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Surface Modification of a Liquid-Crystalline Polymer for Copper Metallization

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ABSTRACT: The effects of different surface modifications on the adhesion of copper to a liquid-crystalline polymer (LCP) were investigated with X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy, contact-angle measurements, and pull tests. High pull-strength values were achieved when copper was sputter-deposited onto plasma and reactive-ion-etching (RIE)-pretreated LCP surfaces. The values were comparable to the reference pull strengths obtained with laminated copper on the LCP. The adhesion was relatively insensitive to the employed feed gas in the pretreatments. The surface characterizations revealed that for RIE and plasma treatments, the enhanced adhesion was attributable to the synergistic effects of the increased surface roughness and polar component of the surface free energy of the polymer. However, if the electroless copper deposition was performed on RIE- or plasma-treated surfaces, very poor adhesion was measured. Good adhesion between the LCP substrate and electrolessly deposited copper was achieved only in the case of wet-chemical surface roughening as a result of the creation of a sufficient number of mechanical interlocking sites, together with a significant loss of oxygen functionalities, on the surface. © 2003 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 623–636, 2003
Keywords: adhesion; liquid-crystalline polymers (LCP); X-ray photoelectron spectroscopy (XPS); plasma; surfaces

INTRODUCTION

The technological basis of future portable electronics will be established on high-performance integrated circuits that are densely connected to other components in low-cost and highly functional modules. However, while we strive for ever better performance and functionality, more fundamental requirements are also encountered in packaging and printed wiring board fabrication. Even though novel packaging solutions and high-density microvia boards have been developed recently, broader bandwidths, especially needed for future wireless communication devices, demand disruptive solutions.[1,2] One such solution is to integrate very thin flexible silicon chips and chemically deposited passive components inside high-density build-up substrates.[3–5] This can be carried out by either fully additive or semiadditive techniques utilizing photodefinable polymers and chemical metal deposition processes in the fabrication of the modules.[6,7] High-performance materials such as liquid-crystalline polymers (LCPs) can be used as base substrates for these modules. It is emphasized, however, that the great technical advantages provided by highly integrated build-up modules depend primarily on good adhesion between the thin sequential layers of the polymers and metals.

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Thermotropic LCP is a unique, high-performance thermoplastic. Its rigid, rodlike molecules maintain an ordered, anisotropic structure with strong mechanical strength in the direction of the molecular chains. The highly crystalline nature of the LCP offers an excellent combination of physical and chemical properties.[8–10] The especially low dielectric constant and losses of the LCP are important for future high-frequency applications. In addition, these properties are not significantly affected by physicochemical changes in the operational environment. The aforementioned properties make the LCP an ideal substrate material for high-density printed wiring boards.

However, the LCP exhibits poor adhesion with metal layers. For improved adhesion, the most frequently used method for polymers in electronics is the roughening of the surface by a wet-chemical treatment. This consists of three water-based steps: swelling, oxidative etching, and reduction. As a result, the mechanical anchoring of electrolessly deposited metal can occur inside the fine cavities of the roughened polymer surface.[11,12] However, there are an increasing number of applications in which roughened polymer surfaces have a deleterious effect on the electrical performance, especially in high-frequency broadband wireless communication.[13,14]

Accordingly, the sufficient adhesion of metals to a smooth polymer surface has to be achieved.[15] An alternative metalization method is the dry process, which includes plasma or RIE pretreatment and sputter deposition of metal to the activated surface. A pretreatment is performed to modify the surface chemistry and morphology of the polymer. For adhesion improvement, only the outermost surface layer is to be affected, whereas the bulk polymer and its properties are left unaltered. This technique has the advantage of being nonpolluting, and it ensures a more uniform treatment over the sample surface than wet processing, including the ability to produce sufficient adhesion on smooth surfaces.[16,17]

In this study, the effects of wet-chemical, oxygen-plasma, and RIE (oxygen or argon) pretreatments on the adhesion of electroless or sputter-deposited copper to the LCP were investigated. The failure modes were examined with optical microscopy, scanning electron microscopy (SEM), and energy-dispersive spectroscopy. The physicochemical changes on the polymer surfaces were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact-angle measurements.

EXPERIMENTAL

Materials and Methods

Commercial LCP films (BIAC from Gore) with or without copper laminates were studied. The thickness of the LCP film was 125 μm. The LCP (BIAC) used in this work was an aromatic polyester containing additives (e.g., silica filler). The LCP films were relatively thin and flexible; therefore, they were attached onto a base substrate with an adhesive (Araldite) for easier processing. E-glass-reinforced epoxy (FR4 from Nelco) was used as the base substrate.

The fabrication process of the test pads is schematically shown in Figure 1. Three different surface treatments were evaluated for the pretreatment of the LCP. The first was the wet-chemical treatment, which consisted of three water-based steps: swelling (3 min), etching (5–30 min), and reduction (2 min). The wet-chemical treatment of the surfaces was then followed by Sn/Pd activation and electroless copper deposition. The details of the process flow are reported in a previous article.[12] In the second treatment, a barrel-type plasma reactor was used. Samples were placed in a substrate holder surrounded by a tunnel-perforated metal shield between the samples and electrodes. The conditions for the plasma treatment were as follows: the gas source was oxygen, the frequency was 13.56 MHz, the treatment period varied from 5 to 25 min, the radio-frequency (RF) power was 80 W, and the gas pressure was 26 Pa. Two sets of samples were prepared. One set was washed with ethanol for 2 min in an ultrasonic bath after the plasma treatment, and the other was analyzed without being washed. The third surface modification method was reactive ion etching (RIE) with a parallel-plate reactor. Plasma in the RIE system was produced in the region between two electrodes with the introduction of O_2 or Ar. The samples were placed directly below the plasma on a plate shielding the lower electrode, which was powered by a 13.56-MHz RF generator. The surface modification was performed at a flow rate of 15 sccm. The RF power was fixed at 80 W, and the operating pressure was held at 2.7 Pa. The treatment time ranged from 5 to 25 min. The treated surface was then metalized electrolessly or by the sputter deposition of copper to a thickness of 1 μm. The electroless plating process was a wet-chemical deposition process, and the copper deposition was the result of a redox reaction. In this process, the treated sam-

