while 1.0 mol% is accounted for by those corresponding to n in the range 1 to 15 (diamine residue (A1)). There are no components that correspond to n of 51 or more.

BAHF: 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (corresponding to diamine residue (A3))

DABS: 4,4'-dihydroxy-3,3'-diaminodiphenyl sulfone (corresponding to diamine residue (A3))

ABP-N: 1,3-bis(3-aminophenoxy)benzene (not corresponding to any of diamine residues (A1) to (A3))

CHN: cyclohexanone

JER871: dimer acid modified epoxy resin (manufactured by Mitsubishi Chemical Corporation) (corresponding to dimer acid epoxy resin (B))

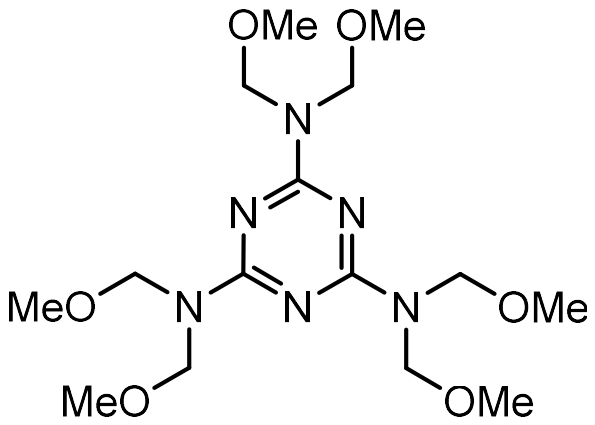
CG500: caldo based epoxy resin (manufactured by Osaka Gas Chemicals Co., Ltd.)

2E4MZ: 2-ethyl-4-methyl imidazole (manufactured by Shikoku Chemicals Corporation

100LM: crosslinking agent having a methylol group as represented by the structural formula given below

[0113]

[Chemical compound 4]



[0114]

In the formula, Me represents a methyl group.

[0115]

Production example 1 (polymerization of polyimide copolymer)

In a reaction vessel equipped with a thermometer, a dry nitrogen inlet, a heating/cooling device using hot water/cooling water, and a stirring device, 95.0 g of APPS2 (containing 108.5

copolymer solution. The solid content in the resulting polyimide polymer solution was measured and found to be 51.4 wt%. CHN was added to adjust the solid content of the polymer solution to 50.0 wt%, followed by stirring to provide a polyimide copolymer solution PIS-19 that had a solid content of 50 wt%. Here, in PIS-19, the diamine residue (A1) accounts for 90.0 mol% and the diamine residue (A2) accounts for 8.5 mol% of all diamine residues, which account for 100.0 mol%, in the polyimide copolymer.

[0134]

Production example 20 (polymerization of polyimide copolymer)

Except for using 103.6 g of APPS2 (containing 118.4 mmol of component A1 and 1.2 mmol of component A2), 15.1 g of APPS3 (containing 0.1 mmol of component A1 and 9.7 mmol of component A2), 16.7 g of BAHF (corresponding to (A3), 49.8 mmol), 5.8 g of ABP-N (diamine residue corresponding to none of (A1) to (A3), 19.9 mmol), and 187 g of CHN, the same procedure as in Production example 1 was carried out to polymerize a polyimide copolymer solution. The solid content in the resulting polyimide polymer solution was measured and found to be 50.9 wt%. CHN was added to adjust the solid content of the polymer solution to 50.0 wt%, followed by stirring to provide a polyimide copolymer solution PIS-20 that had a solid content of 50 wt%. Here, in PIS-20, the diamine residue (A1) accounts for 59.5 mol% and the diamine residue (A2) accounts for 5.5 mol% of all diamine residues, which account for 100.0 mol%, in the polyimide copolymer.

[0135]

Production example 22 (polymerization of polyimide copolymer)

Except for using 121.9 g of APPS2 (containing 139.2 mmol of component A1 and 1.4 mmol of component A2), 22.4 g of APPS3 (containing 139.2 mmol of component A1 and 1.4 mmol of component A2), 12.0 g of BAHF (corresponding to (A3), 35.8 mmol), 2.3 g of ABP-N

(diamine residue corresponding to none of (A1) to (A3), 8.0 mmol), and 204 g of CHN, the same procedure as in Production example 1 was carried out to polymerize a polyimide copolymer solution. The solid content in the resulting polyimide polymer solution was measured and found to be 51.2 wt%. CHN was added to adjust the solid content of the polymer solution to 50.0 wt%, followed by stirring to provide a polyimide copolymer solution PIS-22 that had a solid content of 50 wt%. Here, in PIS-22, the diamine residue (A1) accounts for 70.0 mol% and the diamine residue (A2) accounts for 8.0 mol% of all diamine residues, which account for 100.0 mol%, in the polyimide copolymer.

