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**METHOD OF INCREASING THE ADHESION STRENGTH BETWEEN
EPOXY ENCAPSULANT AND ORGANIC SUBSTRATE BY GRAFT
COPOLYMERIZATION TECHNIQUE**

BACKGROUND OF THE INVENTION

A conventional integrated circuit (IC) package typically comprises several different types of materials. These materials include organic polymer encapsulants, metal frames, silicon dies, polymeric die attach materials and organic laminated substrates, as in the chip-on-board (COB) and Ball Grid Array (BGA) packages. The reliability of the package is intimately connected with the integrity of the interfaces between dissimilar materials. The presence of these different materials with vastly different thermal and chemical properties makes the interfaces vulnerable to delamination. For example, thermal expansion properties of silicon die and organic die-attach polymeric adhesive are quite different; silicon has a much lower coefficient of thermal expansion (CTE). Thus, when the package is exposed to a temperature excursion, these materials expand at different rates and the interface is subjected to stresses. Often, the stresses lead to debonding at the interface and resultant package failures.

The natural propensity of an IC package to absorb moisture has been known to create reliability problems. It has been shown by many researchers that polymer-metal interfaces are degraded by the absorbed moisture. Absorbed moisture in IC packages has also been known to lead to "pop-corn" failures. This occurs when the absorbed

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moisture expands at high temperature (e.g. during SMT solder reflow which occurs at temperature above 220° Celsius, discussed in greater detail below) causing delaminations and cracks in the package body.

FIGS. 1A-1D illustrate pop-corn cracking in a surface mount packaged semiconductor device 10. The surface mount package of device 10 includes a package body 12 which in this example is formed from a resin molding compound. The package body 12 encapsulates a semiconductor integrated circuit 14 bonded by a die-attach adhesive to a die pad 16. The package body 12 also supports leads 18, 20 which are part of a leadframe and allow electrical connection of the integrated circuit 10 to external circuitry.

FIG. 1A illustrates moisture absorption by the package body 12. The moisture is shown by arrows 22 and may be diffused into the package body 12 from an ambient or controlled environment while the device 10 is being stored between manufacturing operations.

FIGS. 1B-1D show a possible mechanism of pop-corn cracking during a solder reflow operation. The solder reflow operation is carried out at a temperature in the range between about 220° C to 260° C such that solder used in prior manufacturing steps will reflow. The reflow improves the strength and conductivity of any solder connections within the device 10. FIG. 1B shows that heating device 10, during the solder reflow operation, to a temperature of 220° C or more creates a high water vapor pressure in the pores of package body 12 at the interfaces with die attach pad 16 as well as in the bulk resin molding compound material. The interfaces tend to be



weaker than the bulk material due to factors such as poor adhesion, high pore densities and interfacial stress resulting from mismatch in the coefficient of thermal expansion (CTE) of the resin package body 12 and the die attach pad 16. The interface between the die-attach pad 16 and package body 12 is generally one of the weakest interfaces in the device 10. FIG. 1B indicates that peeling can occur at the interface 24 between die-attach pad 16 and package body 12 during the solder reflow operation.

FIG. 1C shows that the evaporation of absorbed moisture in combination with the peeling shown in FIG. 1B leads to a doming effect in region 26. A crack 28 begins to form in package body 12 at an interface with die-attach pad 16. FIG. 1D shows that the combination of high pressure steam exerted by vaporizing moisture and the accompanying thermal stresses become greater than the package body 12 can withstand, and the crack 28 then extends to an outer surface of the package to thereby vent the steam. It is apparent from FIGS. 1A-1D that moisture absorption by a plastic surface mount package can cause package failure, and that the relatively weak interface between the encapsulant and die-attach pad is often the point at which the failure originates. However, a reduction in moisture permeation and absorption in the package will reduce pop-corn failures.

