Description

CIRCUIT SUBSTRATE

Technical Field

[0001] The present invention relates to a circuit substrate.

Background Art

[0002] Since polyimide is excellent in mechanical strength, thermal properties and electric properties, it has been widely used in the field such as electric and electronics devices as an application for a film, an insulating resin layer of a circuit substrate and the like. From now on, it is expected that polyimide will be widely used in a field in which heat resistance is required, and an excellent polyimide has been developed.

[0003] For example, along with the advancement of miniaturization, high performance and densification, an electronics device using a print circuit board is growing in use as a circuit board material made of a polyimide film that enables high-density mounting of components and elements. In particular, as an application for an electronic material, it is desired that the dimensional stability to heat and water, and workability by high transparency are improved.

[0004] Conventionally, it has been known that an inorganic substance is added to polyimide in order to improve the thermal properties and mechanical properties of polyimide. However, when an inorganic substance such as a clay mineral, as it is, is added to polyimide, the affinity of the clay mineral to polyimide is low, thus causing problems that the clay mineral was not homogeneously dispersed in polyimide and the characteristics of polyimide was not improved.

[0005] In Japanese Patent Laid-Open Publication No. 2006-57099, there is disclosed the addition of a layered silicate which is increased in affinity with a resin by chemically modifying (organizing) a thermoplastic resin containing a thermoplastic polyimide in advance.

Patent Citation 1: Japanese Patent Laid-Open Publication No. 2006-57099.

Disclosure of Invention

[0006] However, in the above Japanese Patent Laid-Open Publication No. 2006-57099, since the organized clay mineral contains alkyl ammonium with low heat resistance, it had problems that a polyimide film was deteriorated in heat resistance and mechanical properties and discolored.

[0007] An object of the present invention is to provide a circuit substrate containing no organic compound with low heat resistance and having an insulating resin layer which is excellent in compatibility in both transparency and elastic modulus at high temperature.

[0008] According to the present invention, there is provided a circuit substrate containing an insulating resin layer,

wherein said insulating resin layer contains polyimide and a clay mineral, said insulating resin layer has an elastic modulus of not less than 0.3 GPa and not more than 30 GPa at 450 degrees C and said insulating resin layer with a thickness of 20 micrometers has a light transmittance of not less than 40 % at a wavelength of 650 nm.

[0009] The present invention provides a circuit substrate having an insulating resin layer which is excellent in compatibility in both transparency and elastic modulus at high temperature.

Best Mode for Carrying Out the Invention

[0010] Hereinafter, there will be explained a film used as an insulating resin layer of a circuit substrate of the present invention.

[0011] The film preferably has an elastic modulus of not less than 0.3 GPa at 450 degrees C. By so doing, the film is excellent in elasticity at high temperature and dimensional stability. In addition, the film preferably has an elastic modulus of not more than 30 GPa at 450 degrees C. The reduction in the flexibility of the film due to too high an elastic modulus may be prevented.

[0012] When the thickness of the film is 20 micrometers, the film preferably has a light transmittance of not less than 40 % at a wavelength of 650 nm and more preferably of not less than 45 %. By so doing, the operation by visual confirmation through an insulating resin layer composed of such a film is feasible, thereby further improving the accuracy of the operation. Incidentally, the light transmittance when the thickness of the film is 20 micrometers is a light transmittance obtained by converting a light transmittance of a film with a thickness of 15 to 25 micrometers to that of a film with a thickness of 20 micrometers by using the following equation (3).

Absorbance (E) = $\log I_0/I = kCL$ (3)

For a light of intensity I obtained by passing a monochromatic light of intensity I_0 through a sample having molar concentration C and thickness L, the relationship of the above equation (3) is established. The percentage of I_0/I represents a light transmittance (%T), $\log I_0/I$ represents an absorbance and k represents a molar absorbance coefficient. Especially when the sample is a dilute solution, the relationship to which the above equation (3) is applied is called the Lambert-Beer Law.

[0013] It has been conventionally difficult to obtain a semiconductor device such as a circuit substrate by using an insulating resin layer which is compatible in both a high elastic modulus at high temperature and a high light transmittance. On the contrary, the present invention solves such a problem by improving the dispersibility of a clay mineral in polyimide, for example. As a method of improving the dispersibility, for

example, a film may be obtained by preparing a mixture solution of a polyimide precursor solution and a dispersion solution of a clay mineral which is not subjected to the organic modification and subsequently drying the solvents from the mixture solution. The details will be explained later.

[0014] The thickness of the film is not particularly limited, but is typically in the range of 5 to 150 micrometers, and preferably, a film having a thickness in the range of 8 to 50 micrometers is typically used.

