

DESCRIPTION

PREVENTING AGENT FOR EPOXY RESIN BLEEDING OUT

TECHNICAL FIELD

[0001]

The present invention relates to a preventing agent for epoxy resin bleeding out and a method for preventing epoxy resin bleeding out for use in die bonding steps in which an IC chip is bonded and fixed by an epoxy resin to a semiconductor wiring substrate such as a lead frame or printed circuit board.

BACKGROUND ART

[0002]

In die bonding steps, in which an IC chip is bonded and fixed by an epoxy resin to a semiconductor wiring substrate such as a lead frame or a printed circuit board, ooze of the resin or additives (epoxy resin bleeding out) occurs upon application of the epoxy resin when a bonding surface (which has been generally plated with gold, silver, copper or palladium) has an excessively high surface roughness or when a surface is contaminated with organic material, such as a discoloration inhibitor or a sealant. This epoxy resin bleeding out causes the die bonding strength to decline and causes defects in the ensuing wire bonding step. In order to prevent this epoxy resin bleeding out, the capillary phenomenon has been inhibited by reducing the surface roughness of the bonding surface and the contaminants have been removed by cleaning the surface. However, the surface roughness of the bonding surface cannot be unconditionally reduced because it can blemish the die bonding strength and the image recognition performance of the assembly machinery. Surface cleaning has been a problem because it impairs the effects of the discoloration treatment or sealing treatment.

[0003]

In order to solve these problems, Patent Document 1 discloses that epoxy resin bleeding out can be prevented, without altering the surface roughness of the substrate surface or cleaning off a discoloration-inhibiting film or a sealing film, by immersing the substrate in a solution whose main components are carboxylic acid and thiol, or the like and then bringing an organic film of 1 to several molecules thick to adsorb. It is also disclosed that this does not impair the assembly characteristics such as the wire bondability and the moldability, because the adsorbed organic film is extremely thin.

[0004]

However, the use of low-stress, low-elasticity, low-viscosity die bonding resins (referred to below as low-stress die bonding resins) has become widespread in order to ameliorate problems such as warpage that have accompanied the recent trends of semiconductor chip upsizing and thinner semiconductor packages. Many of these low-stress resins contain components that are prone to ooze, which has caused a tendency of epoxy resin bleeding out. The technology of the above Patent Document 1 is unable to accommodate the use of low-stress die bonding resins, and epoxy resin bleeding out still ends up occurring when this technology is used therewith. The development for a preventing agent for epoxy resin bleeding out that also accommodates low-stress die bonding resins is therefore desired.

Patent Document 1: Japanese Patent Publication No. H11-195662

SUMMARY OF THE INVENTION**[0005]**

The present invention provides a preventing agent for epoxy resin bleeding out that can prevent the appearance of epoxy resin bleeding out without

impairing the die bonding strength or the assembly characteristics or the effects from a sealant treatment or a treatment to inhibit discoloration, and that can accomplish this outcome even when a low-stress die bonding resin as described above is used in a die bonding step in which an IC chip is bonded and fixed by an epoxy resin to a semiconductor wiring substrate such as a lead frame or printed circuit board.

[0006]

As a result of focused investigations, the present inventors discovered a group of organic compounds that have an even better ability to prevent bleeding out than before, even with use of low-stress die bonding resins, in the process of preventing epoxy resin bleeding out by immersing a substrate in a solution containing the preventing agent for epoxy resin bleeding out in order to make an organic film adsorb on the surface of a plating layer. That is, the present invention was achieved based on the discovery of compounds that have a higher epoxy resin bleeding out preventing efficiency than the carboxylic acids, thiol compounds, and so forth described in the preceding reference.

The present invention is described in the following.

[0007]

(1) A preventing agent for epoxy resin bleeding out for a die bonding process, comprising a fluorine-containing organic compound that has a fluorohydrocarbon group $C_xH_yF_z-$ ($x = 3$ to 24 , $y = 0$ to 48 , $z = 1$ to 49 , $y + z \leq 2x + 1$) having not less than 3 and not more than 24 of carbon, and a polar group $R-$.