These issues of material mismatch and moisture are particularly relevant to a Ball Grid Array (BGA) package. FIG. 2 illustrates a typical schematic diagram of an overmolded plastic (OMPAC) BGA package 30, wherein an epoxy based encapsulant (molding compound) 34 is molded on one side of the glass/epoxy substrate 38



carrying the silicon die. The OMPAC BGA package includes an IC chip 32 mounted on the top side of substrate 38 and connected to the upper solder resists 40 by wire bonds 44. A further solder resist 40 is layered on the bottom of substrate 38 and includes a plurality of solder balls 36. Main interfaces with which molding compound 34 contact include the solder resists and the IC chip. It is important for molding compound 34 to adhere closely to each interface and in particular, it is desirable that adhesion to the molding compound - solder resist interface of the surface of substrate 38 be as high as possible.

The adhesion strength or integrity of these various interfaces ultimately decides the reliability of the package. Degradation of the interface leads to defects such as delamination and cracks, especially at solder reflow temperatures. The robustness of the package is therefore critically linked to the integrity of these interfaces. Accordingly, a superior adhesion strength between the interfaces lead to better reliability. It follows that a weak adhesion between the molding compound and the solder resist renders the package susceptible to delamination, and especially to cracking during solder reflow.

Overmolded BGA packages are not the only examples where adhesion of the epoxy based IC encapsulant and solder resist layer is crucial. Other examples of susceptible packages include Glob Top BGA, chip-on-board (COB), tape automated bonding (TAB), or indeed any package wherein a solder resist film is used in conjunction with an epoxy based encapsulant. These include the use of underfill encapsulation for flip chip and die attache substrates.



However, BGA package reliability is considerably inferior to that of the established metal lead frame based packages, such as QFP. In general, overmolded BGA packages barely meet IPC level 3 requirement. For example, as described in "Reliability and Moisture Sensitivity Evaluation of 225-pin, 2 Layered Overmolded (OMPAC) Ball Grid Array Package" by B. Poborets, Q.S.M. Ilyas, M. Potter and J. Argyle, 45th ECTC, 434-439 (1995), a typical moisture experiment subjected a BGA package to a temperature of 30°C and a relative humidity of 60% for 192 hours; followed by three solder reflows. The BGA package experienced 50% delamination under the die due to moisture-induced package delamination cracking that occurred during the three solder reflows.

To overcome such typical delamination, prior art solutions have been primarily limited to experimenting with different solder resist and molding compound materials. For example, in the article "Development of Molding Compounds for BGA" by K. Oota and K. Shigeno, 45th ECTC, 78-85 (1995), four different molding compounds were tested with varying results. Unfortunately, the list of available molding compounds for packaging applications is very limited. Out of the handful of compounds that are commercially available, most do not fare very well in terms of strong adhesion properties at the molding compound - solder resist interface. This has been one of the major reasons for the poor reliability of packages involving overmolded BGA. Further, the choices in the solder resist materials are even more limited.

Currently, plasma is used for surface cleaning and treatment of organic laminated substrates to improve the adhesion of the substrate to an to epoxy IC



encapsulant. This process is called surface activation. However, the properties of a plasma treated surface is very time-dependent. As described in "Plasma Processing Notes: Surface Activation", March Instrument, Inc., 995-70, the plasma activated surface is unstable, causing the benefits of surface activation to disappear in a matter of hours.

In COB, TAB, and underfill/flip chips, the same situation exists; namely, adhesion optimization is sought primarily by a mix and match of the constituting materials. Process parameters have also been varied but have been limited to curing temperatures-profiles parameters, molding-dispersion parameters, and the like.

In any of the above adhesion techniques, the adhesion between the molding compound - solder resist interface arises from relatively weak Van der Wall type of interaction between the two materials. These Van der Wall interactions are insufficient to prevent undue stress due to thermal mismatch of the different materials or pop-corn failures due to moisture.