[0015] The film has a hygroscopic expansion coefficient of preferably not less than 5 ppm/% RH and not more than 20 ppm/% RH and more preferably of not less than 5 ppm/% RH and not more than 15 ppm/% RH at a relative humidity of 20 to 60 %. By so doing, the deformation of the film at the time of drying and moisture absorption is unlikely to occur and the dimensional stability of the film may be maintained. For example, the film may be applied to the miniaturization and densification of a circuit substrate.

[0016] The film preferably has a linear expansion coefficient in the range of 10 to 100 ppm/degree C at a temperature of 380 to 430 degrees C. By so doing, the deformation of the film due to the change in temperature is unlikely to occur and the dimensional stability may be maintained. For example, in the process of mounting a circuit substrate, the warpage and peeling-off of the film due to heating may be prevented.

[0017] The film has a water absorption of preferably not less than 0 % and not more than 2 % and more preferably of not more than 1.5 %. By so doing, the deterioration of electric properties such as dielectric constant due to water absorption may be prevented, thereby improving the dimensional stability.

[0018] Since an insulating resin layer composed of such a film is excellent in compatibility in both transparency and elastic modulus at high temperature, it may be widely applied in the field such as electric and electronics devices.

For example, it may be used as an insulating resin layer of a circuit substrate, a flexible circuit substrate further containing a metal layer and a chip-on-film substrate (COF substrate) and the like. These circuit substrates may contain at least one or more layers of the insulating resin layer without any limitation.

[0019] In the present invention, as the precursor of polyimide, there are used a publicly-known polyimide polymer synthesized by using a diamine compound and an acid dianhydride and/or a polyimide precursor containing a polyamide acid copolymer.

[0020] The polyimide precursor preferably contains a polyimide polymer synthesized from one or more kinds of diamine compounds and one or more kinds of tetracarboxylic acid dianhydrides and/or a polyamide acid copolymer.

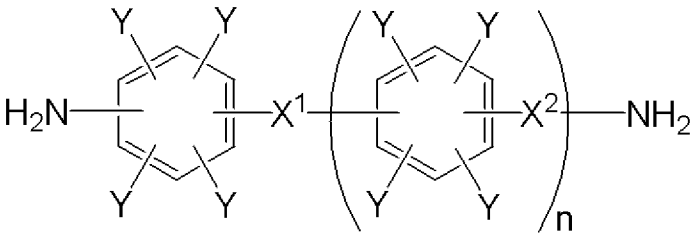
[0021] In the present invention, as the diamine compound used as a raw material of a polyimide polymer and/or a polyamide acid copolymer, there may be mentioned, for example, 1,3-bis(3-aminophenoxy)benzene, 4,4-bis(3-aminophenoxy)biphenyl,

3,3-diaminobenzophenone, p-phenylenediamine, 4,4'-diaminodiphenylether,
1,3-bis(3-(3-aminophenoxy)phenoxy)benzene,
1,3-bis(3-(4-aminophenoxy)phenoxy)benzene, 5,7-diamino-1,1,4,6-tetramethyl indaine, 1,3-bis(4-(3-aminophenoxy)phenoxy)benzene,
1,3-bis(3-(2-aminophenoxy)phenoxy)benzene,
1,3-bis(4-(2-aminophenoxy)phenoxy)benzene,
1,3-bis(2-(2-aminophenoxy)phenoxy)benzene,
1,3-bis(2-(3-aminophenoxy)phenoxy)benzene,
1,3-bis(2-(4-aminophenoxy)phenoxy)benzene,
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1,4-bis(2-(4-aminophenoxy)phenoxy)benzene,
1,2-bis(3-(3-aminophenoxy)phenoxy)benzene,
1,2-bis(3-(4-aminophenoxy)phenoxy)benzene,
1,2-bis(3-(2-aminophenoxy)phenoxy)benzene,
1,2-bis(4-(4-aminophenoxy)phenoxy)benzene,
1,2-bis(4-(3-aminophenoxy)phenoxy)benzene,
1,2-bis(4-(2-aminophenoxy)phenoxy)benzene,
1,2-bis(2-(2-aminophenoxy)phenoxy)benzene,
1,2-bis(2-(3-aminophenoxy)phenoxy)benzene,
1,2-bis(2-(4-aminophenoxy)phenoxy)benzene,
1,3-bis(3-(3-aminophenoxy)phenoxy)-2-methylbenzene,
1,3-bis(3-(4-aminophenoxy)phenoxy)-4-methylbenzene,
1,3-bis(4-(3-aminophenoxy)phenoxy)-2-ethylbenzene,
1,3-bis(3-(2-aminophenoxy)phenoxy)-5-sec-butylbenzene,
1,3-bis(4-(3-aminophenoxy)phenoxy)-2,5-dimethylbenzene,
1,3-bis(4-(2-amino-6-methylphenoxy)phenoxy)benzene,
1,3-bis(2-(2-amino-6-ethylphenoxy)phenoxy)benzene,
1,3-bis(2-(3-aminophenoxy)-4-methylphenoxy)benzene,
1,3-bis(2-(4-aminophenoxy)-4-tert-butylphenoxy)benzene,
1,4-bis(3-(3-aminophenoxy)phenoxy)-2,5-di-tert-butylbenzene,
1,4-bis(3-(4-aminophenoxy)phenoxy)-2,3-dimethylbenzene,
1,4-bis(3-(2-amino-3-propylphenoxy)phenoxy)benzene,

