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# United States Patent [19]

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[54] LIGHT TRANSMISSIVE EPOXY RESIN COMPOSITIONS AND OPTICAL SEMICONDUCTOR DEVICES ENCAPSULATED THEREWITH

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**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 651,438, Feb. 7, 1991.

[30] **Foreign Application Priority Data**

Aug. 24, 1990 [JP] Japan ..... 2-223052

[51] **Int. Cl.**[5] ..... **C08K 9/06**

[52] **U.S. Cl.** ..... **523/214;** 523/219; 523/444

[58] **Field of Search** ..... 523/214, 219, 444

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,842,837 6/1989 Shimizu et al. ..... 423/335
4,985,751 1/1991 Shiobara et al. ..... 357/72

OTHER PUBLICATIONS

Best, M. F., Condrate, R. A. Sr.; "A Raman Study of $TiO_2$-$SiO_2$ Glasses Prepared by Sol-Gel Processes"; Journal of Materials Science Letters, 4, 1985, 994–998.

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[57] **ABSTRACT**

In a light transmissive epoxy resin composition comprising (A) an epoxy resin and (B) a curing agent are blended (C) an organic phosphorus anti-discoloring agent and (D) silica-titania glass beads surface treated with an organic silicon compound. The composition restrains coloring in composition form and discoloration in cured form while curing into clear low stressed products having high light transmittance. Optical semiconductor devices encapsulated with the cured epoxy resin composition are reliable.

**9 Claims, 1 Drawing Sheet**

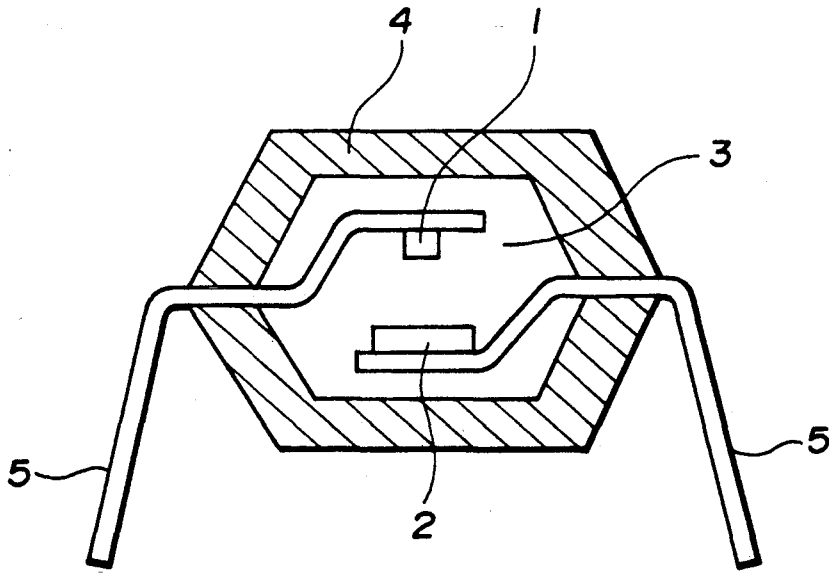
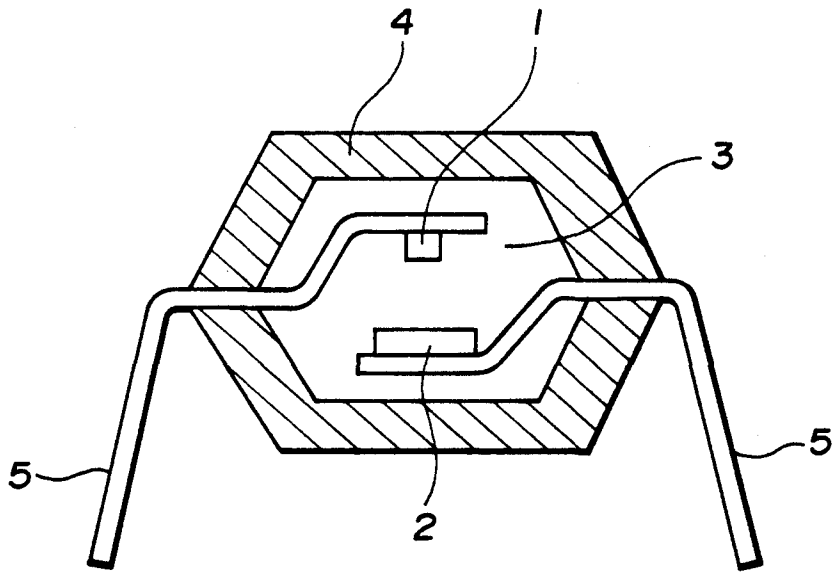


FIG.1



# LIGHT TRANSMISSIVE EPOXY RESIN COMPOSITIONS AND OPTICAL SEMICONDUCTOR DEVICES ENCAPSULATED THEREWITH

## CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of copending application Ser. No. 07/651,438, filed Feb. 7, 1991 pending.

