Abstract:
The invention relates to an oligomeric adduct of bismaleimide and a diamine which is prepared via a Michael addition reaction. The maleimide is extended with the diamin; in some embodiments, the maleimide is extended by an amine in combination with a thiol. The adducts are suitable for use as adhesives, coatings, and encapsulant, particularly for use within the microelectronics packaging industry as a coating for the inactive face of a silicon wafer.
BACKGROUND OF THE INVENTION

[0001] This invention relates generally to oligomeric compounds that are adducts of bismaleimide compounds and diamines. The oligomers are end-capped with maleimide functionality and are extended using amino linkages. These compounds are useful as adhesives, coatings, and encapsulants for various fabrication steps in the semiconductor packaging industry.

[0002] Bismaleimides represent one class of thermosetting resins that have found use in the microelectronic packaging industry. Bismaleimides are capable both of homopolymerization in the presence of free radicals or photoinitiators and of polymerization with other free-radical curing monomers (e.g., acrylates, methacrylates, styrenics, vinyl ethers, vinyl esters, allyl monomers, olefins, and the like). They may also be polymerized in the presence of co-monomers via Diels-Aider, -ene, and Michael addition mechanisms. As used in this specification and the claims, curing will mean polymerization.

[0003] Commercially available maleimide thermosetting resins are noted for their high modulus, and excellent resistance to thermal degradation. However, these thermoset compositions are also brittle, which causes them to fracture with shock after cure. Higher molecular weight maleimides would help to solve the brittleness problem, but for many compositions, the additional molecular weight requires higher levels of diluent to achieve dispensability. With higher levels of diluent, outgassing of the diluent upon cure increases, which increases the likelihood of voids in the cured maleimides. Voids lead to potential failure of the adhesive or encapsulant prepared from the maleimide and failure of the ultimate electronic device.

[0004] Another suitable use for solid maleimide oligomers is in next generation wafer backed coating (WBC) formulations. WBC formulations typically are adhesives applied directly to the inactive face of a silicon semiconductor wafer before the wafer is singulated into individual dies. Requirements for this material include controlled solubility for better open print times, greater toughness allowing higher dicing speeds, and
improved flow. Accordingly, there is a continuing need for maleimide compounds that can address the challenges facing the microelectronic packaging industry.

SUMMARY OF THE INVENTION

[0005] This invention is an oligomeric adduct of a bismaleimide and a diamine, or a bismaleimide and a diamine and a dithiol, prepared via a Michael addition reaction. The maleimide is extended with the diamines, or with the diamine in combination with a dithiol. The oligomers are suitable for use as adhesives, coatings, and encapsulants, and have particular use within the semiconductor packaging industry.

[0006] In one embodiment, this invention is a curable composition suitable for adhering semiconductor dies or semiconductor packages to a substrate, or for coating the inactive side of a semiconductor wafer prior to singulation into individual dies, known as wafer-backed coating (WBC). The curable composition comprises the adduct of a bismaleimide and a diamines, or of a bismaleimide and a diamine and a dithiol, a curing agent, optionally a filler, and optionally a solvent.

[0007] The molar ratio of starting maleimide to amine, or to amine and thiol, may be any that produces an oligomer effective in molecular weight, viscosity, solubility, and toughness for the intended end use. That ratio can be any within the range of 1:1 to 99:1. The amine and thiol can be present in any selected proportion. In one embodiment the ratio will be in the range of 1:1; in another embodiment the ratio will be in the range of 2:1; and in yet another embodiment the ratio will be in the range of 5:1. It will be understood by those skilled in the art that as molecular weight increases, solubility may decrease, and viscosity and toughness (as measured by modulus) will increase.

DETAILED DESCRIPTION OF THE INVENTION

[0008] In designing the oligomeric adducts of bismaleimide and diamine, or of bismaleimide and diamines and dithiol, the practitioner may use one or more bismaleimides with one or more diamines and dithiols within the molar ratios described above. The ability to use a number of bismaleimides, diamines, and dithiols as starting materials expands the repertoire of oligomeric adducts open to the practitioner and permits the design of products with specific performance properties related to solubility, viscosity, and toughness.
Bismaleimides suitable for use include solid aromatic bismaleimide (BMI) resin powders for having the structure in which X is an aromatic group.