1,2-bis(3-(3-aminophenoxy)phenoxy)-4-methylbenzene,
1,2-bis(3-(4-aminophenoxy)phenoxy)-3-n-butylbenzene,
1,2-bis(3-(2-amino-3-propylphenoxy)phenoxy)benzene and the like.
One or two or more kinds of these diamine compounds may be used.

[0022] In addition, as at least one of the diamine compounds, preferably used is a compound represented by the following general formula (1)

[Chem.1]

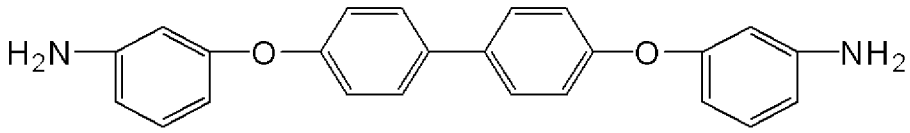


(1)

(in the formula (1), X^1 and X^2 are each independently selected from the group consisting of a single bond, an oxygen atom, a sulfur atom, a carbonyl group, a sulfonyl group and a hydrocarbon group which may have been substituted with a halogen atom, Ys are each independently selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, a nitro group and a hydrocarbon group which may have been substituted with a halogen atom, and n represents an integer of 0 to 8).

[0023] As at least one of the diamine compounds, especially preferably used is a compound represented by the following general formula (2)

[Chem.2]



(2)

[0024] In addition, when two or more kinds of the diamine compounds are used, at least one or more kinds of them are preferably selected from 1,3-bis(3-aminophenoxy)benzene, 4,4-bis(3-aminophenoxy)biphenyl, 3,3'-diaminobenzophenone, p-phenylenediamine and 4,4'-diaminodiphenylether.

[0025] In the present invention, as the acid dianhydride used as a raw material of a polyimide polymer and/or a polyamide acid copolymer, a publicly-known acid dianhydride may be used without any limitation.

[0026] As the acid dianhydride, there may be mentioned, for example, pyromellitic acid dianhydride, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic acid dianhydride, bis(3,4-dicarboxyphenyl)ether dianhydride, bis(3,4-dicarboxyphenyl)sulfide dianhydride,

bis(3,4-dicarboxyphenyl)sulfone dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 4,4'-bis(3,4-dicarboxyphenoxy)biphenyl dianhydride, 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, butane-1,2,3,4-tetracarboxylic dianhydride, pentane-1,2,4,5-tetracarboxylic dianhydride, cyclobutanetetracraboxylic acid dianhydride, cyclopentane-1,2,3,4-tetracarboxylic dianhydride, cyclohexane-1,2,4,5-tetracarboxylic dianhydride, cyclohex-1-ene-2,3,5,6-tetracarboxylic dianhydride, 3-ethylcyclohex-1-ene-3-(1,2),5,6-tetracarboxylic dianhydride, 1-methyl-3-ethylcyclohexane-3-(1,2),5,6-tetracarboxylic dianhydride, 1-methyl-3-ethylcyclohex-1-ene-3-(1,2),5,6-tetracarboxylic dianhydride, 1-ethylcyclohexane-1-(1,2),3,4-tetracarboxylic dianhydride, 1-propylcyclohexane-1-(2,3),3,4-tetracarboxylic dianhydride, 1,3-dipropylcyclohexane-1-(2,3),3-(2,3) - tetracarboxylic dianhydride, dicylohexyl-3,4,3',4'-tetracarboxylic dianhydride, bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic dianhydride, bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride, bicyclo[2.2.2]octo-7-ene-2,3,5,6-tetracarboxylic dianhydride and the like.

[0027] Among these, one or two or more kinds of the tetracarboxylic acid dianhydrides may be used. As the tetracarboxylic acid dianhydride, especially preferable are pyromellitic acid dianhydride, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride. The reaction mole ratio of a diamine compound to a tetracarboxylic acid dianhydride is typically in the range of 0.75 to 1.25.

[0028] In the present invention, any other ingredients may be contained in a polyimide polymer and/or a polyamide acid copolymer depending on the purpose.

