

DESCRIPTION

RESIN-BLEEDOUT PREVENTING AGENT AND METHOD FOR PREVENTING RESIN-BLEEDOUT

TECHNICAL FIELD

[0001] The present invention relates to a resin-bleedout preventing agent and method for preventing resin-bleedout in the die-bonding process whereby a lead frame, printed wiring board or other semiconductor wiring substrate is bonded with resin to an IC chip.

BACKGROUND ART

[0002] Semiconductor chips are normally bonded to lead frames, printed wiring boards and other substrates with die bonding resin. The bonding surface of the substrate is normally plated with gold, silver, palladium, copper, nickel or the like, but if the surface is too rough or if the surface has been contaminated with an organic material such as a plating additive, anti-tarnishing agent or sealant, bleeding (resin-bleedout (RBO)) of resin or additives can occur when die bonding resin is applied in the die bonding process. Such RBO detracts from die bonding strength and adversely affects the subsequent steps of wire bonding and molding.

[0003] Conventional means of preventing RBO have included reducing the surface roughness of the plated surface at the bonding area to control capillary action, and washing the surface to remove contaminants. However, the surface roughness of the bonding surface cannot always be reduced because this affects die bonding strength and the image recognition capability of the

assembly machine. The problem with washing the surface has been that the anti-tarnishing coat and sealant coat are also lost.

[0004] To resolve these problems, Patent Document 1 shows that RBO can be prevented by immersing the substrate in a solution consisting mainly of a carboxylic acid, thiol or the like to thereby adsorb an organic coat of 1 to a few molecules, without altering the surface roughness of the substrate or washing off the anti-tarnishing coat or sealant coat, and without adversely affecting the wire bonding, molding and other assembly properties because the adsorbed organic coat is extremely thin.

[0005] As a result of further research, the inventors in this case have also shown that a fluoroalkyl compound having a polar group has a greater RBO-preventing effect than the carboxylic acid, thiol compound or the like of Patent Document 1 (Patent Document 2).

However, fluoroalkyl compounds may pose wastewater treatment problems because they contain fluorine.
Patent Document 1: Japanese Patent Publication No. H11-195662A

Patent Document 2: Japanese Patent Publication 2007-52890A

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] It is an object of the present invention to provide a resin-bleedout preventing agent that poses few problems for waste-water treatment and does not adversely affect die bonding strength or assembly properties even

using a low-stress type die bonding resin, or detract from the effects of anti-tarnishing and sealant treatment.

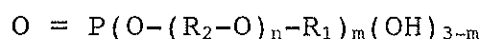
MEANS FOR SOLVING THE PROBLEMS

[0007] The inventors in this case arrived at the present invention after discovering, as a result of exhaustive research, a group of organic compounds having a resin-bleedout preventing effect that pose fewer problems for waste-water treatment than fluorine-containing compounds and do not detract from the effects of anti-tarnishing and sealant treatment or adversely affect die bonding strength or assembly properties even using a low-stress type die bonding resin in a process for preventing resin bleed-out by immersing a substrate in a solution containing a resin bleed-out preventing agent to thereby adsorb an organic coat on a plated surface.

That is, the present invention is as follows.

[0008] (1) A resin-bleedout preventing agent containing the phosphoric acid ester represented by the following general formula:

[C1]



(wherein R_1 represents a C4-30 saturated or unsaturated hydrocarbon group, R_2 represents a lower alkylene group, n is an integer from 0 to 10 and m is an integer from 1 to 3).

[0009] (2) The resin-bleedout preventing agent according to (1) above, wherein R_1 of the aforementioned phosphoric acid ester is either a C8-20 alkyl group, alkenyl group or alkynyl group, R_2 is an ethylene group,

n is an integer from 1 to 6 and m is an integer from 1 to 3.

