New Build-up Insulation Material Based on Cyclo-Olefin Polymer for High-Performance IC Packages

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Abstract

A variety of mobile devices such as smart phones, ultra thin laptops, and tablet PCs have been introduced to the world wide market, and the demands are gaining momentum. In technological perspectives, the trend is going to increased amount of data transfer and further miniaturization of the devices for more comfortable browsing and convenience. With this trend, a build-up insulation film material that plays an important role in interposer substrates for semiconductor packaging, is required to have higher performance to cover 1) low transmission loss, 2) extremely small line and space (L/S) with an ultra-smooth copper surface, and 3) low coefficient of thermal expansion (CTE). It has been very challenging to develop build-up film materials to meet all requirements. We have developed a new build-up insulation film material based on a unique polymer, cyclo-olefin polymer (COP), which has much lower moisture absorption, Dk, and Df than standard epoxy-based materials. The COP-based build-up insulation material has shown outstanding performance; low tangent loss (0.0045 at 5 GHz), 4 um/4 um in L/S with ultra smooth surface for copper plating (Ra < 100 nm), copper peel strength (7 N/cm), and low CTE (17 ppm/deg.C). It has also been found that the COP-based material demonstrates a wide process window for semi-additive process (SAP) that could help ensure easy manufacturing of interposer substrates besides the outstanding performance. For instance, as the material has strong chemical resistance against desmear solution, it does not significantly alter/damage surface roughness, plated copper peel strength, and via morphology. The newly developed build-up insulation material can be promising not only for bearing high electric performance to more sophisticated mobile devices, but also for contributing to high yield manufacturing thanks to easy processability, based on the new polymer, COP.

1. Introduction

Copper line width and thickness are getting smaller and smaller in response to miniaturization of device size and high density wiring [1]. With this trend, however, one of the current challenges is reducing conductor loss.

On the other hand, as signal transfer speed increases with higher frequency [2], signal current is likely to pass through near-surface portion of wiring. It can usually be called “skin effect”. It is reported that the skin effect is negligible in case wiring width is wide enough [3] but it would impact significantly on devices with a finer pitch wiring in the near future [4]. Furthermore, an effective conductor resistance doubles when surface roughness between insulation and conductor layers becomes larger than skin layer depth where electric current flows [5]. In this respect, the surface roughness of wiring is getting extremely important in regard to lowering a signal propagation loss [6,7].

Smooth surface of insulation materials is also necessary to create a fine line pattern. Normally copper wiring can be formed by semi-additive process (SAP) onto build-up films. In this process, an adhesion between copper wiring and insulation layer can be achieved with an anchoring effect, or mechanical bonding, by using micro-etching process based on permanganate solution treatment. However, electro-less copper plated layer (seed layer) formed onto the roughened surface results in much longer time to remove residual copper completely at etching process. That makes it difficult to form fine line patterns due to an over-etching effect of wiring. Although wiring formation by a spattering method might also be promising to get smooth copper surfaces, it has not been adopted because of quite high cost and long process time. From those backgrounds, next generation insulation materials have been required for high-density and miniaturized packages achievable with ultra-fine patterns.

2. New Polymer for Next Generation Build-Up Insulation Material

A matrix polymer consisting of build-up insulation materials plays an important role in determining electric performance and reliabilities. Cyclo-olefin polymers (COP) provided by ZEON Corporation are categorized as a hydro-carbon polymer and have a unique cyclic structure in the backbone unlike linear or branched polyethylene and polypropylene polymers [8]. As the COP does not have polar groups and shows extremely low dielectric constant, dielectric loss, and water absorption, it can be a promising polymer for next generation of high-speed IC packages. We have developed a build-up insulation material based on the COP and proved that the material outperforms conventional epoxy-based insulation materials. The new build-up insulation material shows higher chemical resistance than existing epoxy-based materials because of having no polar groups such as carbon-carbon double-bonds, ether groups, and ester groups. It has been shown that the insulation material cannot be roughened significantly with permanganate solution and can keep quite smooth surface even after desmear process. Although Polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE) also show high micro-etching resistance, those are not easy to apply electro-less copper plating.

