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"COMPOSITION OF MATERIALS FOR FORMING PROTECTIVE
FILM IN SEMICONDUCTOR DEVICE"

1 This invention relates to a composition of
materials for forming a protective film in a semi-
conductor device, more particularly to a composition
of materials for forming a protective film in a
5 semiconductor device not causing erroneous operations
(soft errors) by incidence of α -rays from outside
of a semiconductor element.

 Recently it has become known that when
incidence of α -rays into semiconductor memory
10 elements takes place, reversal of information of
"1" $\rightarrow$ "0" or "0" $\rightarrow$ "1", that is, soft errors, is
often caused. A major source of the α -rays is
trace amounts of uranium and thorium contained in
a ceramic case or an inorganic filler contained in
15 a thermosetting resin used for packaging the elements.
Thus, various methods for reducing the uranium and
thorium contents have been proposed, but since
there are many technically difficult problems,
this problem is not solved completely.

20 On the other hand, soft errors can be
prevented by considering circuit design of semi-
conductor elements. But this method brings about
defects of increasing the chip area, and the like,
so that it is not used practically except for a
25 very special case.

1 It is known that organic materials
generally have lower contents of uranium, thorium,
etc., which are α -rays sources other than inorganic
materials, and even if uranium, thorium, etc. are
5 contained in the organic materials, their contents
can relatively easily be reduced by purification
operations of constituting raw materials such as
distillation, recrystallization, reprecipitation of
the materials, and the like and that the organic
10 materials have a function of absorbing α -rays. Thus,
there have been done many trials of forming an organic
layer between a packaging layer and a semiconductor
element to absorb α -rays by the organic layer and
to prevent soft errors of the element, and some of
15 them gain practical use.

Semiconductor memory elements are
packaged by ceramics, thermosetting resins, etc.,
for securing moisture resistance. In the case of
ceramic packaging, the packaging temperature is
20 about 350°C in the case of using gold-tin eutectic
crystal as packaging adhesive, but the packaging
temperature is about 450°C in the case of using
low-melting glass as packaging adhesive. In the case
of thermosetting resin packaging, curing is
25 conducted by heating at about 200°C. Therefore,
the organic material used for absorbing α -rays should
have properties for sufficiently withstanding
such heat-treating temperatures. As the organic

1 material for such a purpose, polyimide series
resins are mainly used.

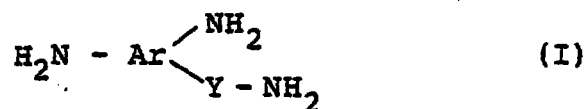
On the other hand, as passivation film,
there are used films of silicon oxide, silicon
5 nitride, and the like in semiconductor memory elements.
Generally speaking, polyimide series resins have
very poor adhesive properties to these passivation
films. In order to give good adhesive properties,
it is necessary to use a coupling agent such as
10 silanes, organic chelates of metals, etc. As
mentioned above, so far as conventional polyimide
series resins are used, the step of forming a
coupling agent layer is inevitable, which results in
not only making the process complicated but also
15 causing a danger of forming a new source for α -rays
when organic chelate compounds of metals are used
as coupling agent because the removal of materials
emitting α -rays contained in inorganic materials is
very difficult as mentioned above. Further since
20 the decomposition temperature of silane coupling
agents is 300 to 350°C, the silane coupling agents
cannot withstand the ceramic packaging temperature,
particularly in the case of using low-melting glass.

This invention provides a composition of
25 materials for forming a protective film in a
semiconductor device, a cured product of said
composition being excellent in adhesive properties,
heat resistance withstanding the heat-treatment

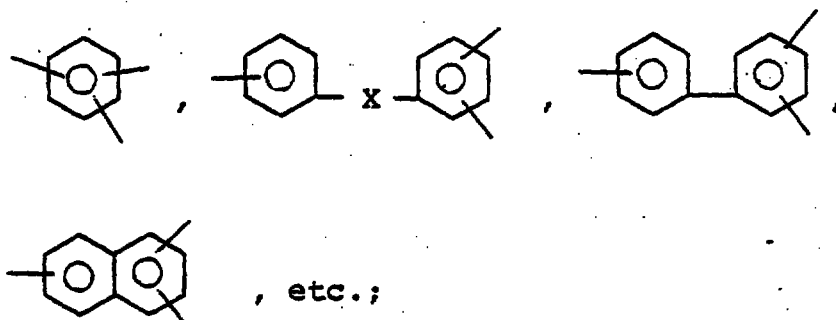
- 1 temperature at the time of packaging and preventing soft errors due to α -rays.

