



## Surface modification and characterization of photodefinable epoxy/copper systems

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### Abstract

The effects of the wet-chemical and plasma treatments on the adhesion of electroless and sputter-deposited copper to the photodefinable epoxy have been investigated. The wet-chemical treatment increased the amounts of oxygen-containing functionalities on the epoxy surface mainly during the early stage of etching. With the longer etching the pronounced surface roughness was revealed in the form of microcavities. The plasma treatment increased significantly the polar component of surface free energy of the epoxy and produced low surface roughness. The physicochemical changes of the epoxy combined with the experimental adhesion results indicated that in the case of the electroless deposition the mechanical interlocking was the main adhesion mechanism. Sputter-deposited copper exhibited the highest pull strengths on the epoxy when the plasma pretreatment with oxygen was employed. The enhancement of the surface polarity of the epoxy and the enlarged surface contact area due to the increased roughness were the most important factors in the adhesion.

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### 1. Introduction

Even though novel packaging solutions and high-density microvia boards have been developed recently, rapidly increasing performance and functionality requirements of wireless devices, in particular, demand the development and implementation of disruptive materials and manufacturing solutions [1–3]. One such solution is to integrate silicon chips and passive components inside high-density build-up substrates [4]. This can be carried out either with the fully additive or semi-additive techniques utilizing photodefinable polymers and metal deposition processes [5,6]. It is emphasized, however, that the great technical advantages provided by these highly integrated build-up modules depend primarily on good adhesion between the thin sequential layers of polymers and metals.

The adhesion of metals to polymers is usually weak because of the surface inertness of polymers. Numerous methods have been developed to modify polymer sur-

faces, such as the wet chemical, plasma, corona, UV/ozone and laser treatments [7–17]. Due to simplicity and low cost, the wet chemical treatment followed by Sn/Pd activation and electroless metal deposition is one of the most frequently used industrial processes for the metallization of printed circuit boards. The main contribution to the adhesion of electroless copper to the polymer in the case of wet processing is provided by the mechanical anchoring of copper into the fine cavities of the roughened polymer surface [18]. However, applications like high-frequency broadband wireless communication suffer from rough interfaces [1,19,20]. Accordingly, sufficient adhesion of metals to smooth polymer surfaces has to be achieved. The alternative metallization method is the dry process, which includes e.g. plasma or reactive ion etching pretreatment prior to sputter deposition of copper onto the activated surface. This technique has the advantage of being able to achieve sufficient adhesion to smooth surfaces [21–24].

In the present work, the effects of chemical and plasma treatments on the adhesion of copper to the photodefinable epoxy (PDE) will be investigated. The failure modes will be examined by means of the optical

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microscopy, scanning electron microscopy (SEM), and energy-dispersive spectroscopy. The polymer surfaces are characterized by the X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), and with contact angle measurements. The results are correlated with the measured pull strength values to gain better understanding of the adhesion mechanisms.

## 2. Experimental

### 2.1. Materials and methods

The E-glass reinforced epoxy (FR4 from NELCO) was used as the base substrate. The PDE solution (Multiposit XP 98752 from Shipley) was spin-coated on to the base substrate to a thickness of approximately 10  $\mu\text{m}$ . The polymer is a heterogeneous novolac type epoxy photoresist that contains, e.g. flexibiliser and silica filler additives. During the photolithographic processing, the crosslinking occurs through a cationic ring-opening mechanism of epoxy and the flexibiliser (i.e. low molecular weight oligomer) crosslinks into the final matrix through epoxy functional groups [25]. As a result, the polymer acts as a photodefinable negative resist material. After spin-coating, the board was soft-baked at 90 °C for 30 min, ultraviolet (UV)-exposed (13.3  $\text{mW}/\text{cm}^2$ ), hard-baked and finally cured at 130 °C for 2 h.

Two methods of surface treatment were employed. The first one is the wet chemical treatment, which consists of three water-based steps: swelling (1 min); etching (1–7 min), and reduction (2 min). The wet chemical treatment of surfaces was then followed by the Sn/Pd activation and electroless copper deposition. The details of the process flow are reported in the previous paper [18]. In the second treatment, a barrel type plasma reactor was used. Samples were placed in the substrate holder surrounded by a tunnel-perforated metal shield between 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 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 the washing. The treated surface was then metallized electrolessly or by sputter-deposited with copper to a thickness of 1  $\mu\text{m}$ . The electroless plating process is a wet chemical deposition process and the copper deposition is the result of redox reaction. In this process, the treated samples were immersed in the catalyst solution (Circuposit TM 3344) containing colloidal palladium–tin particles at 45 °C for 5 min to attach the colloidal palladium–tin particles on the polymer surfaces. After the activation step, the samples were rinsed with the distilled water to remove