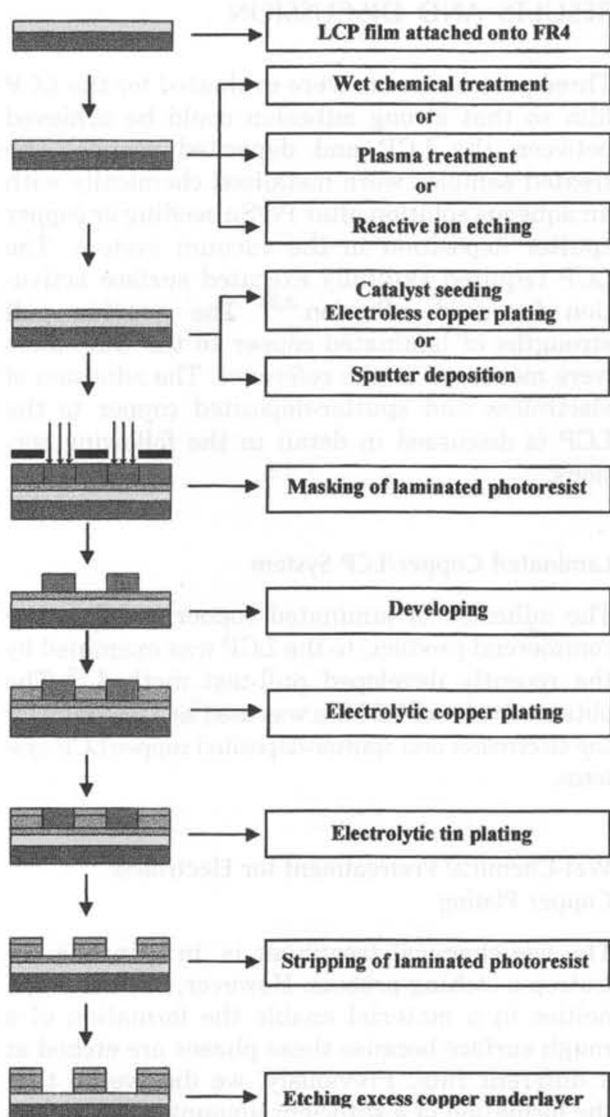

Figure 1. Schematic representation of the fabrication process of the test pads.

ples were immersed in a catalyst solution (Circuposit TM 3344) containing colloidal palladium–tin particles at 45 °C for 5 min to attach the colloidal palladium–tin particles onto the polymer surfaces. After the activation step, the samples were rinsed with distilled water to remove excess Pd/Sn particles and immersed in an electroless plating solution (Cuprothick 84) consisting of an aqueous basic copper sulfate solution and formaldehyde at 36 °C for 15 min. Copper metal was deposited by the copper cation reduction process on the polymer surface at a plating rate of 4–5 μm/h. In the case of sputter deposition, the samples were processed *in vacuo* under the following conditions: base pressure = 1.5×10^{-4} Pa, work pressure = 0.43 Pa, direct-current power = 2000 W, and argon gas rate = 60 sccm. After metalization, a dry-film photoresist was laminated onto it and exposed through a photomask. The trench structure of the resist was formed by development. Copper was then electrolytically plated onto the electroless or sputter-deposited copper that was revealed at the bottom of the resist trenches so that a thicker copper layer would be achieved. As an etching resist, a tin layer was electrolytically plated onto the copper surface, and the dry-film photoresist was then stripped off. Finally, the excess copper was removed with a copper etching solution (Ultraincide 35/35 from Alfachimici), and test pads were formed with a diameter of 2 mm. The adhesion test pads with sufficient surrounding substrate were then cut out from the fabrication panel. Copper wire was finally microsoldered to the test pads with a eutectic SnPb solder for attachment to the pull-test equipment.[12]

Characterization

The MTS 858 tensile test machine was used to measure the pull strength, that is, the adhesion of copper to the LCP. The specimen was fixed to the test setup, and a copper wire was then clamped in the grip and pulled at a constant ramp rate of 0.001 mm/s. The force required to break the weakest interface was recorded. The test pad area was calculated under the assumption that the pad was circular. The pull strength was evaluated as the average tensile strength of the 12 specimens prepared under the same conditions. The schematic representation of the adhesion test configuration is given in Figure 2.

The topographies of the treated LCP surfaces (tilted at 45°), as well as the fracture surfaces of the metalized polymer, were examined with a field-emission SEM instrument (JSM-6330F, JEOL) operated at 1 or 15 kV.

The surface topography of the untreated and treated LCP surfaces was characterized on a Nanoscope IIIa atomic force microscope (Digital Instrument D3100 Inc). In each case, an area of 5 μm × 5 μm was scanned with silicon tips in the tapping mode. The surface roughness of the samples was evaluated in terms of the arithmetic mean of the roughness and the root-mean-square (RMS) of the roughness.

The contact angles of water and diiodomethane (DIM) on the LCP surfaces were measured by the sessile drop method with an Advanced

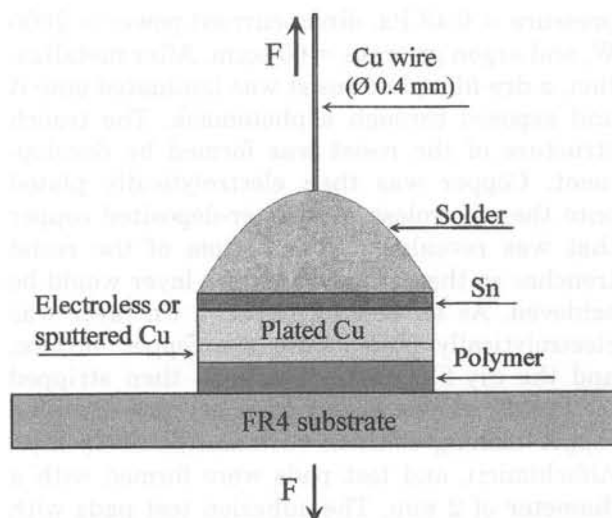

Figure 2. Schematic representation of the adhesion test configuration.

