

EPOXY RESIN COMPOSITION

TECHNICAL FIELD

5 The present invention relates to an epoxy resin composition for sealing semiconductor devices, and to a semiconductor device sealed by an epoxy resin composition.

BACKGROUND

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Existing epoxy resin compositions are inherently flammable and therefore require the addition of a flame retardant to reduce flammability.

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The combustion process of plastic essentially starts by an endothermic reaction or so called pyrolysis endothermic processes and decomposition. Flammable gases that form from the plastic react with oxygen in the air, which then ignite, leading to the exothermic processes of flame propagation and heat release.

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Only a few types of flame retardants are used in epoxy resin compositions: flame retardants containing halogen, flame retardants containing phosphorous, flame retardants containing nitrogen, and inorganic flame retardants (e.g. metal oxides).

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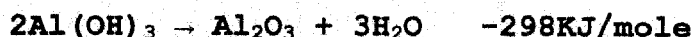
Synergists comprising a halogen containing flame retardant (and in particular those containing bromine) and an antimony oxide flame retardant are commonly used in industry; they show good flame retardancy but generate harmful products when burnt, including hydrogen bromide, polybromine dibenzofurans, and polybromine dibenzodioxins.

30

Furthermore, antimony oxide is suspected of being a carcinogen.

Non-halogen containing flame retardants
5 (containing, for example, nitrogen and phosphorus) have been developed, but these release corrosive and partly toxic compounds when burnt, such as nitrogen oxide and phosphoric acid.

10 Aluminum hydroxide, which is environmentally friendly and non-toxic, retards a fire mainly due to its endothermic decomposition to aluminum oxide and water:



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This reaction takes place between about 180°C and 200°C. Owing to the endothermic breakdown of aluminum hydroxide, the polymer component of the epoxy resin composition containing aluminium hydroxide is cooled, so
20 fewer pyrolysis products are formed. Aluminum oxide, in addition to producing charring, acts as an insulating protective layer. Furthermore, water vapor formed in the decomposition of the aluminium hydroxide dilutes any flammable gases given off by the burning epoxy resin
25 composition.

JP 2003-155426A discloses the use of aluminum hydroxide as a flame retardant in an epoxy resin composition. The epoxy resin composition comprises 5-20wt%
30 of aluminum hydroxide based on the total resin composition. The use of this amount of aluminum hydroxide in the epoxy resin composition achieves the relevant Underwriters Laboratories Inc. standard (i.e. UL-94

entitled "Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances") at only 3.2mm thickness. When the epoxy resin composition comprised less than 5%, the material failed the UL-94 flammability test; if the aluminium hydroxide content was more than 20%, the material had poor moldability and a low value on hot hardness.

For the UL-94 flammability test, as the thickness of the test pieces decrease, the difficulty for passing this test increases.

It is an object of the present invention to provide an epoxy resin composition comprising an inorganic flame retardant that can pass the UL-94 flammability test at a significantly lesser thickness.

SUMMARY

According to one aspect of the invention, there is provided an epoxy resin composition for sealing a semiconductor device, comprising:

- (A) an epoxy resin;
- (B) a phenolic resin curing hardener;
- (C) an inorganic filler;
- (D) an aluminum hydroxide flame retardant;
- (E) a curing accelerator; and
- (F) a releasing agent;

wherein:

the epoxy resin (A) is present in an amount of about 0.8 to about 1.2 times the epoxy equivalents per hydroxyl group equivalent of the total phenolic resin (B), the inorganic filler (C) is present in an amount of about 30

to about 75% by weight of the epoxy resin composition, the aluminum hydroxide flame retardant (D) is present in an amount of about 21 to about 45% by weight of the epoxy resin composition, the curing accelerator (E) is present
5 in an amount of about 0.2 to about 0.5% by weight of the epoxy resin composition, and the releasing agent (F) is present in an amount of less than about 1.0% by weight of the epoxy resin composition.

10 A further aspect of the present invention provides use of the epoxy resin composition for sealing semiconductor devices.