the excess Pd/Sn particles, and immersed in the electroless plating solution (Cuprothick 84) consisting of an aqueous basic copper sulfate solution and formaldehyde at 36 °C for 15 min. Copper metal is deposited by the copper cation reduction process on the polymer surface with the plating rate of 4–5  $\mu\text{m}/\text{h}$ . In the case of sputter deposition, the samples were processed in vacuum under the following conditions: base pressure =  $1.5 \times 10^{-4}$  Pa, work pressure = 0.43 Pa, DC power = 2000 W and argon gas rate was 60 sccm. After the metallization a dry film type of photoresist (RISTON MM140 from DuPont) was laminated on to it and exposed through a photo mask. The trench structure of the resist was formed by developing. Copper was then electrolytically plated on to the electroless or sputter-deposited copper that was revealed at the bottom of the resist trenches so as to achieve a thicker copper layer. As an etching resist, a tin layer was plated onto the copper surface, and the dry film photoresist was then stripped off. Finally, the excess copper underlayer was removed with copper etching solution (Ultracide 35/35 from ALFACHIMICI) to form test pads with a diameter of 2 mm. Adhesion test pads with sufficient surrounding substrate were then cut out from the fabrication panel. Copper wire was finally micro-soldered to the test pads with a eutectic SnPb solder for attachment to the pull test equipment. The detailed flow chart of the fabrication process of the test pads has been reported previously [18,21].

### 2.2. Characterization

The tensile test machine (Table Top System 858 from MTS) was used to measure the pull strength between copper and the PDE. The specimen was fixed to the test set-up, 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 by assuming that the pad was circular. The pull strength was evaluated as the average tensile strength of the twelve specimens prepared under the same conditions. The schematic representation of the adhesion test configuration has been reported elsewhere [21].

The topographies of the treated PDE surfaces (tilted at 45°), as well as the fracture surfaces of the metallized polymer, were examined using a field emission SEM (JSM-6330F, Jeol. Ltd), operated at 1 kV.

The surface topography of the untreated and treated PDE surfaces was characterized on a Nanoscope IIIa atomic force microscope (Digital Instrument D3100 Inc.). In each case, an area of  $5 \times 5 \mu\text{m}^2$  was scanned using silicon tips in the tapping mode. The surface roughness of the samples was evaluated in terms of the arithmetic mean of the roughness ( $R_a$ ) and the root-mean-square (RMS) of the roughness.

The contact angles of water and diiodomethane on the PDE surfaces were measured by the sessile drop method with a VCA 2500XE video contact angle system (Advanced Surface Technology Inc. goniometer). For each sample, the advancing contact angle value is the average of eight measurements recorded from different locations on the sample surface with a standard deviation of 1–3°. From the measured contact angle, the surface free energy ( $\gamma_s$ ) was calculated using the geometric mean model [26,27]. The volume of the liquid drop used in the measurement was 0.1  $\mu\text{l}$ . The surface free energy ( $\gamma_s$ ) in the model is assumed to be the sum of the dispersion ( $\gamma_s^d$ ) and polar ( $\gamma_s^p$ ) components. The dispersive and polar components of the surface free energy of the different liquids ( $\gamma_L$ ) adopted herein are  $\gamma_{\text{L}} = 72.8 \text{ mJ/m}^2$ ,  $\gamma_{\text{L}}^d = 21.8 \text{ mJ/m}^2$ ,  $\gamma_{\text{L}}^p = 51.0 \text{ mJ/m}^2$  for distilled water, and  $\gamma_{\text{L}} = 50.8 \text{ mJ/m}^2$ ,  $\gamma_{\text{L}}^d = 49.5 \text{ mJ/m}^2$ ,  $\gamma_{\text{L}}^p = 1.3 \text{ mJ/m}^2$  for diiodomethane [27,28].

The X-ray photoelectron spectra of both untreated and treated PDE surfaces were recorded using an AXIS 165 X-ray photoelectron spectroscope (KRATOS Analytical). The monochromatic Al K $\alpha$  X-ray source was operated at an anode voltage of 12.5 kV and 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 being employed. The core level spectra were obtained with a pass energy of 20 eV and a step size of 0.1 eV being employed. A photoelectron take-off angle of 90° was used for all the analyses. All XPS peaks were referenced to a C 1s signal at a binding energy of 285 eV, representing the C–C and C–H bonds in hydrocarbons.

