Adhesion Enhancement Between Electroless Copper and Epoxy-based Dielectrics

Harley Hayden, Ed Elce, Sue Ann Bidstrup Allen, and Paul A. Kohl

Abstract—The adhesion between electrolessly deposited copper and an epoxy-containing dielectric material has been investigated. In particular, the role of mechanical anchoring and chemical bonding in these systems has been examined. The contribution of each of these mechanisms to adhesion has been identified. Probelec, a phenolic-novolac epoxy polymer, and Avatrel, an addition polymerized norbornene polymer with an epoxy side-group, have been tested in this study. Traditional swell and etch treatments have been used to enhance mechanical anchoring through pore-type roughness development on the phenol-novolac epoxy, but were found to be ineffective in roughening the Avatrel surface. The critical difference between the two polymers is the epoxy-backbone (for the phenolic epoxy) versus the epoxy side-group (for the norbornene backbone polymer). In order to create roughness on the Avatrel surface, a novel technique utilizing a blend of Avatrel and Probelec was investigated. This technique created pore-type roughness and enhanced mechanical anchoring on the Avatrel surface. NTI\textsubscript{3} plasma treatments were utilized to enhance the chemical bonding contribution to adhesion and produce surfaces with peel strengths of 0.15–0.25 N/mm with minimal roughness generation. Finally, a combined wet-chemical and plasma treatment protocol was investigated to enhance chemical bonding and mechanical anchoring on the same surface. Samples with adhesion greater than 0.5 N/mm with roughness less than 50 nm were produced with both Avatrel and Probelec. Through the use of a combined wet-chemical and plasma-surface treatment the polymer surface has been optimized for adhesion while minimizing roughness.

Index Terms—Adhesion, dielectric materials, electroless copper, plasma processing.

I. INTRODUCTION

NEW technologies and processes are being developed to meet the demand for high density interconnects for integrated circuits (ICs). At the board and package level, sequential buildup structures (SBUs) and microvias have been integrated into the manufacture of printed circuit boards (PCBs) as one means of achieving high density interconnections. These features are typically formed on a PCB with alternating dielectric and copper layers. A key to the performance and reliability of these SBUs is the adhesion between the deposited copper and the dielectric materials. Surface roughness causes scattering of electrons at high frequency; however, roughness improves the mechanical anchoring of the metal film. As the feature density and off-chip frequency increase, the average feature size shrinks, and the interface between the metal and dielectric materials must become smoother to avoid feature dislocation and surface scattering. Future dielectric materials must also have improved electrical properties, in particular permittivity and loss, in order to enable the smaller features and higher frequency performance.

Achieving a smooth metal-dielectric interface is especially challenging because the metal-to-dielectric adhesion is achieved through a combination of chemical bonding and mechanical anchoring [1]–[3]. Enhancing adhesion while minimizing roughness requires advances in chemical bonding and reduced dependence on mechanical anchoring. In order to achieve this, it is important to identify the individual contributions of each mechanism to adhesion. In the case of traditional phenolic epoxy materials and electroless copper metallization, it has been shown that physical anchoring accounts for the majority of adhesion [4], [5]. Improving adhesion with these materials is typically achieved through physical modification of the dielectric surface.

