Metallization Technologies on a Smooth Resin Surface for the Next Generation of Flip Chip Packaging

Michio Horiuchi, Tomoo Yamasaki, and Yuichiro Shimizu

Abstract
To realize higher wiring density, both finer line/space resolution and a smoother resin-metal interface are needed. These requirements, however, conflict to each other: sufficiently fine lines are difficult to form on a rough surface, while a smooth surface generally results in poor peel strength. The feasibility of various metallization processes that promote adhesion on smooth resin surfaces is examined. Their practical applicability to manufacturing high wiring-density packages is also assessed and the related issues that need to be improved are discussed.

Keywords: High-Density Wiring, Fine Line, Adhesion Promotion, Peel Strength, Smooth Surface, Environment

1. Introduction
In order to continue increases in the performance of electronic devices, higher wiring density and efficient data transmission are necessary. The chip-to-package area array connection pitch will become less than 100 μm in the next seven years. At the same time, the required transmission frequency will reach around 40 GHz.[1] To satisfy these requirements, a line/space pitch of less than 10 μm on a very smooth surface will be indispensable. The resin face under the conductor lines is commonly roughened to promote adhesion of the metallization. The roughness, however, hinders the forming of the fine lines. Also, as seen in Fig. 1, depositing an intricate electroless copper seed layer on the roughened surface tends to leave copper residue at the inter-line spaces in SAP (semi-additive process) for the fine patterning, and the residue may cause inter-line electrical shorting. Furthermore, the roughness can induce significant resistive losses at high frequencies. Fig. 2 shows the skin-depth (δ) of copper given by

\[ \delta = \frac{\rho}{\pi f \mu} \]

where \( \rho \) is resistivity, \( f \) is frequency and \( \mu \) is permeability.[2] The dimensions of the ridges at the copper-resin interface are larger than the skin-depth. Consequently the current will follow the contour of the ridges and increase the effective resistance and inductance, resulting in considerable transmission losses. If there is a higher-resistivity coating on the surfaces of the ridges, it will exacerbate this effect.[3] With finer line width, the effect of the roughness on the transmission properties will become significantly larger as shown in Fig. 3. Nevertheless, a smooth surface will induce some other issues in the manufacturing processes. Missing or dislocated lines with decreased width on a very low profile surface occurs often.

![Fig. 1 Intricate distribution of electroless Cu on conventionally roughened surface of resin containing different filler size and content.](image)

![Fig. 2 Skin depth of Cu for high frequency transmission range and roughness (Ra) of resin surface.](image)
due to poor adhesion strength as shown in Fig. 4. Accordingly, metallization technologies promoting adhesion are strongly desired for next-generation packaging.

2. Technologies to enhance adhesion strength

Various approaches to enhancing the peel strength of copper formed on smooth resin surfaces have been reported.[4–16] The approaches can be summarized into two types: surface pre-treatment and the addition of an adhesion-promoting layer on the smooth surface.

2.1 Surface pre-treatment

The surface pre-treatment can further be classified into two processes: surface submicron roughening and surface chemical modification.

2.1.1 Surface roughening

In the ordinary process, surface roughening is done by chemical etching at the same time as desmearing the via-bottoms. In submicron surface roughening, a somewhat mild chemical condition compared with the conventional process is adopted using a conventional permanganate-etch bath. Submicron roughening is also performed through a dry process using plasma, where surface roughness and morphology varies depending on plasma conditions and types (isotropic or anisotropic). In many cases, however, these submicron roughening processes lead to decreased peel strength as surface roughness decreases, and are usually combined with adhesion promoting processes described later.

2.1.2 Surface chemical modification

Some wet chemical treatments modify polymer surfaces chemically without roughening. The adhesion strength of electroless-plated Ni on a wet, chemically-pretreated polyimide surface has been reported to be dominated by the chemical bonding effect rather than the mechanical interlocking effect, with the chemical bonding associated with a carboxyl group.[4]

As a dry process for surface modification, UV irradiation has been widely used to make the surface hydrophilic. Although it depends on the targeted material, UV irradiation induces chemical groups, such as –OH, –C=O and –COO, on the surface of the resin and assists its adhesion with copper.[5] This is generally known as a time-dependent process. UV irradiation is also reported to be able to form nano-level anchors on resin surfaces. According to Inoue et al., a copper layer that was formed on a UV-irradiated polyimide surface showed a peel strength of about 1 kN/m with only the nano-anchor effect.[6]