It is known to chemically modify the surface of synthetic polymer substrates to incorporate specific physicochemical properties, such as hydrophilicity, biocompatibility, adhesion and lubricative properties. Such chemical modifications include acid etching, X-ray irradiation, ultraviolet irradiation, electron beam bombardment, ozone treatment, corona discharge and plasma treatments. Recently, surface modification of synthetic polymer substrates have been performed using a method known as "surface graft polymerization". For example, the article entitled, "Surface Structures of Fluoropolymer, Polyolefin and Polyester Films After Modification



by Graft Polymerization", E.T. Kang, K.G. Neoh, K.L. Tan, F.C. Loh and D.J. Liaw, 5
Polym. Adv. Technol., 837-842 (1994), describes the characteristics of polymer
structures that have been treated with the graft polymerization process. However, the
Kang et al. article does not describe any specific relationship between graft
5 polymerization and adhesion, nor does Kang et al. suggest a workable technique for
increasing the adhesion properties in a semiconductor package between the molding
compound - solder resist interface.

It is therefore an object of the present invention to provide a process that
enhances the adhesion properties between an organic substrate and an epoxy
10 encapsulate.

Another object of the invention is to provide a bonding process for IC packages
by graft copolymerization.

A further object of the invention is to ensure that the surface of the grafted
organic substrate is substantially permanently stable.

15 An additional object of the invention is to reduce stress arising from thermal
mismatch between different materials in IC packages.

Yet a further object of the invention is to reduce pop-corn failure arising from
moisture absorption in IC packages.

Various other objects, advantages and features of the present invention will
20 become readily apparent from the ensuing detailed description and the novel features
which will be particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

These and other objectives are realized by a method of enhancing adhesion properties between an organic substrate, such as a solder resist, and an epoxy encapsulant, such as a molding compound, in an integrated circuit package, by graft copolymerization. The surface of the organic substrate is first optionally activated by, for example, treating the substrate with ozone. The activated substrate is then grafted with a predetermined monomer solvent, such as a solvent having glycidyl methacrylate, so that the encapsulant, when bonded to the substrate, will adhere securely thereto.

In another embodiment of this invention, a method of enhancing adhesion properties between an organic substrate and an epoxy encapsulant by graft copolymerization, first coats the surface of the substrate with a predetermined monomer in vapor form. The coated substrate is then grafted by exposing the substrate to near-UV illumination. Thereafter, the encapsulant is bonded to the graft modified substrate with chemically enhanced adhesion.

These embodiments describe a procedure whereby the adhesion strength of epoxy based solder resist and epoxy based encapsulants can be significantly enhanced by an inventive graft copolymerization technique for IC packages, in order to improve the package reliability. This procedure is based on a chemical modification of the substrate/solder resist surface and therefore, offers the most versatile solution to the interface adhesion deficiencies in package interfaces. Grafted polymers with epoxide



functionality on the solder resist reacts via covalent bonding with the hardener in the epoxy IC encapsulant to strongly bond to the IC encapsulant.

Chemical covalent bonding at the interface constitutes the best possible means of adhesion between two surfaces and is typically orders of magnitude stronger than conventional Van der Waals type of interaction. Another major advantage of the graft copolymerization method is that surface modification after grafting treatment is permanently stable, in sharp contrast to the time-dependent characteristic of surface activation by plasma treatment and etching.

BRIEF DESCRIPTION OF THE DRAWINGS

The following detailed description, giving by way of example and not intended to limit the present invention solely thereto, will best be understood in conjunction with the accompanying drawings in which:

FIGS. 1A-1D illustrate exemplary "pop-corn" cracking in a surface mount integrated circuit package;

FIG. 2 shows a conventional overmolded BGA package;

FIGS. 3A-3D schematically illustrates the chemical reactions formed by the grafting process in accordance with the present invention; and

FIG. 4 illustrates a grafted integrated circuit package in accordance with the present invention.