[0136]

Production example 23 (polymerization of polyimide copolymer)

Except for using 142.5 g of APPS2 (containing 162.8 mmol of component A1 and 1.6 mmol of component A2), 26.8 g of APPS3 (containing 0.2 mmol of component A1 and 17.2 mmol of component A2), 5.7 g of BAHF (corresponding to (A3), 17.0 mmol), and 222 g of CHN, the same procedure as in Production example 1 was carried out to polymerize a polyimide copolymer solution. The solid content in the resulting polyimide polymer solution was measured and found to be 52.0 wt%. CHN was added to adjust the solid content of the polymer solution to 50.0 wt%, followed by stirring to provide a polyimide copolymer solution PIS-23 that had a solid content of 50 wt%. Here, in PIS-23, the diamine residue (A1) accounts for 82.0 mol% and the diamine residue (A2) accounts for 9.5 mol% of all diamine residues, which account for 100.0 mol%, in the polyimide copolymer.

The mole fraction of each monomer component is listed in Table 1.

[0137]

[Table 1]

[Table 1]

	Fractions (mol%) of monomers in all diamine residues (100 mol%)							X in formula of (A1):(A2)=X:1
	acid dianhydride	chain end	diamine corresponding to diamine residue (A1)	diamine corresponding to diamine residue (A2)	diamine corresponding to diamine residue (A3)	diamine corresponding to none of A1, A2, and A3	Sum of diamine corresponding to diamine residue (A1) and diamine corresponding to diamine residue (A2)	
PIS-1	89.5	20	54.7	22.3	23.0	0.0	77	2.5
PIS-2	89.5	20	92.1	3.9	4.0	0.0	96	23.6
PIS-3	89.5	20	79.2	2.8	18.0	0.0	82	28.3
PIS-4	89.5	20	59.7	35.3	5.0	0.0	95	1.7
PIS-5	89.5	20	86.2	10.8	3.0	0.0	97	8.0
PIS-6	89.5	20	69.3	2.7	28.0	0.0	72	25.7
PIS-7	89.5	20	69.4	5.6	25.0	0.0	75	12.4
PIS-8	89.5	20	79.3	13.7	7.0	0.0	93	5.8
PIS-9	89.5	20	86.2	3.8	10.0	0.0	90	22.7
PIS-10	89.5	20	79.2	5.8	15.0	0.0	85	13.7
PIS-11	89.5	20	79.2	5.8	15.0	0.0	85	13.7
PIS-12	89.5	20	44.9	35.1	20.0	0.0	80	1.3
PIS-13	89.5	20	97.0	2.0	1.0	0.0	99	48.5
PIS-14	89.5	20	84.1	0.9	15.0	0.0	85	93.4
PIS-15	89.5	20	50.0	45.0	5.0	0.0	95	1.1
PIS-16	89.5	20	79.4	20.6	0.0	0.0	100	3.9
PIS-17	89.5	20	59.5	5.5	35.0	0.0	65	10.8
PIS-18	89.5	20	94.0	3.0	3.0	0.0	97	31.3
PIS-19	89.5	20	90.0	8.5	1.5	0.0	98.5	10.6
PIS-20	89.5	20	59.5	5.5	25.0	10.0	65.0	10.8
PIS-22	89.5	20	70.0	8.0	18.0	4.0	78.0	8.8
PIS-23	89.5	20	82.0	9.5	8.5	0.0	91.5	8.6

[0138]

Examples 1 to 30 and Comparative examples 1 and 8

Additives were added to the polyimide copolymer solutions prepared in Production examples 1 to 23, followed by stirring to provide varnishes that, including the additives, had a solid content of 50 parts by weight. The varnishes were filtered through a PTFE filter with a pore size of 1 μm. The varnishes were examined to make evaluations for the retention of semiconductor elements, adhesive residue, and heat resistance. The proportions of the components of the varnishes and results of the various evaluations are summarized in Tables 2 to 4.