[0029] As the clay mineral which is not particularly limited, preferable is a layered clay mineral and there may be mentioned serpentine-kaolin group clay minerals such as lizardite, amesite, chrysotile, kaolinite, dickite and halloysite; smectite group clay minerals such as saponite, hectlite, montmorillonite and beidellite; vermiculite group clay minerals such as trioctahedral vermiculite and dioctahedral vermiculite; and mica group clay minerals such as swelling mica, golden mica, illite, white mica and paragonite. Among these clays, especially preferable is smectite group clay minerals or at least one kind selected from the group of swelling mica, vermiculite and halloysite. By so doing, the elastic modulus at high temperature is improved. Still more

preferably, among the smectite group clay minerals, there may be mentioned montmorillonite. The effect on elastic modulus at high temperature and dimensional stability is further increased.

One or two or more kinds of these clay minerals may be used.

[0030] The content of a clay mineral is not particularly limited, but is preferably not less than 1 part by weight and more preferably not less than 2.5 parts by weight, based on 100 parts by weight of the total of the insulating resin layer. By so doing, the heat resistance and elastic modulus at high temperature are improved. In addition, the content of the clay mineral is preferably not more than 30 parts by weight and more preferably not more than 20 parts by weight, based on 100 parts by weight of the total of the insulating resin layer. By so doing, the clay mineral is excellent in the balance between transparency and elastic modulus at high temperature and is suitable for the operation by visual confirmation, for example, when used for a circuit substrate, thereby enabling to provide a material excellent in dimensional stability.

[0031] A circuit substrate is prepared as follows.

A sheet or film used as an insulating resin layer of a circuit substrate may be obtained by preparing a mixture solution by admixing a solution (A) in which a polyimide precursor is dissolved in a first solvent with a dispersion solution (B) obtained by dispersing a clay mineral which is not subjected to the organic modification in a second solvent, and then spreading the mixture solution on a substrate such as a metal foil or an insulating layer followed by drying the solvents. After the above drying, further heat treatment may be carried out.

The circuit substrate has at least one layer of the insulating resin layer obtained as above and any number of the insulating resin layers may be overlapped. In addition, other insulating layer and metal layer may be laminated.

[0032] Further, the circuit substrate may be prepared by thermally compressing a metal foil and/or a laminate onto the insulating resin layer. Even in this case, further another insulating layer and metal layer may be laminated onto the insulating resin layer.

[0033] The insulating resin layer may be directly laminated onto the metal layer or prepared onto an adhesion layer. In addition, when the circuit substrate is a multilayer substrate, the insulating resin layer may be used at any layer and further may be used many times.

[0034] A summary of the method of producing an insulating resin layer for a circuit substrate will be explained.

A process of producing a film used as an insulating resin layer in the embodiment includes the following steps:

(A) a step of dissolving a polyimide precursor in a first solvent,

(B) a step of dispersing a clay mineral which is not subjected to the organic modi-

fication in a second solvent,

(C) a step of preparing a mixture solution by admixing the solution obtained by the above step (A) with the dispersion solution obtained by the above step (B), and

(D) a step of forming a film by spreading the mixture solution obtained by the above step (C) on a substrate followed by drying the solvents.

[0035] Next, the steps (A) to (D) will be explained in detail.

[0036] (A) Step of dissolving a polyimide precursor in a first solvent

A solution is obtained by dissolving the polyimide precursor in the first solvent. The dissolution method is not particularly limited but may be carried out by a publicly-known method.

[0037] The first solvent is a solvent that dissolves the polyimide precursor and is mixable with the second solvent. In addition, preferably the functional group contained in the first solvent does not react with the polyimide precursor. As the first solvent, there may be mentioned, for example, a basic solvent such as pyridine, trialkylamine, beta-picoline and alkylpyperidine, or N,N-dimethylacetoamide, N,N-dimethylformamide, N-methyl-2-pyrolidone or the like. These may be used alone or by mixing one or two or more kinds.

When the second solvent in the step (B) consists of only water, a basic solvent is preferable and includes pyridine, trialkylamine, beta-picoline, alkylpyperidine and the like.

[0038] (B) Step of dispersing a clay mineral which is not subjected to the organic modification in a second solvent

The organic modification is a treatment to homogeneously disperse clay minerals in the resin by subjecting clay minerals to the chemical treatment to increase the affinity with a resin and thus preventing the clay minerals from coagulating each other in a solution. For example, there is mentioned a treatment in which sodium ions and the like contained in clay minerals are substituted by alkylammonium. The clay minerals not subjected to the organic modification are clay minerals not subjected to such treatment.

