METHOD OF COATING FINE WIRES AND CURABLE COMPOSITION THEREFOR

BACKGROUND

Wire bonding is a low cost and flexible method for interconnection of semiconductors. In this technique a semiconductor die is electrically connected to circuitry on a substrate by fine electrically conductive wires. More wires in a package and smaller wire gaps are the trend in the integrated circuit packaging industry.

To protect the semiconductor and the wires from physical and environmental damage, they are collectively encapsulated in a thermosetting resin such as, for example, an epoxy resin. Common techniques include glob-top and dam and fill. In glob-top encapsulation, a volume of encapsulant is deposited on top of a component. The material flows downward, covering the component.

The effect of wire density is becoming increasingly apparent, especially on the flow pattern of the encapsulant during encapsulation processes and, hence, on the amount of wire sweep (that is, physical movement of the wires). A major factor limiting wire density of this widely used interconnect technology is wire sweep, which can lead to shorting during the encapsulation processes.

SUMMARY

In one aspect, the present disclosure provides a method of protecting wires during packaging of a semiconductor device, the method comprising:

providing a curable composition comprising at least one epoxy monomer, at least one free-radically polymerizable monomer, an effective amount of photoinitiator for the free-radically polymerizable monomer, an effective amount of thermal curative for the at least one epoxy monomer, wherein the curable composition is electrically non-conductive and essentially free of solvent;

providing a chip assembly comprising a substrate having a semiconductor die attached thereto, the semiconductor die being electrically connected to the substrate by a plurality of conductive wires;

spraying the curable composition onto at least the plurality of conductive wires;

free-radically polymerizing at least a portion of the at least one free-radically polymerizable monomer to convert the curable composition into a B-staged curable composition; and

thermally curing at least a portion of the at least one epoxy monomer.

In certain embodiments, the method further comprises encapsulating the semiconductor die. In certain embodiments, the curable composition is essentially free of particulates. In certain embodiments, the curable composition further comprises a flow additive (for example, an acrylic polymer). In certain embodiments, the at least one epoxy monomer comprises a monoepoxide and a polyepoxide. In certain embodiments, the at least one free-radically curable monomer comprises at least one (meth)acrylate monomer and at least one N-vinyllactam. The at least one (meth)acrylate monomer may comprise a poly(meth)acrylate monomer and a mono(meth)acrylate monomer.

In another aspect, the present disclosure provides a curable composition comprising at least one epoxy monomer, at least one free-radically polymerizable (meth)acrylate, at least one free-radically polymerizable N-vinyllactam, a flow additive comprising an acrylic polymer, an effective amount of photoinitiator, an effective amount of thermal curative for the at least one epoxy monomer, wherein the curable composition has a viscosity of less than 1000 millipascal-seconds, is essentially free of particulates, and is essentially free of solvent.

Advantageously, a curable composition according to the present disclosure contains little or no solvent and is sprayable. Once sprayed, the curable composition can be B-staged to prevent flow and provide protective insulation and increased stiffness for the wires that reduce or eliminate shorting caused by wire sweep. And, if desired, the epoxy monomer(s) in the B-staged curable composition may be co-polymerized with an epoxy encapsulant, thereby fixing the wires in the encapsulant.

DETAILED DESCRIPTION

Curable compositions suitable for use with the present disclosure comprise at least one epoxy monomer, an effective amount of thermal curative for the epoxy monomer(s), at least one free-radically polymerizable monomer, and an effective amount of photoinitiator for the free-radically polymerizable monomer.

Useful epoxy monomers include, for example, alicyclic and aromatic monoepoxides and polyepoxides, and combinations thereof.