### 3. Results and discussion

#### 3.1. Surface characterization

##### 3.1.1. Topography—SEM and AFM

SEM micrographs of the untreated and the chemically treated epoxy surfaces are shown in Fig. 1. The untreated surface exhibited a smooth topography and its RMS roughness value was 4 nm. The roughness increases as the etching time increases and almost levels off after 3 min of etching (Fig. 2). The surface is adequately roughened and a sufficient number of microscopic root-like cavities are observed after 3 min of etching with a corresponding roughness (RMS) of 180 nm (Fig. 1c and Fig. 2). When the etching time increases to 7 min, the bulk structure of the epoxy is destroyed and adhesion improvement lost (see Fig. 1e for topographical information).

In the barrel plasma etching configuration, a perforated metal tunnel was added to shield the grounded samples from ion bombardment. Therefore, the etching is primarily due to the chemical reaction between the etchant gas (oxygen) and the samples rather than the

physical sputtering of the samples. The chemical etching by the reactive neutral oxygen species (i.e. atomic, molecular and free radicals) causes oxidation and subsequent chain scission of outmost macromolecules [29–31]. The AFM image of the plasma-treated surface is presented in Fig. 3. The change in the topography as a result of the plasma treatment was noticed as the formation of pits on the polymer surface. The pits were observed to grow in height with increasing treatment time, accompanied by the occurrence of small protrusions. These loosely bounded protrusions were formed from low-molecular-weight oxidized products that could be washed away with ethanol by means of an additional ultrasonic agitation. This can be seen by comparing the AFM micrographs of oxygen plasma-treated polymer surfaces before and after washing with solvent (Fig. 3b and c). The corresponding RMS roughness, however, increased slightly, from 7 to 10 nm, as a result of the washing.

##### 3.1.2. Chemistry—XPS

XPS analyses were performed to investigate the state of chemical bonding and the compositional changes of the modified polymer surface. The C 1s spectrum for untreated polymer was peak-fitted to the four components, assigned to the C–C (285 eV), C–O (286.6 eV), C=O/O–C–O (287.7 eV) and  $-(\text{C}=\text{O})-\text{O}-$  (289.4 eV) bonds [32]. The peak at 291.5 eV is the shake-up satellite due to conjugated double bonds in the polymer. The percentages of the different functionalities in the C 1s core level are shown in Fig. 4. In the case of the chemical treatment, the intensity of the C–C peak is decreased and those of oxygen-containing functional groups are increased (Fig. 4b). The O/C ratio is increased from 0.19 to 0.29 after 1 min of etching, but remains almost constant after that (Table 1). This indicates that most of the chemical changes take place within a very short etching time and that with longer etching times the main effect is increased roughness.

As shown in Fig. 4c, following the plasma treatment with oxygen, the C 1s spectrum of the surface is changed significantly. The higher binding energy carbon species increase and additionally highly oxidized species also start to appear. These changes reflect the effects of the oxidation of the sample surface during the plasma exposure. The general mechanism of the formation of functional groups on the surface during the plasma treatment can be interpreted by two steps: the atomic oxygen initiates the reactions by abstracting hydrogen atoms from a polymer chain, leaving a radical species. Thus, the reactive sites facilitate the additional uptake of oxygen species that are available in the plasma to form the oxygen functional groups on the surface. As compared to the untreated epoxy surface, the C 1s of the treated surface can be fitted by one more oxidized