Exemplary aromatic groups include:
[0011] Bismaleimide resins having these X bridging groups are commercially available, and can be obtained, for example, from Sartomer (USA) or HOS-Technic GmbH (Austria)

[0012] Additional exemplary maleimides include those having the generic structure

\[ \left( \begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{O}
\end{array}
\end{array} \right)_{n}^{X^1} \]

in which \( n \) is 1 to 3 and \( X^1 \) is an aliphatic or aromatic group. Exemplary \( X^1 \) entities include, poly(butadienes), poly(carbonates), poly(urethanes), poly(ethers), poly(esters), simple hydrocarbons, and simple hydrocarbons containing functionalities such as carbonyl, carboxyl amide, carbamate, urea, or ether. These types of resins are commercially available and can be obtained, for example, from National Starch and Chemical Company and Dainippon Ink and Chemical, Inc.

[0013] Specific preferred maleimides include

\[ \text{N} \quad \text{O} \quad \text{O} \quad \text{O} \]

in which \( C_{36} \) represents a linear or branched chain (with or without cyclic moieties) of 36 carbon atoms,

\[ \text{N} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \]

Suitable diamines are any of those having the structure $\text{NH}_2 - \text{X} - \text{NH}_2$ in which $\text{X}$ is an aliphatic or aromatic hydrocarbon. The structure and molecular weight of the diamines can be any suitable for use in the desired final composition. A wide variety of diamines is available commercially. In some embodiments, the diamine is selected from the group consisting of $2,2$-bis [4-(4-aminophenoxy) phenylpropane], $4,4'$-diaminodiphenyl-methane, and $2,2$-bis [4-(4-aminophenoxy) phenylmethane], $4,4'$-diamino-3,3'-dimethylidiphenylmethane, $4,4'$-(1,3-phenylenedioxy)-d tantane, 1,4 phenylene diamine.

Suitable dithiols are any of those having the structure $\text{SH} - \text{X} - \text{SH}$ in which $\text{X}$ is an aliphatic or aromatic hydrocarbon. The structure and molecular weight of the dithiols can be any suitable for use in the desired final composition. A wide variety of dithiols is available commercially. In some embodiments, the dithiol is selected from the group consisting of $4,4'$-thiobisbenzenethiol, 2-mercaptoethyl sulfide, or Thioplast G4 from Akcros Chemicals.

Initiators for curable compositions containing N-vinylformamide compounds are compounds that can produce radical or cationic initiating species, when triggered by heat (thermal initiators) or electromagnetic radiation (photoinitiators). The initiator will be present in an amount of 0.01 to 10% by weight of the total resin.

Suitable radical thermal initiators include peroxides, such as benzoyl peroxide, lauroyl peroxide, octanoyl peroxide, butyl peroctoate, dicumyl peroxide, acetyl peroxide, para-chlorobenzoyl peroxide and di-t-butyl diperphthalate; 1,1-di-(tert-amyl-peroxy)-cyclohexane; azo compounds such as azoisobutylonit pIe, 2,2-azobispropane, 2,2'-
Commercially available azo initiators are those available from Wako Specialty Company, such as those sold under the tradenames VA-044, VA-057, VA-085, V-70, VF-096, V-65, V-601, V-59, V-40, VF-096, V-30, and those available from Akzo Nobel, such as those sold under the tradenames Perkadox ACCN, Perkadox AIBN, Perkadox AMBN-GR, and those available from Dupont, such as those sold under the tradenames Vazo-52, Vazo-64, Vazo-67 and Vazo-88.


In some embodiments, both photoinitiator and thermal initiation may be desirable. For example, curing of a photoinitiator-containing adhesive can be started by UV irradiation, and a later processing step, curing can be completed by the application of heat to accomplish a free-radical cure. Both UV and thermal initiators may therefore be added to the adhesive composition.

For some applications, one or more fillers or spacers, or both, may be added to the curable composition and usually are added for improved Theological properties, stress reduction, and bondline control. Examples of suitable nonconductive fillers include alumina, aluminum hydroxide, silica, vermiculite, mica, wollastonite, calcium carbonate, titania, sand, glass, barium sulfate, zirconium, carbon black, organic fillers, and organic polymers including but not limited to halogenated ethylene polymers, such as, tetrafluoroethylene, vinylidene fluoride, vinyl fluoride, vinylidene chloride, and vinyl chloride. Examples of suitable conductive fillers include carbon black, graphite, gold, silver, copper, platinum, palladium, nickel, aluminum, silicon carbide, boron nitride, diamond, and alumina. The particles may be of any appropriate size ranging from nano size to several mm, depending on whether they are used as fillers or spacers (spacers typically being the larger size particles with more uniformity of size). The choice of such size for any particular end use is within the expertise of one skilled in
the art. Filler may be present in any amount determined by the practitioner to be suitable for the chosen end use.