This invention relates to a light transmissive epoxy resin composition suitable for encapsulating optical semiconductor devices such as LED, CCD, and photocouplers. It also relates to an optical semiconductor device encapsulated with the epoxy resin composition in cured state.

## BACKGROUND OF THE INVENTION

Epoxy resins are well known in the art to have improved electrical properties, humidity resistance and heat resistance. Among others, epoxy resin compositions of the acid anhydride curing type are widely used in encapsulating optical semiconductor devices because of their light transparency.

Often anti-discoloring agents are added to such light transmissive epoxy resin compositions in order to prevent them from changing their color toward brown upon high-temperature treatment into cured products. The known anti-discoloring agents are organic phosphorus compounds, hindered phenols and thioethers. The inventors have found that the organic phosphorus anti-discoloring agents are most effective among these agents.

It is also a common practice to produce low stressed epoxy resins compositions by blending inorganic filler such as silica therein, thereby reducing a coefficient of linear expansion.

Epoxy resin compositions having inorganic fillers such as silica loaded therein, however, cure to opaque products although both the epoxy resin and filler components are transparent. This is because most cured epoxy resins have a refractive index ($n^{25}_D$) of about 1.5 to 1.7 and its difference from the refractive index of filler (for example, $N^{25}_D \approx 1.458$ for $SiO_2$ causes light scattering. This suggests that if a filler having a refractive index approximate to that of cured epoxy resins were blended, cured products would be transparent.

In this regard, the inventors found that silica-titania glass having a high refractive index is an effective inorganic filler. In general, sol-gel methods are known for preparing transparent glass species having varying indexes of refraction. The sol-gel methods produce glass by starting with a solution of organic and inorganic compounds of metals, causing hydrolysis and polymerization of the compounds in the solution to form a sol having fine particles of metal oxide or hydroxide suspended, causing the reaction to proceed further to convert the sol into a gel, and heating the porous gel into an amorphous glass or polycrystalline body. The inventors previously proposed a method for preparing high transparency silica-titania glass beads in the above-referred application Ser. No. 07/651,438. This method produces silica-titania glass beads by furnishing a mixed solution of metal alkoxides (silicon alkoxide and titanium alkoxide), alcohol and water, gradually evaporating alcohol from the solution, causing hydrolysis and polycondensation to form a sol and then a wet gel, and drying the gel, followed by grinding and firing of the dry gel. By changing the mix proportion of silicon alkoxide and titanium alkoxide, silica-titania glass beads can be controlled to a desired refractive index, that is, match with the refractive index of cured epoxy resins.



It was expected that by blending such silica-titania glass beads in epoxy resin compositions as a filler, there would be obtained epoxy resin cured products high transparency, a low coefficient of linear expansion, and low stress.

In attempts to blend silica-titania glass beads in epoxy resin compositions along with organic phosphorus anti-discoloring agents which were found to be most effective in preventing the epoxy resin compositions from discoloring upon high-temperature treatment, it was found that the interaction between the organic phosphorus anti-discoloring agent and silica-titania glass beads gave rise to yellowing phenomena. Unlike the above-mentioned browning of cured products upon high-temperature treatment, serious color development occurred even at room temperature as long as both the components co-existed, resulting in a substantial lowering of light transmittance of the cured products.

The filled epoxy resin compositions also suffered from the problem that the cured products became turbid and low in light transmittance due to light scattering caused by separation and gaps occurring at the interface between the resin component and the filler.

Therefore, a mere combination of an organic phosphorus anti-discoloring agent with silica-titania glass beads failed to provide a light transmissive epoxy resin capable of meeting all the requirements of anti-discoloring upon high-temperature treatment, high transparency, and low coefficient of linear expansion. The filled epoxy resin compositions as such were impractical for semiconductor encapsulating purposes.