Surface Technology goniometer equipped with a VCA 2500XE video contact-angle system. For each sample, the contact-angle value was the average of eight measurements recorded from different locations on the sample surface with a standard deviation of 1–3°. From the measured contact angles, the surface free energy (γ_S) was calculated with the geometric mean model.[18,19] The volume of the liquid drop used in the measurement was 0.1 μL. γ_S in the model was assumed to be the sum of the dispersion (γ_S^d) and polar (γ_S^p) components. The dispersive (d) and polar (p) components of the surface free energy of the different liquids (γ_L) adopted herein were $\gamma_L = 72.8$ mJ/m^2, $\gamma_L^d = 21.8$ mJ/m^2, and $\gamma_L^p = 51.0$ mJ/m^2 for distilled water and $\gamma_L = 50.8$ mJ/m^2, $\gamma_L^d = 49.5$ mJ/m^2, and $\gamma_L^p = 1.3$ mJ/m^2 for DIM.[19,20]

The X-ray photoelectron spectra of both untreated and treated LCP surfaces were recorded with an Axis 165 X-ray photoelectron spectroscope. The monochromatic Al Kα X-ray source was operated at an anode voltage of 12.5 kV and at a current of 8 mA. Survey spectra were acquired from 0 to 1100 eV with a pass energy of 80 eV and a step size of 1 eV. The core level spectra were obtained with a pass energy of 20 eV and a step size of 0.1 eV. A photoelectron takeoff angle of 90° was used for all the analyses. All XPS peaks were referenced to a C1s signal at a binding energy of 285 eV, representing the C—C and C—H bonds in hydrocarbons.

RESULTS AND DISCUSSION

Three pretreatments were evaluated for the LCP film so that strong adhesion could be achieved between the LCP and deposited copper. The treated samples were metalized chemically with an aqueous solution after Pd/Sn seeding or copper sputter deposition in the vacuum system. The LCP required skillfully executed surface activation for good adhesion.[3,21] The average pull strengths of laminated copper to the LCP films were measured as the reference. The adhesion of electroless and sputter-deposited copper to the LCP is discussed in detail in the following sections.

Laminated Copper/LCP System

The adhesion of laminated copper (used in the commercial product) to the LCP was examined by the recently developed pull-test method.[12] The obtained value of 7.2 MPa was used as a reference for the electroless and sputter-deposited copper/LCP systems.

Wet-Chemical Pretreatment for Electroless Copper Plating

The wet-chemical treatment is, in principle, an isotropic etching process. However, the heterogeneities in a material enable the formation of a rough surface because these phases are etched at a different rate. Previously, we discovered that the formation of a sufficient amount of microcavities on the polymer surface is a necessity for good adhesion between low surface free energy surfaces, such as those of polymers and electrolessly deposited copper,[22,23] unless the surfaces are activated by more complex approaches.[24,25] Other methods such as plasma and RIE treatments produce primarily chemical modification instead of significant amounts of microcavities. In addition, sputter-deposited copper exhibits poor adhesion on the chemically treated LCP because of the considerable loss of oxygen-containing functionalities on the surface. Therefore, the wet-chemical pretreatment is emphasized for electrolessly deposited copper in this study.

SEM and AFM micrographs of the untreated and chemically treated epoxy surfaces are shown in Figures 3 and 4(a,b), respectively. The untreated surface contained random indentations over the entire surface, and its RMS roughness

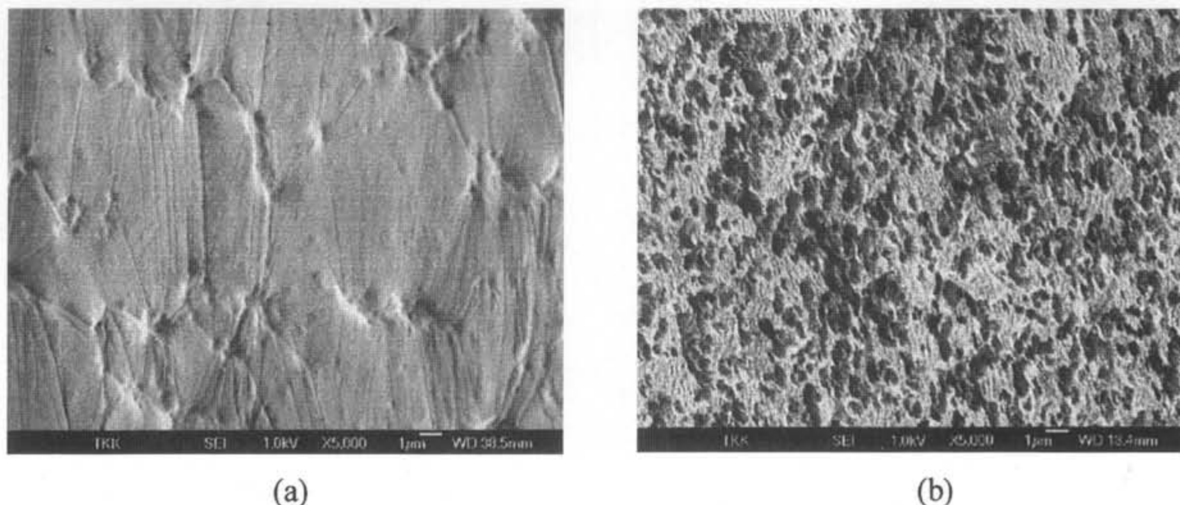

Figure 3. Surface topography of the LCP: (a) untreated and (b) chemically treated (etching time = 20 min).

was 14 nm, as detected by AFM. The initial level of roughness was not enough for good adhesion with electroless copper metalization. There was a marked increase in the surface roughness as a function of the etching time until 20 min, after which the roughness decreased (Fig. 5).

The chemical modification of the LCP surface by the wet-chemical treatment (20 min), as observed by XPS, is shown in Figure 6 and Table 1. The results show a considerable loss of oxygen-containing functionalities on the surface. The atomic ratio (O1s/C1s) decreased significantly from 0.35 to 0.24. The clearly visible C1s peak for carbonyl (C=O) was especially strongly affected. It almost completely disappeared after 20 min of treatment, whereas the intensity in the C1s envelope increased at 289.4 eV. The remaining oxygen was present mainly in the form of C—O and O—C=O, as detected from the C1s spectrum (Fig. 6). The observed changes of the O1s peak were in good agreement with those of the C1s peak as the broad peak of the untreated sample transformed into a doublet. The results obtained from the C1s and O1s spectra imply that the wet-chemical treatment caused bond breaking in the vicinity of the carbonyl and its oxidation to ester groups. The loss of oxygen on the surface, however, could be attributed to chain scission of the polymer backbone and removal of the formed low molecular weight products.

In the electroless plating process, a reduction reaction of copper ions to copper metal with formaldehyde occurs with the assistance of a palladium–tin catalyst that is attached onto the polymer surface. Therefore, a copper metal layer is chemically deposited on the surface as a result of the redox reaction. The adhesion of the electrolessly deposited copper to the LCP without a surface treatment was very poor. The adhesion increased noticeably with continued etching up to 20 min, as a function of increased roughness, after which there was a remarkable decrease in adhesion (Fig. 7). Densely appearing microcavities could clearly be observed after 20 min of etching [Fig. 3(b)]. However, as the bulk structure was affected by the continued etching, the adhesion was lost with excessive treatment.