[0021] Die attach and WBC applications require oligomeric maleimides imparting strength, toughness, and heat resistance, but which also dissolve in low boiling solvents and exhibit excellent workability. The oligomeric maleimides extended with diamines and dithiols of this invention are typically solid resins and are suitable for WBC compositions. The molecular weight and viscosity of the inventive oligomeric maleimides extended with diamines and dithiols can be tailored by proper selection of the maleimide(s) and diamine or dithiol extender(s) used in the Michael addition reactions and their relative molar ratios.

[0022] The invention maleimide/diamine adduct is present in the composition from 2 weight percent to about 98 weight percent (wt %) based on total weight of the composition. In other embodiments, one or more co-monomers may be present in the composition from 10 wt% to about 90 wt% based on total weight of the composition. Such comonomers include, for example, acrylates, methacrylates, maleimides, vinyl ethers, vinyl esters, styrenic compounds, allyl functional compounds, and the like.

[0023] The time and temperature curing profile for each composition will vary, and different compositions can be designed to provide the curing profile that will be suited to the particular industrial manufacturing process. In general, these compositions will cure within the range of 70°C to 250°C and curing will be effected within the range of ten seconds to three hours.

[0024] In certain embodiments, the adhesive compositions may contain compounds that lend additional flexibility and toughness to the resultant cured adhesive. Such compounds may be any thermoset or thermoplastic material having a Tg of 50°C or less, and typically will be a polymeric material characterized by free rotation about the chemical bonds, the presence of ether groups, and the absence of ring structures. Suitable such modifiers include polyacrylates, pofy(butadiene), polyTHF (polymerized tetrahydrofuran, also known as poly(1,4-butandiol)), CTBN (carboxy-terminated butadiene-acrylonitrile) rubber, and polypropylene glycol. When present, toughening compounds may be in an amount up to about 15 percent by weight of the invention maleimide/diamines adduct.
Inhibitors for free-radical cure may also be added to the adhesive compositions described herein to extend the useful shelf life of compositions containing the invention compounds. Examples of these inhibitors include hindered phenols such as 2,6-di-tert-butyl-4-methylphenol; 2,6-di-tert-butyl-4-methoxyphenol; tert-butyl hydroquinone; tetrakis(methylene-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))benzene; 2,2'-methylenebis(6-tert-butyl-p-cresol), and 1,3,5-trimethyl-2,4,6-tris(3',5'-di-tert-butyl-4-hydroxybenzyl)benzene. Other useful hydrogen-donating antioxidants include derivatives of p-phenylenediamine and diphenylamine. It is also well known in the art that hydrogen-donating antioxidants may be synergistically combined with quinones, and metal deactivators to make a very efficient inhibitor package. Examples of suitable quinones include benzoquinone, 2-tert-butyl-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone, and 2,5-dichloro-1,4-benzoquinone. Examples of metal deactivators include N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine, oxalyl bis(benzylidenehydrazide); and N-phenyl-N'-(4-toluenesulfonyl)-p-phenylenediamine. Nitroxyl radical compounds such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyl, free radical) are also effective as inhibitors at low concentrations. The total amount of antioxidant plus synergists typically falls in the range of 100 to 2000 ppm relative to the weight of total base resin. Other additives, such as adhesion promoters, in types and amounts known in the art, may also be added.

EXAMPLES

In all of the following examples, "n" in the structure is an integer that will vary and in each reaction mix, there will be oligomers with different "n" values. Thus, for purposes herein, n is a variable integer. Although the exact integer for each reaction product will be indefinite because of this mix, an average integer can be determined based on the stoichiometry of the starting materials and by the molecular weight of the product, and in general n will be in the range of 1 to 5.
The above maleimide/diamine adduct was prepared from a maleimide having the structure in which $C_{36}$ represents a linear or branched chain (with or without cyclic moieties) of 36 carbon atoms, hereinafter BMI-1, and 4,4’ diamino-diphenylmethane according to the following procedure.

BMI-1 (100.0 grams, 0.1087 mol), 4,4’ diaminodiphenylmethane (<10.77 grams, 0.05435 mol) and toluene (100 mL) were charged to a 500 mL 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The reaction flask was purged with nitrogen while mixing at 400 rpms in an oil bath preheated to 90°C. By the time the reaction temperature reached 65°C, all solids were dissolved forming a clear gold solution. Five drops of acetic acid were then added. At a temperature of 80°C, the reaction time was started and heating and mixing were continued for 48 hours. During this time, the reaction changed from a clear gold solution to a dark red-orange solution. After cooling to room temperature, the reaction solution was decanted away from minor gel on the flask sides and solvent was stripped from the solution on a roto-evaporator. The result was 121 grams of viscous dark amber liquid. This product was vigorously mixed in ethanol (300 mL) for 30 minutes and then left to settle for 60 minutes. The opaque yellow ethanol top layer was decanted from the viscous dark brown bottom layer and discarded. This mix/settle/decant cycle was repeated three more times. It appeared that the ethanol washes removed residual diamine based on TLC (toluene/THF 1/1 vol). Solvent was stripped from the product on a roto-evaporator at 40°C and a Kugelrohr at 60°C. Sixty grams of dark red-brown oil product were obtained. The structure was confirmed by $^1$H NMR.
EXAMPLE 2. SYNTHESIS OF