DETAILED DESCRIPTION OF THE INVENTION

FIGS. 3A-3D schematically illustrates the chemical reactions leading to the bonding of the graft-modified solder resist layer to the IC epoxy based encapsulant. In the graft copolymerization process employed here, glycidyl methacrylate monomers (GMA) with an epoxide function group was used to react with the solder resist layer. However, other monomers such as glycidyl acrylate and methallyl glycidyl ether, and the like, may be used as well. During transfer molding and curing of the epoxy molding compound, the amine curing agent in the hardener of the epoxy molding compound will react with the grafted epoxide function groups of the GMA in the same way as in a normal molding compound curing reaction. As a result, the adhesion of the solder resist to the molding compound will be substantially enhanced.

The mechanism of graft copolymerization is to transplant polymers of interest (for example, ones that will increase adhesion properties) in sufficient quantities and with enhanced spatial distribution on the substrate surface to allow subsequent surface functionalization. The process results in a permanently modified substrate surface, as described with reference to FIGS. 3A-3D.

FIG. 3A shows the solder resist (SR) substrate 45 prior to any treatment or modification. In FIG. 3B, the SR substrate is optionally treated with ozone, O_3 , 48. Such treatment activates the SR substrate by causing a chemical reaction on the surface, as shown in activated SR substrate 50. Instead of ozone, the surface of the SR substrate may be treated with plasma, corona discharge, UV-irradiation, X-ray irradiation or electron beam bombardment.



Further, prior to the optional SR substrate activation, the SR substrate 45 may be etched, if desired, by chemical or plasma etching (not shown) to provide a rough surface to further enhance friction and adhesion between the SR substrate and the molding compound.

5 FIG. 3C illustrates the grafting procedure in this inventive process. Monomer glycidyl methacrylate (GMA) 54 is illustrated for use as the grafting monomer solvent to be "grafted" onto the activated SR substrate 50. As previously stated, other monomers may also be used provided that they bond with the activated SR substrate and subsequently bond with the molding compound. As shown by graft-modified SR
10 substrate 55, GMA 54 is chemically bonded with activated SR substrate 50. This chemically modified surface of the SR substrate will subsequently form covalent bonds to the epoxy molding compound (EMC) 58 in FIG. 3D. To expedite the grafting step, UV light 52 may be concentrated on the substrate. Additionally, thermal light may provide the excitation necessary to speed up the grafting process.

15 EMC 58 is shown having an inherent amine curing agent from the EMC hardener, chemically illustrated as $\text{CH}_2\text{-O-NHRNH}_2$. As shown by reference numeral 60, the amine curing agent compound reacts with the graft-modified SR substrate 55 to form strong covalent bonds therebetween.

20 The process of FIGS. 3A-3D, employed a graft copolymerization technique carried out by the so-called solvent process, i.e. grafting monomers onto the SR substrate using a GMA grafting solvent. Example 1, described below, recites the results of an experiment utilizing the solvent process of FIGS. 3A-3D. Further, a



solvent-free process (not shown) may be utilized which is similar to the solvent process illustrated in FIGS. 3A-3D, except that the GMA monomer in FIG. 3C is transferred onto the substrate in vapor form by vaporization instead of by a monomer solvent, as described hereinlater with reference to Example 2. Whether the solvent or solvent-free process is used, the resultant grafted polymers are stable in nature which subsequently stabilizes the bonded interfaces.

EXAMPLE 1

In this experiment, the approximate process conditions of an overmolded BGA substrate test specimen were as follows:

Activation:

Ozone pretreatment in an ozone generator (Fischer, Model 500)

Oxygen flow rate: 50 liters/hour

Ozone generation rate: 2.5 grams/hour

Temperature: Room temperature

Treatment time: 10 minutes

Graft Copolymerization:

Graft copolymerization in a photochemical reactor

Grafting solution: 20 vol.% GMA in 1,4-dioxane

UV lamp: Schoeffel 150W

Temperature: Room temperature

Grafting time: 40 or 60 minutes



Post Cure Molding:

Temperature: 175° C

Bonding time: 5 hours

5 After grafting, the samples were dipped in 1,4-dioxane solvent for cleaning and to remove the ungrafted homopolymers. The transfer time from activation to graft copolymerization may be up to 3-4 hours resulting in good stability properties of the activated substrate. However, the grafting time can be greatly reduced if a high power UV or thermal lamp is employed.