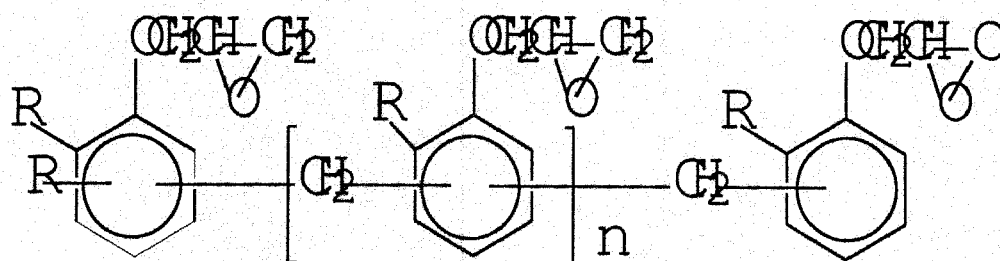
Another aspect of the present invention provides
15 a semiconductor device sealed with the epoxy resin composition.

FIGURE

20 Figure 1 is a schematic diagram of a semiconductor device sealed with the epoxy resin composition.

DETAILED DESCRIPTION

25 Epoxy resins are well known in the art. The epoxy resin (A) is typically selected from the group consisting of ortho-cresol novolac-type epoxy resin, bisphenol-type epoxy resin, phenol novolac-type epoxy resin,
30 multifunctional-type epoxy resin, naphthalene-type epoxy resin, triazine nucleus-type epoxy resin and mixtures thereof. Preferably, the epoxy resin (A) is an ortho-cresol novolac-type epoxy resin, represented by the following Formula I:



Formula I

wherein

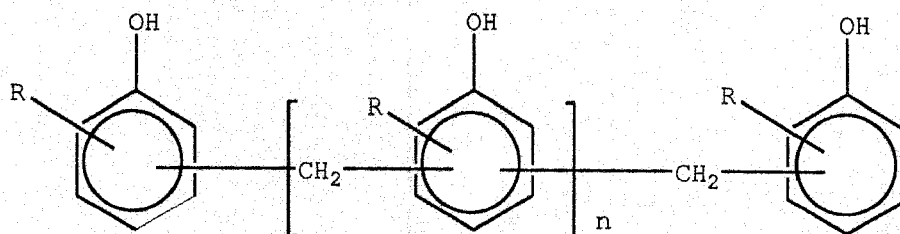
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n is an integer of 0 to 10; and

each R is independently selected from hydrogen, halo, alkyl and haloalkyl.

Phenolic resin curing hardeners are also well known in the art. The phenolic resin curing hardener (B) is preferably selected from the phenol-novolac type resin family. Other typical phenolic resin curing hardeners suitable for the epoxy resin composition of the present invention include, but are not limited to, paraxylene-modified phenolic resin, tri(hydroxyphenyl) methane type phenolic resin, dicyclopentadiene-modified phenolic resin, multifunctional epoxy resin, naphthalene type phenolic resin or triazine nucleus type epoxy resin. A preferred phenol-novolac resin is represented by the following

20 Formula II:



Formula II

wherein

n is an integer of 0 to 10; and

each R is independently selected from hydrogen, halo, alkyl and haloalkyl.

5

The term "halo" or "halogen" includes a chloro, a bromo, an iodo or a fluoro atom.

10 The term "alkyl" refers to straight chain, branched chain or cyclic hydrocarbon groups having from 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms. Illustrative of such alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, 15 cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

With regard to the blending ratio of the epoxy resin (A) to the total phenolic resin curing hardener (B), the epoxy resin is used in an amount of about 0.8 to about 20 1.2 times, preferably about 0.9 to about 1.1 times, the epoxy equivalents per hydroxyl group equivalent of the total phenolic resin (B). If the blending ratio of the epoxy resin (A) to the phenolic resin curing hardener (B) is outside this range of amounts, properties such as 25 curability tend to deteriorate.

A variety of inorganic fillers are commercially available. The inorganic filler (C) used in the epoxy resin composition is preferably selected from the group 30 consisting of fused silica powder; spherical silica powder; crystalline silica powder; secondary agglomerated silica powder; porous silica powder; silica powder obtained by grinding secondary agglomerated silica powder

or porous silica powder and alumina powder and the like. Fused silica powder, spherical silica powder and mixtures of these powders are more preferable. The amount of the inorganic filler (C) present in the epoxy resin composition is about 30 to about 70% by weight, preferably about 30 to about 60% by weight, of the epoxy resin composition. The use of an amount in this range of amounts provides a balance between the soldering stress resistance and moldability of the epoxy resin composition. Although inorganic fillers may comprise aluminum hydroxide, it is to be understood that in the present invention, the inorganic filler (C) does not comprise aluminum hydroxide.