[0139]

[Table 2]

[Table 2]

	polyimide copolymer solution (solution with solid content 50 wt%)	epoxy resin	crosslinking agent (C)	other additive	solvent
	top: type bottom: content	top: type bottom: content	top: type bottom: content	top: type bottom: content	top: type bottom: content
Example 1	PIS-1 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 2	PIS-2 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 3	PIS-3 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 4	PIS-4 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 5	PIS-5 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 6	PIS-6 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 7	PIS-3 48.07g	JER871 0.72g	-	2E4MZ 0.24g	CHN 0.96g
Example 8	PIS-3 46.30g	JER871 1.62g	-	2E4MZ 0.23g	CHN 1.85g
Example 9	PIS-3 34.24g	JER871 7.71g	-	2E4MZ 0.17g	CHN 7.88g
Example 10	PIS-3 39.68g	JER871 4.96g	-	2E4MZ 0.20g	CHN 5.16g
Example 11	PIS-3 31.85g	JER871 8.76g	100LM 0.16g	2E4MZ 0.16g	CHN 9.08g
Example 12	PIS-3 41.22g	JER871 4.12g	100LM 0.06g	2E4MZ 0.21g	CHN 4.39g
Example 13	PIS-3 39.07g	JER871 3.91g	100LM 1.37g	2E4MZ 0.20g	CHN 5.47g
Example 14	PIS-3 40.00g	JER871 4.00g	100LM 0.80g	2E4MZ 0.20g	CHN 5.00g
Example 15	PIS-7 40.98g	JER871 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g
Example 16	PIS-8 40.98g	JER871 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g
Example 17	PIS-9 40.98g	JER871 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g
Example 18	PIS-10 40.98g	JER871 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g
Example 19	PIS-10 32.05g	JER871 8.81g	-	2E4MZ 0.16g	CHN 8.97g
Example 20	PIS-10 32.05g	JER871 8.81g	100LM 0.16g	2E4MZ 0.16g	CHN 8.97g

[0140]

[Table 3]

[Table 3]

	polyimide copolymer solution (solution with solid content 50 wt%)	epoxy resin	crosslinking agent (C)	other additive	solvent
	top: type bottom: content	top: type bottom: content	top: type bottom: content	top: type bottom: content	top: type bottom: content
Example 21	PIS-10 41.32g	JER871 4.13g	-	2E4MZ 0.21g	CHN 4.34g
Example 22	PIS-11 40.98g	JER871 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g
Example 23	PIS-19 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Example 24	PIS-20 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Example 25	PIS-18 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Example 27	PIS-3 32.05g	JER871 8.76g	100LM 0.26g	2E4MZ 0.20g	CHN 8.73g
Example 28	PIS-3 32.05g	JER871 8.76g	100LM 0.40g	2E4MZ 0.20g	CHN 8.59g
Example 29	PIS-22 40.00g	JER871 4.00g	100LM 0.80g	2E4MZ 0.20g	CHN 5.00g
Example 30	PIS-23 40.98g	JER871 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g
Comparative example 1	PIS-12 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Comparative example 2	PIS-13 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Comparative example 3	PIS-14 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Comparative example 4	PIS-15 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Comparative example 5	PIS-16 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Comparative example 6	PIS-17 32.05g	JER871 8.76g	-	2E4MZ 0.16g	CHN 9.08g
Comparative example 7	PIS-10 49.02g	-	100LM 0.25g	2E4MZ 0.25g	CHN 0.49g
Comparative example 8	PIS-10 40.98g	CG500 4.10g	100LM 0.21g	2E4MZ 0.21g	CHN 4.51g

[0141]

[Table 4]

[Table 4]