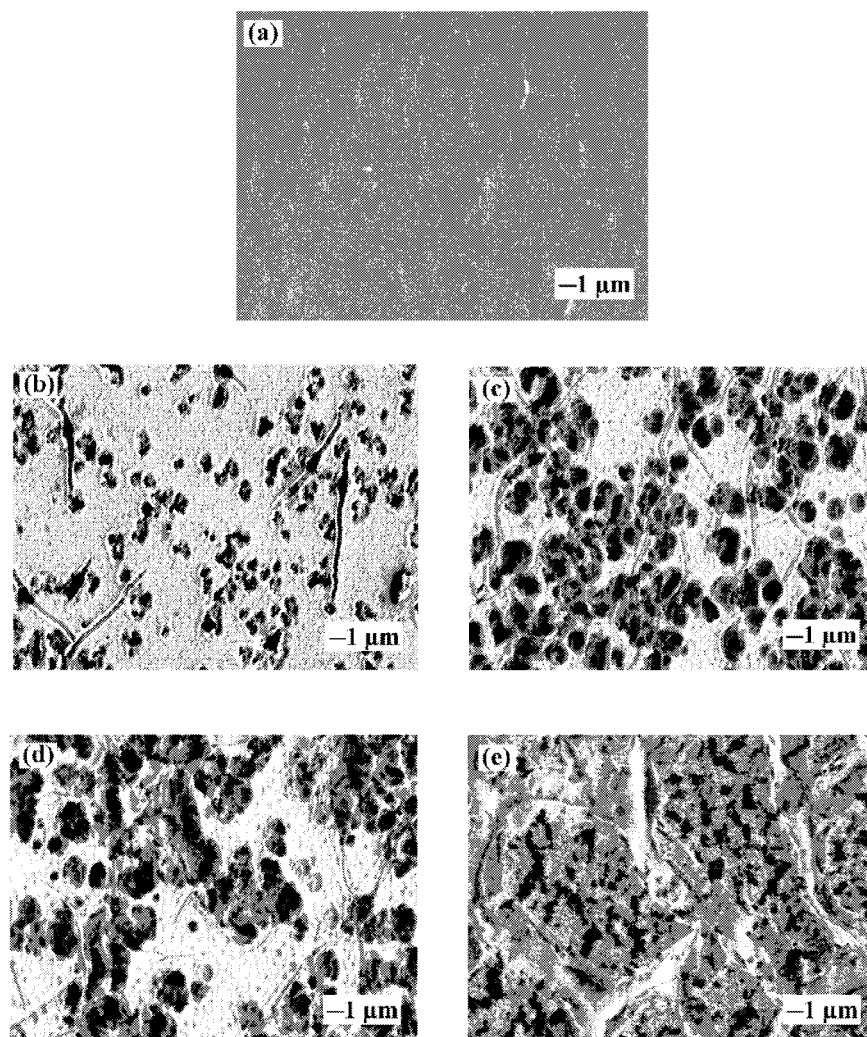


Fig. 1. Surface topography of the PDE (a) untreated, etched for (b) 1; (c) 3; (d) 5; (e) 7 min.

carbon species, i.e. carbonate  $O=COO$  at 290.4 eV. Its concentration increases significantly to 18% within 15 min of exposure to the plasma. Simultaneously, the carbon components at 287.7 and 289.4 eV also increase from 3 and 2% on the untreated surface to 14 and 9%, respectively, after the post-treatment. On the other hand, the proportion of the hydrocarbon species undergoes a large reduction associated with the observed increase in the more oxidized carbon species. The oxidation processes occurring on the polymer surface during the plasma treatment are coupled with the removal of the newly formed oxidized volatile compounds ( $CO$  and  $CO_2$ , etc.). Some of the low molecular weight oxidized

products are still loosely attached onto the surface after the plasma treatment. The high binding energy functional groups correlated with chain fragments are removed by the ethanol washing in the ultrasonic bath (Fig. 4d). As listed in Table 1, the corresponding O/C ratio increases on the surface as the treatment time increases and reaches 56% after 15 min of the treatment. However, the oxygen concentration is reduced to 27%, which is essentially identical to that of the surface treated for 5 min. It indicates that the oxidation products with a low molecular weight are removed, and only the functional groups introduced into the main chain appear in the spectrum after the ethanol washing.

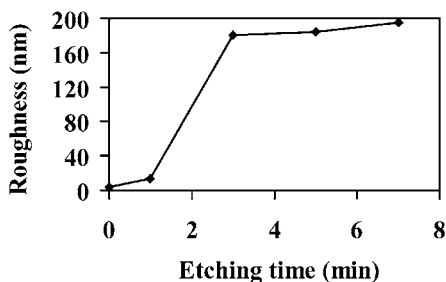


Fig. 2. Roughness (RMS) of the epoxy as a function of etching time in the chemical treatment.

### 3.1.3. Wettability

The measurement of the contact angles of the reference liquids on the surface permits the evaluation of polymer wettability development as a function of surface modification [33]. The wettability of a polymer depends primarily on the state of the surface, e.g. polarity, roughness, and chemical heterogeneity [34–37]. If the contact angle is affected by the roughness, then the measured contact angle is meaningless in terms of the Young's equation and it should not be used to evaluate the surface free energy [38–40]. On rough surfaces, the advancing contact angle is higher than that on a chemically identical but smooth surface. Such angles do not reflect the chemical modification of the surface but the morphological changes [41–43]. In this study, advancing contact angles were measured. After 1 min of the chemical treatment, the water contact angle decreases from 98 to 87°. Etching of longer than 1 min causes an increase in the water contact angle (Table 1). XPS reveals that the O/C ratio increases during the continued etching and saturates after 3 min, with dramatically increased roughness. Therefore, the chemical treatment improves wettability with a short etching time, which reflects the chemical modification of the surface. However, with the long etching time the surface is deeply etched, as is evident from the SEM and AFM examinations and the increased surface roughness of the epoxy starts to influence the wettability.