The aluminum hydroxide is used in the epoxy resin composition as a flame retardant. The amount of aluminum hydroxide is about 21 to about 45% by weight, preferably about 21 to about 40% by weight.

The curing accelerator (E) used in the present epoxy resin composition can be any material as long as it accelerates the reaction between the epoxy group of the epoxy resin (A) and the hydroxyl group of the phenolic resin curing hardener (B). Curing accelerators used for sealing semiconductor devices are well known in the art of the invention. Some examples of suitable curing accelerators include diazabicycloundecene (DBU), triphenylphosphine (TPP), benzyldimethylamine (BDMA), 2-methylimidazole (2-MZ) and the like.

The amount of curing accelerator (E) used in the epoxy resin composition is about 0.2 to about 0.5% by weight, preferably about 0.3% by weight, of the epoxy resin composition. If less than about 0.2% by weight of

curing accelerator (E) is used, the hardness of the resulting molded product decreases and mold release characteristics tend to deteriorate. If more than about 0.5% by weight of curing accelerator (D) is used, the
5 reaction process proceeds at an undesirably fast rate and the fluidity of the epoxy resin composition tends to decrease.

A releasing agent in an epoxy resin composition
10 enhances mold release. It also loosens the polymer chain, and thus can affect the strength of the epoxy resin composition, which in turn can lead to runner breaks in molded epoxy resin compositions.

15 The releasing agent (F) used in the present epoxy resin composition can be a natural wax, a synthetic wax or a combination of both these types of waxes.

For an epoxy resin composition containing
20 aluminum hydroxide in amount of more than 40% by weight of the epoxy resin composition, the amount of releasing agent (F) used in the epoxy resin composition is less than about 1.0% by weight, preferably about 0.2 to about 0.8% by weight, more preferably about 0.5 to about 0.7% by weight,
25 of the epoxy resin composition.

The epoxy resin composition, with the amounts of each of the components as defined above, particularly those of the aluminum hydroxide flame retardant (D) and
30 the releasing agent (F), advantageously achieves a result of V-0 in the relevant Underwriters Laboratories Inc. standard (i.e. UL-94 entitled "Standard for Tests for Flammability of Plastic Materials for Parts in Devices and

Appliances") at 1.0mm while maintaining good moldability, e.g. no runner breaks.

Apart from components (A) to (F), the epoxy resin
5 composition may further comprise, if necessary, various additives such as a silane coupling agent, a coloring agent (e.g. carbon black or red iron oxide), a stress-reducing additive (e.g. silicone oil or rubber), and the like. Such additives are well known in the art of the
10 invention.

In producing the present epoxy resin composition, the individual components are mixed sufficiently and uniformly using hot rollers, a kneader or similar type
15 apparatus. The rolled or kneaded product is then cooled and ground. The molding material subsequently obtained can be used for sealing of semiconductor devices. The meaning of the term "sealing" is well known in the art, and would therefore be understood to include coating, insulating or
20 encapsulating.

The term "semiconductor device" as used herein includes any solid-state electronic or electrical devices, integrated circuits, capacitors, resistors, diodes and
25 transistors.

Figure 1 shows a semiconductor device sealed with a layer of epoxy resin composition.

30 EXAMPLES

The present invention will now be described with reference to the following non-limiting Examples.

Example 1

5 An epoxy resin composition comprising the
components set out Table 1 (and repeated in Table 2 below)
were mixed at room temperature using a mixer. The mixed
powder was then kneaded using a bi-axial roller at a
temperature range between about 80°C and about 130°C. The
kneaded mixture was then cooled and ground to obtain a
10 molding material.

Table 1:

Composition of Epoxy Resin Composition of Example 1

Components of epoxy resin composition	Amount
(A) Cresol novolac-type epoxy resin of Formula I (Softening point: 55°C, epoxy equivalent: 198g/eq)	14.71 parts by weight
(B) Phenolic resin curing hardener of Formula II, reacted with 2 parts of TPP (Softening point: 80°C, hydroxyl group equivalent: 104g/eq)	1.82 parts by weight
(B) Phenolic resin curing hardener of Formula II (Softening point: 92°C, hydroxyl group equivalent: 104g/eq)	6.28 parts by weight
(C) Fused silica powder (excluding aluminum hydroxide) (30/70 mixture of flake and spherical filler)	45.42 parts of weight
(D) Aluminum hydroxide	30.00 parts of weight
(E) 2-Methylimidazole	0.07 parts of weight
(F) Releasing agent (such as natural wax, synthetic wax or combination)	0.70 parts of weight
Carbon black (coloring agent)	0.30 parts of weight
Silane Coupling agent	0.70 parts of weight

15 Examples 2 to 4

The epoxy resin compositions of Examples 2 to 4
comprise the components in the amounts set out in Table 2

(below). These epoxy resin compositions were prepared in a similar manner to the epoxy resin composition of Example 1.