Examples of useful monoepoxides include styrene oxide, allyl glycidyl ether, and glycidyl ethers of cardanol (for example, as "CARDOLITE 2513HP" from Cardolite Corp., Newark, NJ)

Examples of useful alicyclic polyepoxides include monomeric alicyclic polyepoxides, oligomeric alicyclic polyepoxides, and polymeric alicyclic polyepoxides. Exemplary alicyclic polyepoxides monomers useful in practice of the present invention include epoxycyclohexanecarboxylates such as, for example, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (for example, as "ERL-4221" from Dow Chemical Co., Midland, MI.) and 3,4-epoxy-2-methylcyclohexylmethyl 3,4-epoxy-2-methylcyclohexanecarboxylate; diglycidyl ether of cyclohexanedimethanol (for example, as "HELOXY 107" from Hexion Specialty Chemicals, Columbus, OH); and hydrogenated bisphenol A diglycidyl ether (for example, as available as "EPONEX 1510" from Hexion Specialty Chemicals).

Useful aromatic polyepoxides include, for example, monomeric aromatic polyepoxides, oligomeric aromatic polyepoxides, and polymeric aromatic polyepoxides. Exemplary aromatic polyepoxides include the polyglycidyl ethers of polyhydric phenols such as bisphenol A-type resins and their derivatives; epoxy cresol-novolac resins; Bisphenol-F resins and their derivatives; epoxy phenol-novolac resins; and glycidyl esters of aromatic carboxylic acids (for example, phthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, trimellitic acid triglycidyl ester, and pyromellitic acid tetraglycidyl ester), and mixtures thereof. Commercially available aromatic polyepoxides include, for example, those aromatic polyepoxides having the trade designation "EPON" (for example, "EPON 828", "EPON 862", "EPON 1001F, "EPON DPL-862" and "EPON HPT-1079"), available, for example, from Hexion Specialty Chemicals; and aromatic polyepoxides

having the trade designations "DER", "DEN" (for example, "DEN 438", and DEN 439"), and "QUATREX", available, for example, from Dow Chemical Co.

The at least one epoxy monomer is typically present in an amount of from 20 to 50 percent by weight, more typically in an amount of from 30 to 50 percent by weight, and still more typically in an amount of from 35 to 45 percent by weight, based on the total weight of the curable composition, although this is not a requirement.

An effective amount of thermal curative for the at least one epoxy monomer is included in the curable composition such that it can be sufficiently cured to develop a C-stage. Hence, the term "effective amount of thermal curative" refers to at least a minimum quantity. The precise amount will necessarily vary due to formulation and curing variables, but it is typically 10 percent by weight or less based on the total weight of the curable composition.

Useful thermal curatives for the polyepoxide(s) include acid curatives and base curatives. Examples of useful curing agents include boron trifluoride complexes such as, for example, $BF_3 \cdot Et_2O$ and $BF_3 \cdot H_2NC_2H_4OH$; polyamines such as, for example, bis(4-aminophenyl)sulfone, bis(4-aminophenyl)ether, and 2,2-bis(4-aminophenyl)propane; aliphatic and aromatic tertiary amines such as, for example, dimethylaminopropylamine; fluorenediamines; and modified amine curing agents such as those commercially available from Air Products and Chemicals, Allentown , PA, under the trade designation "ANCAMINE " (for example, "ANCAMINE 2337S", "ANCAMINE 2014", and "ANCAMINE 2441") and from Ajinimoto, Japan, "AJICURE" (for example, "AJICURE PN23" and "AJICURE M353"); imidazoles such as, for example, methylimidazole and 2,4-diamino-6-(2'-methylimidazolyl-(1'))-ethyl-s-triazine hexakis(imidazole)nickel phthalate); hydrazines such as, for example, adipohydrazine; guanidines, such as, for example, tetramethylguanidine and dicyandiamide (cyanoguanidine, also commonly known as DiCy); and combinations thereof.

Examples of free-radically polymerizable monomers include mono(meth)acrylate monomers, poly(meth)acrylate monomers (that is, having a plurality of acryl groups), styrene, butadiene, maleimides, maleic anhydride, and N-vinylamides (including N-vinyllactams). As used herein, the term "(meth)acryl" encompasses both methacryl and/or acryl. For example, a poly(meth)acrylate monomer may have only acrylate groups, only methacrylate groups, or a combination of acrylate and methacrylate groups.