We have developed a new build-up insulation material based on a new and unique polymer, COP, and shown that it has ultra-smooth surface with high copper peel strength. Furthermore, with high micro-etching resistance, the new material has shown a wider process margin than existing epoxy-based materials.

Table 1. Property of developed COP-based insulation material

Dielectric constant, Dk [5GHz]	3.4
Dielectric loss tangent, Df [5GHz]	0.0045
Tg (deg. C)	160
CTE (ppm/deg. C) [X-Y 30-150 deg. C]	17
Surface roughness, Ra (nm)	<100
Peel strength (N/cm)	>7
Water absorption (%)	<0.2
Filler content (wt %)	75

3. Insulation Material Properties

Table 1 lists build-up film properties after curing which we have developed.

Dielectric properties were obtained based on a cavity resonator (CPMA Series, KEAD) with N5230A (Agilent Technologies), and glass transition temperature (Tg) and coefficient of thermal expansion (CTE) were measured by a thermal mechanical analyzer (TMA).

Surface roughness data after desmear, Ra was measured by an optical interferotype surface roughness measurement system. Water absorption was measured after soaking in a water bath at 100 deg. C for 1 hour. Water absorption of existing epoxy-based material was 1.1 %. On the other hand, the value of COP-based material was less than 0.2 %.

Coefficient of thermal expansion (CTE) is very important for a chip-package interaction (CPI) where CTE mismatch is currently one of key challenges between silicon chip process and packaging process in reliability.

Generally CTE number of organic materials is much larger than that of metal and ceramic materials. To address the CPI, it is very challenging to get CTE of organic materials closer to those different types of material that have low CTE numbers below 17 ppm/deg.C (CTE of copper). In order to lower the CTE of organic materials, it is important to look at how much filler loading can be achieved in terms of surface-free energy of resin and filler surfaces, filler size distribution, and filler shape. Therefore, we have developed COP-based insulation material to take into account those effects with, for instance, monomer design of COP for surface-free energy and surface treatment of fillers. As a result, high filling was attained.

Fig. 1 shows a thermo mechanical analysis (TMA) test result for COP-based insulation materials. From this measurement, CTE below glass transition temperature range was obtained for both materials. The CTE was 50 ppm/deg.C for 40 wt% filler content material and 17 ppm/deg.C for 75 wt% filler content COP-based material that is identical to copper CTE. It would be very promising for the CPI. Fig. 2 shows a warpage test result in which one piece of insulation film with 40 um thickness was laminated with 10 um thickness copper foil and followed by curing. The 17 ppm COP-based insulation material showed much lower warpage than 50 ppm material. This result explains well that getting closer in CTE number between different materials can contribute significantly to a reduction of stress for warpage generation.

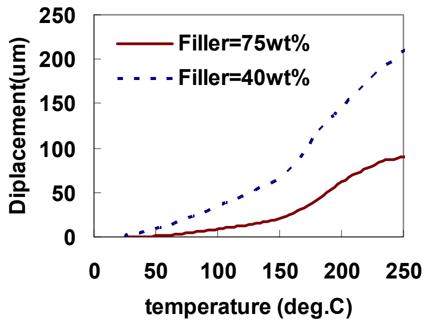


Fig. 1. TMA data comparison between 40 and 75 wt% filler contents of COP-based insulation materials

(a) (b)

Fig. 2. Warpage comparison of (a) 40 and (b) 75 wt% filler contents of COP-based insulation materials