RIE and Plasma Pretreatments for Sputter-Deposited Copper

Plasma etching is primarily due to the chemical reactions between the etchant gas (oxygen) and the sample surfaces in the barrel configuration, in which a perforated metal tunnel is added to shield samples from ion bombardment. In RIE pretreatments, physical etching (i.e., ion bombardment) is involved. With a chemically reactive gas (e.g., O_2), both chemical etching and physical bombardment contribute to the etching. Chain scissions of the outmost macromolecules occurring during the chemical or physical etching process lead to low molecular weight products on the surface.[26–28] If the formed fragments are thoroughly cleaned away and sufficient chemical activation has taken place on the surface, sputter deposition as a high-energy

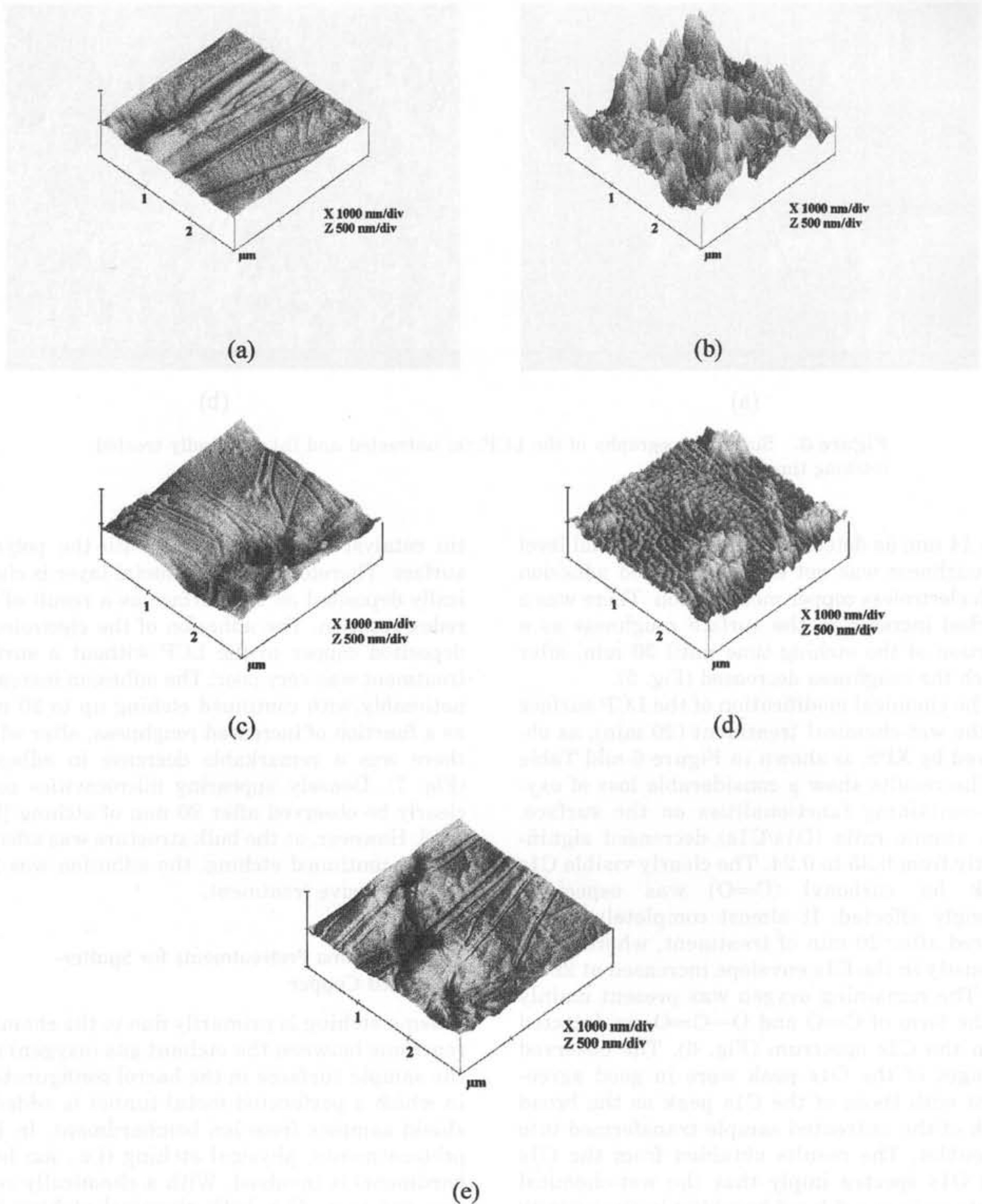

Figure 4. AFM images of the LCP: (a) untreated, (b) chemically treated (etching time = 20 min), (c) plasma-treated (5 min), (d) RIE-treated with O_2 (5 min), and (e) RIE-treated with Ar (5 min).

deposition method leads to good adhesion even on relatively smooth polymer surfaces.[16,22] This, in turn, is beneficial for good electrical performance in high-frequency electronics.

Surface Morphology

The formation of pits on the plasma-treated LCP surface was detected by AFM [see Fig. 4(c)].

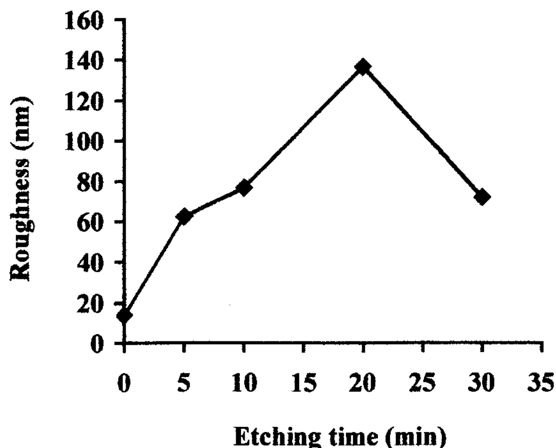

Figure 5. Roughness (RMS) of the LCP after the chemical treatment as a function of the etching time.