In accordance with this invention, there is provided a composition of materials for forming
5 a protective film in a semiconductor device which comprises (i) a polyamide acid-silicone intermediate obtained by reacting:

- (a) a diaminoamide compound of the formula:



wherein Ar is an aromatic residue such as

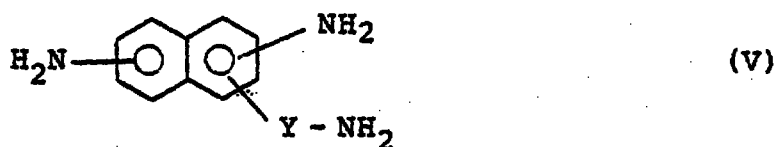
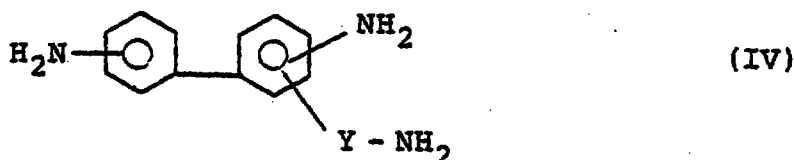
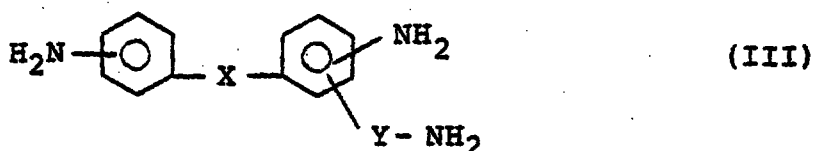
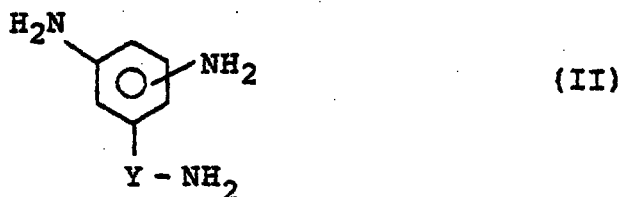


- 10 X is O, CH₂, SO₂, S or CO; Y is SO₂ or CO, and one of amino groups and the Y-NH₂ group are positioned at ortho position each other,
- (b) a diaminosiloxane,
- (c) a diamine, and
- 15 (d) an aromatic tetracarboxylic acid dianhydride, and
- (ii) a solvent.

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1 The polyamide acid-silicone intermediate used in this invention can be produced by a known process, for example, a process disclosed in U.S. Patent No. 4,338,426.

5 The component(a), diaminoamide compounds of the formula (I), includes the following compounds:



In the above formulae (II) to (V), Y is SO₂ or CO, X is O, CH₂, SO₂, S or CO, and the Y-NH₂ group is positioned at the ortho position as to one NH₂ group.

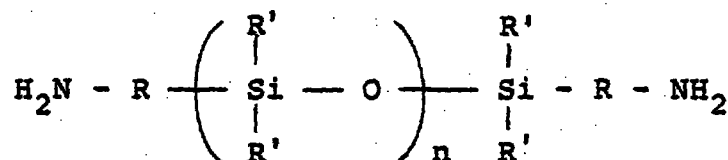
10 Examples of the diaminoamide compounds (I) are