	evaluation results							
	evaluation for retention of semiconductor elements number of chips held on pressure sensitive adhesive		evaluation for adhesive residue		heat resistance		chemical resistance	
	press-bonded at room temperature	press-bonded at 100°C	area containing adhesive residue	rating	1% weight loss temperature	rating	Proportion of residual film	rating
	number	number	%		°C		%	
Example 1	88	95	0	A	325	B	95	B
Example 2	98	97	0	A	310	B	91	B
Example 3	95	95	0	A	324	B	96	A
Example 4	93	95	0	A	300	B	93	B
Example 5	97	97	3	A	308	B	91	B
Example 6	97	93	0	A	328	B	97	A
Example 7	97	99	12	B	410	A	91	B
Example 8	97	99	7	A	403	A	94	B
Example 9	96	97	0	A	335	B	94	B
Example 10	95	96	0	A	360	A	95	B
Example 11	94	95	0	A	329	B	99	A
Example 12	97	99	0	A	373	A	97	A
Example 13	95	98	0	A	360	A	99	A
Example 14	95	98	0	A	362	A	99	A
Example 15	90	95	0	A	381	A	98	A
Example 16	98	100	0	A	365	A	97	A
Example 17	96	99	0	A	373	A	98	A
Example 18	98	100	0	A	375	A	98	A
Example 19	93	95	0	A	330	B	95	B
Example 20	93	96	0	A	328	B	100	A
Example 21	99	100	0	A	380	A	98	A
Example 22	98	100	0	A	340	B	99	A
Example 23	98	100	30	C	350	A	91	B
Example 24	83	90	0	A	370	A	92	B
Example 25	97	97	20	C	362	A	91	B
Example 27	97	99	0	A	375	A	99	A
Example 28	94	97	0	A	363	A	99	A
Example 29	92	94	0	A	366	A	99	A
Example 30	99	100	0	A	370	A	99	A
Comparative example 1	20	40	0	A	301	B	99	A
Comparative example 2	97	100	1	A	270	C	85	C
Comparative example 3	100	100	0	A	290	C	99	A
Comparative example 4	95	98	0	A	275	C	96	A
Comparative example 5	99	100	89	D	280	C	60	D
Comparative example 6	15	35	0	A	287	C	97	A
Comparative example 7	95	98	100	D	419	A	55	D
Comparative example 8	45	50	0	A	390	A	99	A

CLAIMS

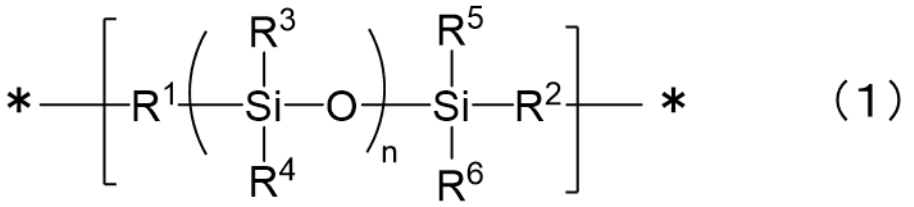
[Claim 1]

A pressure sensitive adhesive comprising a polyimide copolymer (A) having at least an acid dianhydride residue and a diamine residue and also comprising a dimer acid epoxy resin (B),

wherein the diamine residue has a diamine residue (A1) as represented by the formula (1) in which n is a natural number of 1 or more and 15 or less (hereinafter referred to as the diamine residue (A1)), a diamine residue (A2) as represented by the formula (1) in which n is a natural number of 16 or more and 50 or less (hereinafter referred to as the diamine residue (A2)), and a diamine residue (A3) having a phenolic hydroxyl group (hereinafter referred to as the diamine residue (A3)), and

wherein the diamine residue (A1) accounts for 50.0 mol% or more and 95.0 mol% or less, the diamine residue (A2) accounting for 5.5 mol% or more and 40.0 mol% or less, and the diamine residue (A3) accounting for 1.0 mol% or more and 30.0 mol% or less, of all diamine residues, which account for 100.0 mol%, in the polyimide copolymer (A),

[Chemical compound 1]



(1)

wherein in the formula (1), R^1 and R^2 may be identical to or different from each other and they each represent an alkylene group containing 1 to 30 carbon atoms or a phenylene group; R^3 to R^6 may be identical to or different from each other and they each represent an alkyl group containing 1 to 30 carbon atoms, a phenyl group, or a phenoxy group; and * denotes a bonding part.

[Claim 2]

A pressure sensitive adhesive as set forth in claim 1, comprising 5 parts by weight or more and 50 parts by weight or less of a dimer acid epoxy resin (B) relative to 100 parts by weight of the polyimide copolymer (A).

[Claim 3]

A pressure sensitive adhesive as set forth in either claim 1 or 2, further comprising a crosslinking agent (C) having either an alkoxy methyl group or a methylol group.