5 Comparative Examples 1 to 3

 The epoxy resin compositions of Comparative Examples 1 to 3 comprise the components in the amounts set out in Table 2 (below). These epoxy resin compositions
10 were prepared in a similar manner to the epoxy resin composition of Example 1.

Tests

15 All of the Examples (Examples 1 to 4 and Comparative Examples 1 to 3) were then subjected to the following tests, the results of which are also set out in Table 2 (below).

20 • *Spiral Flow Measurement*

 This test was conducted on an amount of each epoxy resin composition, which gave a cull thickness of about $3 \pm 0.3\text{mm}$.

25

 A spiral flow mold die was placed in a molding machine and heated up to about 175°C . When the temperature reached about $175 \pm 2^{\circ}\text{C}$, the epoxy resin composition was poured into a transfer pot and a plunger was lowered. The
30 epoxy resin composition was molded for about 120 seconds and then the mold press was opened. The spiral flow length (up to the lustrous tip) was measured after the mold die

was taken out from the molding machine.

• *Flammability Test*

(Underwriters Laboratory flammability rating;

UL-94 V-0, UL-94 V-1)

From each Example of epoxy resin composition, five specimens with dimensions of about 127mm x 12.7mm x 1.0mm were molded using a 37 ton molding machine. Before the test was conducted, all specimens were treated at the following condition: temperature of about $23 \pm 2^{\circ}\text{C}$ with about $50 \pm 5\%$ relative humidity for at least 48 hours.

Each specimen was clamped vertically and burnt for about 10 ± 0.5 seconds. A record was taken of the flaming time and of any burnt residue dropping of each specimen. After the flaming of the specimens died out, the burner was immediately placed under the specimen again. The burner was removed after about 10 seconds and a record was taken of the flaming time, the glowing time and of any burnt residue dropping of each specimen.

The same procedure was repeated for all specimens.

In order to pass the UL-94 V-0, the results must be within the following criteria.

Criteria conditions	V-0
After-flame time for each individual specimen t_1 or t_2	≤ 10 seconds
Total after-flame time for any condition set (t_1 plus t_2 for the five specimens)	≤ 50 seconds

After-flame time plus after-glow time for each individual specimen after the second flame application ($t_2 + t_3$)	≤ 30 seconds
After-flame or after-glow of any specimen up to the holding clamp	No

• *Moldability Check*

Tablets having a diameter of about 40mm and weighing about 65g each were made from the Examples of epoxy resin compositions.

These tablets were molded on a 100LQFP with a dummy leadframe at a temperature of about 165°C for about 100 seconds.

With regard to the results, the term "GOOD" was used to indicate that no runner break occurred after the ejected pins were ejected out and the term "NG" was used to indicate that runner breaks occurred after the ejected pins was ejected out.

Tablets prepared from the Examples of epoxy resin compositions, each having a diameter of about 48mm and weighing about 75g, were used to seal TEG die for 16p PDIP devices (16-pin Plastic Dual Inline Package). These assembled units were then subjected to the following High Temperature Storage Test (HTSL) and Pressure Cooker Test (PCT).

• *High Temperature Storage Test (HTSL)*

The sealed 16p PDIP devices were stored in a controlled elevated temperature (up to about 175°C) for an

extended time (up to about 500 hours) without electrical bias. Interval resistance measurements were taken and final measurements were conducted at the conclusion of the test.

5

Damage, such as package cracks, junction thermal resistance increase or depolymerisation were considered a failure.

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• **Pressure Cooker Test (PCT)**

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Sealed 16p PDIP devices were stored in saturated steam, at a pressure of about 103 ± 7 kPa and a temperature of about 125°C in a sealed autoclave containing deionised water. The devices were suspended at a minimum height of about 1cm above the initial water level in the chamber. Interval electrical measurements were made and the devices were stored for up to about 100 hours.