The water contact angles on the epoxy surface as a function of the plasma treatment time are plotted in Fig. 5. The contact angle on the epoxy surface decreases notably, from 98° to a plateau of 19°, after 5 min of the plasma treatment. The decrease in the contact angle is mainly attributed to the strong increase of polar component of surface free energy. However, any further increase in surface free energy resulting from the plasma treatment is limited due to the formation of the low molecular weight oxidized products on the surface. This prevents the gaseous species from reacting with it. Washing with ethanol actually caused an increase in the water contact angle from 19 to 38° after 5 min of the

plasma treatment, but the values were much lower than those of the untreated samples. The increase in the water contact angle by the washing is due to removal of the oxidized fragments from the treated epoxy surface, as detected by XPS (Fig. 4). During the sample storage (30 days under laboratory conditions), the treated sur-

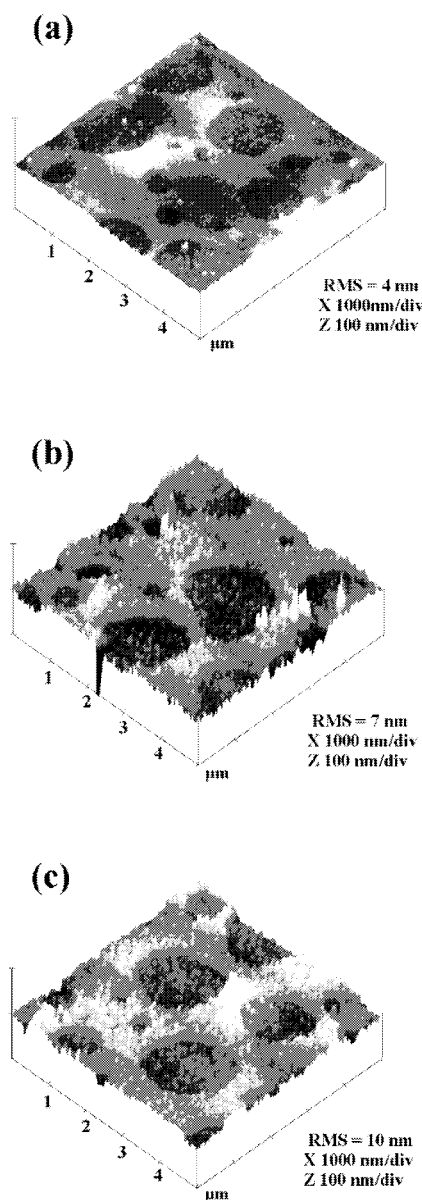


Fig. 3. AFM images of the epoxy; plasma treated with oxygen for (a) 5 min; (b) 15 min (unwashed); (c) 15 min (washed with ethanol).