Plasma treatment is also known as an effective manner to modify resin surfaces chemically. Technologies such as reverse sputtering and plasma bombardment are also included in this category. Depending on the plasma condition, a polymer surface can be made to be hydrophilic or hydrophobic. While halogen gases and fluoro-carbons such as CF4 or the other halo-carbons are used as etching gases for surface roughening, Ar, O2 and N2 plasmas are effective for chemical modification. It has been observed that the surface nitrogen concentration increases during N2 or NH3 plasma treatment, resulting in improved adsorption of Sn and Pd, which are used as the catalysts for electroless copper deposition. This enhanced Pd adsorption has been attributed to the –N=C< sites induced on the polyimide surfaces.[7] Utilizing the NH3 plasma treatment and polymer-blend technologies, Hayden et al., have obtained a sufficient peel strength (0.51 kN/m) of a copper layer formed on a very smooth (rms roughness 13.8 nm) epoxy resin substrate surface.[8]

2.2 Adhesion promotive layer addition

To promote the adhesion strength, it has been proposed to add various chemical groups onto polymer material surfaces. Many different types of processes have also been examined as methods to form the chemical group layer on a smooth surface. Graft copolymerization, impregnation and simple (spray-, dip-, drop- or spin-) coating are typical well-examined processes. As the initiating chemicals, acrylates, vinyl imidazoles, vinylpyridines, amines, porphyrins,
organometals, and silane coupling agents have been applied. According to some recent reports, impregnated amino-group-containing imidazole, grafted polyacrylate, “organic molecules,” and organometals including tin and silane have provided copper peel strengths on smooth surfaces of 0.42–0.51 kN/m on Ra 59 nm,[11] 1.1 kN/m on Rz < 100 nm,[12] 0.61 kN/m on Ra < 200 nm,[13] and 0.8–1 kN/m on Ra 50 nm,[14] respectively. These seem to provide promising adhesion characteristics, though they cannot be compared directly since their resin substrate materials and pretreatment conditions differ from each other.

In surface graft copolymerization, an applying polymer can be chosen independently of the substrate material and the formed polymer adheres strongly to the substrate with covalent bonds,[15] while it forms coordinate bonds with the catalytic metal for the subsequent electroless copper deposition. Its representative process is shown in Fig. 5, where vinyl imidazole is applied as the initiating monomer. After plasma treatment, coated monomers are polymerized with UV irradiation and heating. The attached imidazole group can be clearly recognized in XPS (X-ray photoelectron spectroscopy) N1s spectra as shown in Fig. 6, where the two peaks seen after the modification correspond to the two nitrogen atoms included in the imidazole ring.

Active metal (also called “contact metal”) is another practical promotive layer. Typical metal species are Ti, Cr, Ta, Zn, Sn, and they are usually deposited on the substrate by sputtering prior to forming a copper seed layer for electrolytic copper plating. Ti is known as a metal which has strong affinity for oxygen and tends to form oxides with oxygen-containing polymers. It has nevertheless been reported that Ti-C bonds have been detected by both AES (Auger electron spectroscopy) and XPS surface analysis in Ti-LCP (liquid crystal polymer) interface, suggesting a reactant adhesion layer will depend on the substrate materials and process conditions.[16]

Fig. 7 shows microstructures of copper-epoxy resin interfaces formed through the above-mentioned technologies and the initial peel strengths that we have obtained with them. Spherical silica particles are included in the epoxy resin substrate as fillers to control its coefficient of thermal expansion (CTE). Both samples prepared through processes A and B showed nano-level anchors and higher peel strength compared with that shown by the conventionally processed samples. Smoother interfaces are observed in the samples obtained with processes C and D, but are morphologically influenced by the coexisting silica particles. The peel strength obtained with process D was

![Fig. 5](image1.png)  
**Fig. 5** Representative surface modification process through graft copolymerization.

![Fig. 6](image2.png)  
**Fig. 6** XPS N1s spectra observed with vinyl imidazole-grafted resin surface.

<table>
<thead>
<tr>
<th>Process</th>
<th>Interface</th>
<th>Peel strength [kN/m]</th>
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<tbody>
<tr>
<td>conventional</td>
<td></td>
<td>0.48</td>
</tr>
<tr>
<td>A</td>
<td>C</td>
<td>0.69</td>
</tr>
<tr>
<td>B</td>
<td></td>
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<tr>
<td>C</td>
<td></td>
<td>0.04</td>
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<tr>
<td>D</td>
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<td>0.50</td>
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![Fig. 7](image3.png)  
**Fig. 7** Interface structure of Cu-resin that are treated with various processes and their peel strength.
comparable to that obtained conventionally, whereas that for process C was inferior to the conventional process.

3. Challenges from the viewpoint of package manufacturing

Even if adequate adhesion strength of copper layer formed on a smooth surface is achieved with simple test samples, various further capabilities are simultaneously required to realize high-density packaging.