Useful free-radically polymerizable mono(meth)acrylates include, for example, phenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and (meth)acrylic esters of non-tertiary alcohols having from about 4 to about 12 carbon atoms in the alcohol moiety, and combinations thereof. Included in this latter class of (meth)acrylic esters are butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, decyl (meth)acrylate, and dodecyl (meth)acrylate.

Useful free-radically polymerizable poly(meth)acrylate monomers include, for example, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,2-ethylene glycol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, and urethane and epoxy di(meth)acrylate oligomers available under the trade designation "EBECRYL" (for example, "EBECRYL 230", "EBECRYL 3605", and "EBECRYL 8804") from UCB Radcure, Smyrna, Ga., and "CN" (for example, "CN 104") from Sartomer Co., Exton, PA, and combinations thereof.

Examples of N-vinylamides include N-vinylpyrrolidone, N-vinylcaprolactam, and N-vinylformamide.

Typically, a combination of one or more free-radically polymerizable monomer(s) is used. The at least one free-radically polymerizable monomer is typically present in an amount of from 30 to 70 percent by weight, more typically in an amount of from 40 to 65 percent by weight, and still more typically in an amount of from 50 to 60 percent by weight, based on the total weight of the curable composition, although this is not a requirement.

An effective amount of photoinitiator for the at least one free-radically curable monomer is included in the curable composition such that it can be sufficiently cured to B-stage (that is, sufficiently cured that it will soften but not melt if heated) the curable composition upon photopolymerization. Hence, the term "effective amount of photoinitiator" refers to at least a minimum quantity. The precise amount will necessarily vary due to formulation and curing variables, but it is typically 10 percent by weight or less based on the total weight of the curable composition. Typically, lower molecular weight photoinitiators are used in total amounts of about 0.001 to about 4 percent by weight based on the total weight of the curable composition, while higher molecular weight photoinitiators are used in total amounts of about 0.1 percent to about 8 percent by weight based on the total weight of the curable composition.

Useful photoinitiators include, for example, substituted acetophenones such as 2,2-dimethoxy-2-phenylacetophenone; benzoin ethers such as benzoin methyl ether and substituted benzoin ethers such as anisoin methyl ether; substituted alpha-ketols such as 2-methyl-2-hydroxypropiophenone; benzophenone and its derivatives; phosphine oxides; polymeric photoinitiators; and combinations thereof. Many useful photoinitiators are commercially available from sources such as, for example, Ciba Specialty Chemicals, Tarrytown, NY, under the trade designation "IRGACURE" (for example, "IRGACURE 184", "IRGACURE 651", "IRGACURE 369", and "IRGACURE 907") and "DAROCUR" (for example, "DAROCUR 1173", "DAROCUR MBF", "DAROCUR TPO", and "DAROCUR 4265"), and under the trade designation "ESCACURE" from Sartomer Co., Exton, PA.

In order to serve as electrical insulators, curable compositions are electrically nonconductive.

While not required, the curable compositions may further contain minor amounts of one or more additive(s) such as, for example, surfactant(s), flow additive(s), dye(s), pigment(s), inhibitor(s), and /or coupling agent(s).

Any optional flow additive may be included in the curable composition, for example, to facilitate even coating of the wires. Typically, any such flow additive will be in an amount of less than 3 percent, more typically in an amount of less than 1 percent based on the total weight of the curable composition. One exemplary useful flow additive is an acrylic polymer in solution available as "TEGO ZFS 460" from Tego Chemie Service GmbH, Essen, Germany.

Advantageously, the curable compositions are formulated as essentially solvent-free, or even totally free of solvent. As used herein, the term "essentially solvent-free" means containing less than about one percent by total weight of solvent based on the total weight of the curable composition. The term "solvent" refers collectively to any volatile organic compound(s) (not reactive with other components that are present) added for the purpose of solvating at least some of the remaining components of a composition. Examples include toluene, heptane, ethyl acetate, methyl ethyl ketone, acetone, and mixtures thereof.