4,4'-diaminodiphenyl ether-3-sulfonamide,

- 1 3,4'-diaminodiphenyl ether-4-sulfonamide,
3,4'-diaminodiphenyl ether-3'-sulfonamide,
3,3'-diaminodiphenyl ether-4-sulfonamide,
4,4'-diaminodiphenylmethane-3-sulfonamide,
5 3,4'-diaminodiphenylmethane-4-sulfonamide,
3,4'-diaminodiphenylmethane-3'-sulfonamide,
3,3'-diaminodiphenylmethane-4-sulfonamide,
4,4'-diaminodiphenylsulfone-3-sulfonamide,
3,4'-diaminodiphenylsulfone-4-sulfonamide,
10 3,4'-diaminodiphenylsulfone-3'-sulfonamide,
3,3'-diaminodiphenylsulfone-4-sulfonamide,
4,4'-diaminodiphenylsulfide-3-sulfonamide,
3,4'-diaminodiphenylsulfide-4-sulfonamide,
3,3'-diaminodiphenylsulfide-4-sulfonamide,
15 3,4'-diaminodiphenylsulfide-3'-sulfonamide,
1,4-diaminobenzene-2-sulfonamide,
4,4'-diaminodiphenyl ether-3-carbonamide,
3,4'-diaminodiphenyl ether-4-carbonamide,
3,4'-diaminodiphenyl ether-3'-carbonamide,
20 3,3'-diaminodiphenyl ether-4-carbonamide,
4,4'-diaminodiphenylmethane-3-carbonamide,
3,4'-diaminodiphenylmethane-4-carbonamide,
3,4'-diaminodiphenylmethane-3'-carbonamide,
3,3'-diaminodiphenylmethane-4-carbonamide,
25 4,4'-diaminodiphenylsulfone-3-carbonamide,
3,4'-diaminodiphenylsulfone-4-carbonamide,
3,4'-diaminodiphenylsulfone-3'-carbonamide,
3,3'-diaminodiphenylsulfone-4-carbonamide,

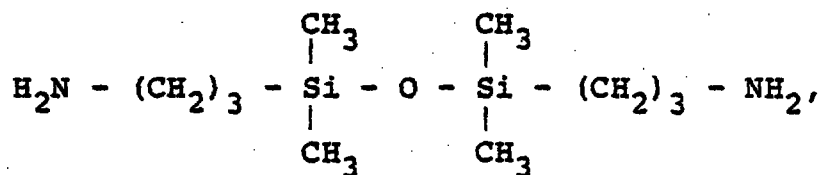
- 1 4,4'-diaminodiphenylsulfide-3-carbonamide,
 3,4'-diaminodiphenylsulfide-4-carbonamide,
 3,3'-diaminodiphenylsulfide-4-carbonamide,
 3,4'-diaminodiphenylsulfide-3'-sulfonamide,
 5 1,4-diaminobenzene-2-carbonamide, and the
 like. These diaminodiamide compounds can be used
 alone or as a mixture thereof.

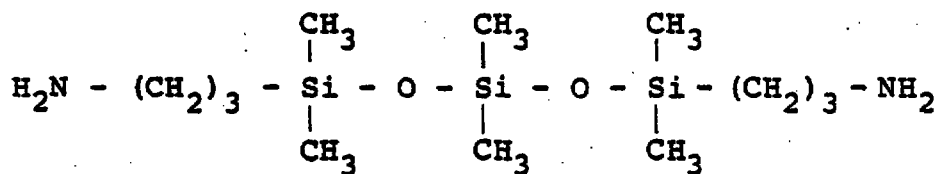
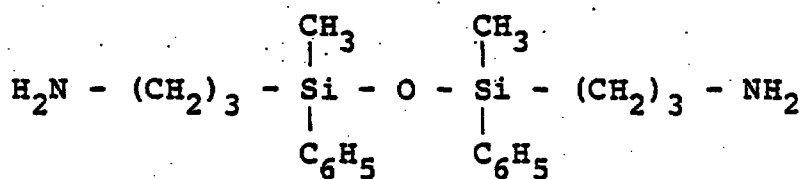
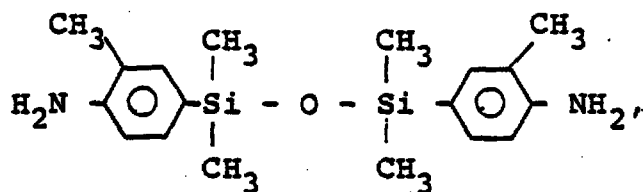
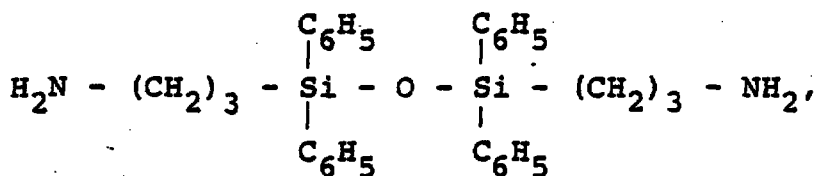
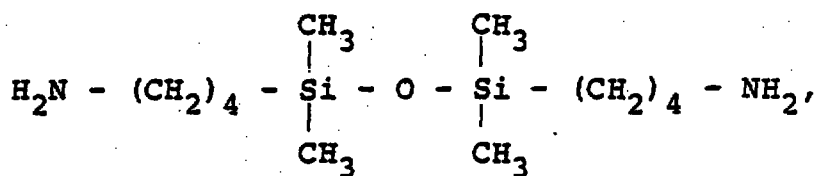
The diaminosiloxane (b) usable in this
 invention can be represented by the formula:



- 10 wherein R is a bivalent hydrocarbon group such as
 alkylene preferably having 1 to 5 carbon atoms;
 phenylene, phenylene substituted by alkyl, and R' is
 a monovalent hydrocarbon group such as alkyl
 preferably having 1 to 5 carbon atoms, phenyl, phenyl
 15 substituted by alkyl, each R or R' may be the same
 or different, and n is an integer of 1 or more.

Examples of these diaminosiloxanes are as
 follows:





- 1 These diaminosiloxanes can be used alone or as a mixture thereof.

These diaminodisiloxanes can be synthesized by the process described in, for example, U.S. Patent No. 3,185,719.

1 As the diamine (c), there can be used conventionally used ones, for example, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfide,
5 benzidine; m-phenylenediamine, p-phenylenediamine, 1,5-naphthalenediamine, 2,6-naphthalenediamine, and the like.

 These diamines can be used alone or as a mixture thereof.

10 As the tetracarboxylic acid dianhydride (d), there can be used conventionally used ones, for example, pyromellitic acid dianhydride, 3,3',4,4'-diphenyltetracarboxylic acid dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, cyclo-
15 pentanetetracarboxylic acid dianhydride, 1,2,5,6-naphthalenetetracarboxylic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 2,3,5,6-pyridinetetracarboxylic acid dianhydride, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 3,4,9,10-
20 perpylenetetracarboxylic acid dianhydride, 4,4'-sulfonyldiphthalic acid dianhydride, and the like.

 Among them, 3,3',4,4'-diphenyltetracarboxylic acid dianhydride is more preferable from the viewpoint of heat resistance of a cured product of the polyamide
25 acid-silicone intermediate. These tetracarboxylic acid dianhydrides can be used alone or as a mixture thereof.

 In this invention, about equimolar amount of

1 tetracarboxylic acid dianhydride is used per mole
of the total of the diaminoamide compound, the
diaminosiloxane and the diamine (or a total of the
diamine components (a), (b) and (c)).

5 It is preferable to use 5 to 30% by mole of
the diaminoamide compound (a) and 0.1 to 50% by mole
of the diaminosiloxane (b) based on the total amounts
of the diamine component, i.e., the diaminoamide (a),
the diaminosiloxane (b) and the diamine (c).

10 In this invention, an inert solvent can
be used. The solvent is not always required to
dissolve the abovementioned four kinds of monomers
(a) to (d), but preferable solvents are those
which can dissolve the produced polyamide acid-
15 silicone intermediate.

