Novel Photosensitive Solder Resist with High Reliability for Semiconductor Package(II)

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The increasing demands for small, thin, and high performance electronic equipment raise the specification on higher density pattern, narrow pad pitch and fine line and space of the semiconductor package substrates. Accordingly the outermost layers of solder resists are needed to have 1) excellent Highly Accelerated Stress Test(HAST) resistance performance with thinner film, 2) high crack resistance at the Thermal Shock Test(TST), and 3) high resolution for fine pattern. For HAST resistance, we reduced chlorine ion and improve anti-hydrolysis properties in solder resist. This new technology significantly improves ion migration resistance resulting in a higher HAST reliability even with a thinner solder resist film. For crack resistance, a simulation has been designed to analyze the mechanism of cracking as well as a target of physical properties of the solder resist possessing superior crack resistance. High crack resistance was successfully achieved at the TST using the solder resist with elastomer forming nano-phased separation and filler surface treatment. For high resolution, we optimized exposure wavelength and the refractive index of the material and successfully demonstrated good resolution in accordance with the design size.

Keywords : Solder Resist, Package, HAST Resistance, Crack Resistance, High Resolution

1. Introduction

Solder resist is a curable resin composition typical in green color which is formed at the outermost layer of a printed circuit board [1], [2]. The main function of the solder resist is to selectively expose the specific part of the circuit on a printed circuit board (copper patterns) to enable soldering to a packaged component, while suppressing solder spreading to other areas for a protection purpose.

Since the semiconductor packages were developed into the area array packages such as Chip Size Package(CSP) and Ball Grid Array (BGA) in the 1990s, increased density and performance of package substrate have been developed. Accordingly the solder resist has been given much more important roles that may influence the performance and functions of the printed circuit board, which represents its departure from a simple role as a curable resin composition. The enhancement of various performance factors are much expected. For example, the solder resist is needed to have 1) excellent HAST

resistance between the fine line and space (L/S) circuit, 2) high crack resistance at the TST, and 3) high resolution for higher density. For HAST resistance, we reduced chloride ion concentration in the material and enhanced hydrolysis resistance. For crack resistance, we optimized the elastomer using nano-phased separation [3] and filler surface treatment. For high resolution, we optimized particle size and refractive index of the filler to reduce light scattering.

We demonstrate development of high performance solder resist that meets stringent specifications for next generation high density semiconductor devices in this paper.

2. Roadmap to the Development of Solder Resist for Package Substrates

Table 1 and Table 2 show the road maps to the solder resist development for the next-generation CSP and BGA substrates.

Table 1. Roadmap to FC-CSP Package Application

TAIYO's spec	Year	2013	2014	2015	2016	2017
L/S (μm) @BHAST		12/12-8 / 8				5 / 5
Min. SRO (μm)		60	60	50	50	<40
SR Thickness on Cu (μm)		10-15	5-10	5-7.5	5	<5
SR Tg (deg.C)		100	140-150	150-175	150-175	175-200
SR CTE alpha 1 (ppm)		55	25-45	15-20	15-20	<15
SR Elastic Modulus (GPa)		3.0-4.0	4.0-5.0	10.0<	10.0<	10.0<
SR Tensile Strength (MPa)		70	70-80	90-100	90-100	100<
SR Elongation (%)		3.0-4.0	3.0-4.0	3.0<	3.0<	3.0<

Table 2. Roadmap to FC-BGA Package Application

TAIYO's spec	Year	2013	2014	2015	2016	2017
L/S (μm) @BHAST		10 / 10				5 / 5
Min. SRO (μm)		60	60	55	55	<50
SR Thickness on Cu (μm)		15	10	7.5	7.5	5
SR Tg (deg.C)		100	130-140	150-160	150-160	160-170
SR CTE alpha 1 (ppm)		55	40-45	35-40	35-40	<30
SR Elastic Modulus (GPa)		3.0-4.0	4.0-5.0	3.5-4.0	3.5-4.0	5.0-6.0
SR Tensile Strength (MPa)		50	75-80	90-95	90-95	100<
SR Elongation (%)		3.0-4.0	3.0-4.0	5.0-6.0	5.0-6.0	7.0<