[0008]

(2) The preventing agent for epoxy resin bleeding out according to (1), wherein the polar group $R-$ is a polar group that contains one selected from the group of sulfur (S), nitrogen (N), phosphorus (P) and oxygen (O).

[0009]

(3) The preventing agent for epoxy resin bleeding out according to (2), wherein the polar group R- is one selected from the group of mercapto group, amino group, nitrogen-containing heterocyclic group, phosphate ester group and carboxyl group.

[0010]

(4) The preventing agent for epoxy resin bleeding out according to (3), wherein the nitrogen-containing heterocyclic group is one selected from the group of imidazolyl group, triazolyl group, tetrazolyl group and derivative thereof.

[0011]

(5) The preventing agent for epoxy resin bleeding out according to any of (1) to (4), further comprising a discoloration inhibitor or a sealant.

[0012]

(6) The preventing agent for epoxy resin bleeding out according to (5), wherein the discoloration inhibitor contains a nitrogen-containing heterocyclic compound.

[0013]

(7) The preventing agent for epoxy resin bleeding out according to (6), wherein the nitrogen-containing heterocyclic compound is one selected from the group of imidazole derivative, triazole derivative, tetrazole derivative and thiazole derivative.

[0014]

(8) A method of preventing epoxy resin bleeding out, comprising the step of:

immersing a wiring substrate in a solution containing the preventing agent for epoxy resin bleeding out according to any of (1) to (7), or

spraying or applying a solution containing said preventing agent for epoxy resin bleeding out on a wiring

substrate.

[0015]

(9) A wiring substrate, treated to prevent epoxy resin bleeding out by

immersing the wiring substrate in a solution containing the preventing agent for epoxy resin bleeding out according to any of (1) to (7), or

spraying or applying a solution containing said preventing agent for epoxy resin bleeding out on the wiring substrate.

[0016]

(10) A wiring substrate, wherein the preventing agent for epoxy resin bleeding out according to any of (1) to (7) is adsorbed on a surface thereof.

[0017]

(11) A semiconductor package, which uses the wiring substrate according to (9) or (10).

Effect of the invention

[0018]

The execution of a treatment using the preventing agent for epoxy resin bleeding out according to the present invention to prevent epoxy resin bleeding out, in which an organic compound having the capacity to prevent epoxy resin bleeding out is adsorbed on the surface of a semiconductor wiring substrate such as a lead frame or printed circuit board, achieves prevention against epoxy resin bleeding out in die bonding processes, even with respect to low-stress die bonding resins, and to do this without impairing the effect from a sealant treatment or a treatment to inhibit discoloration. In addition, there are no damages on the assembly characteristics, such as the wire bondability and moldability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Figure 1 shows the method of measuring the amount of epoxy resin bleeding out in the evaluation of resistance to epoxy resin bleeding out in the examples.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

[0020]

The preventing agent for epoxy resin bleeding out of the present invention includes a fluorine-containing organic compound that has a fluorohydrocarbon group $C_xH_yF_z-$ ($x = 3$ to 24 , $y = 0$ to 48 , $z = 1$ to 49 , $y + z \leq 2x + 1$) having not less than 3 and not more than 24 of carbons, and a polar group R-.

[0021]

As the aforementioned fluorohydrocarbon group, fluoroalkyl groups, double bond-containing fluoroalkenyl groups, and triple bond-containing fluoroalkynyl groups are exemplified, among them, fluoroalkyl groups are preferred. These fluorohydrocarbon groups may be straight chain or may have a side chain, as long as the fluorohydrocarbon group as a whole contains 3 to 24 carbons. The number of carbons x in the fluorohydrocarbon group is 3 to 24 and particularly preferably is 5 to 12. The epoxy resin bleeding out preventing effect is reduced when carbons are too few, while the moldability (adhesiveness of the molding resin) is reduced when carbons are too many. As for the number of fluorines z , the epoxy resin bleeding out preventing effect is higher when more fluorine is present; however, in the case of a long molecule with a large number of carbons, too many fluorines reduce the moldability, and for this reason the number of fluorines z is preferably 11 to 25.

[0022]

For example, $F(CF_2)_6-$, $F(CF_2)_8-$, $F(CF_2)_{10}-$, $F(CF_2)_6(CH_2)_2-$,

$F(CF_2)_8(CH_2)_2-$, and $F(CF_2)_{10}(CH_2)_2-$ can be preferably used as the aforementioned fluorohydrocarbon group.