The above maleimide/diamine adduct was prepared according to the following procedure from 4,4’ dianodiphenyl-methane and a maleimide, hereinafter BMI-2, having the structure

BMI-2 (50.0 grams, 0.0991 mol), 4,4’ dianodiphenylmethane (9.81 grams, 0.0495 mol) and toluene (50 mL) were charged to a 250 mL 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The reaction flask was purged with nitrogen while mixing at 200 rpms in an oil bath preheated to 90°C. By the time the reaction temperature reached 60°C, all solids were dissolved forming a deep gold solution. Five drops of acetic acid were then added. At 80°C, the reaction time was started and heating and mixing continued for 46 hours. During this time the reaction changed from a clear orange solution to a thin very dark red solution. The reaction solution was then decanted away from black gel formed on the flask sides. Solvent was stripped from the red solution by roto-evaporator for 1 hour at 40°C and by Kugelrohr for three hours at 60°C. The result was 62 grams of thick dark red oil. The oil was next mixed in ethanol (150 mL) for 30 minutes and then left to settle for 30 minutes. The opaque yellow ethanol top layer was decanted from the viscous dark brown bottom layer and discarded. This mix/settle/decant cycle was repeated three more times.
Solvent was stripped from the product using a roto-evaporator at 4°C and a Kugelrohr at 80°C. Sixty grams of product were obtained. The structure was confirmed by 1H NMR.

[0033] EXAMPLE 3. SYNTHESIS OF

![Diagram]

[0034] The above maleimide/diamine adduct was prepared from a maleimide, hereinafter BMI-3, having the structure

![Diagram]

and 4,4' diaminodiphenylmethane according to the following procedure.

[0035] BMI-3 (70.0 grams, 0.1203 mol) and 4,4' diaminodiphenylmethane (11.9 grams, 0.0602 mol) were charged to a 100 ml 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The reaction flask was purged with nitrogen while mixing at 300 rpms in an oil bath preheated to 110°C. By the time the reaction temperature reached 83°C, all solids were dissolved forming a clear red solution. Five drops of acetic acid were then added. At a temperature of 80°C, the reaction time was started and heating and mixing continued for 11 hours. During this time, the reaction changed from a thin red solution to a thick red-orange solution. After cooling to room temperature, the reaction solution was dissolved in dichloromethane (600 ml). This organic solution was washed twice with 10% (wt.) hydrochloric acid to remove residual diamine. Brine was used to break the emulsions formed by the wash. The organic
fraction was dried over magnesium sulfate (50 grams) and filtered. Solvent was then stripped from the clear copper-colored filtrate by roto-evaporator at 40°C and Kugelrohr at 60°C resulting in a thick amber liquid product. The structure was confirmed by 1H NMR.

[0036] EXAMPLE 4 SYNTHESIS OF

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{O} & \quad \text{N} \\
\text{N} & \quad \text{O} \\
\text{O} & \quad \text{N} \\
\text{N} & \quad \text{O}
\end{align*}
\]

from an aromatic-linked maleimide extended with an amine 2,2-bis[4-(4-aminophenoxy)phenylpropane].

[0037] A bismaleimide (obtained as Matrimid 5292A from Huntsman Advanced Materials Americas Inc., CAS# 13676-54-5, and hereinafter BMI 5292A) (26.0 grams, 0.0726 mol), 2,2-bis[4-(4-aminophenoxy)phenylpropane] (14.0 grams, 0.0341 mol), and 2-methoxyethanol (20 grams) were charged to a 100 mL 3-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The flask was secured in an oil bath preheated to 130°C and the contents were mixed at 300 rpms. Gradually, the reaction changed from a yellow paste to a dark brown solution at 105°C. Heating was continued for 2.5 hours while a reaction temperature was maintained between 100° and 110°C. The thick dark red reaction product was cooled to room temperature in the flask. The flask was chilled in dry ice causing the product to freeze and crack. This allowed for easy collection of the cold product from the flask as a hard glassy material. The product was placed in a 1L single neck flask and solvent was stripped on a Kugelrohr for three hours at 70°C. The product was collected, pulverized to a fine gold powder and dried under vacuum at 60-80°C for a total of 16 hours. More than 35 grams of a fine gold powder were thus collected from this reaction. A softening point of 135°-140°C. The structure was confirmed by 1H NMR.