[0039] The second solvent means a solvent that disperses clay minerals not subjected to the organic modification and is soluble with the first solvent. As the second solvent, water may be used. When a solvent for a polyamide acid is not a basic solvent, preferable is a mixture solvent obtained by adding approximately 50 to 1000 of a solvent which may dissolve the polyamide acid to 100 of water after dispersing clay minerals in water. For example, as the solvent added, there may be mentioned N,N-dimethylacetoamide, N,N-dimethylformamide, N-methyl-2-pyrolidone, pyridine, trialkylamine, beta-picoline, alkylpyperidine and the like. When a solvent which may dissolve a polyamide acid is added to an aqueous solution in which clay minerals are dispersed, and clay

minerals are precipitated, the solution after removing the precipitated clay minerals by centrifugation is preferably used.

[0040] Dispersion means a state in which the solvent molecules are incorporated between the clay minerals and clay minerals are homogeneously dispersed in a solvent. The dispersion method is not particularly limited, but there may be mentioned, for example, a method of stirring a solution using a magnetic stirrer, mechanical stirrer, homogenizer and the like. A solution thus obtained is used as a dispersion solution.

[0041] (C) Step of preparing a mixture solution by admixing the solution obtained by the above step (A) with the dispersion solution obtained by the above step (B)

The mixture solution means a homogeneously mixed solution obtained by admixing the solution obtained in the step (A) with the dispersion solution obtained in the step (B). The polyimide precursor is maintained in a state in which it is dissolved in the solution and clay minerals are maintained in a state where they are not coagulated and are homogeneously dispersed in the solution. By so doing, clay minerals may be homogeneously dispersed in polyimide.

[0042] In this embodiment, since the solution obtained in the step (A) and the dispersion solution obtained in the step (B) are separately prepared, the degree of freedom of conditions for the selection of solvents, preparation time and the like is improved and the preparation conditions may be optimized. By so doing, the dispersion stability of the mixture solution may be improved.

The order of the step (A) and the step (B) is not particularly limited. Therefore, the step (B) may be carried out after the step (A) and the step (A) may be carried out after the step (B). In addition, the step (A) and the step (B) may be carried out simultaneously.

[0043] (D) Step of forming a film by spreading the mixture solution obtained by the above step (C) on a substrate followed by drying the solvents

The film formation method is not particularly limited and may be carried out by a publicly-known method. By spreading the mixture solution on the substrate followed by drying the solvents, a film with a fixed thickness may be obtained. A publicly-known method may be selected as appropriate and used depending on the concentration of the mixture solution, type of solvent and the like.

After the step (D), further heat treatment may be carried out. The heating temperature is not particularly limited, but the heat treatment is carried out at a temperature of 100 degrees C to 500 degrees C. A film containing polyimide may be obtained by conducting dehydration imidization.

[0044] The type of a substrate is not particularly limited, but there may be mentioned, for example, glass, metal, plastics and the like. In addition, the drying method is not particularly limited, and there may be used a publicly-known method, for example, by

using air blasting, hot blast, hot nitrogen, far-infrared radiation, high frequency wave and the like.

[0045] As the metal used as the metal layer in the flexible circuit substrate, any metal may be used without particular limitation. As a preferable example, there may be mentioned at least one kind of metal selected from the group consisting of copper, nickel, cobalt, chromium, zinc, aluminum and stainless steel as well as an alloy thereof and more preferable are copper and copper alloy, stainless steel, nickel and nickel alloy (including 42 alloy), aluminum and aluminum alloy and the like. Further more preferable are copper and copper alloy.

[0046] There is no limitation on the thickness of the metal layer if the metal layer is formed in a tape shape, and the metal layer has a thickness of preferably not less than 0.1 micrometers and not more than 150 micrometers, more preferably not less than 2 micrometers and not more than 105 micrometers and further more preferably not less than 3 micrometers and not more than 35 micrometers. The thickness may be selected accordingly from the above range, for example, a thin foil is preferably used for the application requiring wiring processing of a fine pattern and a thick foil is preferably used for the wiring requiring rigidity and the large current application.

[0047] The film as an insulating resin layer used in the present invention is excellent in transparency, elastic modulus at high temperature and dimensional stability (low thermal expansion coefficient). For this reason, since the circuit substrate has at least one layer of such insulating resin layer, it has a significant effect that the deformation of a substrate is unlikely to occur and problems such as wire disconnection, sinking, peeling and plating penetration will not occur, even when a chip is mounted at a high temperature and pressure.

[0048] When an insulating resin layer of the present invention is used for a chip-on-film substrate which is widely used in the TAB (Tape Automated Bonding) tape processing line, the insulating resin layer is easy in operation and excellent in dimensional stability because it has a high elastic modulus at a temperature near the mounting temperature. The temperature near the mounting temperature is not less than 250 degrees C and not more than 500 degrees C, preferably not less than 300 degrees C and not more than 450 degrees C and more preferably not less than 350 degrees C and not more than 450 degrees C.