[0023]

A polar group containing sulfur (S), nitrogen (N), phosphorus (P), or oxygen (O) can be preferably used as the aforementioned polar group R-, for example, one of mercapto group, amino group, nitrogen-containing heterocyclic group, phosphate ester and carboxyl group is preferable. For example, imidazolyl group, triazolyl group, tetrazolyl group, or a derivative of the preceding can be preferably used as the nitrogen-containing heterocyclic group.

A monoester ($-OP(O)(OH)_2$), diester ($(-O)_2P(O)(OH)$), or triester ($(-O)_3P(O)$) can be used for the phosphate ester as the aforementioned polar group.

[0024]

Isomers exist for the imidazolyl, triazolyl, and tetrazolyl, which are nitrogen-containing heterocyclic groups, and any of these isomers can also be used in the present invention, as can mixtures. Considered in terms of synthesis, nitrogen-containing cyclic compounds in which the nitrogen is directly bonded to the fluorohydrocarbon group are easily obtained and preferably used. As the derivatives of the imidazolyl group, triazolyl group, and tetrazolyl group, derivatives which have an alkyl group or phenyl group as a substituent are exemplified.

[0025]

As the fluorine-containing organic compounds suitable for the preventing agent for epoxy resin bleeding out of the present invention, A-SH, A-NH₂, A-OP(O)(OH)₂, (A-O)₂P(O)(OH), (A-O)₃P(O), A-COOH, A-N₂C₃H₃ (1-imidazolyl), A-N₃C₂H₂ (1,2,3-triazol-1-yl), and A-N₄CH (1-tetrazolyl), where A- is the aforementioned fluorohydrocarbon group C_xH_yF_z-, are exemplified.

[0026]

The preventing agent for epoxy resin bleeding out of the present invention is used in the form of a preventing agent solution for epoxy resin bleeding out prepared by dissolving in a solvent such as water or an organic solvent. The concentration of the aforementioned organic compound in this preventing agent solution is 0.1 mg/L to 100 g/L and preferably 10 mg/L to 10 g/L.

The epoxy resin bleeding out preventing effect is absent when the concentration of the aforementioned organic compound is too low. The effect is saturated at overly high concentrations, which are therefore undesirable since no additional effect can be expected.

[0027]

When water is used as the solvent, an organic solvent such as alcohol or ketone, is added as necessary in those cases where the aforementioned organic compound is difficult to dissolve in water. It is enough for the amount of addition to be the concentration required to dissolve the aforementioned organic compound in water, and the concentration is generally 0.1 g/L to 200 g/L and preferably 1 g/L to 50 g/L. The solubility is low when too little is added, while an excess quantity of addition not only does not change the effect of dissolving the aforementioned organic compound, but also results in a too low concentration of the aforementioned organic compound.

[0028]

In addition, in those cases where the aforementioned organic compound is difficult to dissolve in water, an anionic, cationic, or nonionic surfactant, or a mixture thereof, is optionally added at 1 μ g/L to 10 g/L and preferably 10 μ g/L to 1 g/L.

[0029]

A phosphoric acid based, boric acid based, or organic acid based pH buffer is as necessary added to the preventing

agent solution at 0.1 g/L to 200 g/L and preferably 1 g/L to 50 g/L. Too little results in a low pH buffering effect, while the effect is saturated for excess amounts and hence there is no merit to the addition of large amounts.

[0030]

In those cases where metal elutes into the preventing agent solution, a complexing agent such as an amine based, aminocarboxylic acid based, or a carboxylic acid based complexing agent is optionally added at 0.1 g/L to 200 g/L and preferably 1 g/L to 50 g/L as a metal sequestrant. Too little results in little metal sequestration effect by complexing, while the effect is saturated for excess amounts and hence there is no merit to the addition of large amounts.

[0031]

While there is no necessary restriction on the pH of the preventing agent solution for epoxy resin bleeding out, the pH is generally between pH 1 and 14, and treatment at pH 2 to 12 is preferred. When the range is not followed, the substrate is seriously damaged and the preventing effect against epoxy resin bleeding out is low.