A very thin board is used for the CSP substrate. This includes the thin memory board and the coreless board. For the CSP board, thinner solder resist with finer pitches are required, which can be achieved through a higher density. Therefore, for development of the solder resist for the next-generation CSP board, the liquid solder resist was replaced with the dry-film solder resist, which provides higher accuracy of thickness. This enables creation of very flat surfaces with high thickness accuracy even with the thin film. Besides maintaining the accuracy for film thickness by switching to the dry-film solder resist, it is important to match the values to the peripheral materials. High level of filler loading is required at this time, but it gets more difficult to maintain resolution. The technologies for enhancing resolution and maintaining excellent HAST resistance even in the thin film state will be mentioned later in this paper.

For the BGA substrate, some tendencies can be observed including expansion of the chip size, finer pitches with higher density, replace from solder bump to Cu pillar, and thinner solder resist with thinner substrates. Accordingly, the solder resist for the BGA substrate requires crack resistance under the stress applied at the TST. Therefore our development work has been proceeded with a focus on the high tensile strength and elongation from our simulation. Among other required properties is high resolution that is applicable for a small-diameter Solder Resist Opening (SRO). These technologies will also be mentioned later.

3. High Resolution

The solder resist of recent years with lower Coefficient of Thermal Expansion (CTE) adopts the technology that enables high level of filler content. Higher filler content may increase risks to have higher scattering causing resolution degradation, thus it is important to employ appropriate filler technologies to avoid resolution degradation. Therefore, we focus on particle size and refractive index of the filler to achieve high resolution in high level of filler content.

One feasible method is to reduce the diameter of the filler grain. The reason for this is that solder resist is hardened with UV radiation. From data on the differences in light distributions based on the Mie Scattering with a wavelength of 365 nm, it is confirmed that when the grain size is 3 times larger, the light scattering intensity in the forward direction is 1,000 times greater. Thus, the filler with a smaller grain diameter must be considered. Figure 1 shows the resolution with different grain sizes of the filler. By setting the filler particle diameter less than the exposure wavelength, the light scattering was successfully constrained. Even with the opening size of 50μm, excellent resolution was obtained in accordance with the design size.

Figure 1. Resolution with Different Particle Sizes of Filler.

Another likely method is to make adjustments on the refractive index of the filler. The inorganic filler generally causes light refraction because the refractive index is different from the resin used for the solder resist. Therefore dense filling with the inorganic filler can cause halation. Figure 2 shows the resolution for three different types: 1) Filler Not Included, 2) Traditional Filler, and 3) Filler with the same level of refractive index as the resin.

By matching the refractive index of the filler with that of the resin, even with the dense filling of the filler at 70wt%, good resolution was obtained in accordance with the design size.

Figure 2. Resolution for Different Filler Refractive Indexes

For the solder resist using these technologies, even with the opening size of 50μm, excellent resolution was obtained in accordance with the design size (Figure3).

Figure 3. Resolution with Various Exposure Machine

4. Ion Migration Resistance of Fine Pattern with Thinner Film

In the next-generation package substrates with higher density, less than 10μm of L/S are needed. Using Higher Tg solder resist is generally known as a method to

enhance ion migration resistance. In accordance with the road maps, the solder resist has now achieved higher Tg of 150°C compared to a previous Tg of around 100°C. However, only higher Tg is not enough to realize a better ion migration resistance in the fine pattern. Therefore, some measures were taken specially designed for the solder resist to achieve unparalleled ion migration resistance.

Figure 4 shows the chemical reactions observed when voltage is applied to the circuit covered with the solder resist [2]. The major reactions include 1) electrolysis of water, and 2) a reaction to produce copper chloride from Cu ion and chloride ion. Each reaction is described below.

Figure 4. Chemical Reactions Observed When Voltage is Applied to Circuit Covered with Solder Resist.

An important factor for 1) electrolysis of water is the fact that the anode acidifies and the cathode basifies. Originally, the solder resist uses acrylate compound as photosensitive group, and it contains a lot of ester bond. The ester bond has a defect where hydrolysis may occur against a base (Figure 5).