These pits resulted in an increased surface area and, therefore, provided a more favorable surface state for various physical and chemical interactions between the LCP and copper. The use of Ar in the RIE resulted in a surface with a texture similar to that for the plasma treatment with oxygen [Fig. 4(e)], whereas the use of oxygen in the RIE had a great influence on the modification of the surface topography [Fig. 4(d)]. The RMS roughness of the plasma- or RIE-treated surfaces was much greater than that of the untreated surface (Fig. 8).

XPS Analyses

The C1s and O1s core level photoemission spectra for the untreated and treated LCPs are shown in Figure 6. The C1s spectrum for the untreated LCP was peak-fitted to four components assigned to the carbon atoms of the phenyl ring (285 eV), the single-bonded carbons (C—O, 286.6 eV), carbonyls (C=O, 287.7 eV), and the ester group carbons [—(C=O)—O—, 289.4 eV].[29] The small peak occurring at 291.1 eV was a shake-up satellite that occurred as a result of the aromatic ring appearing in the LCP backbone. A rather broad, symmetric, and nonstructured O1s peak was detected for the untreated samples at 532.9 eV. This feature was broad enough to cover the related C—O and C=O subpeaks. The relative amounts of the different functionalities observed by the C1s core level analysis are shown in Table 1. The enrichment of the surface with oxygen-containing functionalities was evident after the plasma treatment with oxygen, which was expected to enhance adhesion.

As mentioned previously, the introduction reactions of new functional groups during plasma treatment are accompanied by the formation of low molecular weight fragments on the surface. If these fragments are not removed before the deposition of a sequential material layer, a weak boundary layer (WBL) is formed, and no significant adhesion improvement is achieved.[30–32] The examination of the formed fragments can give valuable information about the reactions occur-

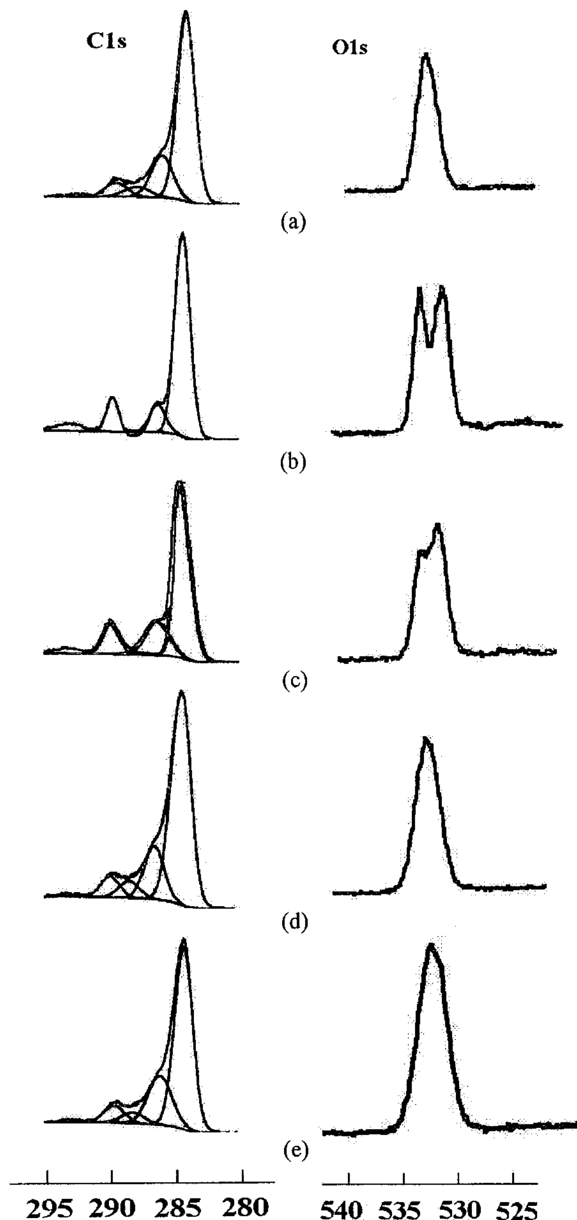

Figure 6. XPS (C1s and O1s) spectra for LCP surfaces: (a) untreated, (b) wet-chemically treated (etching time = 20 min), (c) O_2-plasma-treated (5 min), (d) RIE-treated with Ar (5 min), and (e) RIE-treated with O_2 (5 min).

Table 1. Chemical Compositions of the Untreated and Treated LCP Surfaces

Functional Groups (%)	Binding Energy (eV)	Untreated	Chemically Treated	Plasma-Treated (Unwashed)	Plasma-Treated (Washed)	RIE-Treated (O_2)	RIE-Treated (Ar)
C—C	285	71	78	52	68	65	71
C═O	286.6	18	12	21	19	23	17
C═O	287.7	6	—	5	1	5	6
O═C—O	289.4	5	10	22	12	7	6
Total		29	22	48	32	35	29
O/C		0.35	0.24	0.67	0.30	0.33	0.34

ring at the surface during the treatment. Therefore, untreated and oxygen-plasma-treated and subsequently washed samples are compared in Figure 9. Plasma treatment broke the polymer chains and formed a very hydrophilic fragment layer on the LCP surface, as evaluated by the contact-angle measurements with water ($\theta \approx 15°$), which are shown in Table 2. However, after these fragments were washed away from the surface by ethanol, the remaining surface became less hydrophilic. This can be explained by the removal of the highly oxidized fragments (Fig. 9). Peak-fitted concentrations of each functional group in Figure 9 were calculated and are shown in Table 1. The concentration of C═O and O—C═O functionalities decreased after washing, whereas that of C—O remained almost unaffected. This suggests that the majority of the carboxylate debris that formed was not introduced into the main chain and was easily washed away by ethanol in an ultrasonic bath. The O1s core level spectrum was changed significantly on the samples treated by the oxygen-plasma treatment. A clear shift of the center of the peak to higher binding energies occurred. This was expected to follow from the ester groups that contributed to the intensity at the high binding energy side of the O1s envelope (532–534 eV). These XPS results support the degradation of the polymer backbone from the vicinity of the carbonyl unit and the plasma-induced formation of the ester/carboxyl acid species. The RIE-treated (O_2) LCP C1s spectrum does not show significant changes in comparison with the spectrum of the untreated sample. After the treatment, a broadening of the peaks and an enhancement of oxygen functional groups could be observed. Nevertheless, no formation of oxygen-containing functional groups was observed in detectable quantities in the C1s spectrum of the RIE-treated (Ar) LCP.