The temperature of the preventing agent solution for epoxy resin bleeding out can be in the temperature range in which the aqueous solution can be worked, but the temperature is generally 5 to 90°C and preferably 10 to 60°C. The preventing effect against epoxy resin bleeding out is low when the temperature is too low, while the effect is saturated at overly high temperatures and hence there is no merit to the use of high temperatures as well as the workability is poor.

[0032]

In the case of using an organic solvent as the solvent, alcohols such as methanol, ethanol and isopropanol, and ketones such as acetone and methyl ethyl ketone are exemplified for the organic solvent. When an organic solvent

is used, the temperature of the preventing agent solution for epoxy resin bleeding out is preferably room temperature.

[0033]

The time of treatment with the preventing agent solution for epoxy resin bleeding out can be suitably adjusted from at least 0.1 second to no more than 300 seconds in view of the effect, while from at least 1 second to no more than 120 seconds is preferred, by taking account of process reproducibility and efficiency. A too short time of treatment results in a low epoxy resin bleeding out preventing effect and also impairs process repeatability. A too long time of treatment does not provide any additional effect and leads to a reduced process efficiency.

[0034]

The method of preventing epoxy resin bleeding out comprises immersing a wiring substrate in the preventing agent solution for epoxy resin bleeding out, or spraying the preventing agent solution for epoxy resin bleeding out on the substrate with a shower, a sprayer, or the like, or coating the preventing agent solution for epoxy resin bleeding out on the substrate with a spin coater or the like in order to contact the solution; in each case followed by a water rinse and drying.

[0035]

A discoloration preventing effect and/or a sealant effect can be imparted at the same time as the bleeding out effect by combining a discoloration inhibitor and/or a sealant for metal surfaces such as plating films or metal substrates, with the aforementioned fluorine-containing organic compound that is the main component of the preventing agent for epoxy resin bleeding out.

Known discoloration inhibitors and known sealants can be used here. For example, a nitrogen-containing heterocyclic compound, such as an imidazole derivative, a triazole

derivative, a tetrazole derivative, or a thiazole derivative, is preferably used as the discoloration inhibitor.

[0036]

By the epoxy resin bleeding out preventing treatment as described hereinabove, the fluorine-containing organic compound adsorbs on the plating layer of the wiring substrate surface with the formation of a film comprising the fluorine-containing organic compound that is from 1 to several molecules thick. This increases the contact angle of plating film and epoxy resin, thereby enabling the prevention of epoxy resin bleeding out. Since the adsorbed fluorine-containing organic compound film is extremely thin, it does not affect on the assembly characteristics, such as the wire bondability, moldability, and so forth. The discoloration inhibiting effect and sealant effect are also not impaired. The present invention also encompasses a wiring substrate on which an epoxy resin bleeding out preventing treatment has been executed by the aforementioned method and further encompasses a semiconductor package that uses the same.

EXAMPLES

[0037]

The present invention is described in detail in the following based on examples, but the present invention is not limited to these examples.

Examples 1 to 10

[0038]

A lead frame substrate of copper alloy (Cu:97.7%-Sn:2.0%-Ni:0.2%-P:0.03%) was subjected to copper strike plating as an underlayer to improve the adhesion. The entire lead frame surface was then plated with one of gold, silver and copper. This was followed by a treatment with the preventing agent for epoxy resin bleeding out shown in Table

1 by immersion.

$-N_2C_3H_3$, $-N_3C_2H_2$, and $-N_4CH$ polar groups in the preventing agents for epoxy resin bleeding out used in Examples 8, 9, and 10 are 1-imidazolyl group, 1,2,3-triazol-1-yl group and 1-tetrazolyl group, respectively.

Die bonding was carried out on these substrates, followed by evaluation of the resistance to epoxy resin bleeding out (EBO resistance), the wire bondability (W/B), the moldability, and the resistance to discoloration. The results are shown in Table 1. A "-" in Table 1 in the bath composition indicates that the particular component was not added, while a "-" in the evaluations indicates that the sample was not evaluated.

[0039]

The resistance to epoxy resin bleeding out was evaluated by the following method.