(3) A resin-bleedout preventing agent according to (1) or (2) above, also containing a nitrogen-containing heterocyclic compound-type anti-tarnishing agent comprising any of a tetrazole derivative, triazole derivative, imidazole derivative and thiazole derivative.

[0010] (4) A method for preventing resin-bleedout by applying a resin-bleedout preventing treatment using a resin-bleedout preventing agent according to any one of (1) through (3) above.

(5) A substrate that has been subjected to resin-bleedout preventing treatment using a resin-bleedout preventing agent according to any one of (1) through (3) above and has a coat of the resin-bleedout preventing agent.

EFFECT OF THE INVENTION

[0011] Using the resin-bleedout preventing agent of the present invention, resin-bleedout in the die bonding process can be prevented without detracting from the effects of anti-tarnishing treatment or sealant treatment by applying a resin-bleedout preventing treatment whereby an organic compound having a resin-bleedout preventing function is adsorbed on the surface of a lead frame, printed wiring board or other semiconductor wiring substrate.

Moreover, the wire bonding properties, molding properties and other assembly properties are not adversely affected. In addition, because the resin-bleedout preventing agent is of the non-fluorine type it poses few problems for waste-water treatment.

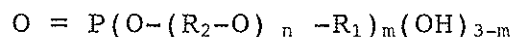
BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 illustrates a method for measuring resin-bleedout when evaluating the anti-resin-bleedout effects of the examples.

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] The resin-bleedout preventing agent of the present invention contains a phosphoric acid ester represented by the following formula:

[C2]



(wherein R_1 represents a C4-30 saturated or unsaturated hydrocarbon group, R_2 represents a lower alkylene group, n is an integer from 0 to 10 and m is an integer from 1 to 3).

[0014] R_1 represents a C4-30 saturated or unsaturated hydrocarbon group. Of these, a C8-20 saturated or unsaturated hydrocarbon group is preferred. If there are too few carbon atoms the resin-bleedout preventing effect will be poor, while if there are too many the molding properties (adhesiveness of molding resin) will be reduced.

[0015] The saturated or unsaturated hydrocarbon group may have two or more double bonds or triple bonds, and may be a straight chain or may have side chains. A cyclic hydrocarbon group or aromatic hydrocarbon group may also be linked to the main chain, but a straight-chain alkyl group, alkenyl group or alkynyl group is preferred, and a straight-chain alkyl group is especially preferred. The positions of the double bonds and triple

bonds in an alkenyl group or alkynyl group are not particularly limited.

R_2 is a C1-4 lower alkylene group, and is preferably a methylene group, ethylene group or propylene group or more preferably an ethylene group.

[0016] n represents an integer from 0 to 10 and preferably an integer from 1 to 6.

m represents an integer from 1 to 3. This phosphoric acid ester is useful either as a monoester, diester or triester, and if obtained as a mixture it can be used as is without the need for separation. When m is more than 1, R_1 , R_2 and n may be different.

[0017] The resin-bleedout preventing agent of the present invention is dissolved in a solvent such as water to be used as a resin-bleedout preventing agent solution. The concentration of the phosphoric acid ester in this resin-bleedout preventing agent solution is preferably 1 mg/L to 100 g/L, or more preferably 10 mg/L to 10 g/L. If the concentration is less than 1 mg/L the RBO preventing effect will be weak, while more than 100 g/L is not desirable because the effect is saturated and no additional effects can be expected beyond that level.

[0018] The resin-bleedout preventing agent of the present invention may also contain a metal anti-tarnishing agent. Specifically, a known anti-tarnishing agent can be used for this anti-tarnishing agent, but a nitrogen-containing heterocyclic compound-type anti-tarnishing agent comprising any of a tetrazole derivative, triazole derivative, imidazole derivative and thiazole derivative is preferred.

Examples of such anti-tarnishing agents include tetrazole, benzotriazole, benzimidazole, benzothiazole, mercaptobenzothiazole and the like.