Wettability

To evaluate the changes in the wettability of the modified surfaces, we conducted a further characterization of the LCP surfaces by water and DIM

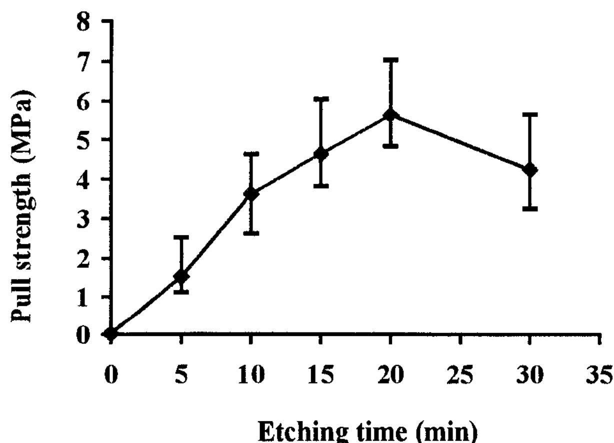

Figure 7. Pull strength of electroless copper to the LCP as a function of the etching time in the chemical treatment.

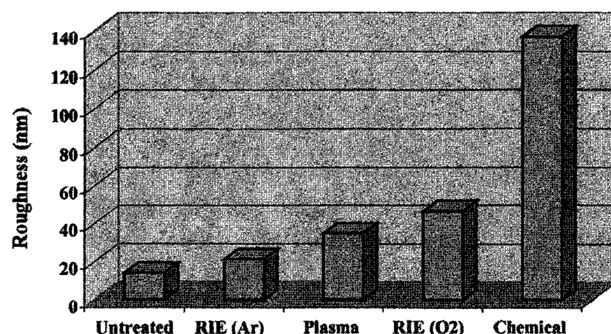

Figure 8. Roughness (RMS) of the untreated, plasma-treated, or RIE-treated (5 min) and wet-chemically treated (etching time = 20 min) LCP surfaces.

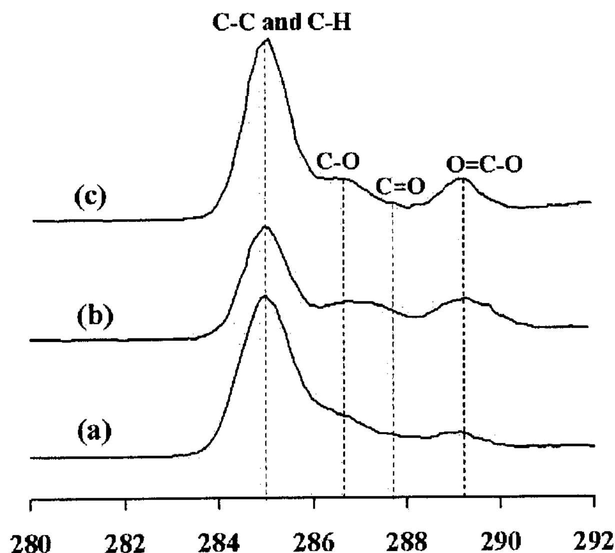

Figure 9. Comparison of the C1s XPS peak shape for the LCP surfaces: (a) untreated, (b) O_2-plasma-treated (5 min), and (c) O_2-plasma-treated (5 min) and ethanol-washed.

contact-angle measurements and surface free energy calculations. Although there was no direct correlation between wettability and adhesion, the contact-angle measurements could be used to monitor the changes of the surface. It is well known that the wettability of a polymer depends primarily on the state of the surface (e.g., chemistry, polarity, roughness, and chemical heterogeneity).[33–37]

The contact angles of water and DIM on the treated LCP surfaces as a function of the treatment time are shown in Table 2. The water contact angle on the LCP surface decreased significantly, from 54° to a plateau of 15°, after 5 min of the oxygen-plasma treatment, whereas the DIM contact angle remained almost constant. Washing with ethanol actually caused an increase in the water contact angle, but the values remained much lower than that of the untreated samples. This is because the hydrophilic fragments that were formed could be washed away ultrasonically with ethanol, and the modified surface was revealed, as detected by XPS. The usage of oxygen in the RIE resulted in a considerable reduction in the contact angles of water and DIM within 5 min of the treatment, whereas the employment of argon caused a relatively slight decrease in the contact angles. The increase in the contact angles with the prolonged treatment time indicated that the effectiveness of the treatment on wettability was lost with the continued etching. Furthermore, the geometric-mean model was used to calculate the surface free energy for the surfaces. As a result of the plasma and RIE treatments, γ_S and γ_S^p increased markedly, and γ_S^d decreased (Fig. 10). It appears that the increase in the amount of hydrophilic functional groups increased the surface free energy of the LCP surface, especially the polar force by the dipole–dipole interaction of hydrogen bonding with water. As a result, polarity of the treated surfaces increased, and this was anticipated to have a beneficial effect on adhesion. However, the competition between degradation and functionalization reactions limited further evolution of the O/C ratio and the surface free energy. The RIE-treated (Ar) LCP surface showed effective results for increasing the polar component of the surface free energy, even though the amount of oxygen-containing components on the surface was almost equal to that of the untreated surface. This can be explained by the fact that a probe liquid could be drawn into the irregularities on the surface; therefore, if changes of oxygen functional groups were present in these regions, those could be detected by the

Table 2. Contact Angles of Water and DIM on the Treated Surface as a Function of the Treatment Time

		Contact Angle (°)			
Treatments	Time (min)	H_2O	SD[a]	DIM	SD
Untreated	—	54	2.5	46.1	2.2
Wet chemical	5	61.2	3.4	43.9	1.8
	10	71.6	4.4	46.5	2.9
	15	69.5	4.1	45.4	3.6
	20	68.5	3	35.9	2.8
Plasma					
Unwashed	5	15.0	1.7	48.3	1.9
	10	12.0	2.8	43.2	1.2
	15	14.5	3	46	1.9
	20	12.5	2.9	42.5	2.5
	25	13	1.4	44.6	3.8
Washed	5	29.4	1.5	32.2	2
	10	36.7	2.8	43.2	4.3
	15	41.2	2.3	35.4	1.9
	20	40.6	1.1	37.4	1.7
	25	44.8	3.5	32.4	2.6
RIE with Ar	5	47.0	2.2	37.8	1.6
	10	52.5	3.5	42.8	1.6
	15	47.3	2.3	39.2	1.2
RIE with O_2	5	13.3	1.7	9	1.0
	10	48.5	2.9	36.3	2.3
	15	46.3	2.2	37.4	1.5

[a] SD = standard deviation.