A commercially available epoxy resin for low-stress die bonding (Ablebond 8340 from Ablestik) was applied with a syringe on the plating surface which was treated with the preventing agent for epoxy resin bleeding out, followed by a thermal cure in air for 30 minutes at 175°C on a hot plate. The epoxy resin-coated region was then inspected with a metal microscope (100X). With regard to the epoxy resin bleeding out observed at the circumference of the epoxy resin for die bonding, as shown in Figure 1 (in Figure 1, the epoxy resin for die bonding is seen as a black circle and the narrow region that is palely seen around this black circle is the epoxy resin bleeding out zone), the amount of ooze (amount of EBO) was measured at the region in which the epoxy resin bleeding out was most pronounced and the amount was evaluated on the following scale.

- : less than 10 μm
- △ : at least 10 μm , but less than 100 μm
- × : at least 100 μm

[0040]

The wire bondability was evaluated by the following method.

Wire bonding was carried out using 25 μ m gold wires by thermocompression with ultrasonics (temperature of 200°C; load of 50 g; time of 10 ms), and the pull strength was then measured with a pull tester and was evaluated on the following scale.

- : at least 10 gf
- × : less than 10 gf

[0041]

The molding characteristics were evaluated by the following method.

The plating surface which had been treated with the preventing agent for epoxy resin bleeding out was coated with a commercially available epoxy resin for molding (EME-6300 from Sumitomo Bakelite), followed by a thermal cure for 5 hours at 175°C. The shear strength was then measured and evaluated on the following scale.

- : at least 10 kgf/cm²
- × : less than 10 kgf/cm²

[0042]

The discoloration inhibiting effect was evaluated by the following method.

The sample was exposed to humidity for 96 hours at 90% humidity and 40°C, followed by inspection of the appearance and evaluation on the following scale.

- : no discoloration
- × : discoloration

Comparative Example 1**[0043]**

Treatment with an preventing agent for epoxy resin bleeding out was carried out as in Example 1, except that the

treatment with the preventing agent for epoxy resin bleeding out shown in Table 1 was executed with using a carboxylic acid as the main component. The sample was evaluated in the same way as in Example 1, and the results are shown in Table 1.

Comparative Example 2

[0044]

Using the substrate shown in Table 1, the same procedure as in Example 1 was carried out, except for the treatment with the preventing agent for epoxy resin bleeding out was not performed. The sample was evaluated in the same way as in Example 1, and the results are shown in Table 1.

Table 1-1

		Examples			
		1	2	3	4
bath composition	substrate, or plating surface	gold	gold	silver	silver
	main component	$F(CF_2)_8-COOH$: 0.1 g/L	$F(CF_2)_8-SH$: 0.1 g/L	$F(CF_2)_8-SH$: 0.1 g/L	$F(CF_2)_8-NH_2$: 0.1 g/L
	solvent	isopropyl alcohol: 1 g/L	—	—	isopropyl alcohol: 1 g/L
	pH buffer	potassium pyrophosphate: 1 g/L	—	potassium tetraborate: 1 g/L	—
	complexing agent	—	—	—	—
	surfactant	polyoxyethylene nonylphenyl ether: 1 mg/L	—	polyoxyethylene nonylphenyl ether: 1 mg/L	—
treatment conditions	discoloration inhibitor	—	—	mercaptobenzo- thiazole: 0.1 g/L	—
	pH	9.0	9.0	9.0	9.0
	treatment temperature (°C)	25	25	25	25
	treatment time (s)	30	30	30	30
results of the evaluations	resistance to EBO	△	○	△	○
	W/B	○	○	○	○
	moldability	○	○	○	○
	resistance to discoloration	○	○	○	○

[0046]