10 The graft-modified substrate samples were subsequently overmolded using commercially available molding compounds. Standard transfer molding conditions and equipment were employed. FIG. 4 illustrates the completed BGA package 65 having superior adhesion properties between the molding compound 74 and the solder resist layer 68 via grafted polymer layer 66. As shown, the solder resist layer is mounted
15 on top of copper clad layer 70 (which provides a molding compound - copper interface) on glass/epoxy substrate 72.

 After the standard post mold cure step, the molded samples were subjected to a "pull test" by using an Instron Tensile Tester. This test methodology has been developed in order to quantitatively measure the interface adhesion strength between
20 the molding compound and the substrate. These measurements record the adhesion strength of the interface. The recorded values and the failure locations provide



information pertaining to the interface adhesion, as shown in TABLE 1, where "SR" represents the solder resist and "MC" represents the molding compound.

TABLE 1

S. No.	Pristine		Treatment 1		Treatment 2	
	No Treatment		Grafting time: 40mm		Grafting time: 60 min.	
	Adhesion, N/cm ²	Failure Mode	Adhesion, N/cm ²	Failure Mode	Adhesion, N/cm ²	Failure Mode
1	77.5	SR/MC	386.0	Mixture of Cu/SR and SR/MC	442.3	Mixture of Cu/SR and SR/MC
2	73.5	"	545.5	"	703.4	"
3	72.8	"	277.2	"	211.1	"
4	318.1	"	734.2	"	787.4	"
5	208.2	"	1006.0	"	131.2	Cu/SR
6	41.9	"	619.1	"	379.7	"
7	56.8	"	694.8	"	1004.0	"
8	153.3	"	1008.0	"	220.3	"
9	187.5	"	160.2	"	845.1	"
10	135.4	"	843.0	Cu/SR	412.3	"
11			470.5	"		
Mean	132.5		613.1		513.7	
Std Dev	86.7		279.1		301.6	
Min	41.9		160.2		131.2	
Max	318.1		1008.0		1004.0	



After modification by graft copolymerization, the adhesion strength at the molding compound - solder resist interface was increased by at least four times over the interface involving pristine test coupons without the inventive process.

Accordingly, the pull test confirms that the failure interface of the BGA test coupon shifts from the solder resist/epoxy molding compound interface in the pristine sample, to the solder resist/copper interface or to a mixture of solder resist/copper and solder resist/epoxy molding compound interfaces in the graft-modified sample. The failure interface corresponds to the weakest interface in the adhesion strength. The shifting of the failure interface from the solder resist/epoxy molding compound interface to other interfaces in the graft-modified substrate supports the adhesion strength test results. It also indicates that good adhesion of the solder resist to the epoxy molding compound is achieved through the graft copolymerization technique.

EXAMPLE 2

In the alternative solvent-free process for surface graft copolymerization, a BGA substrate with a pre-activated surface is first coated with a thin layer or thin film of liquid GMA monomers, for example by exposing the substrates to a monomer vapor under reduced pressure in an inert atmosphere chamber. Surface graft copolymerization is achieved by exposing the monomer-coated substrates to near-UV illumination for a period of about 30 minutes in the same inert atmospheric chamber. The unreacted monomers, oligomers and ungrafted homopolymers on the substrate



surface after graft copolymerization are then removed from the substrate surface by stripping with an organic solvent. The stripping solvents are chosen from the family of solvent for the GMA polymer, including 1,4-dioxane and acetone, and the like.