[0019] The content of this anti-tarnishing agent in the resin-bleedout preventing agent solution is preferably 1 mg/L to 100 g/L or more preferably 10 mg/L to 10 g/L. Below 1 mg/L the anti-tarnishing effect will be weak, while more than 100 g/L is not desirable because the effect is saturated and no additional effects can be expected beyond that level.

In addition to the resin-bleedout preventing effect, the anti-tarnishing effect can also be provided at the same time by containing the anti-tarnishing agent.

[0020] When water is used as the solvent, if the phosphoric acid ester does not dissolve easily in water an alcohol, ketone or other organic solvent may also be added as necessary. The added amount can be any concentration that allows the phosphoric acid ester to be dissolved in water, but normally 0.1 g/L to 200 g/L is preferred and 1 g/L to 50 g/L is more preferred. If less is added solubility will be low, while adding more will not produce any further effect in terms of dissolving the phosphoric acid ester.

[0021] If the phosphoric acid ester does not dissolve easily in water, moreover, 1 μ g/L to 10 g/L or preferably 10 μ g/L to 1 g/L of an anionic, cationic or nonionic surfactant or a mixture of these can be added as necessary. If less is added solubility will be low, while adding more will not produce any further effect in terms of dissolving the phosphoric acid ester.

[0022] A phosphoric acid, boric acid or organic acid pH buffer may also be added as necessary to the resin-

bleedout preventing agent solution in the amount of 0.1 g/L to 200 g/L or preferably 1 to 50 g/L in order to improve the pH buffer properties of the liquid. Below 0.1 g/L the pH buffer effect will be low, while above 200 g/L a plateau is reached and no further effects can be expected.

[0023] A metal masking agent can be used as necessary in cases in which metal is eluted in the resin-bleedout preventing solution. Basically a known metal masking agent can be used in this case, and in particular it is desirable to add 0.1 g/L to 200 g/L or preferably 1 g/L to 50 g/L of an amine, aminocarboxylic acid or carboxylic acid complexing agent. Below 0.1 g/L the metal complexing ability will be low, while above 200 g/L the effect is saturated and no additional effects can be expected.

[0024] The pH of the resin-bleedout preventing agent solution need not be particularly limited, but is normally between pH 1 and pH 14 or preferably pH 2 and pH 12. Outside this range, there will be more damage to the materials and less resin-bleedout preventing effect.

The temperature of the resin-bleedout preventing agent solution can be any temperature range that is possible in an aqueous solution, but is normally 5 to 90°C or preferably 10 to 60°C. If the temperature is too low the effect on resin-bleedout will be less, while temperatures above 90°C adversely affect operability without providing any advantages.

[0025] The treatment time with the resin-bleedout preventing agent solution can be adjusted appropriately between 0.1 and 300 seconds according to the effects, and 1 to 60 seconds is desirable from the standpoint of

operation reproducibility and efficiency. Below 0.1 seconds the effect on resin-bleedout will be less and the operation will be difficult to reproduce, while above 300 seconds the effects plateau and operating efficiency is poor.

[0026] In the method for preventing resin-bleedout of the present invention a wiring substrate is immersed in a resin-bleedout preventing agent solution, or a resin-bleedout preventing agent solution is sprayed, showered or spin-coated or the like on a substrate, after which the substrate can be water washed and dried.

Examples of wiring substrates include lead frames, printed wiring boards and other semiconductor wiring substrates, and the surface of the substrate which is to be given the resin-bleedout preventing treatment is preferably one that has been plated with gold, silver, palladium, copper, nickel or the like.

[0027] By means of a resin-bleedout preventing treatment such as that described above, the phosphoric acid ester is adsorbed on the plated surface of a wiring substrate to thereby form a coat consisting of a phosphoric acid ester with a thickness of 1 to a few molecules. Consequently, it is possible to increase the contact angle between the plated surface and the die bonding resin, and control bleeding of the die bonding resin. Because the coat of adsorbed phosphoric acid ester is extremely thin, the wire bonding properties, molding properties and other assembly properties are not adversely affected. The anti-tarnishing effects and sealant effects are also not affected. The present invention encompasses a wiring substrate that has been subjected to resin-bleedout preventing treatment by the

aforementioned methods to form a coat of the preventing agent, as well as a semiconductor package using such a substrate.