Table 1-2

substrate, or plating surface		Examples			
		5	6	7	8
bath composition	main component	gold	silver	copper	copper
		$F(CF_2)_8(CH_2)_2-OPO(OH)_2$ 0.1 g/L	$F(CF_2)_6(CH_2)_2-OPO(OH)_2$ 0.1 g/L	$[F(CF_2)_8(CH_2)_2-OPO(OH)_2]$ $F(CF_2)_6(OH)_2$:0.1 g/L	$F(CF_2)_8(CH_2)_2-OPO(OH)_2$ 0.1 g/L
	solvent	—	—	isopropyl alcohol: 1 g/L	—
	pH buffer	potassium pyrophosphate: 1 g/L	—	potassium pyrophosphate: 1 g/L	—
	complexing agent	—	—	4Na ethylene- diamine- tetraacetate: 1 g/L	—
	surfactant	—	—	—	—
	discoloration inhibitor	—	—	benzotriazole: 0.1 g/L	—
	pH	9.0	9.0	9.0	9.0
	treatment temperature (°C)	25	25	25	25
	treatment time (s)	30	30	30	30
results of the evaluations	resistance to EBO	○	○	○	○
	W/B	○	○	—	—
	moldability	○	○	○	○
	resistance to discoloration	○	○	○	○

Table 1-3

substrate, or plating surface	Examples		Comparative Examples	
	9	10	1	2
bath composition	main component	copper $F(CF_2)_8-N_3C_2H_5$: 0.1 g/L	copper $F(CF_2)_8(CH_2)_2-N_4CH$: 0.1 g/L	gold $H(CH_2)_8-COOH$ no treatment
	solvent	isopropyl alcohol: 1 g/L	—	isopropyl alcohol: 1 g/L
	pH buffer	potassium tetraborate: 1 g/L	—	potassium pyrophosphate: 1 g/L
	complexing agent	4Na ethylene-diamine-tetraacetate: 1 g/L	4Na ethylene-diamine-tetraacetate: 1 g/L	—
	surfactant	—	—	—
treatment conditions	discoloration inhibitor	—	—	—
	pH	9.0	9.0	—
	treatment temperature (°C)	25	25	—
	treatment time (s)	30	30	—
results of the evaluations	resistance to EBO	○	○	—
	W/B	—	—	×
	moldability	○	○	—
	resistance to discoloration	○	○	○
			○	×

CLAIMS

1. A preventing agent for epoxy resin bleeding out for a die bonding process, comprising a fluorine-containing organic compound that has a fluorohydrocarbon group $C_xH_yF_z-$ ($x = 3$ to 24 , $y = 0$ to 48 , $z = 1$ to 49 , $y + z \leq 2x + 1$) having not less than 3 and not more than 24 of carbons, and a polar group $R-$.
2. The preventing agent for epoxy resin bleeding out according to claim 1, wherein the polar group $R-$ is a polar group that contains one selected from the group of sulfur (S), nitrogen (N), phosphorus (P) and oxygen (O).
3. The preventing agent for epoxy resin bleeding out according to claim 2, wherein the polar group $R-$ is one selected from the group of mercapto group, amino group, nitrogen-containing heterocyclic group, phosphate ester group and carboxyl group.
4. The preventing agent for epoxy resin bleeding out according to claim 3, wherein the nitrogen-containing heterocyclic group is one selected from the group of imidazolyl group, triazolyl group, tetrazolyl group and a derivative thereof.
5. The preventing agent for epoxy resin bleeding out according to any of claims 1 to 4, further comprising a discoloration inhibitor or a sealant.
6. The preventing agent for epoxy resin bleeding out according to claim 5, wherein the discoloration inhibitor contains a nitrogen-containing heterocyclic compound.
7. The preventing agent for epoxy resin bleeding out according to claim 6, wherein the nitrogen-containing heterocyclic compound is one selected from the group of imidazole derivative, triazole derivative, tetrazole derivative and thiazole derivative.
8. A method of preventing epoxy resin bleeding out,

comprising the step of:

immersing a wiring substrate in a solution containing the preventing agent for epoxy resin bleeding out according to any of claims 1 to 7, or

spraying or applying a solution containing said preventing agent for epoxy resin bleeding out on a wiring substrate.

9. A wiring substrate, treated to prevent epoxy resin bleeding out by

immersing the wiring substrate in a solution containing the preventing agent for epoxy resin bleeding out according to any of claims 1 to 7, or

spraying or applying a solution containing said preventing agent for epoxy resin bleeding out on the wiring substrate.

10. A wiring substrate, wherein the preventing agent for epoxy resin bleeding out according to any of claims 1 to 7 is adsorbed on a surface thereof.

11. A semiconductor package, which uses the wiring substrate according to claim 9 or 10.