O_2. The LCP surface was taken from a peeled interface of Cu/LCP having an interface strength of 200 g/cm. The energy of Ar ion etching source was 3 keV, and the current was 20 mA. The atomic concentrations of Cu, O_2, and C on delaminated LCP surface at the beginning of the depth profile measurement were 60%, 30%, and ~2%, respectively. This implies the presence of Cu oxides on LCP surface, as previously shown in Fig. 10(e). Native oxide formation due to atmospheric exposure after peeling seems to be etched out within a few tenths of a second. The necessity of long etching time is indicative of thick oxide layers of Cu on LCP. Cu and O_2 reduce with etching time, while C increases. As expected,
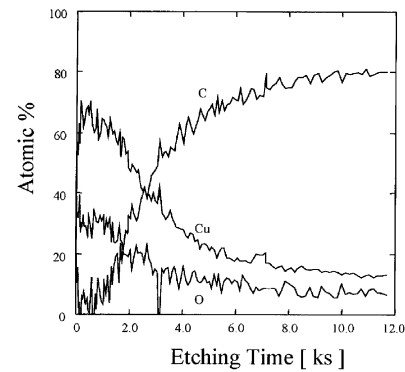

Fig. 11. Depth profile of delaminated LCP heated in Ar gas and then in O_2 gas prior to heating.

Cu 2p3/2, and C1s peaks cross over near 2500 s, and then decrease and increase, respectively, with increasing etching time. Then, the C1s peak for LCP attains the highest value. Cu counts higher than 10% were found after etching for 3 h, which reasonably postulates the islands formation of deposited Cu on LCP.

IV. CONCLUSION

The heating influence on bonding strength was investigated to clarify the bonding mechanism of Cu and LCP in air, argon, nitrogen, hydrogen, and oxygen gases at 240 °C after bonding (because absorption of LCP below 100° is insignificant). To eliminate stress induced by bonding and stacking, heat treatment was found to be important. The peel strength of Cu/LCP was enhanced in the heating sequence of oxygen, air, nitrogen, and argon gas environments. Drastic decrease in adhesion was found in Cu/LCP heated in O_2 gas following heating in Ar and N_2 gases. In this case, adhesion decreased to the level found in nonheated samples. XPS analyses showed that RF plasma modifies the LCP surface probably into carbon rich having dangling bonds with reduced oxygen. This surface favorably may react with deposited Cu and the annealing environments may enhance or suppress the reaction resulting in strong adhesion or poor adhesion. Depth profile analysis on previously oxygen-annealed peeled LCP surface revealed much thicker Cu oxide layers than normal. These new oxidized Cu layers, produced by oxidation of the deposited Cu can be attributed to the diffusion of oxygen through the LCP. On the other hand, no oxidation layer of Cu is expected across the interface of the samples heated in other gas environment because of the bulk fracture in LCP.

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