[0038] Examples: Synthesis of
from an aromatic-linked maleimide extended with an amine 2,2-bis[4-(4-aminophenoxy) phenylpropane.

[0039] A bismaleimide (obtained from National Starch and Chemical Co. as SR 525, CAS# 3006-93-7, hereinafter BMI 525) (26.0 grams, 0.0969 mol), 2, 2-bis[4-(4-aminophenoxy) phenylpropane] (14.0 grams, 0.0341 mol), and 2-methoxyethanol (20 grams) were charged to a 100 mL 3-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The flask was secured in an oil bath preheated to 125°C and the contents were mixed at 300 rpsi. Gradually, the reaction changed from a yellow slurry to a darkening orange slurry at 105°C. Heating was continued for 6.0 hours while a reaction temperature was maintained between 105° and 115°C. The reaction product, a thick dark orange-red syrup was cooled to room temperature in the flask. The product solution was transferred to a 250 mL single neck flask and solvent was stripped on a Kugelrohr for one hour at 60°C. After a brief foaming episode, product was collected as a dark orange solid, pulverized and dried under vacuum at 60°-80°C for a total of 16 hours. More than 35 grams of a fine gold powder was obtained from this reaction. A softening point of 115°-125°C was observed. The structure was confirmed by 1H NMR.

[0040] EXAMPLE 6. SYNTHESIS OF

![Diagram](image)

from an aromatic-linked maleimide extended with an amine 2,2-bis[4-(4-aminophenoxy) phenylpropane.

[0041] A bismaleimide (obtained from Daiwakasei Industry Co. Ltd, as 5100, CAS# 105391-33-1, hereinafter BMI 5100) (26.0 grams, 0.0588 mol), 2, 2-bis[4-(4-aminophenoxy) phenylpropane] (14.0 grams, 0.0341 mol), and 2-methoxyethanol (20 grams) were charged to a 100 mL 3-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The flask was secured in an oil bath preheated to 125°C and the contents were mixed at 200 rpsi. Gradually, the reaction changed from a tan-gold slurry to a clear dark red solution at 105°C. Heating was
continued for 75.0 hours while the reaction temperature was maintained between 105° and 120°C. When the amine was exhausted, the reaction product was a thick dark red liquid. To aid recovery, the reaction flask was chilled in dry ice. In this way, the viscous liquid was frozen, cracked and easily obtained as solid chunks from the reaction flask. The solids were then transferred to a 1000 ml single neck flask which was placed on a Kugelrohr. The solids melted back to a liquid and residual solvent was stripped at 80°C. After stripping, product was collected as a brown powder and dried in a vacuum oven at 60-80°C. More than 35 grams of product with a softening point of 180-190°C was obtained from this reaction. The structure was confirmed by ¹H NMR.

[0042] EXAMPLE 7. SYNTHESIS OF

![Chemical structure diagram]

from an aromatic-linked maleimide extended with an amine 4,4’ diamino-diphenylmethane

[0043] BMI 5292A (30.00 grams, 0.0838 mol), 4,4’diaminodiphenylmethane (8.3 grams, 0.0419 mol), and 2-methoxyethanol (19 grams) were charged to a 100 ml 3-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The contents of the reaction flask were mixed at 300 rpms in an oil bath preheated to 125°C. By the time the reaction temperature reached 105°C, the mixture formed a thin dark red solution. At that temperature, reaction time was started and heating and mixing continued. The reaction was monitored using thin-layer chromatography (toluene/tetrahydrofuran, 1/1 vol.). After 7 hours, all amine was exhausted and the reaction changed from a yellow paste to a viscous dark red liquid. The reaction solidified upon cooling and was transferred to a 1-neck 500 mL reaction flask as a clay-like solid. Residual solvent was stripped from the flask using a roto-evaporator for two hours and then a Kugelrohr for 1.5 hours, both at 60°C. The resulting gold-brown solids were then pulverized and residual solvent was removed using a vacuum oven heated to 80°C. Nearly 35 grams of light brown powder with a softening point of 180-190°C were obtained. The structure was confirmed by ¹H NMR.
EXAMPLE 8.

in a 50% solids solution, from an aromatic-linked maleimide extended with amine 4,4′-diaminodiphenylmethane.