This physical modification occurs through a multistep swell and etch process that generates root mean squared roughness up to 500 nm with peel strengths as large as 1.5 N/mm [6]. The development of pore-type roughness on the surface of a traditional epoxy has been well documented in the literature. Siau et al. has postulated a mechanism for pore development in which the swelling agent rearranges polar groups in the polymer into packets and the etch solution then preferentially attacks these packets forming pores [7], [8]. The schematic in Fig. 1 shows the proposed etch mechanism for the epoxy system. The site of attack for the etch solution is the ether linkage formed by the opening of the epoxide ring during the curing process. In traditional epoxy materials, this ether linkage is located in the polymer backbone, allowing the etch reaction to remove a small segment of the polymer chain and expose the next linkage for subsequent etch attack. In this manner, the etching process works down the polymer chain, eventually removing the entire chain and beginning the process of forming pores on the surface. This swell and etch process on epoxy materials typically creates a surface with pore-type roughness, where the pores can be micrometers in diameter and depth [3]. It is these large pores, with feature sizes in the range of the skin depth of copper at high frequencies, which cause electron scattering and signal distortion. This effect is increasingly important because the off-chip frequency is projected to increase by 25% per year for the next decade reaching 41 GHz by 2017. This corresponds to a decrease in copper skin depth from 1000 nm in 2007 to 315 nm...
Minimizing the need for large pores is a key to achieving high performance substrates using current materials. One method for reducing the need for large pores and the mechanical anchoring they provide is to increase chemical bonding, which has the ability to enhance adhesion without creating roughness on the surface [1], [10]–[12]. In order to enhance chemical bonding between a dielectric material and electroless copper, the concentration of active chemical groups on the surface of the polymer must be increased. Wet-chemical treatments such as graft polymerization, coupling agents, and surface synthesis techniques have been studied by numerous researchers as means of increasing the content of certain active groups on the surface [2], [13]–[16]. Plasma treatments have also been utilized with a variety of materials to activate surfaces [17]–[21]. A common link in many of these studies is the role of nitrogen containing functionalities on the surface. These have been shown to enhance catalyst adsorption on polymer materials and to enhance adhesion by as much as 0.5 N/mm in some systems [17], [19]. Although the exact interaction mechanism between electroless copper and these nitrogen groups is unclear, it appears that both nitrogen–palladium and nitrogen–copper complexes are formed on the surfaces, aiding adhesion [14], [22], [23]. Previous work with polyimides has shown that 5-min 80-W NH₃ plasma treatments are effective for enabling catalyst adsorption and enhancing adhesion through nitrogen incorporation [17]. In this study, similar NH₃ plasma treatment conditions have been utilized on polymer surfaces in an attempt to increase nitrogen concentrations and enhance chemical bonding.

The goal of this work is to utilize both chemical and mechanical bonding in order to enhance adhesion while minimizing the necessary surface roughness of the dielectric material. Two material sets have been studied in this investigation, Probelec 81/7081 (Huntsman), a traditional phenol-novolac epoxy, and Avatrel 2190P (Promerus LLC) an addition polynorbornene-based epoxy. The chemical structure for each of these materials is given in Fig. 2. Probelec contains epoxy groups in the backbone of the polymer, while Avatrel is an advanced epoxy material that has a polynorbornene backbone with epoxy side-groups used for crosslinking. Although the goal of strong adhesion with smooth surfaces for these two materials is the same, the approach and challenges are quite different. With Probelec, a rough, highly adherent interface is readily available through traditional surface treatments. The challenge here is to understand why the material behaves differently during the swell and etch process and to identify suitable processing methods for enhancing contributions of mechanical anchoring and chemical bonding to adhesion.
II. EXPERIMENTAL

Probelec 81/7081 from Huntsman International LLC was spin coated onto a FR-4 substrate board at a spin speed of 1500 rpm to yield a 15-μm-thick film. The Probelec film was soft-baked at 100 °C in a box oven under ambient air for 30 min, exposed to a dose of 1400 mJ/cm² from a 365-nm light source (Spectra-Physics model 92521), hard-baked at 100 °C for 60 min, and cured at 145 °C under ambient air for 55 min. Avatrel 2190 P from Promerus was spin coated onto a silicon wafer at a spin speed of 1500 rpm to yield a 15-μm-thick film. The Avatrel film was soft-baked at 100 °C on a hotplate for 10 min, exposed to a dose of 200 mJ/cm² from a 365-nm light source (lamp maker), hard-baked in a box oven at 100 °C for 20 min, and cured in a Lindberg tube furnace under ambient nitrogen at 165 °C for 60 min. Blends of Avatrel and Probelec (identified as AP henceforth) were prepared with mechanical mixing (magnetic stir bar) for 24 h and ultrasonic mixing for up to 8 h. The mixtures were then immediately spin-coated at 1000 rpm and cured in the same manner as the pure Avatrel material.