3.1 Reliability

Among various methods we examined to promote the adhesion strength of the copper layer, some of them showed considerable degradation during one or more of the reliability tests: TC (temperature cycle), TS (Thermal shock cycle), HAST (highly accelerated temperature and humidity stress test), or reflow cycles. The typical failure mode was peeling off along the copper-resin interface. Some samples, however, showed an obvious intra-resin break, and resin fragments were observed on the peeled copper face. The microstructure of this break mode corresponds to a cohesive break that usually results in higher peel strength. This poor correlation between the microstructure and the actual strength strongly suggests a weak boundary layer being formed during the process.

3.2 Processability

Although adhesion performance was quite durable, some materials showed poor processability for high-density wiring. For example, as shown in Fig. 8a, a dry film resist (DFR) in photolithography became hard to remove, probably caused partly by the excessively promoted adhesion to the film. By contrast, if the adhesion-promoting layer has poor affinity to the resist film, washing away or floating issues could occur, resulting in defocusing and poor resolution, like the examples shown in Figs. 8b, c, and d. This affinity relation is a bit complicated. While stronger adhesion is preferable for the resin-copper, copper-resin, copper-solder resist, and resin-solder resist interfaces, adhesion strength should be appropriate (not too strong or too weak) for resin (or seed layer)-patterning resist. Since the surface characteristics of silica are different than those of most resin types, differences in particle size distribution and the total content (volume fraction) of silica included in the resin affect the adhesion properties. To avoid this, an additional filler-free layer was applied onto the conventional resin layer including filler, where the latter layer has a role in controlling TCE and rigidity. This added layer also provides a highly smooth surface when modified only chemically. Nevertheless, this heterolayer structure sometimes shows difficulty in the laser via hole forming process due to a difference in their ease of abrasion, as seen in Fig. 9. There was a case in which an element included in the promotion layer could not be sufficiently removed, leading to poor connection durability at the via-bottom (Fig. 10). The interference caused by the introduced adhesion promoter in the processing should be analyzed and solved in order to achieve high-density wiring. Although some modification of the existing processes should be tried for cost-effective solutions, additional processes will be needed when the optimum condition is out of the modification range. For instance, an additional etch-

Fig. 8 Issues relating to material or processing conditions that are newly introduced for the adhesion promotion; a. DFR removal failure, b. floated DFR failure, c. DFR resolution error and d. missing line.

Fig. 9 Cross sectional view of laser drilled via of a. heterolaminated layer, and b. conventional single layer including filler.

Fig. 10 Residue of a newly applied element on a via-bottom.
ing process to remove the element included in the adhesion promoting layer should be introduced if the analysis indicates the inability of the existing process to complete the removal. Fig. 11 demonstrates fine copper lines 4\( \mu \)m wide with 4\( \mu \)m spaces formed on conventionally roughened, un-roughened, and additionally stacked-up filler-free resin layer surfaces.

3.3 Performance

Even within the same magnitude of roughness, it is reported that peel strength varies depending on the roughened surface morphology, and pore-type roughness is superior to a peak-valley structure in respect to mechanical anchoring.[8] Since such a difference in roughness morphology may lead to a difference in the relative conductor-resin interface area, its effect on transmission performance, especially S21 at high frequencies, should be analyzed. Also, even if the surface has a very low roughness profile or is very smooth, the effects on the transmission properties of the actual impedance of alloy/intermetallic or of other adhesion-promoting layers newly introduced between the resin layer and the conductor metal should be considered. Dimensional control of transmission lines in the manufacturing process becomes more important.

3.4 Environmental standpoint and cost

The requirements to minimize the environmental burden have become more rigorous. Substances newly adopted in the manufacturing process need, at least, to satisfy the demands of the existing legislation or rules restricting the use of hazardous substances, such as RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronic equipments) and REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). Additionally, substances that impact on climate should be avoided. For instance, fluorocarbons that are broadly used as etching gases have extremely high global warming potentials (GWPs). Fig. 12 compares GWPs and safety levels given with NFPA (National Fire Protection Association) standards among various fluorocarbons. In spite of its high chemical stability and bio-inertness, CF4 has a very high GWP of 6500, so that its thorough decomposition is necessary. Taking these actions is possible and the corresponding equipment is commercially available, but the question here is its cost-effectiveness. Similar consideration will be needed for performance-cost balance. For instance, although Ti can be an efficient adhesion promoter on a smooth surface, it cannot be removed by typical etchants for seed copper removal, so that an additional etch bath containing a different etchant such as HF will be needed. In a case like this, some other cost reductions in another part of the manufacturing process will be strongly desired to compensate for the additional process cost.

4. Conclusion

Some methods providing sufficient copper peel strength on smooth surface have become available. To apply them to the next generation of packaging practically, however, various process improvements and optimizing are still needed.

References