[0049] Since the insulating resin layer of the present invention is transparent, the metal wiring may be recognized by image through the insulating resin layer after the circuit processing as above, thereby enabling the layout when a chip is mounted by an inner lead bonder.

[0050] According to the present invention, by the compatibility in both transparency and a high elastic modulus at high temperature which were not obtained in a molded product

composed of a complex of a conventional polyimide and clay minerals, a polyimide-clay mineral complex may be applied to a film and a circuit substrate and the like. In addition, the polyimide-clay mineral complex improves the workability by visual confirmation because of its transparency and prevents the reduction in elasticity due to heating, and therefore, may be applied to the miniaturization and densification of electric and electronics devices and the like.

Mode for the Invention

[0051] Hereinafter, the present invention will be explained in more detail with reference to Examples, but the present invention is not limited at all by these Examples. Incidentally, the abbreviations in Examples mean the followings.

DMAc: dimethylacetoamide

NMP: N-methyl-2-pyrrolidone

APB: 1,3-bis(3-aminophenoxy)benzene

m-BP: 4,4'-(3-aminophenoxy)biphenyl

ODA: 4,4'-oxydianiline(4,4'-diaminodiphenylether)

PPD: p-phenylenediamine

BTDA: 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride

BPDA: 3,3',4,4'-biphenyltetracarboxylic acid dianhydride

PMDA: anhydrous pyromellitic acid

APB-BMI: 1,3-bis(3-maleimidephenoxy)benzene

Further, each evaluation in Examples was performed as follows.

[0052] (Viscoelasticity Measurement: Measurement of Storage modulus at 450 degrees C)

For the evaluation of the elastic modulus, the temperature distribution measurement in a tensile deformation mode was performed by using RSA-II manufactured by Rheometrics Corp. The measurement was made under the condition of a temperature range of 30 to 500 degrees C, a heating rate of 3 degrees C /min, a strain of 0.02 % under control of auto-strain and a frequency of 1 Hz. In addition, the storage modulus E' was determined at 450 degrees C using a test specimen having a length of 20 mm and a width of 5 mm.

[0053] (Thermal Expansion Coefficient Measurement)

The average coefficient of linear elongation (CTE) at a temperature in the range of 100 to 250 degrees C and 380 to 430 degrees C was determined by a tensile method in which the extension (shrinkage) of the film was measured by changing the temperature in the range of 50 to 500 degrees C while applying a certain loading to both ends of the film by using a thermomechanical analyzer (TMA-50, manufactured by Shimadzu Corporation).

[0054] (Light Transmittance Measurement)

The light transmittance at a wavelength of 650 nm was determined by measuring a light transmittance of a film having a thickness shown in Table 1 by using an ultraviolet-visible spectrophotometer (UV-2200, manufactured by Shimadzu Corporation). The light transmittance converted to that of a film with a thickness of 20 micrometers was calculated from the thickness and light transmittance of the film by using the following equation (3).

Absorbance (E) = log I_0/I = kCL (3)

For a light of intensity I obtained by passing a monochromatic light of intensity I_0 through a sample having molar concentration C and thickness L, the percentage of I_0/I represents a light transmittance (%), Log I_0/I represents an absorbance and k represents a molar absorbance coefficient.

[0055] (Confirmation of a dispersion state of clay minerals)

A prepared polyimide/clay composite film was trimmed using a Leica Ultracut UCT ultra-microtome. The resulting microtome thin sections were placed on 200 mesh copper grids and examined the dispersion state of clay minerals by using a transmission electron microscope (TEM) (CM300-FEGTEM, manufactured by Philips Co., Ltd.) at an acceleration voltage of 300 kV.

[0056] (Hygroscopic Expansion Coefficient Measurement)

A length of a film was measured by using a thermomechanical analyzer equipped with humidity control unit (TMA-2200S, manufactured by Shimadzu Corporation) at a relative humidity of 20, 40 and 60 %. A slope of a line, that is, a hygroscopic expansion coefficient (CHE) (ppm/% RH), was determined by plotting the measured length of films against the relative humidity and by applying linear approximation to the points plotted.

[0057] (Water absorption Measurement)

The water absorption of a film stored for more than 1 week under the atmosphere of a temperature of 23 degrees C and a relative humidity of 50 % was measured at 250 degrees C by using a heating vaporization moisture content measuring device (manufactured by Hiranuma Sangyo Co., Ltd.).