Wet-chemical treatments were carried out using three different solutions, a swelling solvent (Shipley MLB 211 and Cupositol Z) at 80 °C, a potassium permanganate etch bath (Shipley Circuposit 3308 A and B) at 80 °C, and a neutralizing bath (Shipley 3314) at room temperature. Plasma treatments were carried out in a Unaxis plasma-enhanced chemical vapor deposition (PECVD) chamber. The typical NH₃ plasma treatment parameters were: 20 sccm NH₃ flow rate, 200 mTorr chamber pressure, 150 °C substrate temperature, 30–200 W RF power, and 0.5–5 min treatment times. Following wet chemical or plasma treatments, the samples were activated with a Sn/Pd catalyst (Shipley Cataposit 44) at 46 °C for 20 min. Finally, the samples were plated with 1 μm of electrolessly deposited copper (Shipley Circuposit 3350 chemistry) at 46 °C. The copper thickness was increased to 40 μm for the peel tests through electroplating. Additionally, samples were annealed at 150 °C for 1 h following both the electroless and electropolating copper deposition steps.

The effect of these treatments was monitored by four analytical techniques. The adhesion strength of the copper to the polymer was measured with a 90° peel test using an Instron (Model 5842) instrument following the ASTM B 533-85 standard [24]. In this test, a 10-mm-wide strip of copper was pulled at the rate of 25 mm/min and the average force was calculated and divided by the peel strip width to yield the peel strength in N/mm. Analysis of the chemical state of the surface was performed with a Perkin Elmer XPS system (Model PHI 1600). A Molecular Imaging Picoplus AFM in the tapping mode was utilized to quantify the root mean square (rms) roughness of the surface and for qualitative analysis of the morphology of that roughness. The AFM tip diameter was less than 10 nm. Finally, a scanning electron microscope (SEM) (Zeiss SEM Ultra 60) was utilized to analyze the morphology of the polymer surfaces.

III. RESULTS

Roughness formation on Probelec and Avatrel surfaces following a swell and etch treatment is quantified in Fig. 3. RMS roughness values for Probelec increase with increasing etch treatment times, reaching a maximum of 800 nm with extended etching. Traditional treatment conditions of a 480-s swell and a 600-s etch produce rms roughness of 400 nm with corresponding adhesion of up to 1.5 N/mm. The surface roughness that forms in Avatrel, however, is more than an order of magnitude less than with Probelec, with a maximum rms roughness development of 35 nm. These treatment conditions produced no measurable adhesion between Avatrel and electroless copper. The roughness morphology also depends on the kind of material (Fig. 4). The Probelec surface develops a pore-type roughness forming large, deep pores with extended etching times. The Avatrel surface, however, does not exhibit pore-type roughness formation. Instead, surface roughness increases are realized in the form of peak-valley structures, which are uniform across the surface.

In order to form pore-type roughness on a surface containing Avatrel, AP mixtures were used. Fig. 5 shows the resulting surfaces when these mixtures are exposed to a 2000-s swell and 2000-s etch treatment. Fig. 5(a) shows a sample with 5% Probelec in the mixture. Only one pore can be seen in this 100-μm² scan after the swell and etch process. Fig. 5(b) is for the 10% Probelec sample, which shows the presence of approximately 30 pores in the 100-μm² scan. Fig. 5(c) is for a sample with 20% Probelec yielding 40 pores in the 100-μm² scan. In each case, the pores are of the same approximate size, 200–500-nm diameter and are evenly dispersed across the polymer surface. Changing the concentration of Probelec in the mixture affects pore concentration and not pore size or depth. Fig. 5(d) is a 3-D AFM image of the 20% Probelec sample illustrating that the pores formed on the surface are a maximum of 65 nm deep.

Mechanical and ultrasonic mixing techniques were studied with the 20% Probelec AP mixture in order to understand the
effect on pore size and distribution. Fig. 6 presents two SEM images of the polymer surface following 24 h of mechanical mixing and a 2000-s swell and 2000-s etch treatment. The smooth, dark field in these images is the Avatrel material, which is largely unaffected by the swell and etch process. The lighter areas are Probelec regions that have been etched to create roughness. It can be seen in Fig. 6(a) that there are many large Probelec particles, up to 50 μm in diameter, still present following purely mechanical mixing. Fig. 6(b) is a higher magnification image of one of these particles that shows the rough features created when large areas of Probelec are left in the mixture. AFM images indicate that in addition to these large Probelec areas, there are also well dispersed, smaller particles as evidenced by the small pores seen in Fig. 5. Fig. 7 shows SEM images of a solution that was mechanically mixed for 24 h and then subjected to ultrasonic agitation for a further 8 h. Fig. 7(a) shows a wide field SEM image with Probelec features as large as 10 μm. The majority of this surface contains very small features, as shown in Fig. 7(b), with a diameter of 200–500 nm. AFM scans confirm the presence of well-dispersed 200–500-nm Probelec areas on the surface. Thus ultrasonic mixing breaks up the largest Probelec particles, creating more uniformly sized pores on the surface. Despite these advances in roughness development, the surfaces of the AP mixture did not enable catalyst adsorption or electroless copper deposition without further treatment. Thus, the role of purely mechanical bonding could not be quantified using this approach alone.