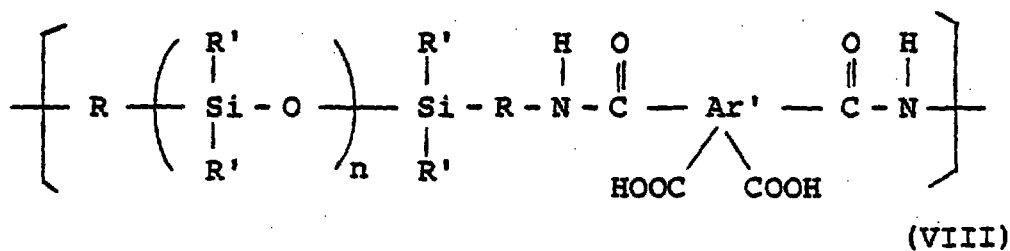
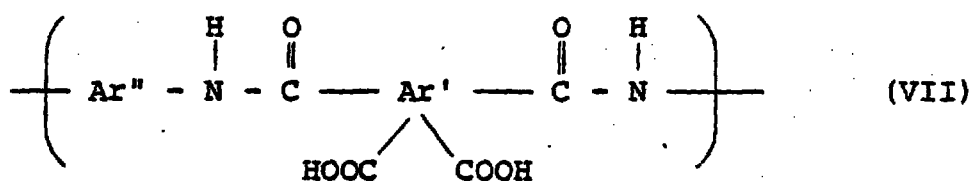
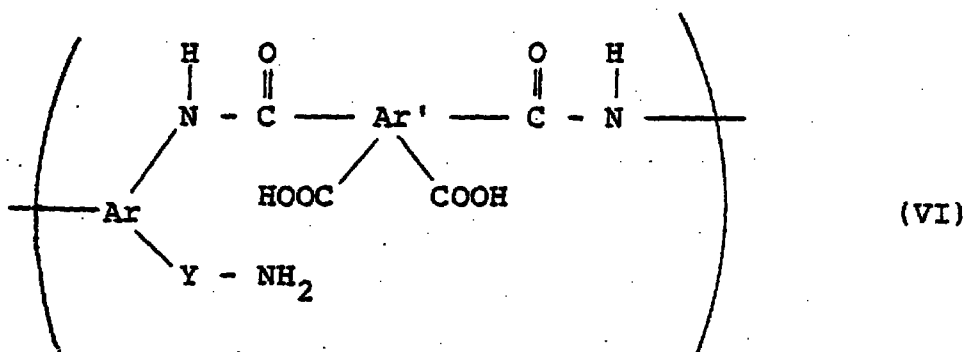
Examples of inert solvents are N-methyl-2-
pyrrolidone, N,N-dimethylacetamide, N,N-dimethyl-
formamide, N,N-diethylformamide, dimethyl sulfoxide,
hexamethylphosphoramide, tetramethylene sulfone,
20 and the like. These solvents can be used alone
or as a mixture thereof.

These inert solvents can be used in the
reaction of the components (a) to (d) or can be used
as the component (ii) in the composition of this
25 invention.

In a preferred process of this invention,
a diaminoamide compound (a), a diaminosiloxane (b),
a diamine (c) and a tetracarboxylic acid dianhydride

5 temperature or lower. Under such conditions, the reaction proceeds rapidly with increasing the viscosity of the reaction system gradually to produce the polyamide acid-silicone intermediate.

10 used in this invention has, for example, the following recurring structural units of the formulae (VI) to (VIII):

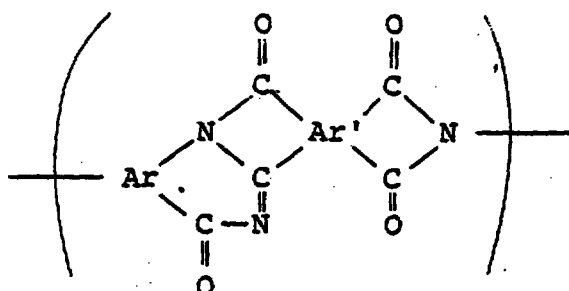


- 1 In the above-mentioned formulae, Ar, Ar' and Ar" are independently aromatic residues derived from the raw materials mentioned above. R is a divalent hydrocarbon group such as alkylene preferably
- 5 having 1 to 5 carbon atoms; phenylene, phenylene substituted by C₁₋₅ alkyl; R' is a monovalent hydrocarbon group such as alkyl preferably having 1 to 5 carbon atoms, phenyl, phenyl substituted by C₁₋₅ alkyl; and Y is SO₂ or CO.

10 The composition of materials for forming a protective film in a semiconductor memory device of this invention can be coated on a surface of a semiconductor element by a conventional process such as a dispenser process, or the like, heat-

15 treated for removing a solvent dissolving the polyamide acid-silicone intermediate, followed by dehydration and ring closure to give a protective film layer of polyimide-isoindoloquinazolinedione-silicone copolymer. For example, the structural

20 unit of the formula (VI) contained in the polyamide acid-silicone intermediate is changed to the following structural unit with heating:



1 The composition of materials for forming
a protective film in a semiconductor device preferably
contains uranium and thorium as a total amount 1 ppb or less,
(ppb means parts per American billion i.e. parts per one
5 thousand million parts) more preferably 0.2 ppb or less.
This is because when the total amounts of uranium and
thorium are 1 ppb or less, more preferably 0.2 ppb
or less, the influence of α -rays causing soft
errors radiated from the protective film is reduced
10 remarkably. When the total amounts of uranium
and thorium in the composition of this invention is
more than 1 ppb, more preferably more than 0.2 ppb,
the total amounts of uranium and thorium can be
reduced by purification of the above-mentioned
15 monomers (a) to (d), or the solvent used.