In practice, the curable composition is typically prepared from its constituent parts using a conventional mixing technique, for example, gentle rolling, roller milling, or ball

milling. In some cases, it may be useful to heat the polyepoxide and/or free-radically polymerizable monomers (for example, up to about 80 °C) to facilitate mixing.

To facilitate flow, and reduce the chance of spray nozzle clogging, the curable composition is typically essentially free of (that is, containing less than one percent by weight of the total weight of the curable composition), or even completely free of particulates, however this is not a requirement. Further, the viscosity of the curable composition is typically less than 1000 centipoise (1000 millipascal-seconds), more typically less than 500 millipascal seconds, although this is not a requirement.

The chip assembly has a substrate with a semiconductor die attached thereto. The semiconductor die is typically electrically connected to the contact pads on the substrate by a plurality of conductive wires (typically gold wires, although other conductive metals and alloys may also be used). Examples of such assemblies are well known in the integrated circuit packaging art and are discussed, for example, in U. S. Pat. No. 6,750,533 B2 (Yu-Po et al.) in col. 1, line 12 to col. 2, line 34.

A curable composition is applied to the conductive wires, and optionally onto the at least a portion of the substrate and /or semiconductor die by spraying. Examples of useful spraying techniques include, spray jet and air brush spraying.

Once applied to the chip assembly, the curable composition is then exposed to actinic radiation (for example, ultraviolet and/or visible light) that decomposes at least a portion of the photoinitiator and causes free-radical polymerization of the at least one free-radically polymerizable monomer sufficient to result in a B-staged (that is, sufficiently cured that it will soften but not melt if heated) curable composition. Sources of actinic (for example, ultraviolet (UV)) radiation include, for example, low, medium, or high pressure mercury lamps, lasers, and xenon flash lamps.

Optionally, at this point the B-staged curable composition may be heated (for example, in an oven) under conditions (for example, time and temperature) to sufficiently cure the epoxy monomer(s) to achieve a C-stage cure (wherein the curable material has become relatively insoluble and infusible). In such a case, an encapsulant (for example, an epoxy resin glob top) may be applied to the chip assembly to encapsulate the semiconductor die and conductive wires.

Alternatively, the encapsulant may be applied to the chip assembly while the curable composition remains in the B-stage and then the combination is heated to achieve

a C-stage cure. In such a case the curable composition will typically chemically bond to an epoxy encapsulant thereby reducing the likelihood of subsequent delamination (for example, due to thermal cycling).

It will also be noted, that even in the former instance wherein the B-staged curable composition is cured to the C-stage prior to applying an epoxy encapsulant, there may typically be some residual epoxide groups available for grafting to the epoxy encapsulant.

Objects and advantages of this invention are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and, details, should not be construed to unduly limit this invention.

EXAMPLES

Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight.

EXAMPLE 1

Composition A was prepared by combining: 42.5 parts of an epoxy monomer (a polymer of dicyclopentadiene concentrate, phenol and epichlorohydrin, "TACTIX 756" from Huntsman Advanced Materials Americas, Brewster, NY); 44.2 parts of phenoxyethyl acrylate ("AGEFLEX PEA" from Ciba Specialty Chemicals, Tarrytown, NY); 10.8 parts of N-vinylcaprolactam; 1.2 parts of 1-cyanoethyl-2-ethyl-4-methylimidazole ("MEZCN" from Shikoku Chemicals Corp., Kagawa, Japan); 0.9 parts of photoinitiator (CAS No. 119313-12-1, "IRGACURE 369" from Ciba Specialty Chemicals); and 0.4 parts of an acrylic polymer in solution (flow additive) ("TEGO ZFS 460" from Tego Chemie Service GmbH, Essen, Germany). The composition had a viscosity of less than 1000 millipascal-seconds.

A first portion of Composition A was sprayed using a sprayer ("PREVAL SPRAYER" from Precision Valve Corp., Yonkers, NY) onto a first gold-plated metal coupon.