## SUMMARY OF THE INVENTION

We have found that by treating silica-titania glass beads on their surface with an organic silicon compound and blending the surface treated beads along with an organic phosphorus anti-discoloring agent in a light transmissive epoxy resin composition comprising a compound having at least two epoxy groups in a molecule, an acid anhydride curing agent, and a curing promoter, there is obtained a light transmissive epoxy resin composition which can not only restrain the color development due to the interaction between silica-titania glass beads and the organic phosphorus anti-discoloring agent, but also enhance the interfacial adhesion between the resin component and the filler beads and which cures to transparent, low stressed products while preventing any discoloration upon high-temperature treatment. Consequently, optical semiconductor devices encapsulated with such epoxy resin compositions a cured state can perform their function to a greater extent than the devices encapsulated with prior art light transmissive epoxy resin compositions.

Therefore, the present invention provides a light transmissive epoxy resin composition comprising

(A) a compound having at least two epoxy groups in a molecule,

(B) an acid anhydride curing agent,

(C) an organic phosphorus anti-discoloring agent, and

(D) silica-titania glass beads surface treated with an organic silicon compound.

An optical semiconductor device encapsulated with a cured product of the light transmissive epoxy resin composition is also contemplated.

## BRIEF DESCRIPTION OF THE DRAWING

The only FIGURE, FIG. 1 is a schematic cross-sectional elevation of a photo-coupler used in Example 15.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Component (A) of the light transmissive epoxy resin composition of the invention is a compound having at least two epoxy groups per molecule. It may be selected from conventional well-known epoxy resins which may be either liquid or solid. Illustrative examples include epoxy resins synthesized from epichlorohydrin and bisphenols including various novolak resins, cycloaliphatic epoxy resins, and epoxy resins having halogen atoms such as chlorine and bromine atoms incorporated therein, alone or in admixture of two or more.

Preferred are least colored bisphenol type epoxy resins which are commercially available as Epikote 828, Epikote 1001, and Epikote 1004 (trade name, Yuka Shell Epoxy K.K.), RE 310S and RE 304S (trade name, Nihon Kayaku K.K.), and DER 332, DER 661 and DER 664 (trade name, Dow Chemical Co.).

Component (B) is an acid anhydride curing agent which may be selected from well-known ones commonly used for epoxy resins. Examples of the curing agent include phthalic anhydride, trimellitic anhydride, and pyromellitic anhydride, with aromatic ring-free anhydrides such as hexahydrophthalic anhydride and tetrahydrophthalic anhydride being preferred.

In the practice of the invention, a curing promoter may be blended for the purpose of promoting reaction between epoxy resin (A) and curing agent (B), if desired. Examples of the curing promoter include imidazole and its derivatives such as 2-ethyl-4-methylimidazole, 2-phenylimidazole, and 1-cyanoethyl-2-methylimidazole; tertiary amine derivatives such as 1,8-diaza-bicyclo(5.4.0)-undecene-7 and benzyl-dimethylamine; and phosphine derivatives such as triphenyl phosphine and nonyl diphenyl phosphine. It will be appreciated that acid anhydride curing agent (B) and the optional curing promoter may be added in commonly used amounts. Preferably, component (B) is 10 to 100 parts by weight per 100 parts by weight of component (A). The curing promoter, if any, is up to 10 parts especially 0.1 to 10 parts by weight per 100 parts by weight of components (A) and (B) combined.

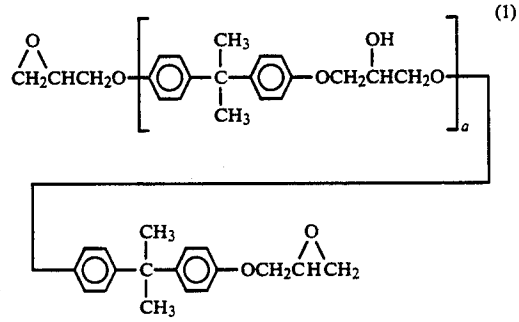
A light transmissive epoxy resin composition of component (A), component (B) and an optional curing promoter all as defined above is further blended with (C) an organic phosphorous anti-discoloring agent and (D) silica-titania glass beads surface treated with an organic silicon compound in order to provide a light transmissive epoxy resin composition of the invention. As a result of blending components (C) and (D), the composition cures to low stressed products capable of maintaining high transparency in a stable manner.