The purification of the monomers (a) to
(d) can be conducted by a so-called recrystallization
process wherein a monomer is dissolved in a suitable
solvent with heating, the resulting solution is
20 filtered, and the filtrate is cooled to precipitate
the monomer. There is no particular limit to

1 the conditions employed. The purification of the
solvent can be conducted by distillation.

The composition of this invention may
contain a coupling agent such as silane compounds,
5 e.g. aminosilane, epoxysilane, etc.

The composition of this invention is
coated on a semiconductor element in the form of a
varnish, dehydrated and ring-closed to form a
protective film of polyimide-isoindoloquinazo-
10 linedione-silicone copolymer. The thickness of the
protective film is preferably 30 μm or more, more
preferably 40 μm or more in order to show a preferable
effect for shielding α -rays.

The packaging layer in a semiconductor
15 device having the protective film obtained by using
the composition of this invention is constituted by
a ceramic package, a metal package such as a
metallic can, etc., a resin package such as an epoxy
resin mold, etc.

20 Particularly preferable effects can be
obtained when a semiconductor device is constituted
by using the composition of this invention for
forming a protective film, a ceramic package as
packaging layer and low-melting glass as packaging
25 adhesive.

Further, the composition of this invention
shows more effective function when used in semi-
conductor memory elements having a higher level

- 1 of integration in memory circuits. More concretely,
the composition of this invention is more effective
when used in semiconductor memory elements having
a degree of integration (a memory capacity) of
5 1 K-bit or more in the case of a bipolar type and
a degree of integration of 16 K-bits or more in
the case of a MOS type.

This invention is illustrated by way of
the following Examples, in which all percents are
10 by weight unless otherwise specified.

Example 1

- Using a three-necked flask equipped with
a thermometer, a stirrer and a calcium chloride
tube, 2.43 g of 4,4'-diaminodiphenyl ether-3-
15 carbonamide obtained by recrystallization using
n-butanol as solvent, 9.51 g of para-phenylenediamine
obtained by recrystallization using ethyl alcohol
as solvent, 0.50 g of 1,3-bis(aminopropyl)-
tetramethyldisiloxane purified by distillation under
20 reduced pressure, and 29.42 g of 3,3',4,4'-bi-
phenyltetracarboxylic acid dianhydride purified by
using acetic anhydride were reacted at room
temperature in 240 g of N-methyl-2-pyrrolidone
purified by distillation under reduced pressure.
25 As a result, there was obtained a polyamide acid-
silicone intermediate solution having a resin
content of 14.5% and a viscosity of 125 poises.

- 1 After removing the solvent from said solution,
the uranium and thorium contents were measured
by radiation analysis. The uranium content was
less than 0.02 ppb and the thorium content was
5 less than 0.05 ppb, these values of 0.02 ppb and
0.05 ppb being detecting limits, respectively.

Then, the solution was coated on a surface
of MOS type RAM having a degree of integration of
16 K-bits and heat-treated at 100°C for 2 hours,
10 200°C for 1 hour and 350°C for 1 hour to form a
protective film layer of polyimide-isoindoloquinazoline-
dione-silicone copolymer having a thickness of
about 40 μ m. Subsequently, the resulting semi-
conductor element was packaged by using a ceramic
15 package containing low-melting glass as packaging
adhesive at about 450°C.

The soft error rate of the resulting
semiconductor device was 30 fits (1 fit means a
unit showing that an error takes place per 10^9
20 hours per one element).

On the other hand, a naked semiconductor
memory element not packaged by a ceramic package was
allowed to stand in water vapor heated at 120°C
under a pressure of 2.2 atmospheres for 20 hours.
25 Then the thus treated element was subjected to a
peeling-off test using an adhesive Cellophane* type
but no peeling of the protective film layer from
the semiconductor memory element was observed.

* "CELLOPHANE" is a registered Trade Mark.

- 1 This showed that high adhesive properties were maintained after such severe heating in water vapor.