BMI 5292A (30.00 grams, 0.0838 mol), 4,4′diaminodiphenylmethane (8.3 grams, 0.0419 mol), and propylene carbonate (38.3 grams) were charged to a 500 mL 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The contents of the reaction flask were mixed at 200 rpm in an oil bath preheated to 125°C. By the time the reaction temperature reached 105°C, the mixture formed a thin dark red-orange solution. At that temperature, reaction time was started and heating and mixing continued. The reaction was monitored using thin-layer chromatography (toluene/tetrahydrofuran, 1/1 vol.). After nine hours, all amine was exhausted and the reaction changed from an initial yellow slurry to a viscous dark red liquid. While hot, the viscous product was transferred to an HDPE bottle. Nearly 65 grams of a 50% solution of the product in propylene carbonate were obtained. The solution of the BMI/amine adduct is expected to provide greater efficiency in preparing, processing and formulating. The structure was confirmed by 1H NMR.

EXAMPLE 9. SYNTHESIS OF
from two different aromatic-linked maleimides (BMI 5292A, BMI 5100) extended with amine 2,2-bis[4-(4-aminophenoxy)phenylpropane]

[0047] BMI 5292A (15.0 grams, 0.0419 mol), BMI 5100 (18.5 grams, 0.0419 mol), 2,2-bis[4-(4-aminophenoxy)phenylpropane] (17.2 grams, 0.0419 mol), and 2-methoxyethanol (26 grams) were charged to a 250 mL 3-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The flask was secured in an oil bath preheated to 125°C and the contents were mixed at 300 rpms. Gradually, the reaction changed from a yellow mixture to a light orange slurry at 105°C. Heating was continued for approximately nine hours while a reaction temperature was maintained between 105° and 115°C. The reaction product, a thick dark red liquid was transferred to a 250 mL single neck flask. 2-Methoxyethanol was used for rinsing. Solvent was stripped from the reaction using a rotovapor at 60°C. Product was collected as a dark orange powder and dried under vacuum at 60°-80°C for a total of 16 hours. More than 40 grams of powder with a softening point of 150-160°C were obtained from this reaction. The structure was confirmed by ¹H NMR.

[0048] EXAMPLE 10 SYNTHESIS OF

in a 50% solids solution, from two aromatic-linked maleimides (BMI 5292A and BMI 5100) extended with amine 2,2-bis[4-(4-aminophenoxy)phenylpropane].

[0049] BMI 5292A (15.0 grams, 0.0419 mol), BMI 5100 (18.5 grams, 0.0419 mol), 2,2-bis[4-(4-aminophenoxy)phenylpropane] (17.2 grams, 0.0419 mol) and propylene carbonate (50.7 grams) were charged to a 500 mL 4-neck round-bottom reaction flask
equipped with a thermometer, mechanical mixer, and condenser. The contents of the reaction flask were mixed at 200 rpms in an oil bath preheated to 125°C. By the time the reaction temperature reached 105°C, the mixture formed a thin dark red-orange solution. At that temperature, reaction time was started and heating and mixing continued. The reaction was monitored using thin-layer chromatography (toluene/tetrahydrofuran, 1/1 vol.) After 31.5 hours, all amine was exhausted. The reaction changed from a gold-yellow slurry to a viscous dark red syrup. While hot, the viscous product was transferred to an HDPE plastic bottle. The structure was confirmed by 1H NMR. Nearly 95 grams of a 50% solution of the product were obtained. The solution of the BMI/amme adduct is expected to provide greater efficiency in preparing, processing, and formulating.

EXAMPLE 11
SYNTHESIS OF

from two different aromatic-linked maleimides (BMI 5292A, BMI 5100) extended with amine 4, 4′diaminodiphenylmethane to

BMI 5292A (15.0 grams 0.0419 mol), BMI 5100 (18.5 grams, 0.0419 mol), 4,4′ diaminodiphenylmethane (8.3 grams, 0.0419 mol), and 2-methoxyethanol (50 grams) were charged to a 500 ml 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The flask was secured in an oil bath preheated to 125°C and the contents were mixed at 200 rpms. Gradually, the reaction changed from a yellow-orange mixture to a thin clear red-orange solution at 105°C. Heating was continued for 7.5 hours while a reaction temperature was maintained between 105° and 115°C. The reaction product, a thick dark red liquid was transferred to a 500 ml single neck flask. 2-Methoxyethanol was used for rinsing. Solvent was stripped from the reaction using a roto-evaporator at 60°-70°C. Product was collected as a dark amber powder and dried under vacuum at 75°C. More than 35 grams of powder with a
softening point of 130°-140°C were obtained from this reaction. The structure was confirmed by ¹H NMR.