NH₃ plasma treatments were utilized to enhance catalyst adsorption and chemical bonding on the polymer surfaces. Fig. 8 presents two XPS survey scans for Probelec, before and after plasma treatment. Before plasma treatment, the Probelec shows the presence of two elements, carbon (73.2%) and oxygen (26.8%). Following plasma treatment, the surface contains three elements, carbon (68.7%), oxygen (23.3%), and nitrogen (8.0%). Fig. 9 shows XPS survey scans for Avatrel. As with Probelec, there are two elements on the surface before plasma treatment, carbon (91.9%) and oxygen (8.1%), and three present after the plasma, carbon (72.8%) oxygen (22.1%), and nitrogen (5.1%). These plasma treatments also increased adhesion with the electroless copper. The Probelec peel strength increased from 0 to 0.11 N/mm, and the Avatrel peel strength increased from 0 to 0.26 N/mm. In both cases, the rms roughness of the surface remained below 20 nm following plasma treatments. Increasing plasma power was found to create less chemical modification and more roughness on the Avatrel surface (Table I). These conditions enabled plating but did not create any measurable adhesion, indicating that this
Fig. 6. SEM images of Avatrel/Probelec (20% Probelec) mixture with 24-h mechanical mixing following a 2000-s swell and 2000-s etch treatment: (a) 114× magnification, (b) 1160× magnification.

level of peak-valley roughness (<20 nm rms) does not facilitate mechanical anchoring.

A combined wet-chemical and plasma treatment was investigated with Probelec and the AP mixture in order to create surfaces capable of both mechanical anchoring and chemical bonding. Table II shows the Probelec adhesion results following swell and etch treatments with and without a 5-min 80-W NH₃ plasma treatment. Samples with shorter etch times and lower initial adhesion exhibit reductions in adhesion and roughness following the plasma treatment. For example, the sample with 100-s etch alone exhibited a peel strength of 0.66 N/mm and roughness of 63 nm; however, following plasma treatment the peel strength was reduced to 0.27 N/mm and roughness was reduced to 38 nm. Meanwhile, adhesion on samples with high roughness levels was found to be unaffected by the plasma treatment. This effect is evidenced in the samples that had been etched for 300 s, which have the same peel strength with and without the plasma treatment.

Table III presents XPS results for combined treatment samples with etch treatment times no greater than 80 s. It can be seen that each sample following plasma treatment has approximately the same nitrogen concentration (7%–9%). Also, the oxygen and carbon concentrations are consistent throughout the samples with only small decreases in each following plasma treatment. These decreases are due to the nitrogen added to the surface during plasma treatment. The palladium concentration is also consistent from sample to sample with concentrations ranging from 1.3% to 1.9%. Finally, the last three rows of this table illustrate the effect of varying plasma treatment time on the samples with combined wet-chemical and plasma treatment.
TABLE I
PEEL STRENGTH, RMS ROUGHNESS, AND XPS RESULTS FOR AVATREL AND AP MIXTURES

<table>
<thead>
<tr>
<th>Material</th>
<th>Plasma Treatment</th>
<th>Atomic Concentrations (At %)</th>
<th>RMS Roughness (nm)</th>
<th>Adhesion (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avatrel</td>
<td>No Treatment</td>
<td>C 95.8 O 4.2 N 0</td>
<td>1.1</td>
<td>0</td>
</tr>
<tr>
<td>AP Mixture</td>
<td>No Treatment</td>
<td>C 76.1 O 23.9 N 0</td>
<td>15.2</td>
<td>0</td>
</tr>
<tr>
<td>Avatrel</td>
<td>80 W NH₃</td>
<td>C 72.5 O 21.9 N 5.7</td>
<td>9.3</td>
<td>0.26</td>
</tr>
<tr>
<td>AP Mixture</td>
<td>80 W NH₃</td>
<td>C 75.4 O 18.2 N 6.4</td>
<td>13.8</td>
<td>0.51</td>
</tr>
<tr>
<td>Avatrel</td>
<td>300 W NH₃</td>
<td>C 73.5 O 24.8 N 1.7</td>
<td>16.3</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE II
PEEL STRENGTHS AND RMS ROUGHNESS VALUES FOR PROBELEC WITH AND WITHOUT PLASMA TREATMENT (ALL SAMPLES RECEIVED A 30-s SWELL TREATMENT)