[Claim 4]

A pressure sensitive adhesive as set forth in either claim 1 or 2, wherein the total amount of the diamine residue (A1) and the diamine residue (A2) accounts for 70.0 mol% or more and 98.0 mol% or less of all diamine residues, which account for 100.0 mol%, in the polyimide copolymer (A) and also wherein the molar ratio between the

diamine residue (A1) and the diamine residue (A2) is in the range of 5:1 to 30:1.

[Claim 5]

A pressure sensitive adhesive as set forth in claim 3, comprising 0.1 part by weight or more and 5.0 parts by weight or less of the crosslinking agent (C) relative to 100 parts by weight of the polyimide copolymer (A).

[Claim 6]

A substrate coated with a pressure sensitive adhesive layer, comprising a support substrate having thereon a pressure sensitive adhesive layer made of a pressure sensitive adhesive as set forth in either claim 1 or 2.

[Claim 7]

A substrate coated with a pressure sensitive adhesive layer as set forth in claim 6, wherein the pressure sensitive adhesive layer present on the support substrate has a thickness of 0.1 μm or more and 10 μm or less.

[Claim 8]

A layered body comprising semiconductor elements held on the pressure sensitive adhesive layer surface of a substrate coated with a pressure sensitive adhesive as set forth in claim 6.

[Claim 9]

A layered body as set forth in claim 8, having a patterned pressure sensitive adhesive layer.

[Claim 10]

A production method for a layered body, comprising:

a step for placing a laser-transmissive substrate laid with semiconductor elements at least containing a laser-transmissive substrate and semiconductor elements stacked in this order and a substrate coated with a pressure sensitive adhesive layer as set forth in claim 1 in such a manner that the surface of the former where the semiconductor elements are exposed and the surface of the latter where the pressure sensitive adhesive layer is exposed face each other, and
a subsequent step for applying laser light to the laser-transmissive substrate by irradiating that surface of the laser-transmissive substrate laid with semiconductor elements which is opposite to the surface where the semiconductor elements are exposed so that the semiconductor elements are transferred to the substrate coated with a pressure sensitive adhesive layer.

[Claim 11]

A production method for a layered body as set forth in claim 10, further comprising a step for removing part of the pressure sensitive adhesive layer.

[Claim 12]

A production method for a semiconductor device using a layered body as set forth in

claim 8, comprising:

a step for placing the layered body and the circuit board in such a manner that the surface of the former where the semiconductor elements are exposed faces the latter and establishing an electric connection between the semiconductor elements and the circuit board by thermocompression bonding, and

a subsequent step for removing the substrate part coated with a pressure sensitive adhesive layer from the semiconductor elements.

[Claim 13]

A circuit board coated with a pressure sensitive adhesive layer, comprising a circuit board having thereon a pressure sensitive adhesive layer made of a pressure sensitive adhesive as set forth in either claim 1 or 2.

[Claim 14]

A layered body comprising a circuit board coated with a pressure sensitive adhesive layer as set forth in claim 13 and semiconductor elements held on the surface thereof where the pressure sensitive adhesive layer is exposed.

[Claim 15]

A production method for a semiconductor device using a layered body as set forth in claim 14, comprising:

a step for applying a pressure in the stacking direction to the layered body to break the pressure sensitive adhesive layer in order to bring the circuit board into contact with the semiconductor elements so that an electric connection is established between the circuit board and the semiconductor elements.

[Claim 16]

A production method for a semiconductor device, comprising:

a step for placing a layered body including a substrate, a pressure sensitive adhesive layer wherein the pressure sensitive adhesive is according to claim 1, and a plurality of semiconductor elements stacked in this order and a circuit board in such a manner that the surface of the former where the semiconductor elements are exposed faces the latter,

a step for heating and press-bonding the semiconductor elements and the circuit board at a temperature of 80°C or more and less than 300°C to establish an electric connection between them, and

a subsequent step for removing the pressure sensitive adhesive layer and the substrate part present in the layered body from the semiconductor elements.

[Claim 17]

A production method for a semiconductor device, comprising:
a step for applying a pressure in the stacking direction to a layered body including a circuit board, a pressure sensitive adhesive layer wherein the pressure sensitive adhesive is according to claim 1, and a plurality of semiconductor elements in this order to break the pressure sensitive adhesive layer in order to bring the circuit board into contact with the semiconductor elements so that an electric connection is established between the circuit board and the semiconductor elements.

[Claim 18]

A production method for a semiconductor device as set forth in either claim 16 or 17, wherein the pressure sensitive adhesive layer contains polyimide.