Figure 5. Decomposition Mechanism of Ester Bond

Figure 6 shows the cross-section view of the substrate with different level of the ester bond, before and after the HAST. Some waviness was observed with the existing resin composition. It was caused by decomposed ester bonds after HAST. In contrast, the resin composition with a hydrolysis-free structure has less waviness even after HAST.

Figure 6. Cross-section Images of Substrate Before and After HAST with Different Amounts of Ester Bond.

2) Production of Cu-chloride shown in was observed as migration of Cu on the anode. The chloride ions stimulating migration are the impurities in the solder resist. Thus it is important that the amount of the chloride ions contained in the solder resist. Figure 7 shows the cross-section views of the conventional resin composition and the resin composition using the newly developed resin after HAST. On the conventional resin composition with high total chlorine concentration, Cu diffusion was confirmed on the anode. In contrast, the newly developed resin composition achieved a much lower chlorine concentration and less diffusion of Cu.

Figure 7 Cross-section views of the existing resin composition and the new resin composition after HAST.

Figure 8 shows the Mean Time To Failure (MTTF) for the amount of total chlorine of the conventional and the new resin composition. It was confirmed that, compared with the conventional resin composition, the new resin component maintained high MTTF for the same amount of total chlorine. This result means the new resin achieves higher HAST reliability.

Figure 8. MTTF for the Amount of Total Chlorine of Conventional Resin and New Resin.

Figure 9 shows the result of the HAST for the solder resist for the current CSP substrates. Even with the fine pattern, the solder resist with the new technology achieved 3 times higher HAST reliability than the conventional solder resist, under the conditions of Temperature 130°C, Humidity 85%, and Voltage 5V at the same time, outstanding HAST resistance was realized with the 5μm thin film on Cu.

Figure 9. Result of HAST for Solder Resists

5. High Crack Resistance

The crack resistance is highly expected especially for the solder resist for the BGA substrate. This is based on the current tendency towards enlarged chips, higher density and finer pitches. Therefore, we have designed a simulation to analyze the mechanism of cracking as well as the target of physical properties of the solder resist possessing superior crack resistance.

First, analysis was conducted on the stress applied to the solder resist during the TST in the simulation. Figure 10 shows the interrelation between temperature and stress in the solder resist during the TST. As a result of the simulation, the highest stress was observed in the solder resist at the lower temperature in the thermal shock cycling.

Figure 10. Interrelation between Temperature and Stress in Solder Resist during TST

Next, another analysis was performed with a simulation where the stress at lower temperature and the physical properties of the solder resist were observed. Figure 11 shows interrelation between the stress at lower temperature and the physical properties of the solder resist. As a result, within the physical properties of the solder resist, close interrelations were confirmed among the CTE, the elastic modulus at lower temperature, and stress occurrence [4].

Figure 11. Interrelations between Stress at Lower Temperature and Physical Properties of Solder Resist

In order to enhance crack resistance, the following two targets are defined to the physical properties of the solder resist:

- 1) Sufficient tensile strength and elongation in the lower temperature region, and
- 2) Low CTE and low elastic modulus in the all ranges of temperature regions.

By strengthening the resin composition with elastomer, 1) sufficient tensile strength and elongation is obtained. Elastomer can substantially enhance fracture toughness using nano-phase separation with the resin composition in the solder resist. In this experiment, some positive effects of elastomer were observed for the resin composition without filler. Figure 12 shows the tensile strength and elongation with the different amounts of elastomer content. The resin composition with more than 10wt% of elastomer show more than 5 times higher elongation than the resin composition without elastomer. Figure 12 also shows the SEM images of the tensile fracture surface for different amounts of elastomer content. The substantial plastic deformation was observed for the resin composition with more than 10 wt% of elastomer.

Figure 12. Tensile Strength and Elongation with Different Amounts of Elastomer Content

Figure 13 shows the results of DMA measurement for the different amounts of elastomer content. Generally adding elastomer drastically reduces T_g in the resin composition. In the method using nano-phase separation of the elastomer, however, T_g is successfully maintained.