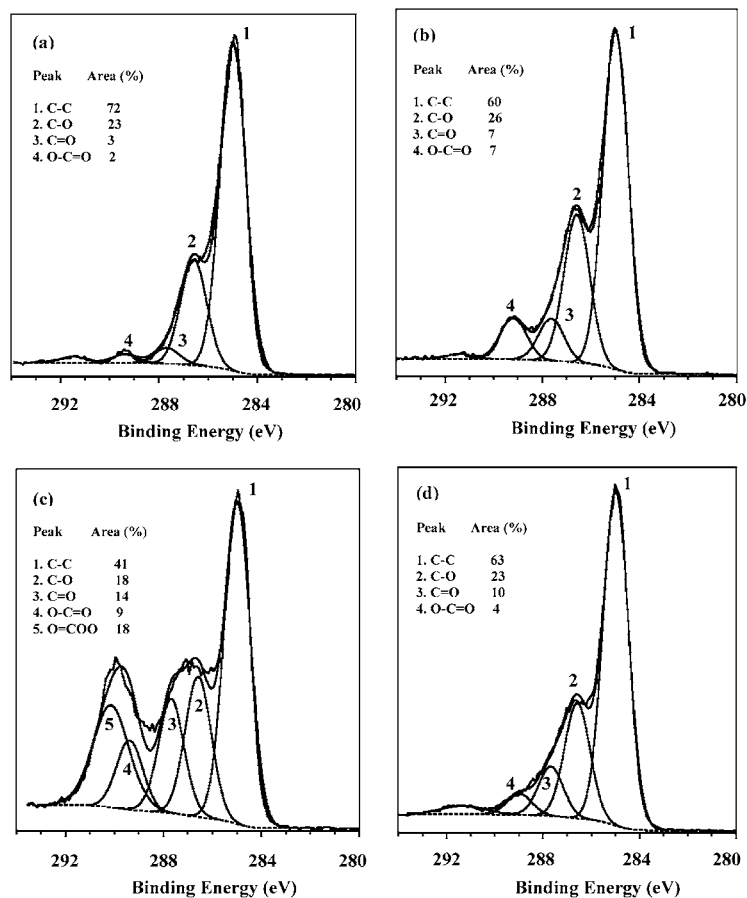


Fig. 4. XPS (C 1s) spectra of the epoxy (a) untreated; (b) chemically treated (etching time 1 min); (c) O<sub>2</sub> plasma treated (15 min); (d) O<sub>2</sub> plasma treated (15 min) followed by ethanol washing.

face underwent surface reorganization, which resulted in the absence of some polar groups from the surface [44]. This is expected—on the basis of the second law of thermodynamics—as the surface free energy strives to minimum. As a result, a gradual increase in the water contact angle was observed. However, the water contact angle of the stored samples is 48° for the 5 min treated sample obtained for post-treatment storage, still 50° lower than that of the untreated polymer. This means that the surface hydrophilicity produced during the modification does not vanish after long-term exposure (30 days) to air.

### 3.2. Adhesion results

#### 3.2.1. Wet-chemical pretreatment

The samples treated by the chemical treatment were metallized chemically using the aqueous solution after

the Pd/Sn ‘seeding’ or sputter-deposited copper in the vacuum system. The effects of the deposition methods on the adhesion of copper to the chemically treated epoxy are compared in Fig. 6. The comparison shows the opposite adhesion behavior between the metallization methods. The details are discussed in the following paragraphs.

**3.2.1.1. Electroless deposition.** In the electroless plating process, reduction reaction of copper ions to copper metal with formaldehyde occurs with the assistance of palladium–tin catalyst that is attached on the polymer surface. Hence, copper metal layer is chemically deposited on the surface as a result of the redox reaction. The adhesion of electroless copper to the epoxy without any surface pretreatment is very poor. Within 1 min of the etching, the adhesion is not increased significantly by the increase of concentration of oxygen-containing func-

Table 1

Water contact angle, O/C atomic ratio on the surface, evaluated surface free energy ( $\gamma_s$ ) of the PDE and the failure modes of the epoxy/copper systems

Treatments	Treatment time (min)	WCA (°)	O/C ratio	$\gamma_s^p$ (mJ/m <sup>2</sup> )	$\gamma_s$ (mJ/m <sup>2</sup> )	Failure mode
Untreated		97.6	0.19	0.4	34.1	Adhesive <sup>a</sup> Cohesive <sup>b</sup>
Chemical treatment	1	87.3	0.29	1.4	41.7	Mixed (Adhesive/Cohesive) <sup>a</sup> Cohesive <sup>b</sup>
	3	93.6	0.27	n.d. <sup>c</sup>	n.d. <sup>c</sup>	Cohesive
Plasma treatment	5 (washed)	38.3	0.26	26.8	62.7	Adhesive <sup>a</sup> Cohesive <sup>b</sup>
	15 (washed)	38.2	0.27	25.9	63.6	Adhesive <sup>a</sup> Cohesive <sup>b</sup>
	15 (unwashed)	18.8	0.56	37.8	71.1	Adhesive <sup>a</sup> Cohesive <sup>b</sup>

<sup>a</sup> Metallization is electroless copper.

<sup>b</sup> Metallization is sputter-deposited copper.