Example 12.

in a 50% solids solution, from two aromatic-linked maleimides (BMI 5292A and BMI 5100) extended with amine 4,4′ diaminodiphenylmethane.

BMI 5292A (15 0 grams, 0.0419 mol), BMI 5100 (18.5 grams, 0.0419 mol), 4,4′ diamino-diphenylmethane (8.3 grams, 0.0419 mol), and propylene carbonate (41.8 grams) were charged to a 500 ml 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The contents of the reaction flask were mixed at 200 rpms in an oil bath preheated to 125°C. By the time the reaction temperature reached 105°C, the mixture formed a thin red-orange solution. At that temperature, reaction time was started and heating and mixing were continued. The reaction was monitored using thin-layer chromatography (toluene/tetrahydrofuran, 1:1 vol.). After 12 hours, all amine was exhausted and the reaction changed from a gold-yellow slurry to a viscous dark red syrup. While hot, the viscous product was transferred to a high density polyethylene bottle. The structure was confirmed by ¹H NMR. Nearly 80 grams of a 50% solution in propylene carbonate were thus obtained. The solution of the BMI/amine adduct is expected to provide greater efficiency in preparing, processing and formulating.
from an aromatic-linked maleimide (BMI 5292A) extended with two different amines, 2,2-bis[4-(4-aminophenoxy)phenylpropane] and 4,4' diaminodiphenylmethane.

BMI 5292A (40.0 grams, 0.1117 mol), 2,2-bis[4-(4-aminophenoxy)phenylpropane] (11.5 grams, 0.0279 mol), 4,4'diaminodiphenylmethane (5.5 grams, 0.0279 mol), and 2-methoxyethanol (30 grams) were charged to a 250 mL 3-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The flask was secured in an oil bath preheated to 125°C and the contents were mixed at 200 rmps. Gradually, the reaction changed from a pale yellow slurry to a dark red solution at 105°C. Heating and mixing were continued for two hours at a reaction temperature maintained between 105° and 115°C. The reaction product, a dark red-orange liquid was transferred to a 500 mL single neck flask 2-Methoxyethanol was used for rinsing. Solvent was stripped using a roto-evaporator for four hours at 60°C. Product was collected, pulverized to a gold orange powder and further dried under vacuum at 75°C. More than 40 grams of powder was obtained from this reaction. The structure was confirmed by 1H NMR.
from an aromatic-linked maleimide extended with two different amines 2,2-bis[4-(4-
aminophenoxy)phenylpropane] and 4,4'diaminodiphenylmethane.

[0057] BMI 5100 (49.4 grams, 0.117 mol), 2,2-bis[4-(4-aminophenoxy)phenylpropane] 
(11.5 grams, 0.0279 mol), 4,4'diaminodiphenylmethane (5.5 grams, 0.0279 mol), and 2-
methoxyethanol (30 grams) were charged to a 250 mL 3-neck round-bottom reaction 
flask equipped with a thermometer, mechanical mixer, and condenser. The flask was 
secured in an oil bath preheated to 125°C and the contents were mixed at 200 rpms. 
With heating, the reaction changed from a pale yellow slurry to a clear orange-red 
solution at 105°C. Heating and mixing were continued for 28 hours at a reaction 
temperature maintained between 105° and 115°C. The reaction product, a dark red 
viscous liquid was transferred to a 500 mL single neck flask. 2-Methoxy-ethanol was 
used for rinsing. Solvent was stripped using a roto-evaporator for four hours at 60°C. Solids 
were collected, pulverized to a gold orange powder and further dried under vacuum at 
75-80 °C. More than 40 grams of powder with a softening point of 145°-155°C were 
obtained from this reaction. The structure was confirmed by 1H NMR.

[0058] EXAMPLE 15. SYNTHESIS OF

in a 50% solids solution, from an aromatic-linked maleimide extended with amine 2,2-
bis[4-(4-aminophenoxy)phenylpropane].

[0059] BMI 5292A (360.0 grams, 1.0056 mol), 2,2-bis[4-(4-aminophenoxy) 
phenylpropane] (206.4 grams, 0.5028 mol), and propylene carbonate (566.4 grams) were 
charged to a 2L 4-neck round-bottom reaction flask equipped with a thermometer, 
mechanical mixer, and condenser. The contents of the reaction flask were mixed at 200 
rpms in an oil bath preheated to 125°C. By the time the reaction temperature reached 
105 °C, the mixture formed a thin dark red-orange solution. At that temperature, reaction 
time was started and heating and mixing continued. (Note: the contents temperature 
gradually increased to approximately 122°C) The reaction was monitored by measuring 
solution viscosity at 50°C from samples taken hourly. After 21.5 hours, the solution
viscosity at 50°C measured 4580 mPa.s (cPs) and the reaction was stopped. While hot, the dark red viscous product was easily discharged. Nearly 900 grams of a 50% solution of product were obtained and a sample was characterized. The structure was confirmed by $^1$HNMR. The Mw was 20,646 with an MWD of 7.3 as determined by GPC.