Figure 13. Results of DMA Measurements with Different Amounts of Elastomer Content

2) The CTE reduction method enhances wettability of the resin and the filler using filler surface treatment. Figure 14 shows CTE with different amounts of filler content, with and without surface treatment. It is observed that the CTE reduction effect is higher with the resin composition with filler surface treatment than those without filler surface treatment. Figure 14 shows CTE for different surface treatment, where the filler content is 70wt% each for the entire composition. Here, it was confirmed that CTE values vary depending on an existence of surface treatment.

Figure 14. Result of CTE with Different Amounts of Filler Content and Different Filler treatments

Figure 15 shows the SEM image of the tensile fracture surface with and without filler surface treatment. An interface between the resin and the filler was observed on the fracture surface without filler surface treatment. In contrast, an interface between the resin and the filler was not observed on the fracture surface with filler surface treatment.

Figure 15. SEM Images of Tensile Fracture Surface with and without Filler Surface Treatment

It was assumed that filler surface treatment was fundamental.

Figure 16, and 17 show the tensile strength and elongation at the lower temperature, and the TMA measurement, respectively. The new solder resist was designed based on simulation by 1) enhancing the tensile strength and elongation under the lower temperature, and 2) lower CTE.

Figure 16. Results of Tensile Test at Lower Temperature for Solder Resist with Enhanced Anti-crack Resistance

	Conventional SR	New SR
α_1	55-60 ppm	35-40 ppm
α_2	130-140 ppm	100-110 ppm
Tg	100-110°C	150-160°C

Figure 17. Results of TMA Measurement for Solder Resist with Enhanced Crack Resistance

The TST using the new solder resist was conducted for a model assuming the flip chip package. The details of the tested chip and substrate are described below (Figure 18 and Figure 19):

"Chip for Evaluation"

- * Chip Size: 20mm
- * Chip Thickness: 0.725mm±0.025mm
- * Pad Size: 80μm
- * Number of Pads: 2208 X 4 = 8832 PADS
- * Pad Pitch/Array: 200μm Pitch
- * Height of Bumps: 45μ [Cu Pillar]
- * Bump Composition: Cu+Sn-Ag [Cu Pillar]

Figure18. Chip Appearance and Chip Pad Specifications

"Substrate for Evaluation"

- * Substrate Structure: 4-2-4 Bu Base
- * Substrate Size: 50mm X 50mm X Approx. t1.0mm
- * Pad Size: φ10μm
- * Resist Opening Size: φ80μm
- * Pad Pitch: 200μm
- * Surface Treatment: Au Flush

Figure 19. Substrate Appearance and Substrate Pad Specifications

Implemented in accordance with the process shown in Figure 20, and the TST was conducted.

Figure 20. Mounting Workflow of Test Coupon for TST

The number of cracks after the TST is shown in Figure 21. For the solder resist strengthened with the filler surface treatment technology, no cracks were observed even after performing 1,000 cycles of TST, on the mount board with Cu Pillar connection. Thus, an overwhelmingly higher crack resistance was achieved compared with the conventional products.

Figure 21. Number of Cracks after TST

6. Conclusion

This paper has introduced a possible approach towards the high HAST reliability, the high crack resistance, and the high resolution for the solder resist designed for the next-generation packaging substrate. For HAST resistance, we have successfully established technology to enhance ion migration reliability through reduction of chlorine ion impurities and enhancement of anti-hydrolysis properties. For the crack resistance, a simulation has been designed to analyze the mechanism of cracking. Outstanding crack resistance was successfully achieved at the TST, with the solder resist strengthened based on the results from our simulation. For the resolution, during the patterning, attention is focused on the exposure wavelength and the refractive index to produce good resolution.

With the advancement in technologies, the package substrates will get more complicated in the future. It is expected that the solder resist for the package substrates should have higher performance and more important

functions. In order to understand the properties in the state of package substrate, combination testing with peripheral materials (build-up material, underfill, and epoxy molding compound (EMC) etc.) will be more important.

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