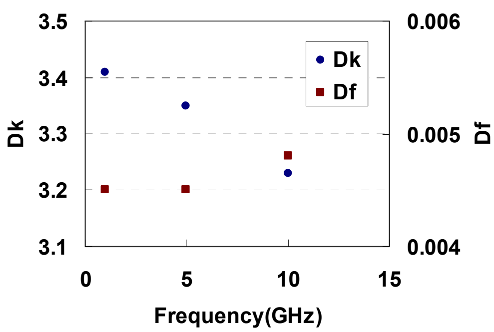
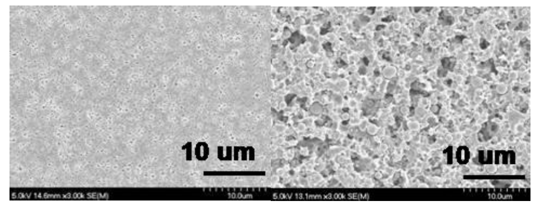


Fig. 3. Frequency dependence of Dk and Df

Fig. 3 shows a frequency dependence of dielectric constant (Dk) and dielectric loss (Df) of COP-based insulation material. The Df was below 0.005 in the measured frequency range, and the number is much lower than currently available epoxy-based insulation material. It can be clearly explained that COP which is used as a base polymer has extremely low Df (0.0001-2).

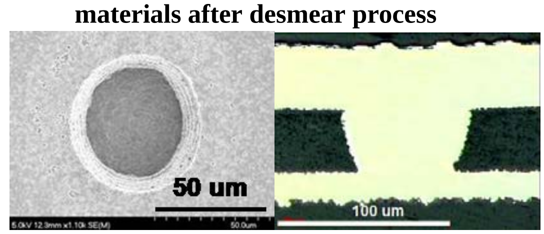
4. Flat Surface and Blind Via after Desmear Process

Fig. 4 shows SEM observation for planar surface of (a) developed COP-based material and (b) existing epoxy-based material after desmear. The micro-etching condition was 80 deg. C and 15 minutes for both cases. As one can clearly see from those photos, COP-based material showed much smoother surface than epoxy-based material; in order to compare the surface roughness, Ra numbers of both materials were measured and were 80 nm and 600 nm, respectively. Generally surface of epoxy-based materials can be largely roughened by permanganate solution at desmear process since it possesses polar groups that can easily be broken chemically with the solution. In contrast, COP-based material can keep smooth surface after desmear process.



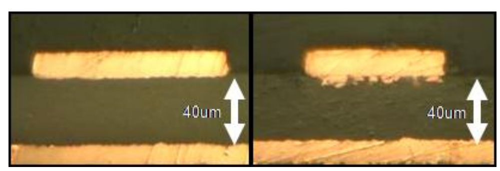
(a) (b)

Fig. 4. SEM images of surface for (a) developed COP-based and (b) existing epoxy-based insulation materials after desmear process



(a) (b)

Fig. 5. (a) SEM image of a blind via from the top after CO_2 laser drilling and desmear and (b) cross-section after plating (optical micro scope)



(a) (b)

Fig. 6. Cross-section photos of copper lines for (a) COP-based and (b) epoxy-based insulation materials

Fig. 5 (a) shows SEM images of a blind via from the top after carbon dioxide (CO_2) laser drilling and desmear. Fig. 2 (b) shows an optical microscope image of cross-section after plating. One can see that smear can be totally removed.

Fig. 6 shows cross-section photos after forming copper wiring layer that is based on semi-additive process (SAP) on top of material surface. It can be clearly seen that COP-based material shows much smoother surface than epoxy-based material. Since signal transmission loss depends significantly on a degree of surface roughness, i.e., a skin effect, the surface roughness needs to be much lower as well as fine line formation capability.

In order to explain the different behaviors of both materials in surface roughness, desmear rate of cured film surface was measured and compared. The desmear rate was obtained by weight loss of the materials after passing through desmear process once. Micro-etching condition was fixed at 80 deg. C and 15 minutes. COP-based material showed 6 mg/cm^2 in weight loss, while epoxy-based material showed 15 mg/cm^2. This result was also confirmed by a surface elemental analysis (ESCA) in which epoxy-based material had more polar groups and bonds likely etched. Those results definitely support that COP-based material has higher chemical resistance against micro-etching solution than epoxy-based material.