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Failure was considered when an open circuit was detected and by external degradation of the packages, such as corroded device leads or the formation of conducting matter between the leads.

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Table 2:

Composition of Epoxy Resin Compositions
and Results of Tests

Formulation	Unit									
		1	2	3	4	1	2	3		
Cresol novolac-type epoxy resin (Softening point: 55°C ,	%	14.7	14.3	-	12.8	-	14.3	14.3		

epoxy equivalent: 198g/eq)								
Cresol novolac-type epoxy resin (Softening point: 70°C, epoxy equivalent: 210g/eq)	%	-	-	16.4	-	16.4	-	-
Phenolic resin curing reacted with 2 parts of TTP (Softening point: 80°C, epoxy equivalent: 104g/eq)	%	1.8	1.8	2.2	1.8	2.2	1.8	1.8
Phenolic resin curing hardener (Softening point: 92°C, epoxy equivalent: 104g/eq)	%	6.3	5.7	-	5.2	-	5.6	5.6
Phenolic resin curing hardener (Softening point: 110°C, epoxy equivalent: 104g/eq)	%	-	-	6.3	-	6.3	-	-
Fused silica powder	%	45.4	41.4	32.9	52.9	61.2	41.1	28.1
Aluminum hydroxide	%	30	35	40	25	11.2	35	48
2-Methylimidazole	%	0.07	0.05	-	0.05	-	0.03	-
Releasing Agent (Natural wax or Synthetic wax or combination of both)	%	0.7	0.7	0.7	0.7	1.2	1.2	0.7
Silane Coupling Agent	%	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Carbon black (coloring agent)	%	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Others (Low stress additive, etc)	%	-	-	0.5	0.5	0.5	-	0.5
Properties								
Spiral Flow	cm	70	60	60	50	60	70	60
UL-94 Flammability Test (3.2mm)	V0/V1	V-0	V-0	V-0	V-0	V-1	V-0	V-0
UL-94 Flammability Test (1.6mm)	V0/V1	V-0	V-0	V-0	V-0	V-1	V-0	V-0
UL-94 Flammability Test (1.0mm)	V0/V1	V-0	V-0	V-0	V-0	V-1	V-0	V-0
Moldability (Runner Break) check on 100LQFP	-	Good	Good	Good	Good	Good	NG	NG
HTSL @ 500hrs (175°C, 16p DIP, SiN)	-	0/10	0/10	0/10	0/10	0/10	0/10	NA
PCT @ 96hrs (121°C, 100% RH, 20V, 16p DIP, SiN)	-	0/10	0/10	0/10	0/10	0/10	0/10	NA

It will be understood by persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

CLAIMS:

1. An epoxy resin composition for sealing a semiconductor device, comprising:

- 5 (A) an epoxy resin;
(B) a phenolic resin curing hardener;
(C) an inorganic filler;
(D) an aluminum hydroxide flame retardant;
(E) a curing accelerator; and
10 (F) a releasing agent;

wherein:

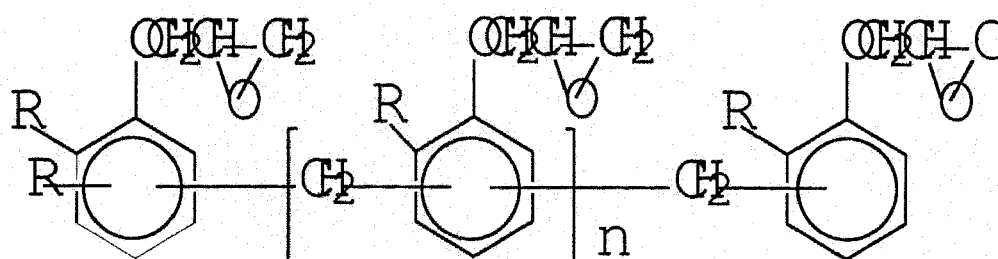
the epoxy resin (A) is present in an amount of about 0.8 to about 1.2 times the epoxy equivalents per hydroxyl group equivalent of the total phenolic resin (B), the
15 inorganic filler (C) is present in an amount of about 30 to about 75% by weight of the epoxy resin composition, the aluminum hydroxide flame retardant (D) is present in an amount of about 21 to about 45% by weight of the epoxy resin composition, the curing accelerator (E) is present
20 in an amount of about 0.2 to about 0.5% by weight of the epoxy resin composition, and the releasing agent (F) is present in an amount of less than about 1.0% by weight of the epoxy resin composition.