<table>
<thead>
<tr>
<th>Etch Treatment Time (s)</th>
<th>5 min 80 W NH₃ Plasma Treatment</th>
<th>RMS Roughness (nm)</th>
<th>Peel Strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>No</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>Yes</td>
<td>17</td>
<td>0.11</td>
</tr>
<tr>
<td>50</td>
<td>No</td>
<td>40</td>
<td>0.21</td>
</tr>
<tr>
<td>50</td>
<td>Yes</td>
<td>22</td>
<td>0.18</td>
</tr>
<tr>
<td>100</td>
<td>No</td>
<td>63</td>
<td>0.66</td>
</tr>
<tr>
<td>100</td>
<td>Yes</td>
<td>38</td>
<td>0.27</td>
</tr>
<tr>
<td>300</td>
<td>No</td>
<td>350</td>
<td>1.47</td>
</tr>
<tr>
<td>300</td>
<td>Yes</td>
<td>310</td>
<td>1.47</td>
</tr>
<tr>
<td>600</td>
<td>No</td>
<td>450</td>
<td>1.52</td>
</tr>
<tr>
<td>600</td>
<td>Yes</td>
<td>450</td>
<td>1.59</td>
</tr>
</tbody>
</table>

In Fig. 9, XPS survey spectra of Avatrel before and after 80-W NH₃ plasma treatment.

surface concentrations of nitrogen. It can be seen that reducing the treatment time from 5 min to 30 s reduces nitrogen concentration from 9.6% to 8.9%.

Fig. 10 shows the peel test results for Probelec with a swell and etch only treatment and with a combined swell, etch, and plasma treatment. In the swell and etch only data set samples received a 30-s swell treatment and a 30–100-s etch treatment. Roughness under these conditions remained below 100 nm in all cases with adhesion ranging from 0.4 to 0.65 N/mm. The combined treatment data set used the same range of swell and etch conditions, with an additional 30-s 80-W NH₃ plasma treatment. These treatments created improved adhesion when compared to the swell and etch only surface. The offset between the data sets was approximately 0.20 N/mm for a given rms roughness value. Adhesion from electroless copper and Avatrel materials was also measured. Utilizing the 20% Probelec AP mixture with a 2000-s swell, 2000-s etch, and a 30-s 80-W NH₃ treatment peel strength increased to 0.51 N/mm with rms roughness values less than 20 nm (Table I). This peel strength is 0.25 N/mm larger than that obtained with purely chemical bonding from plasma treatments alone.

IV. DISCUSSION

In order to increase adhesion while maintaining smooth surfaces, processes that combine chemical bonding and mechanical anchoring have been investigated. An attempt was made to quantify the contributions of each mechanism through experimentation, with wet-chemical treatments used for mechanical anchoring improvements and plasma treatments for chemical bonding enhancement. The individual contributions to adhesion have been combined to produce optimum surfaces with the minimum necessary roughness and acceptable adhesion.

When comparing the degree of roughness created in Probelec and Avatrel by wet etching it is apparent that different processes are occurring, producing roughness with different magnitudes and morphologies from one material to the other. The Probelec pore-type roughness formation described in the introduction does not occur in Avatrel because of the location and function of the epoxy groups. In Avatrel, unlike Probelec, the epoxy groups are present as side-groups off of the main polymer chain and are mainly responsible for crosslinking of the polymer. Upon curing, approximately 80% of the epoxide rings are opened and used for crosslinking, producing a series of ether linkages connecting polymer chains [25]. The Avatrel material used in this study, which has a molecular weight of 200 000 a.m.u. contains approximately 200 epoxy-related crosslinks per polymer chain when cured. When the etch process attacks one of the ether linkages on these crosslinks, it enables the attack of subsequent linkages on the same crosslink chain (Fig. 11). Once all the ether linkages on a given crosslink are etched there is no mechanism for propagation of the etch process into the main polymer chain and it stops. Etching of the maximum length of polymer side group leads to the loss of the equivalent of an
eight carbon chain with an approximate length of just 1.2 nm, as opposed to Probelec in which the entire polymer chain can be removed in an etching sequence. Removing repeated small lengths of polymer through extending etching leads to the retention of relatively smooth surfaces with only the peak-valley roughness morphology seen in Fig. 4.