5. Wide Process Window for Desmear Process

A relationship between surface roughness and micro-etching temperature was confirmed and the result is shown in Fig. 7. The etching time was fixed at 15 minutes through the measured temperature range. Ra of epoxy-based material increased with micro-etching temperature, but, in contrast, COP-based material kept steady numbers over the temperature range. This result coincides with that from the weight loss and ESCA measurements shown above.

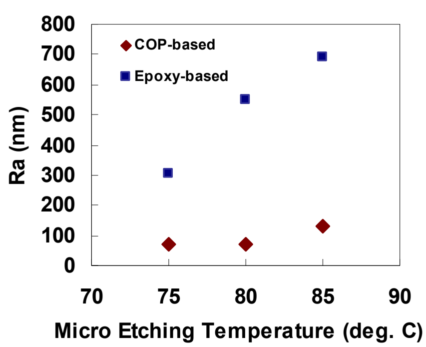
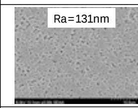
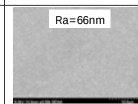
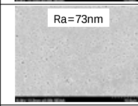
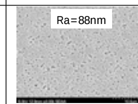
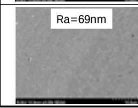


Fig. 7. Micro etching temperature dependence of surface roughness for COP-based and epoxy-based insulation materials

Table 2 is a matrix showing surface roughness (Ra) changes for COP-based material that depend on micro-etching temperature and time. As seen in this matrix, COP-based material exhibits low Ra numbers and cannot be affected significantly by a wide range of micro-etching conditions. That means that the material has a wide process margin that leads to easy manufacturing for substrate manufacturers.

Table 2. SEM images of surface for COP-based materials after various micro-etching conditions

Micro-etch	10min	15min	20min
85C		Ra=131nm 	
80C	Ra=66nm 	Ra=73nm 	Ra=88nm 
75C		Ra=69nm 	Film thickness : 40um Desmear Conditions : ・Swell:60C✕15min ・Micro-etch:✱✱C✕✱✱min ・Reduction:40C✕5min

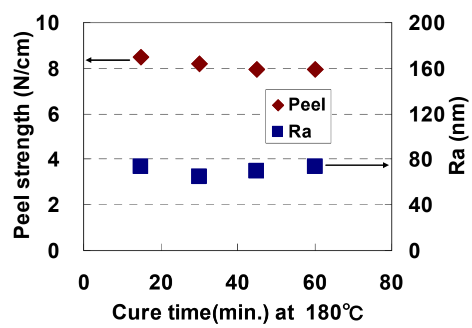


Fig. 8. Cure time dependence of peel strength and surface roughness (Ra)

For high-performance IC packages, adhesion between insulation material and plated copper layer is getting more and more important in terms of passing through a variety of reliability tests. Furthermore, in response to a recent trend that surface roughness gets lower for low transmission loss, keeping high peel strength is a key challenge.

An adhesion between insulation film and plated copper was studied and Fig. 8 shows a dependence of peel strength and surface roughness as a function of cure time. Both the peel strength and surface roughness did not change regardless of cure time. That means that COP-based material has high micro-etching resistance.

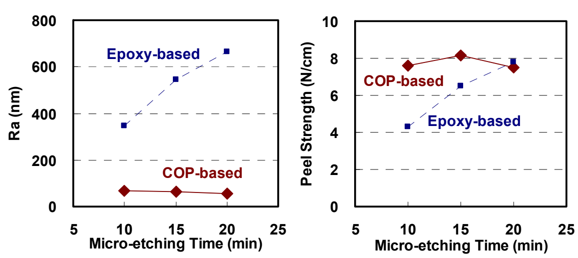
It is considered that the peel strength between COP-based material and plated copper layer comes from two aspects: physical adhesion and chemical adhesion. Physical adhesion is based on an "anchoring effect" of micro-pores formed on the insulation material surface; meanwhile, chemical adhesion is based on chelate complexes formed between plated copper and special functional groups of COP-based material.