A second portion of Composition A was sprayed as done with the first portion onto a second gold-plated metal coupon and irradiated using an "H-type" microwave powered electrodeless lamp, Model F300S, available from Fusion UV Systems, Gaithersburg, MD,

operated at a conveyor speed of 20 ft/min (6.1 m/min) to B-stage the composition. The ultraviolet light dosage was measured using an energy meter ("UV POWER PUCK" from EIT, Sterling, VA) at 485 mJ/cm^2 UV-A and 448 mJ/cm^2 UV-B.

In both cases, Composition A wetted out on the gold-plated metal coupon providing a smooth continuous coating.

EXAMPLE 2

Composition A was prepared by combining: 38.9 parts of an epoxy monomer (a polymer of dicyclopentadiene concentrate, phenol and epichlorohydrin, "TACTIX 756" from Huntsman Advanced Materials Americas); 4.3 parts of an epoxy monomer (epoxidised cardanol diluent, "CARDOLITE 2513HP" from Cardolite Corp., Newark, NJ); 43.1 parts of phenoxyethyl acrylate ("AGEFLEX PEA" from Ciba Specialty Chemicals); 10.6 parts of N-vinylcaprolactam; 1.8 parts of 1-cyanoethyl-2-ethyl-4-methylimidazole ("MEZCN" from Shikoku Chemicals Corp.); 0.9 parts of photoinitiator (CAS No. 119313-12-1, "IRGACURE 369" from Ciba Specialty Chemicals); and 0.4 parts of an acrylic polymer in solution (flow additive, "TEGO ZFS 460" from Tego Chemie Service GmbH). The composition had a viscosity of less than 1000 millipascal-seconds.

A first portion of Composition B was sprayed using a sprayer ("PREVAL SPRAYER" from Precision Valve Corp.) onto a third gold-plated metal coupon.

A second portion of Composition B was sprayed as done with the first portion onto a fourth gold-plated metal coupon and irradiated as in Example 1.

In both cases, Composition B wetted out on the gold-plated metal coupon providing a smooth continuous coating.

The resultant four coated gold-plated metal coupons from Examples 1 and 2 were placed in parallel position in a rack such that the plates tilted greater than 45 degrees from horizontal. The rack was then placed in an oven set at 120 °C for 1 hour. The coatings that were cured to B-stage by irradiation retained their original coated shape during thermal curing. The samples that were not cured to B-stage by irradiation flowed down the gold coupons and dripped off the bottom during thermal curing.

What is claimed is:

1. A method of protecting wires during packaging of a semiconductor device, the method comprising:

providing a curable composition comprising at least one epoxy monomer, at least one free-radically polymerizable monomer, an effective amount of photoinitiator an effective amount of photoinitiator for the free-radically polymerizable monomer, an effective amount of thermal curative for the at least one epoxy monomer, wherein the curable composition is electrically non-conductive and essentially free of solvent;

providing a chip assembly comprising a substrate having a semiconductor die attached thereto, the semiconductor die being electrically connected to the substrate by a plurality of conductive wires;

spraying the curable composition onto at least the plurality of conductive wires;

free-radically polymerizing at least a portion of the at least one free-radically polymerizable monomer to convert the curable composition into a B-staged curable composition; and

thermally curing at least a portion of the at least one epoxy monomer.

2. The method of claim 1, wherein the curable composition is essentially free of particulates.

3. The method of claim 1 or claim2, wherein the curable composition further comprises a flow additive.

4. The method of any one of claims 1 to 3, wherein the at least one free-radically curable monomer comprises at least one (meth)acrylate monomer and at least one N-vinyllactam.

5. The method of any one of claims 1 to 4, wherein the at least one (meth)acrylate monomer comprises a poly(meth)acrylate monomer and a mono(meth)acrylate monomer.

6. The method of any one of claims 1 to 5, wherein the at least one epoxy monomer comprises a monoepoxide and a polyepoxide.

7. The method of any one of claims 1 to 6, further comprising encapsulating the semiconductor die.