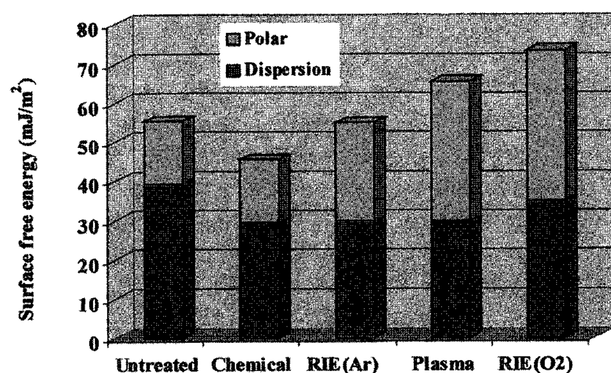

Figure 10. Components of γ_S for the untreated and treated LCP.

contact-angle measurement. However, the depth of the XPS analysis was largely controlled by the takeoff angle, regardless of the surface morphology.

Adhesion

Sputter deposition is a result of the more energetic nature of the deposition method with respect to electroless plating. The untreated LCP surface exhibited several oxygen-containing functionalities on the surface. Sputter-deposited copper exhibited relatively good adhesion (5.1 MPa) to the LCP without surface pretreatment. It was expected that the deposited copper atoms with higher kinetic energy would enable a reaction with the functional groups on the LCP surface. The pull-strength values for sputter-deposited copper as a function of the treatment time are shown in Figure 11. The pull strengths of copper sputter-deposited to the plasma- or RIE-treated LCP increased and reached the maximum value of 7.2 MPa after a 5-min treatment. The adhesion could not be further increased with a prolonged treatment. Moreover, a decrease in the adhesion followed if the plasma treatment was continued for a long period of time (see Fig. 11); this was anticipated to be a result of deteriorated mechanical properties of the LCP. A comparison of the pull strengths of copper deposited to the variously treated LCPs is plotted in Figure 12. The similarity of the pull-strength values was observed as a result of the pretreatments.

We examined the fracture surfaces of the adhesion test specimens with SEM to identify the failure modes and to provide a qualitative assessment of the adhesion of copper to the polymer. The locus of failure was markedly different for the high and low pull strengths (Table 3). Chemically deposited copper delaminated from the untreated or plasma- or RIE-treated surfaces. Sputter-deposited copper was also easily detached from the chemically treated surface. This indicated that the failure occurred as a complete adhesive fracture along the polymer/copper interface [Fig. 13(a)]. An SEM investigation showed thin polymer pieces attached to the back side of the copper pad after the pull test. Such a failure mode was found only in the chemically treated LCP/electroless copper system with a short etching time [Fig. 13(b)]. In this case, which showed adhesive/cohesive mixed failure, the pull strength decreased with the increase in the interfacially failed area. For all the other cases, the fractured LCP side of the test pad showed a fibrillar-like morphology. In the copper side of the fracture surface, severe ductile deformation of the LCP could clearly be noticed [Fig. 13(c,d)]. This indicated that the failure was mainly cohesive within the LCP. The initiation of the failure involved tensile failure of the fibrils and shear failure between the fibrils. The mechanical strength of the LCP matrix played a dominant role, as there appeared a certain upper limit after which the film ultimately broke. In some cases, fracture occurred at the WBL/bulk interface. This was due to the excessive treatment of the polymer, which resulted in a WBL that did not allow strong adherence to the bulk material.

Influence of the Treatments on the Adhesion

It is known that the adhesion of a deposited metal such as copper to a substrate depends on both the

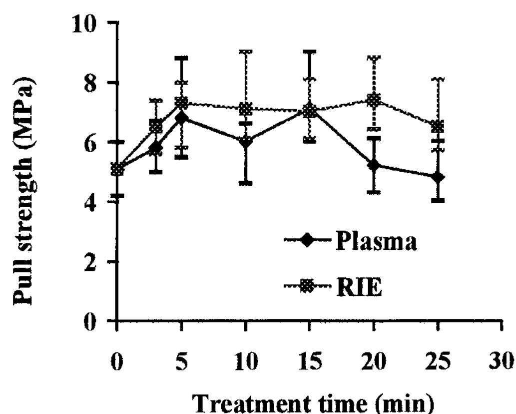

Figure 11. Pull strength of sputter-deposited copper to the LCP as a function of time in the plasma and RIE treatments.

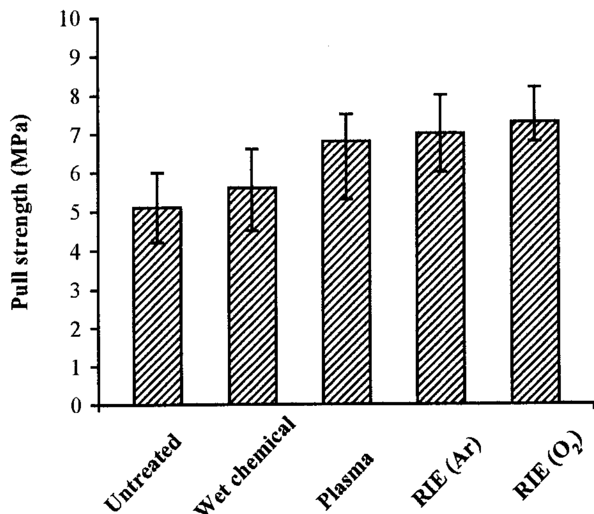

Figure 12. Comparison of the pull strengths of deposited copper to the untreated, wet-chemically treated (the metalization is electrolessly deposited copper; etching time = 20 min), plasma-treated, and RIE-treated (O_2 or Ar, 5 min) polymer.

mechanical and chemical interaction at the interface. In general, oxygen-containing functional groups, for example, are relatively reactive in a complex formation. The presence of these complexes has been reported to correlate with the enhancement of interfacial adhesion.[38–43] However, surface roughening is also important in adhesion improvement because it increases the contact area for chemical interactions and allows mechanical interlocking in some cases. For the plasma- and RIE-treated LCPs, the strong increase in the polar component of the surface free energy and the pull strength were well correlated. The increase of the polar part of the surface free energy, caused by the treatments, was explained by the generation of polar functional groups on the topmost layer of the polymer. However, as the roughness also increased, the adhesion improvement was attributed to a synergistic effect of chemical interactions and mechanical retention. Very poor adhesion was achieved if the electroless copper deposition was conducted on the plasma- or RIE-treated surfaces. However, the adhesion of sputter-deposited copper to the treated surfaces was noticeable improved. It was expected that copper atoms, brought into contact with a substrate with a higher kinetic energy, would enable a reaction with the functional groups arising from the LCP surface. In addition, For sputter-deposition, sufficient adhesion was achieved even if the LCP surface was not treated; this was expected to result from the initial chemical attractiveness of the surface (i.e., the LCP backbone was rich in functional groups). As stated previously, good adhesion between the LCP substrate and electrolessly deposited copper was achieved only in the case of wet-chemical surface roughening as a result of the creation of a sufficient number of sites for mechanical interlocking.