[0058] Synthesis Example 1

Into a flask equipped with a stirrer and a nitrogen introduction tube was added 261.0 g of DMAc as a solvent, and then 20.44 g of ODA and 16.12 g of m-BP were added, followed by stirring and dissolving at 20 to 30 degrees C. Then, 30.84 g of PMDA was added and the raw materials adhered to the inside of the flask were washed off with 11.0 g of DMAc. The resulting mixture was heated to 50 to 60 degrees C and stirred for approximately 1 hour and subsequently 0.44 g of PMDA was added and stirred for approximately 4 hours while maintaining the temperature at 60 degrees C to obtain varnish (a). Next, into another flask equipped with a stirrer and nitrogen introduction

tube was added 263.0 g of NMP as a solvent, and then 19.62 g of PPD was added and dissolved by stirring at 20 to 30 degrees C. Thereafter, 37.0 g of BPDA and 11.06 g of PMDA were added and the raw materials adhered to the inside of the flask were washed off with 10.0 g of NMP. The resulting mixture was heated to 50 to 60 degrees C and stirred for approximately 4 hours to obtain varnish (b). Finally, in another flask equipped with a stirrer and a nitrogen introduction tube, varnish (b) and varnish (a) were mixed at a weight ratio of 77:23. The resulting mixture was heated to 50 to 60 degrees C and stirred for approximately 4 hours to obtain a polyamic acid solution. The resulting polyamic acid solution had a polyamic acid content of 20 % by weight and an E type viscosity at 25 degrees C of 30000 milli pascal-second.

[0059] (Example 1)

The polyamic acid solution produced in Synthesis Example 1 was reprecipitated in methanol and dissolved in pyridine so that the concentration was 10 % by weight of the polyimide after imidization to obtain a polyamic acid/pyridine solution. This solution was used as a first solution.

In addition to this, 1.6 g of montmorillonite which is not subjected to the organic modification was added to 78.4 g of water and stirred at 10,000 rpm for 1 hour by a homogenizer to obtain a 2 % aqueous dispersion solution. This solution was diluted 8-fold with water to obtain a 0.25 % dispersion solution, which was used as a second solution. To 20 g of the first solution was gradually added 20.51 g of the second solution over 30 minutes using a microtube pump to obtain a homogeneous solution. The homogeneous solution was transferred to glass Petri-dishes and dried at room temperature for 1 week under a flow of nitrogen and subsequently thermally treated in an inert oven at 200, 250, 300 and 350 degrees C for 1 hour, respectively, to obtain composite films with a thickness of 15 to 20 micrometers. When the resulting composite films were observed by TEM, it was confirmed that clay minerals were homogeneously dispersed in units from one to a few layers. In addition, the physical properties of the resulting composite films are shown in Table 1.

[0060] (Examples 2 and 3)

The composite film was prepared in the same operation as in Example 1 so that the content of clay minerals to polyimide meets the conditions described in Table 1. The physical properties of the resulting composite film are shown in Table 1.

[0061] (Examples 4 to 6)

By changing Kunipia G in the second solution of Example 1 to a synthetic smectite (Smecton SA, manufactured by Kunimine Industries Co., Ltd.), the composite films were prepared in the same operation as in Example 1 so that the content of clay minerals to polyimide meets the conditions described in Table 1. The physical properties of the resulting composite films are shown in Table 1.

[0062] (Example 7)

A solution was prepared by adding NMP to the polyamic acid solution produced in Synthesis Example 1 and then adjusting the weight of the polyimide after imidization to 10 % by weight. This solution was used as a first solution.

In addition to this, 1.6 g of montmorillonite which is not subjected to the organic modification was added to 78.4 g of water and stirred at 10,000 rpm for 1 hour by a homogenizer to obtain a 2 % aqueous dispersion solution. To this solution was added 80 g of NMP to obtain a 1 % dispersion solution, which was used as a second solution. A homogeneous solution was obtained by slowly adding 10.53 g of the second solution to 20 g of the first solution. This homogeneous solution was applied on a glass substrate and dried by increasing the temperature from 50 to 200 degrees C at a heating rate of 5 degrees C /min and subsequently thermally treated in an inert oven at 200, 250, 300 and 350 degrees C for 1 hour, respectively, to obtain composite films with a thickness of 15 to 20 micrometers. The physical properties of the resulting composite films are shown in Table 1.

[0063] (Example 8)

The composite film was prepared in the same operation as in Example 7 so that the content of clay minerals to polyimide meets the conditions described in Table 1. The physical properties of the resulting composite film are shown in Table 1.

[0064] (Comparative Example 1)

The polyamic acid prepared by the condition of Synthesis Example 1 was applied on a glass substrate so that the dried film thickness is 15 to 21 micrometers and dried by increasing the temperature from 50 to 180 degrees C at a heating rate of 3 degrees C / min in an inert oven and subsequently imidized to obtain a polyimide film. The physical properties of the resulting polyimide film are shown in Table 1.

[0065] (Comparative Example 2)

A solution was prepared by adding NMP to the polyamic acid produced in Synthesis Example 1 and then adjusting the weight of the polyimide after imidization to 19 % by weight. This solution was used as a first solution.