[0028] An effective die bonding resin to use after the resin-bleedout preventing treatment of the present invention may be a low-stress type die bonding resin, the examples of which include an epoxy resin, acrylic resin or the like, with an epoxy resin being preferred.

EXAMPLES

[0029] The present invention is explained below based on examples, but the present invention is not limited by these examples.

[0030] Examples 1 to 6, Comparative Examples 1 and 2

A copper alloy (Cu 97.7%, Sn 2.0%, Ni 0.2%, P 0.03%) lead frame substrate was strike-plated with copper as a base for improving adhesiveness, and the entire lead frame was then plated with silver, gold or copper. Resin-bleedout preventing agent treatment was then carried out by immersion as described in Table 1 below.

These substrates were then die bonded, and the anti-resin-bleedout (anti-RBO) properties, wire bonding (W/B) properties, molding properties and anti-tarnishing properties were evaluated. The results are shown in Table 1. In Table 1, "-" under bath composition means that the component was not added, while "-" under evaluation means that the property was not evaluated.

[0031] In Table 1, R_1 , R_2 and n represent R_1 , R_2 and n in the phosphoric acid ester represented by the aforementioned formula, using a 1:1 monoester:diester mixture as the phosphoric acid ester. The alkyl groups and alkenyl groups of R_1 in the phosphoric acid ester are

all straight-chain, while the alkenyl groups in Examples 5 and 6 are 10-eicosenyl and 11-docosenyl groups having double bonds at or near the center of the chains.

[0032] The anti-resin-bleedout properties were evaluated as follows.

A commercial low-stress die-bonding epoxy resin (Ablebond 8340, Ablestik Co.) was applied to a plated surface that had been subjected to resin-bleedout preventing treatment, and left for 2 hours at room temperature in atmosphere. This was then heat cured for 1 hour in atmosphere at 175°C with a hot plate, the area with the epoxy resin was observed with a metal microscope (100x), and, as shown in Figure 1, the amount of bleeding (RBO) in the area with the most extreme resin bleed-out was measured and evaluated as follows.

O: Less than 10 μm
Δ: At least 10 μm but less than 50 μm
X: 50 μm or more

[0033] The wire bonding properties were evaluated as follows.

Wire bonding was performed by thermosonic compression bonding (temperature 200°C, load 50 g, time 10 ms) using 25 μm gold wire, and the pull strength was measured with a pull tester and evaluated as follows.

O: 10 gf or more
X: Less than 10 gf

[0034] The molding properties were evaluated as follows.

A commercial epoxy resin for molding (Sumitomo Bakelite EME 6300) was applied to a plated surface that had been subjected to resin-bleedout preventing treatment, and heat cured for 5 hours at 175°C, after which

adhesiveness (shearing force) was measured and evaluated as follows.

O: 20 kgf/cm² or more

Δ: At least 10 kgf/cm² but less than 20 kgf/cm²

X: Less than 10 kgf/cm²

[0035] Tarnishing resistance was evaluated as follows.

Following 96 hours of humidification at 40°C, 90% humidity, the external appearance was observed and evaluated as follows.