Comparative Example 1

- 5 4,4'-Diaminodiphenyl ether in an amount of 10.0 g and 10.9 g of pyromellitic dianhydride, both being purified by the same method as described in Example 1, were reacted at room temperature in 118.4 g of N-methyl-2-pyrrolidone purified by
10 distillation to give a polyamide acid solution having a resin content of 14.7% and a viscosity of 135 poises.

- On the same semiconductor memory element as used in Example 1, a coupling agent layer having
15 a thickness of about 200 Å was formed by coating a toluene solution containing 1% of ethylacetoacetate aluminum diisopropylate and heating at 350°C for 1 hour. Then, the above-mentioned polyamide acid solution was coated on the coupling agent layer,
20 heat-treated under the same conditions as used in Example 1 to form a protective film layer of polyimide having a thickness of 45 µm.

Packaging was conducted in the same manner as described in Example 1.

- 25 The soft error rate of the resulting ceramic packaged semiconductor device was 250 fits. The uranium content in the coupling agent layer

1 was 0.3 ppb and that of the polyimide film was
less than 0.02 ppb.

On the other hand, when a polyimide
film was formed on a semiconductor memory element
5 without forming a coupling agent layer in the manner
similar to that described above and allowed to
stand in water vapor heated at 120°C under a
pressure of 2.2 atmospheres for 1 hour, the polyimide
film was peeled off from the semiconductor memory
10 element by the peeling-off test mentioned above.



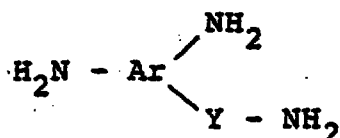
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CLAIMS

1. A composition of materials for forming a protective film in a semiconductor device which comprises

(i) a polyamide acid-silicone intermediate obtained by reacting

(a) a diaminoamide compound of the formula:



wherein Ar is an aromatic residue; Y is SO₂ or CO, and one of the amino groups and the Y-NH₂ group are positioned at ortho position each other, and

(b) a diaminosiloxane, and

(c) a diamine, and

(d) an aromatic tetracarboxylic acid dianhydride,

(c) and (d) being used in each equimolar amounts, and

(ii) a solvent.

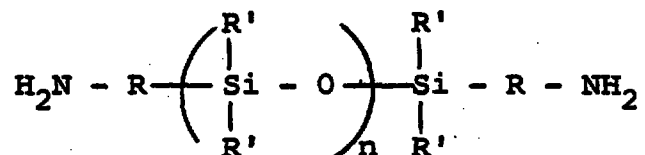
2. A composition according to Claim 1, wherein the composition has a total amount of uranium and thorium 1 ppb or less.

3. A composition according to Claim 1, wherein the composition has a total amount of uranium and thorium 0.2 ppb or less by using purified components (a) to (d) or purified solvent.



- 20 -

4. A composition according to any one of the preceding claims, wherein the diaminosiloxane is represented by the formula:



wherein R is a divalent hydrocarbon group; R' is a monovalent hydrocarbon group; each R or R' may be the same or different; and n is an integer of 1 or more.

5. A composition according to claim 4, wherein the diaminosiloxane is 1,3-bis-(aminopropyl)-tetramethyldisiloxane.

6. A composition according to any one of the preceding claims, wherein the diaminoamide compound is 4,4'-diaminodiphenyl ether-3-carbonamide.

7. A composition according to any one of the preceding claims, wherein the diamine is 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, or a mixture thereof.

8. A composition according to any one of the preceding claims, wherein the aromatic tetracarboxylic acid dianhydride is 3,3',4,4'-diphenyltetracarboxylic acid dianhydride, 4,4'-benzophenonetetracarboxylic acid dianhydride, pyromellitic acid dianhydride, or a mixture thereof.



- 21 -

9. A composition according to claim 1 substantially as hereinbefore described with reference to the Example.

10. A semiconductor device having a protective film of polyimide-isoindoloquinazolinedione-silicone copolymer obtained from a composition according to any one of the preceding claims.

11. A device according to claim 10, wherein the protective film is formed on a bipolar type semiconductor memory element having a degree of integration of 1 K-bit or more.

12. A device according to claim 10, wherein the protective film is formed on a MOS type semiconductor memory element having a degree of integration of 16 K-bits or more.

13. A device according to any one of claims 10 to 12 having a package layer of ceramic and a low-melting glass as packaging adhesive.

14. A device according to claim 10 substantially as hereinbefore described with reference to the Example.