Table 3 shows effects of micro-etching temperature and time on peel strength. The peel strength basically did not change significantly over the temperature range and time frame although there was a little variation. This means that COP-based insulation material has a wide process window. It can be explained that COP has high chemical resistance against micro-etching solution as previously mentioned.

Micro-etching time dependences on surface roughness (Ra) and peel strength were investigated and the results are shown in Fig. 9 (a) and (b), respectively. The temperature of permanganate solution was 80 deg.C through the measurements. COP-based insulation material did not show any changes in this time frame although epoxy-based insulation material increased steadily with micro-etching time. It can be interpreted that in the case of epoxy-based material, peel strength increases as surface is roughened by time, meaning that a mechanical bonding effect, so-called anchoring effect, dominates the increase of peel strength.

Table 3. Effects of micro-etching temperature and time on peel strength

Micro etch	10 min	15 min	20 min
85C		8.0	
80C	7.6	8.2	7.5
75C		7.9	

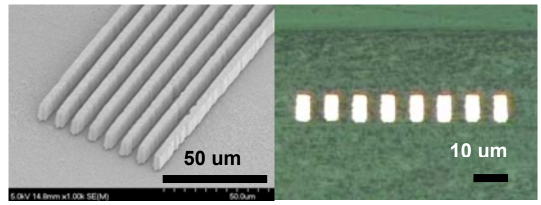


(a) (b)

Fig. 9. Micro-etching time dependence of (a) Ra (b) peel strength for COP-based and epoxy-based insulation materials

6. High-Density Wiring Capability

Fine line formation capability has been investigated with COP-based insulation materials which have ultra-smooth surface. It is well-recognized that the fine line formation depends largely on degree of surface roughness, i.e., the smoother the surface roughness, the finer line-and-space (L/S) can be achieved. The finer L/S can greatly help design and develop high-density packages. Fig. 10 (a) shows SEM photo of 4/4 um pattern in L/S that is based on semi-additive process (SAP) and successfully achieved by COP-based insulation material. Fig. 10 (b) shows an optical microscope image of cross-section of the 4/4 um pattern. This accomplishment can be attributed to two effects, 1) ultra-smooth surface and 2) high peel strength of copper-plated layer on the smooth surface. On the other hand, if the surface roughness is not so low, generally it takes a long time to remove electro-less copper seed layer, resulting in an over-etching of electro-plated copper layer.



(a) (b)

Fig. 10. (a) SEM image of fine line formation at L/S = 4/4 um of copper (thickness =8 um) (b) Cross-section image of fine line (optical micro-scope)

7. Low Signal Propagation Loss

Propagation loss (S21) of COP-based insulation material was measured based on a micro-strip line test vehicle and its schematic representation is shown in Fig. 11. The micro-strip line was designed so as to have 50 ohm in characteristic impedance. Since Dk numbers of COP-based and epoxy-based insulation materials were different, line width for those were adjusted at 84 um and 83 um, respectively. Also insulation layer thickness and transmission length were set at 40 um and 40 mm, respectively, for both materials because signal loss depends significantly on the insulation layer thickness.

Fig. 12 shows S21 parameter variation representing propagation loss, as a function of frequency for both materials. The propagation loss of COP-based insulation material was much lower than that of epoxy-based material, and it can be considered that the difference comes from both surface roughness (skin effect) and Df effects.