25 2. An epoxy resin composition according to claim 1, wherein the amount of aluminum hydroxide is about 21 to about 40% by weight of the epoxy resin composition.

3. An epoxy resin composition according to claim 1
30 or claim 2, wherein the amount of releasing agent (F) in the epoxy resin composition is about 0.2 to about 0.8% by weight of the epoxy resin composition.

4. An epoxy resin composition according to any one of the preceding claims, wherein the epoxy resin (A) is selected from the group consisting of ortho-cresol novolac-type epoxy resin, bisphenol-type epoxy resin, phenol novolac-type epoxy resin, multifunctional-type epoxy resin, naphthalene-type epoxy resin, triazine nucleus-type epoxy resin and mixtures thereof.

10 5. An epoxy resin composition according to claim 4, wherein the epoxy resin (A) is an ortho-cresol novolac-type epoxy resin, represented by the following Formula I:



Formula I

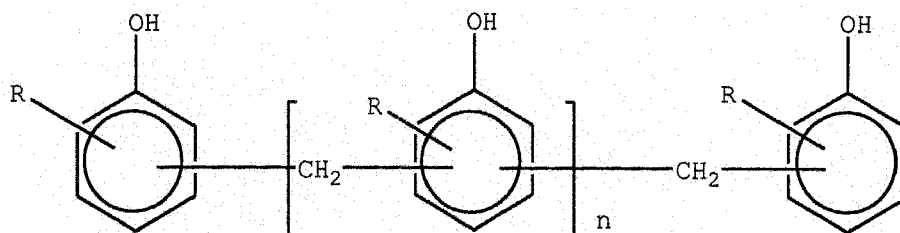
15 wherein

n is an integer of 0 to 10; and

each R is independently selected from hydrogen, halo, alkyl and haloalkyl.

20 6. An epoxy resin composition according to any one of the preceding claims, wherein the phenolic resin curing hardener (B) is selected from paraxylene-modified phenolic resin, tri(hydroxyphenyl) methane type phenolic resin, dicyclopentadiene-modified phenolic resin, multifunctional epoxy resin, naphthalene type phenolic resin or triazine nucleus type epoxy resin and mixtures thereof.

7. An epoxy resin composition according to claim 6, wherein the phenolic resin curing hardener (B) is of the following Formula II:



Formula II

wherein

n is an integer of 0 to 10; and

each R is independently selected from hydrogen, halo, alkyl and haloalkyl.

8. An epoxy resin composition according to claim 7, wherein the phenolic resin curing agent (B) is a mixture of compounds of Formula II.

9. An epoxy resin composition according to any one of the preceding claims, wherein the inorganic filler (C) is selected from the group consisting of fused silica powder; spherical silica powder; crystalline silica powder; secondary agglomerated silica powder; porous silica powder; silica powder obtained by grinding secondary agglomerated silica powder or porous silica powder and alumina powder; and mixtures thereof.

10. An epoxy resin composition according to claim 9, wherein the inorganic filler (C) is fused silica powder,

spherical silica powder or a mixture thereof.

11. An epoxy resin composition according to any one of the preceding claims, wherein the curing accelerator (E) is selected from the group consisting of diazabicycloundecene (DBU), triphenylphosphine (TPP), benzyldimethylamine (BDMA) and 2-methylimidazole (2-MZ).

12. An epoxy resin composition according to any one of the preceding claims, wherein the releasing agent (F) is a natural wax, a synthetic wax or a combination of both types of waxes.

13. An epoxy resin composition according to any one of the preceding claims, wherein the epoxy resin composition passes the UL-94 flammability test at 1.0mm thickness.

14. Use of an epoxy resin composition as defined in any one of claims 1 to 13 for sealing semiconductor devices.

15. Use according to claim 14, wherein the semiconductor device is a solid-state electronic or electrical device, integrated circuit, capacitor, resistor, diode or transistor.

16. A semiconductor device sealed with a layer of an epoxy resin composition as defined in any one of claims 1 to 13.

17. A semiconductor device according to claim 16,

wherein the layer of epoxy resin composition has a thickness of 3.0mm or less.

18. A semiconductor device according to claim 17,
5 wherein the layer of epoxy resin composition has a thickness of 1.0mm or less.