This work illustrates that the epoxy functionality alone is not sufficient for creating high levels of pore-type roughness. If this functionality is present in the polymer backbone it enables pore-formation roughness and enhanced adhesion. Moving this functionality to a side group off of the main polymer chain, however, minimizes the effect of the etch process leaving materials smooth and providing no adhesion enhancement. It is clear that in order to enhance adhesion with advanced materials different techniques are required. A new approach (i.e., using a blend of Avatrel and Probelec) has been taken to form the pore-type roughness needed for mechanical interlocking on the Avatrel surface.

In this approach, a small amount (5%–20% by weight) of Probelec in propylene glycol methyl ether acetate (PGMEA) is mixed with Avatrel in mesitylene. The solvents for these polymers are immiscible leading to the formation of two phases in the mixture, with small droplets of Probelec/PGMEA suspended in the Avatrel/mesitylene bulk phase. Ideally these droplets would be small and uniformly dispersed throughout the bulk phase. A process flow diagram for this approach is shown in Fig. 12. After the mixing, spin-coating, and curing processes described in the experimental procedures section of this report, the AP blend is subjected to a swell and etch treatment that preferentially etches the Probelec areas while leaving the Avatrel areas smooth. The Probelec droplets can be thought of as space-holders which are removed through the etch process to leave pores on the Avatrel surface. The resulting surface contains well-dispersed pores that are 200–500 nm in diameter and 70 nm deep, as shown in Fig. 5. The rms roughness of these surfaces remains low, less than 20 nm, despite the presence of pores because the Avatrel surface is largely unaffected by the etch process. The uniformity of these surfaces and the dispersion of pores is strongly affected by the mixing technique used.

Mechanical mixing alone, as shown in Fig. 6, does not adequately break-up large Probelec particles, leaving 30–50 μm areas of Probelec on the surface. When these large particles are subjected to the swell and etch process they act like the Probelec bulk material, creating large scale pores and extreme roughness. Probelec particles in the 200–500-nm-diameter range are removed completely by the etch process, leaving the same size pore on the surface. The larger particles however, are not completely removed leaving the large pores and high levels of roughness seen in Fig. 6. This leads to inconsistent adhesion, high adhesion over these Probelec areas and normal adhesion elsewhere, and large variance in roughness across the polymer sur-

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**TABLE III**

<table>
<thead>
<tr>
<th>Etch Treatment Time (s)</th>
<th>80 W NH₃ Plasma Treatment</th>
<th>Chemical Species Atomic Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>40</td>
<td>No</td>
<td>73.2</td>
</tr>
<tr>
<td>60</td>
<td>No</td>
<td>74.9</td>
</tr>
<tr>
<td>80</td>
<td>No</td>
<td>37.7</td>
</tr>
<tr>
<td>40</td>
<td>30 s</td>
<td>72.6</td>
</tr>
<tr>
<td>60</td>
<td>30 s</td>
<td>34.1</td>
</tr>
<tr>
<td>80</td>
<td>30 s</td>
<td>68.7</td>
</tr>
<tr>
<td>80</td>
<td>2 min</td>
<td>69.9</td>
</tr>
<tr>
<td>80</td>
<td>5 min</td>
<td>36.5</td>
</tr>
</tbody>
</table>

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Fig. 10. Peel strength versus RMS roughness chart for Probelec samples with and without 30-s 80-W NH₃ plasma treatments.
face, leading to electrical performance and mechanical reliability issues. Adding ultrasonic mixing to the process enables the breakup of more of these large particles, leaving the surface more uniform (Figs. 5 and 7) and minimizing the problems of inconsistent adhesion and roughness across the surface [26].