5 While several embodiments have been chosen to illustrate the invention, it will be understood by those skilled in the art that various changes and modifications can be made herein without departing from the scope or spirit of the invention as defined in the appended claims.





Claims

What is claimed is:

1. A method of enhancing adhesion properties between an organic substrate and an epoxy encapsulant, having an amine curing agent, in an integrated circuit package by graft copolymerization for reducing cracking and delamination in said package, comprising the steps of:

grafting by graft copolymerization predetermined monomers, having an epoxide function group, on the surface of said organic substrate to produce a graft modified substrate having said epoxide function group; and

bonding said epoxy encapsulant to said graft modified substrate;

wherein said amine curing agent in said epoxy encapsulant chemically reacts to said epoxide function group on said graft modified substrate to form covalent bonds which substantially enhances said adhesion properties.

2. The method of claim 1, further comprising the step of activating the surface of said organic substrate to stimulate said surface for subsequent polymerization.

3. The method of claim 2, wherein said organic substrate is an epoxy solder resin.





4. The method of claim 3, wherein each said monomer is a glycidyl methacrylate monomer.

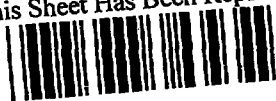
5. The method of claim 4, wherein said epoxy encapsulant is one of an epoxy molding compound encapsulant, an epoxy top-dispensing and printing encapsulant, an underfill encapsulant, and a die attache encapsulant.

6. The method of claim 2, wherein said step of activating activates said organic substrate by one of said ozone treatment, acid etching, X-ray irradiation, U-V radiation, electron beam bombardment, corona discharge, and plasma treatment.

7. The method of claim 2, further comprising the step of surface roughing the non-activated organic substrate by one of chemical and plasma etching.

8. The method of claim 7, further comprising the step of stripping any inherent unreacted monomers, oligomers and ungrafted homopolymers with an organic solvent.

9. The method of claim 8, wherein said organic solvent comprises at least one of 1,4-dioxane and acetone.





10. The method of claim 2, wherein said grafting step further includes the step of illuminating said organic substrate with a U-V lamp to reduce the amount of grafting time.

5 11. A method of enhancing adhesion properties between an organic substrate and an epoxy encapsulant, having an amine curing agent, in an integrated circuit package by graft copolymerization for reducing cracking and delamination in said package, comprising the steps of:

10 coating the surface of said organic substrate with predetermined monomers, having an epoxide function group;

grafting by graft copolymerization the monomer coated substrate by exposing the substrate to near-UV illumination for a predetermined period of time to produce a graft modified substrate having said epoxide function group; and

bonding said epoxy encapsulant to said graft modified substrate;

15 wherein said amine curing agent in said epoxy encapsulant chemically reacts to said epoxide function group on said graft modified substrate to form covalent bonds which substantially enhances said adhesion properties.

20 12. The method of claim 11, further comprising the step of activating the surface of said organic substrate to stimulate said surface for subsequent polymerization.





13. The method of claim 11, wherein said organic substrate is an epoxy solder resin.

14. The method of claim 13, wherein each said monomer is a glycidyl methacrylate monomer.

15. The method of claim 14, wherein said epoxy encapsulant is one of an epoxy molding compound, an epoxy top-dispensing and printing encapsulant, and an underfill material.

16. The method of claim 11, wherein said coating step comprises the step of exposing said organic substrate to a monomer vapor in an inert atmosphere chamber under a pressure lower than the standard atmospheric pressure.

17. The method of claim 15, wherein said organic substrate is exposed to said monomer vapor in said chamber for approximately 30 minutes.

18. The method of claim 11, further comprising the step of stripping any inherent unreacted monomers, oligomers and ungrafted homopolymers with an organic solvent.





19. The method of claim 18, wherein said organic solvent comprises at least one of 1,4-dioxane and acetone.

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