The organic phosphorus anti-discoloring agents (C) include triphenyl phosphite, tridecyl phosphite, diphenylmonodecyl phosphite, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-decyloxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene, etc. alone and mixtures of two or more. The amount of the organic phos- to 10 parts, especially 1 to 6 parts by weight per 100 parts by weight of components (A) and (B) combined.

Component (D) is silica-titania glass beads surface treated with an organic silicon compound. The silica-titania glass beads should preferably have a linear transmittance of at least 70%, especially at least 80% as measured at a wavelength in the range of from 900 nm to 600 nm by a linear transmittance measurement method A.

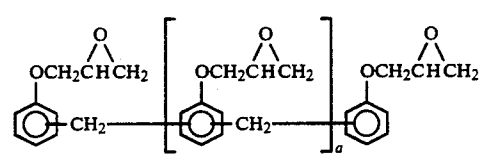
Method A involves the steps of mixing a bisphenol type epoxy resin of the general formula (1) shown below or a novolak type epoxy resin of the general formula (2) shown below with phenylglycidyl ether to form a solution having a difference in refractive index from the silica-titania glass beads within ±0.002; mixing the solution with the silica-titania glass beads which have been ground to a mean particle diameter of 5 to 30 μm in a weight ratio of 1:1; and measuring the linear transmittance of the mixture across a light path length of 1 mm.

Formula (1):



(1)

Formula (2):



(2)

In formulae (1) and (2), a is an integer of from 0 to 10.

Such highly transparent silica-titania glass beads can be prepared by the sol-gel method disclosed in the above-referred copending application Ser. No. 07/651,438 as comprising the steps of hydrolyzing and polycondensing a silicon alkoxide and a titanium alkoxide to form a silica-titania sol, causing the silica-titania sol to gel, drying the gel, grinding the dry gel to a predetermined particle size, and thereafter heating the ground gel at a temperature of 1,050 to 1,250° C. into a sintered glass.

More particularly, the source materials used herein are silicon alkoxides such as $Si(OCH_3)_4$ and $Si(OC_2H_5)_4$ and titanium alkoxides such as $Ti(OC_3H_7)_4$ and $Ti(OC_4H_9)_4$. The silicon and titanium alkoxides are preferably mixed such that $TiO_2$ may range from 10 to 18 mol % of the total of $SiO_2$ and $TiO_2$ in the final product. Silica-titania glass beads with a $TiO_2$ content of less than 10 mol % will sometimes have a refractive index below the minimum level of 1.53 acceptable as the epoxy resin filler. Silica-titania glass beads with a $TiO_2$ content of more than 18 mol % will often have a too high refrac-

The sol or gel is obtained from these source materials by dissolving the silicon and titanium alkoxides in a diluting solvent in the form of an alcohol such as methanol, ethanol, and propanol. Water is added to the solution to form a silica-titania sol through hydrolysis. The sol is then poured into a gelling vessel which is closed. The vessel is placed stationary in a constant temperature dryer where the sol is converted into gel. The temperature during this gelation and subsequent aging should preferably be 60° C. or higher because hydrolysis of alkoxides cannot proceed to completion below 60° C., leaving the likelihood of generating trivalent Ti ions which can cause coloring during subsequent sintering step. Since the aging is intended for completing the hydrolysis, the aging time is preferably at least one hour, more preferably at least 5 hours.

The wet gel resulting from gelation and aging is then dried by any desired method, for example, by removing the lid from the gelling vessel and keeping the vessel open along with the gel contents in the constant temperature dryer until the gel is dry.

Then the dry gel is ground prior to sintering. That is, the dry gel is ground by conventional methods using ball mills or the like to an appropriate particle size, often an average particle size of from 1 to 100 μm, preferably from 5 to 30 μm.

The finely divided dry gel is then heated or fired into sintered glass at a sintering temperature in the range of from 1,050° C. to 1,250° C. At temperature of lower than 1,050° C., the silica-titania glass beads are not fully uniformly consolidated and show low transmittance values as when light is directed to the beads for measuring the transmittance thereof, the light is scattered within the bead interior due to differential refraction at cracks or interstices in the beads. If the sintering temperature exceeds 1,250° C., the anatase phase, which is one of crystalline phases of $TiO_2$, appears, preventing the formation of silica-titania glass beads having high light transmission.