O: No tarnishing

X: Tarnishing

[0036] [Table 1-1]

	Example			
	1	2	3	4
SUBSTRATE/PLATED SURFACE	Silver	Silver	Silver	Silver
BATH COMPOSITION	Main Component			
	R ₁	C ₆ H ₁₃	C ₁₂ H ₂₅	C ₁₆ H ₃₃
	R ₂	-	CH ₂ CH ₂	CH ₂ CH ₂
	n	0	2	2
	Concentration	0.5 g/L	0.5 g/L	0.5 g/L
	Anti-tarnishing agent	-	-	Mercaptobenzo-thiazole: 0.1 g/L
	Solvent	-	-	Isopropyl alcohol: 5 g/L
	pH buffer	Potassium tetraborate: 1 g/L	Potassium pyrophosphate: 1 g/L	-
	Complexing agent	-	Ethylenediamine tetraacetic acid 4Na: 1 g/L	-
	Surfactant	-	Oxyethylene nonylphenyl ether: 1 mg/L	-
TREATMENT CONDITIONS	pH	9.0	9.0	9.0
	Temperature (°C)	25	25	25
	Time (s)	10	10	10
EVALUATION RESULTS	RBO properties	Δ	0	0
	W/B properties	0	0	0
	Molding	0	0	0
	Anti-tarnishing	0	0	0

[0037] [Table 1-2]

SUBSTRATE/PLATED SURFACE	Example				Comparative Example	
	5	6	1	2	1	2
Main component	Gold	Copper	Silver	Silver	Silver	Silver
R ₁	C ₂₀ H ₃₈	C ₂₂ H ₄₃	C ₃ H ₇	C ₃₂ H ₆₅	C ₃ H ₇	C ₃₂ H ₆₅
R ₂	CH ₂ CH ₂	CH ₂ CH ₂	-	CH ₂ CH ₂	-	CH ₂ CH ₂
n	3	4	0	8	0	8
Concentration	0.5 g/L	0.5 g/L	0.5 g/L	0.5 g/L	0.5 g/L	0.5 g/L
Anti-tarnishing agent	-	Benzotriazole: 0.1 g/L	-	-	-	-
Solvent	Isopropyl alcohol: 10 g/L	Isopropyl alcohol: 10 g/L	-	Isopropyl alcohol: 10 g/L	-	Isopropyl alcohol: 10 g/L
pH buffer	Potassium phosphate: 1 g/L	-	-	-	-	-
Complexing agent	-	Ethylene-diamine tetraacetic acid 4Na: 1 g/L	-	-	-	-
Surfactant	-	-	-	-	-	-
pH	9.0	9.0	9.0	9.0	9.0	9.0
Temperature (°C)	25	25	25	25	25	25
Time (s)	10	10	10	10	10	10
RBO properties	0	0	X	0	X	0
W/B properties	0	-	0	X	0	X
Molding	0	Δ	0	X	0	X
Anti-tarnishing	0	0	0	0	0	0

BATH COMPOSITION

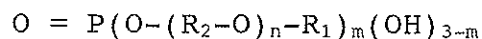
TREATMENT CONDITIONS

EVALUATION RESULTS

CLAIMS

1. A resin-bleedout preventing agent containing a phosphoric acid ester represented by the following general formula:

[C1]



(wherein R_1 represents a C4-30 saturated or unsaturated hydrocarbon group, R_2 represents a lower alkylene group, n is an integer from 0 to 10 and m is an integer from 1 to 3).

2. The resin-bleedout preventing agent according to Claim 1, wherein R_1 of the phosphoric acid ester is any of a C8-20 alkyl group, alkenyl group and alkynyl group, R_2 is an ethylene group, n is an integer from 1 to 6 and m is an integer from 1 to 3.

3. The resin-bleedout preventing agent according to Claim 1 or 2, further containing a nitrogen-containing heterocyclic compound-type anti-tarnishing agent comprising any of a tetrazole derivative, triazole derivative, imidazole derivative and thiazole derivative.

4. A method for preventing resin-bleedout by applying a resin-bleedout preventing treatment using the resin-bleedout preventing agent according to any one of Claims 1 through 3.

5. A substrate that has been subjected to resin-bleedout preventing treatment using the resin-bleedout preventing agent according to any one of Claims 1 through 3 and has a coat of the resin-bleedout preventing agent.