<sup>c</sup> The surface free energy in this case is not evaluated because the very rough surface is expected to cause error in the measured contact angles.

tionalities on the surface. The adhesion increases with the continued etching of the epoxy up to 5 min due to the creation of mechanical anchor sites in sufficient amounts on the epoxy surface. After this, there is a remarkable decrease in adhesion. The microcavities are the result of the more rapid etching of the easily attacked components, e.g. filler and flexibilizers, as compared to the epoxy. It is found that the pull strength depends on the level of microroughness of the epoxy surface (Fig. 6). However, the pull strength decreases as the etching time reaches 7 min, although the roughness of the samples still continues to increase slightly. It is noticed that the bulk structure is severely damaged as the etching time increases to 7 min. The excessive treatment causes a weak boundary layer that is a result of deterioration of mechanical properties of the epoxy and thus leads to the poor adhesion.

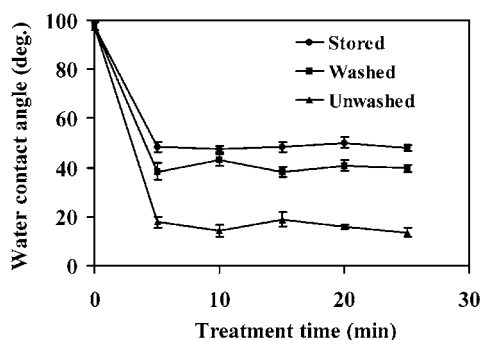


Fig. 5. The water contact angle on the plasma treated surface as a function of the treatment time.

**3.2.1.2. Sputter deposition.** Sputter deposition is, in fact, a result of more energetic nature of deposition method as compared to the electroless plating. In other words, copper atoms are brought into contact with the substrate with high kinetic energy that enables reaction with the functional groups arising from the polymer surface. In the untreated epoxy there are functional groups, such as carbonyls. Therefore, the sputter-deposited copper achieves a relatively high adhesion in this case without any surface pretreatment, i.e. pull strength of 5.6 MPa was obtained. The adhesion of sputter-deposited copper to the chemically etched (1 min) epoxy surface increased to 8.3 MPa without significantly roughening the epoxy surface (Fig. 6). This can be explained by the increase in the relative amounts of the oxygen-containing groups (Fig. 4). During the metallization, the energetic copper atoms can react with the oxygen functional groups to form complex, which improve the

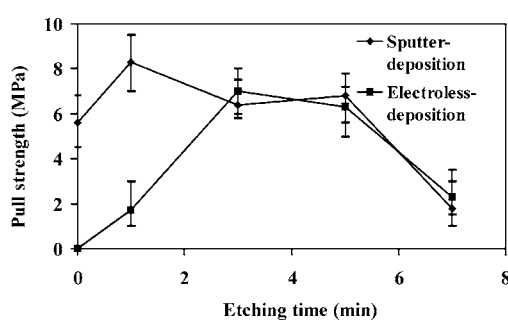


Fig. 6. The pull strengths of the epoxy with electroless and sputter-deposited copper as a function of etching time in the chemical treatment.

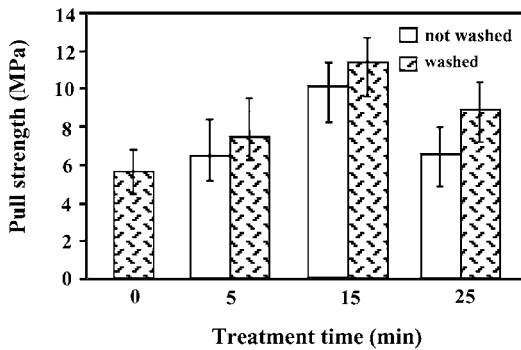


Fig. 7. Comparison of the pull strength of the untreated and plasma treated epoxy (unwashed and washed) with sputter-deposited copper as a function of treatment time.

adhesion. However, the adhesion begins to decrease after 1 min of etching time, even though the O/C ratio is almost constant. The relatively rough surface that is found in this case has a very high specific surface area. However, the sputter-deposited copper cannot completely fill the irregularities of the surface. Due to the presence of voids, the stress concentration occurs and thereby reduces adhesion. To support the hypothesis, it is found that the adhesion strength begins to reduce as the roughness increases, although the chemical composition of the surfaces remains almost identical.

The action of the chemical treatment on the epoxy is twofold. It modifies the surface chemistry and gradually produces the pronounced roughness. The electrolessly deposited copper adheres well to the epoxy only if the surface is roughened sufficiently, which emphasizes the role of the mechanical interlocking. However, sputter-deposited copper exhibits the best adhesion to a relatively smooth but oxygen-rich epoxy surface. The role of the chemical state of bonding at the surface is very important in this case rather than the surface roughness due to the fact that the adhesion starts to decrease as the roughness increases.