Insofar as the sintering temperature falls within the above-defined range, the remaining parameters of the sintering step are not particularly limited. Preferably, electric furnaces or similar firing furnaces which can maintain a constant temperature are used while oxygen gas or a mixture of oxygen and air is introduced into the furnace to establish an oxidizing atmosphere therein effective for preventing the generation of trivalent Ti ions which will otherwise cause coloring. The furnace is typically heated at a rate of 10° to 500° C./hour until the predetermined temperature is reached. The heating or sintering time is usually 10 to 300 minutes in the above-defined temperature range.

The silica-titania glass beads should have a refractive index approximate to the refractive index of cured resin so that the light scattering associated with the silica-titania glass beads in the epoxy resin may be minimized. Desirably, the difference in refractive index should be within ±0.01, more desirably within ±0.005, most desirably within ±0.002.

In the present invention, the silica-titania glass beads on the surface are treated with an organic silicon compound.

The organic silicon compounds used herein are typically silane coupling agents, silanes, and organopolysiloxanes as shown below. One or more of these compounds may be used for surface treatment.

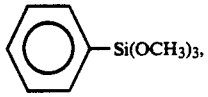
Organosilanes having the following general formula (3):

$$Si(OR^1)_lR^2_{4-l} \quad (3)$$

wherein $R^1$ represents an alkyl group having 1 to 5 carbon atoms, $R^2$ represents an alkyl group having 1 to 12 carbon atoms or an aryl group having 6 to 10 carbon atoms and l is an integer of 1 to 4.

Examples of the organosilanes of formula (3) are shown below.

$Si(OCH_3)_4$, $Si(OCH_2CH_3)_4$, $CH_3Si(OCH_3)_3$,



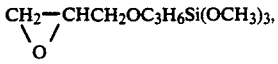
$CH_3(CH_2)_nCH_2Si(OCH_3)_3$ (n=1 to 10), etc.

Organosilanes (silane coupling agents) having the following general formula (4):

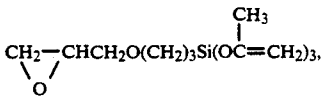
$$X—(CH_2)_p—Si(OR_3)_qR^4_{3-q} \quad (4)$$

wherein X represents an organic group containing at least one group selected from the group consisting of an epoxy group, an amino group, a carboxyl group, a hydroxy group, a mercapto group, a ureido group, a maleimido group and trialkoxysilyl groups and having 0 to 10 carbon atoms, $R^3$ and $R^4$ independently represent a monovalent hydrocarbon group having 1 to 6 carbon atoms such as an alkyl group, an alkenyl group and an aryl group, p is an integer of 1 to 12, and q is an integer of 1 to 3.

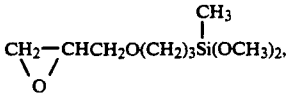
Examples of the silane coupling agents of formula (4) are shown below.



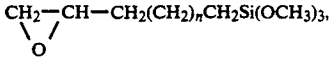
$CH_2—CHCH_2OC_3H_6Si(OCH_3)_3$,



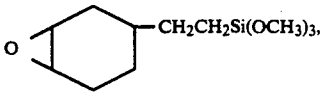
$CH_2—CHCH_2O(CH_2)_3Si(OC(CH_3)=CH_2)_3$,



$CH_2—CHCH_2O(CH_2)_3Si(CH_3)(OCH_3)_2$,



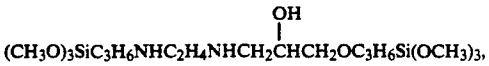
$CH_2—CH—CH_2(CH_2)_nCH_2Si(OCH_3)_3$,



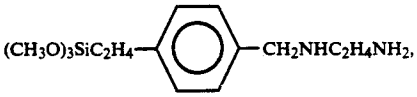
$CH_2CH_2Si(OCH_3)_3$,

$NH_2C_3H_6Si(OCH_3)_3$, $NH_2C_2H_4NHC_3H_6Si(OCH_3)_3$,

$HSC_3H_6Si(OCH_3)_3$,



$(CH_3O)_3SiC_3H_6NHC_2H_4NHCH_2CH(OH)CH_2OC_3H_6Si(OCH_3)_3$,



$(CH_3O)_3SiC_2H_4$ — $CH_2NHC_2H_4NH_2$,

$(CH_3O)_3SiC_3H_6NHC_2H_4NHCH_2CH=CH_2$,

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