CONCLUSIONS

The influence of the different surface pretreatments on the adhesion of copper to the LCP was investigated. The wet-chemical, plasma, and RIE treatments were used to modify the LCP surface for electroless and sputter-deposited copper. The good adhesion in the epoxy/sputter-deposited copper systems was achieved as a result of the plasma or RIE pretreatments and was comparable to the adhesion between the LCP and laminated copper. Both the plasma and RIE treatments increased the surface roughness and polarity of the LCP. The increase in the polar component of the surface free energy of the LCP and the improved pull-strength values correlated well. AFM revealed that increased roughness due to micropits resulted in an increase in the surface contact area and, therefore, provided a more favorable surface state for various physical and chemical interactions between the LCP and copper. Consequently, the improved adhesion was attributed to both chemical and physical effects. Very poor adhesion was obtained if the electroless copper deposition was conducted on the plasma- or RIE-treated surfaces, whereas the sputter dep-

Table 3. Failure Modes for the LCP/Copper Systems

	Untreated	Wet-Chemically Treated	Plasma-Treated O_2	RIE-Treated O_2 or Ar
Electroless deposition	Adhesive	Mixed or cohesive	Adhesive	Adhesive
Sputter deposition	Cohesive	Adhesive	Cohesive	Cohesive

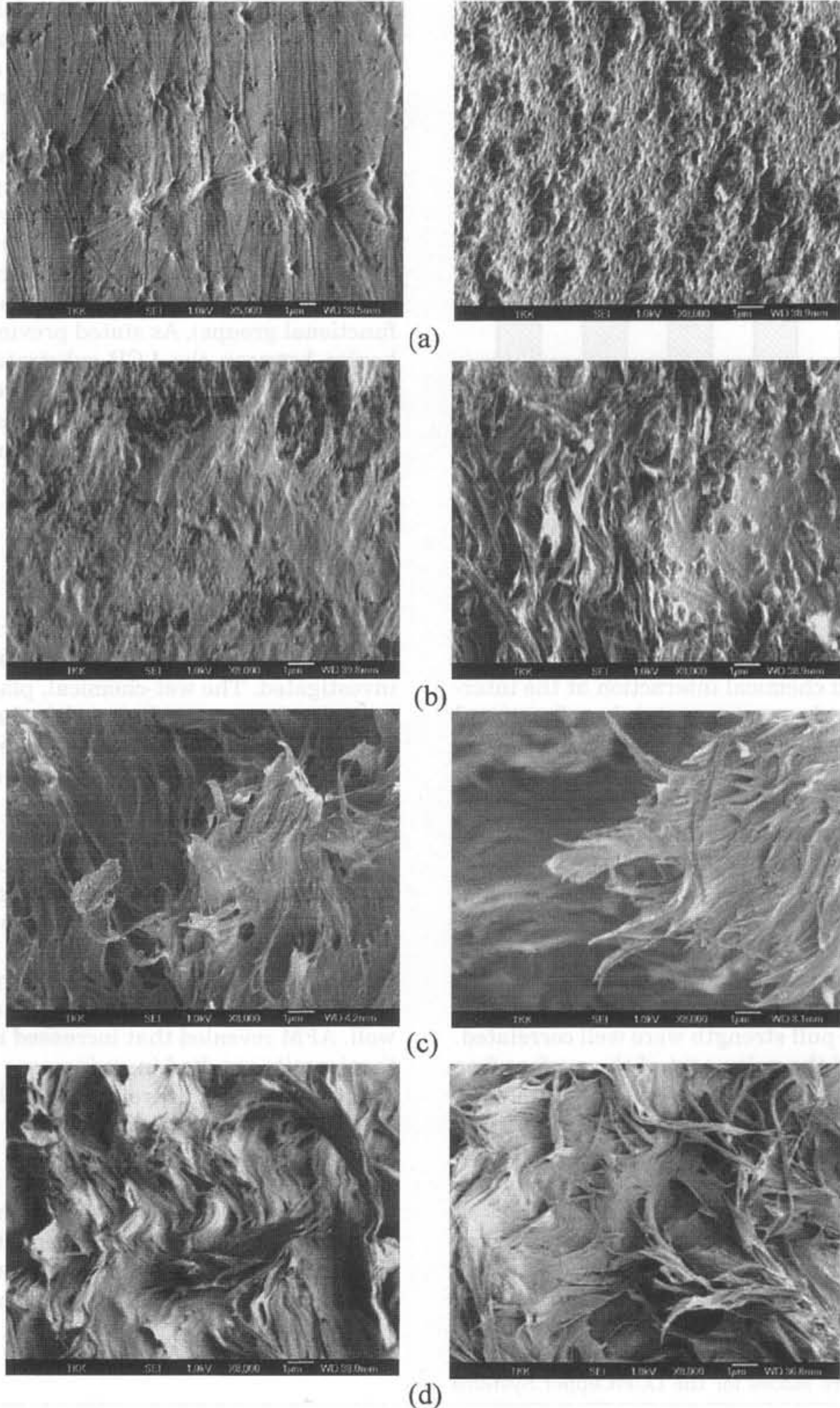

Figure 13. SEM micrographs of the LCP and copper surfaces pulled off from the LCP/copper systems: (a) plasma-treated epoxy/electroless copper system (treatment time = 15 min), (b) chemically treated epoxy/electroless copper system (etching time = 5 min), (c) chemically treated epoxy/electroless copper system (etching time = 15 min), and (d) RIE-treated (Ar) epoxy/sputter-deposited copper system (treatment time = 5 min).

osition led to strong adhesion even without the pretreatments. Good adhesion of electroless copper to the LCP substrate was achieved only with the wet-chemical treatment. The densely appearing microcavities and considerable loss of oxygen on the surface supported the mechanical interlocking mechanism.

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