EXAMPLE 16: SYNTHESIS OF

in a 50% solids solution, from an aromatic-linked maleimide (BMI 5292A) extended with amine 2, 2-bis[4-(4-aminophenoxy)phenylpropane).

BMI 5292A (360.0 grams, 1.0056 mol), 2, 2-bis [4-(4-aminophenoxy)phenylpropane] (206.4 grams, 0.5028 mol), and propylene carbonate (566.4 grams) were charged to a 2L 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The contents of the reaction flask were mixed at 200 rpms in an oil bath preheated to 150°C. By the time the reaction temperature reached 105°C, the mixture formed a thin dark red-orange solution. At that temperature, reaction time was started and heating and mixing continued. (Note the contents temperature gradually increased and during most of the reaction, the temperature ranged between 130° and 132°C) The reaction was monitored by measuring solution viscosity at 50°C from samples taken hourly. After nearly seven hours, the solution viscosity at 50°C measured 4915 mPa.s (cPs) and the reaction was stopped. While hot, the dark red viscous product was easily discharged. Nearly 900 grams of a 50% solution of the product were obtained and a sample was characterized. The structure was confirmed by $^1$HNMR. The Mw of the product was 28,161 with an MWD of 10.19 as determined by GPC.

EXAMPLE 17. SYNTHESIS OF
in a 50% solids solution, from an aromatic-linked maleimide extended with amine 2, 2-bis[4-(4-aminophenoxy)phenylpropane]

[0063] BMI 5292A (360.0 grams, 1.0056 mol), 2, 2-bis[4-(4-aminophenoxy)phenylpropane] (206.4 grams, 0.5028 mol), and propylene carbonate (566.4 grams) were charged to a 2L 4-neck round-bottom reaction flask equipped with a thermometer, mechanical mixer, and condenser. The contents of the reaction flask were mixed at 200 rpms in an oil bath preheated to 140°C. By the time the reaction temperature reached 105°C, the mixture formed a thin dark red-orange solution. At that temperature, reaction time was started and heating and mixing continued. (Note: the contents temperature gradually increased and during most of the reaction, the temperature ranged between 123° and 125°C) The reaction was monitored by measuring solution viscosity at 50°C from samples taken hourly. After 10 hours 15 minutes, the solution viscosity at 50°C measured 4536 mPa s (cPs) and the reaction was stopped. While hot, the dark red viscous product was easily discharged. Nearly 900 grams of a 50% solution of Example 24 were thus obtained and a sample was characterized. The structure was confirmed by 1H NMR. The Mw of Example 24 was 19,975 with an MWD of 7.44 as determined by GPC.

UTILITY

[0064] In one embodiment this invention is a semiconductor silicon wafer having an active face and an inactive face. The inactive face coated with a composition comprising one or more of the inventive oligomeric adducts of bismaleimide and diamine, or of bismaleimide and diamine and dithiol. The coating may be applied by any of those techniques employed to add materials to the backside of silicon wafers, and include stencil printing, spraying, spin-coating, ink jet printing and the like.

[0065] While this invention has been described with respect to these specific examples, it should be clear that other modifications and variations would be possible without departing from the spirit of this invention.
WHAT IS CLAIMED IS:

1. A curable composition comprising
   (a) a compound selected from the group consisting of
and

(b) a curing initiator.

2. A semiconductor silicon wafer having an active face and an inactive face, in which the inactive face is coated with a composition according to claim 1.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
C08G 59/14(2006.01), C08L 79/08(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 8: C08G 59/14, 73/10, C08L 79/08, C07D 207/444, 487/02, C08F 122/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility Models and applications for Utility Models since 1975
Japanese Utility Models and applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKipass (K IPO internal) "bismaleimide and diamine"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
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  "O" document referring to an oral disclosure, use, exhibition or other means
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
24 FEBRUARY 2009 (24.02.2009)

Date of mailing of the international search report
24 FEBRUARY 2009 (24.02.2009)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
Government Complex- Daejeon, 139 Seonsa-ro, Seogu, Daejeon 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
LEE, Su Hyoung
Telephone No. 82-42-481-8148

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