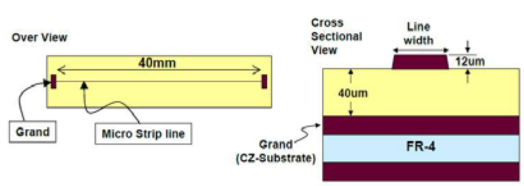


Fig. 11. Micro strip line test vehicle design

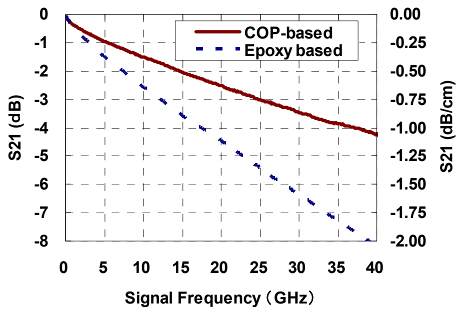


Fig. 12. Propagation loss of COP-based and epoxy-based insulation materials as a function of frequency

8. Reliability

As previously mentioned, the peel strength would impact significantly on reliability in terms of thermal cycling and high humidity conditions. In order to check reliability of COP-based insulation material, highly accelerated stress test (HAST) was performed to see how peel strength changes with time. The test condition was 130 deg. C and 85 % relative humidity. Fig. 13 shows a peel strength variation as a function of time in HAST. The peel strength was steady until 200 hours. Basically peel strength can be considered to have failed for two possible reasons; 1) penetration of water molecules into an interface between insulation material and copper layer, and 2) insulation material absorbs water and that results in a failure of bonding strength with copper layer. This result reveals that low water absorption property of COP-based insulation material leads to keeping high peel strength even at 200 hours.

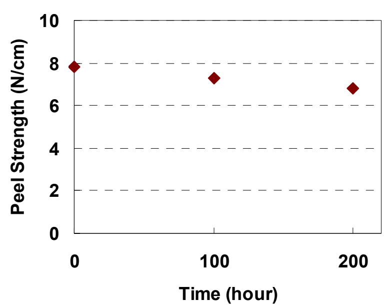


Fig. 13. Peel strength variation as a function of time in HAST

Layer-to-layer insulation reliability was investigated and the results are shown in Fig. 14. Pre-treatment condition has three steps, i.e., 1) baking at 125 deg. C for 6 hours, 2) keeping at 60 deg. C and 60 % relative humidity for 40 hours, and followed by 3) five solder reflow cycles with 260 deg. C peak reflow temperature. HAST condition was 3.3 V in applied voltage, 130 deg. C, and 85 % relative humidity. Insulation film thickness range was 10 to 40 um.

COP-based insulation material remained unchanged until 350 hours even at 10 um thickness, which can be attributed to extremely low water absorption and high insulation resistance of the material. On the other hand, the resistance of epoxy-based material decreased drastically, which can be attributed to its water absorption. As previously mentioned, water absorption of existing epoxy-based material was 1.1 %, and for COP-based material, it was less than 0.2 %. The large difference in water absorption would impact significantly on the reliability test under a high humidity condition.

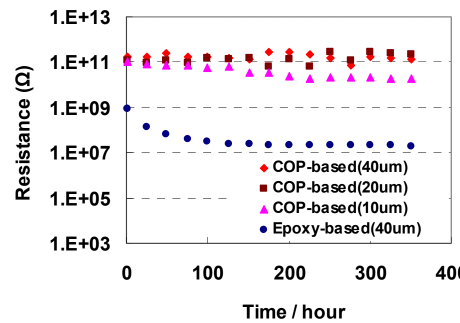


Fig. 14. HAST result of COP-based and epoxy-based materials with different film thickness as a function of time

10. Summary

We have developed a next generation build-up insulation material based on cyclo-olefin polymer as a new polymer matrix which has extremely low water absorption and excellent dielectric properties and proved 1) low propagation loss, 2) extremely small line and space (L/S) with an ultra- smooth copper surface, and 3) low coefficient of thermal expansion (CTE). In addition to these excellent qualities, the COP-based insulation material exhibited a wider process window than conventional epoxy-based insulation material, which can be expected to significantly enhance manufacturing yield.

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