Plasma treatments were studied in order to enable catalyst adsorption and improve adhesion through improved chemical bonding. These treatments on Probelec and Avatrel are shown to increase adhesion by 0.15 and 0.26 N/mm, respectively, while maintaining smooth surfaces. The level of surface roughness created in this process (17 nm for Probelec, 9.4 nm for Avatrel) is quite low. Avatrel materials with similar roughness (16.3 nm) obtained through higher power plasma treatments have shown no adhesion, indicating that this level of peak-valley roughness does not enable mechanical anchoring (Table I). Thus, the adhesion gains realized through these plasma treatments (0.15–0.26 N/mm) can be attributed to chemical bonding improvements on the polymer surface.

Combined treatments, which take advantage of both mechanical anchoring and chemical bonding, were attempted with Probelec and the AP mixture, utilizing the optimum conditions identified in the individual investigations. It was found that the optimum conditions for mechanical anchoring, long swell and etch treatments and rough surfaces, were not suitable for combined treatments. These conditions produced surfaces with more roughness than desired and led to cohesive failure inside the polymer, not adhesive failure at the copper/polymer interface. The effect of plasma treatment which enhances
adhesion at the interface is not measured when failure occurs cohesively (Table II, 300- and 600-s etch data). In order to quantify the effect of these treatments, adhesion must occur adhesively at the interface. Limiting the swell to 30 s and the etch 30-100 s produced samples that failed adhesively with and without plasma treatments, while maintaining rms roughness levels below 100 nm. Utilizing these conditions with a 5-min 80-W NH₃ plasma treatment following the swell and etch proved to reduce adhesion compared to the samples with swell and etch alone (Table II, 50 and 100 s etch data). The 5 min plasma treatment significantly decreases the roughness of the surface (up to 41 nm rms roughness reduction) through plasma etching, reducing mechanical anchoring and adhesion. Limiting the plasma time to 30 s, thereby reducing the time of plasma etching, minimized the smoothing effect while maintaining the desired chemical modifications of the surface. Table III confirms the NH₃ plasma treatment creates similar chemical modifications whether treatment time is 30 s, 2 min, or 5 min treatment times as evidenced by consistent nitrogen concentration increases on the surface.

Utilizing a 30-s swell, 30–100-s etch, and 30-s 80-W NH₃ plasma condition, combined treatments were tested. Fig. 10 compares peel test results with and without the plasma treatment. With a purely swell and etch treatment Probelec exhibits peel strength values between 0.38 and 0.65 N/mm depending on the roughness generated. These peel strength values correspond to the contribution of mechanical anchoring on the surface. Adding the plasma treatment increases adhesion for a given level of rms roughness. The difference in adhesion before and after plasma treatments for a given rms value is a measure of the contribution of chemical bonding to adhesion. In these experiments this contribution was consistently 0.20 N/mm. Thus, this technique is capable of combining the effects of chemical bonding and mechanical anchoring and allowing for the quantification of the contributions of each to adhesion. The resulting surfaces are smooth and adherent, with rms roughness as low as 40 nm and peel strength values over 0.5 N/mm for most samples. The same effect was also realized with the AP mixtures, improving adhesion from 0.26 N/mm with plasma only treatments to 0.51 N/mm with combined treatments (Table I). In this case the 0.26 N/mm corresponds to chemical bonding and the remainder, 0.25 N/mm, is due to enhanced mechanical anchoring contributed by the pores formed on the surface.

V. CONCLUSION

A study of adhesion between epoxy-containing substrates and electrolessly deposited copper has been presented. In this study the contributions of mechanical anchoring and chemical bonding were measured individually in order to determine their relative magnitudes and suitable conditions for producing optimum surfaces. For the first time, a study of the etch process for materials with epoxy functionalities as side-groups off of the main polymer chain has been presented. A mechanism for this process with Avatrel has been postulated and compared with the process for a traditional dielectric material with epoxy in the polymer backbone. Wet-chemical and plasma treatments which provide optimum mechanical anchoring and chemical bonding respectively have been identified. Following this work, a treatment protocol that allows both mechanical anchoring and chemical bonding to contribute to adhesion on the same sample was identified. These conditions produced adhesion of greater than 0.5 N/mm for samples with rms roughness less than 50 nm on the surface by combining the benefits of chemical bonding and mechanical anchoring on one surface. These results aid the process of maintaining adequate adhesion on smooth surfaces for use with future microelectronic applications.

REFERENCES


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