### 3.2.2. Plasma pretreatment

First, it is to be noted that electroless copper gives very poor adhesion to the polymer treated by the plasma treatment. Therefore, the adhesion improvement with the help of plasma treatment followed by the sputter deposition of copper metallization is emphasized in this study. The pull strengths of sputter-deposited copper to the plasma-treated epoxy are shown in Fig. 7. The adhesion of the sputter-deposited copper to the polymer surface is considerably improved by the plasma treatment and reaches 11.5 MPa at 15 min of the treatment. However, when the treatment time is increased further, the adhesion decreases. The reduced adhesion can be

attributed to the formation of a weak boundary layer as a result of excessive treatment [45,46]. It is generally known that complexes are formed between metal film and oxygen-containing functional groups on polymers, and the presence of these complexes correlates with the increase in adhesion [47–51]. On the other hand, surface roughening is also important in enhancing adhesion due to the increase of the contact area. Despite the fact that the chemistry of the plasma-treated surface for 15 min is almost identical to that with 5 min (Table 1), the adhesion is clearly stronger for former because of the increased roughness. Therefore, the significantly improved adhesion is attributed to the increase in the number of polar groups on the surface, together with a favourable surface topography as revealed by the AFM and XPS examinations. The total surface free energy of the system increased significantly especially its polar component (Table 1). Strong correlation was found between the polar component of the epoxy surface free energy and the adhesion. The characterization and adhesion testing results show that the plasma treatment, while creating a more hydrophilic surface, also causes chain scission. This results in low molecular weight oxidized products and, thus, the formation of a weak boundary layer. The adhesion is further increased after washing with ethanol. This enhancement in adhesion is attributed to the removal of the poorly adherent low molecular weight fragments and elimination of the weak point from the epoxy/copper interface [52]. XPS examinations revealed the incorporation of the highly oxidized components providing the evidence that these high binding energy functional groups are associated with chain fragments and are removed by the ethanol washing. It should be emphasized that the adhesion depends not only on the pretreatments but also the copper deposition techniques. Highest pull strength of electroless copper to the epoxy was obtained only by the chemical treatment due to the creation of the sufficient mechanical interlocking sites on the polymer surface. The plasma treatment with oxygen is very effective in increasing the polar component of surface free energy and yields the best adhesion results for the sputter-deposited copper on the studied epoxy.

### 3.3. Fracture surfaces

The fracture surfaces of the specimens were examined with SEM to identify the failure modes and to provide a qualitative assessment of the adhesion of copper to the epoxy. It is observed that the locus of failure is different markedly in the high and low pull strength cases. Electroless copper is found to delaminate from the untreated or plasma treated epoxy surfaces, which indicated a complete adhesive failure along the copper/epoxy interface. For the specimen, which showed adhesive/cohesive mixed failure, the pull strength decreased



with the increase of interfacially failed area (Table 1). In most cases, the failure is cohesive. As the adhesion increases, the locus of the failure shifts from the interface to the bulk polymer and even further to the FR4 substrate. In fact, sometimes the failure also occurs partially inside the substrate, since the glass fibres of the FR4 can be observed on the fracture surface. This suggests that the adhesion strength at the epoxy/Cu interface is much stronger than at the failed site. In some cases, fracture occurs at the WBL/bulk interface. This is because the excessive treatment of the polymer results in a weak boundary layer at the surface that does not strongly adhere to the bulk.

#### 4. Conclusion

The effects of the wet-chemical and plasma treatments on the adhesion of electroless and sputter-deposited copper to the PDE have been investigated. The wet-chemical treatment produced large numbers of micro-cavities to anchor the deposited electroless copper. The dependence of the adhesion on the surface roughness in the epoxy/electroless copper systems revealed the dominant role of the mechanical interlocking. However, such level of the surface roughness which is needed for electroless copper had no beneficial effects on the adhesion in the chemically treated epoxy/sputter-deposited copper system. The plasma treatment was very effective in improving the wettability of the epoxy by increasing the surface polarity. It led to considerably better adhesion of sputter-deposited copper to the epoxy than the chemical treatment. Good correlation between the polar component of surface free energies and the measured pull strength values confirmed the importance of the oxygen-containing polar groups on the adhesion. Likewise, the removal of the low molecular weight fragments from the epoxy surface induced by the plasma treatment contributed to the adhesion. The adhesion of sputter-deposited copper to the plasma treated epoxy was also observed to be further increased with the increased surface roughness. The improved adhesion that can be achieved between the polymer and copper build-up layers is of great importance for the reliability of high density electronic assemblies.

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