In addition to this, 1.6 g of montmorillonite (Kunipia G, manufactured by Kunimine Industries Co., Ltd.) which is not subjected to the organic modification was added to 78.4 g of NMP and stirred for 1 hour by a magnetic stirrer and subsequently treated for 1 hour by an ultrasonic washer to obtain a dispersion solution. This dispersion solution was used a second solution. A homogeneous solution was obtained by adding 4.87 g of the second solution to the 20 g of the first solution. This homogeneous solution was applied on a glass substrate and dried by increasing the temperature from 50 degrees C to 200 degrees C at a heating rate of 5 degrees C/min and subsequently thermally treated at 200 degrees C for 5 hours in an inert oven to obtain a composite film with a

thickness of 15 micrometers. The resulting film was not homogeneous in which montmorillonite was agglomerated.

[0066] (Comparative Examples 3 and 4)

The composite films were prepared in the same operation as in Comparative Example 2 so that the content of clay minerals to polyimide is 5 % by weight and 8 % by weight, respectively. Both of the resulting films were not homogeneous in which montmorillonite was agglomerated.

[0067] (Comparative Example 5)

A solution was prepared by adding NMP to the polyamic acid produced in Synthesis Example 1 and then adjusting the weight of the polyimide after imidization to 19 % by weight. This solution was used as a first solution.

In addition to this, a 2 % dispersion solution was obtained by adding 1.6 g of an organo-montmorillonite treated with dimethyldistearylammonium (S-BEN NX, produced by Hojun Co., Ltd.) to 78.4 g of NMP and stirring for 1 hour while applying ultrasonic treatment. This dispersion solution was used as a second solution. A homogeneous solution was obtained by adding 4.87 g of the second solution to 20 g of the first solution. This homogeneous solution was applied on a glass substrate and dried by increasing the temperature from 50 degrees C to 200 degrees C at a heating rate of 5 degrees C/min and subsequently thermally treated at 200 degrees C for 5 hours in an inert oven to obtain a composite film with a thickness of 16 micrometers. In addition, the physical properties of the resulting composite film are shown in Table 1.

[0068] (Comparative Examples 6 and 7)

The composite films were prepared in the same operation as in Comparative Example 5 so that the content of clay minerals to polyimide meets the conditions described in Table 1. The physical properties of the resulting composite films are shown in Table 1.

[0069] (Example 9)

Into a flask equipped with a stirrer and a nitrogen introduction tube was added 855 g of N,N-dimethylacetoamide as a solvent and 69.16 g of 1,3-bis(3-aminophenoxy)benzene, followed by stirring until the compound was dissolved at room temperature. Then, to the resulting mixture was added 75.84 g of 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, followed by stirring at 60 degrees C to obtain a polyamic acid solution. The content percent of the polyamic acid was 15 % by weight. Then 500 g of the resulting polyamic acid solution was weighed out, followed by adding 11.3 g of 1,3-bis(3-maleimidephenoxy)benzene and stirring at room temperature for 2 hours, to obtain a polyamide acid solution containing a bismaleimide compound.

The polyamide acid solution containing a bismaleimide compound obtained by the above method was applied on the film obtained in Example 3 by a spin coater so that the thickness after drying is 3 micrometers. The applied film was heated from room temperature to 240 degrees C at a heating rate of 6 degrees C/min under a flow of nitrogen in an inert oven, followed by thermally treating at 240 degrees C for 15 minutes to obtain an insulating film in which one surface of the film is a thermoplastic polyimide resin layer. Thereafter, a commercially available electrolysis copper foil (F1-WS with a thickness of 12 micrometers, manufactured by Furukawa Circuit Foil Co., Ltd.) and an insulating film were bonded by heat press to obtain a polyimide-metal laminate.

The 90 degrees peel test was conducted by using the resulting polyimide-metal laminate in accordance with IPC-TM-650 method and the result was 0.3 kN/m.

[0070]

[Table 1]

	Clay Minerals		Water Absorption Rate (%)	CHE (ppm/% RH)	Elastic Modulus (GPa)		CTE (ppm/°C)		Light Transmittance at 650 nm (%)	Film Thickness in measuring Light Transmittance (μm)	Light Transmittance converted to 20 μm(%)
	Clay Mineral Name	Content (wt%)			40°C	450°C	α1 (100 -250 °C)	α2 (380 -430 °C)			
Example 1	Kunipia G	2.5	-	-	7.31	0.33	-	-	71.9	16	66.2
Example 2	Kunipia G	5.0	-	-	9.41	0.59	8	61	54.0	20	54.0
Example 3	Kunipia G	8.0	1	8.5	9.81	1.02	7	44	59.7	20	59.7
Example 4	Smecton SA	2.5	-	-	6.75	0.30	11	-	79.0	15	73.0
Example 5	Smecton SA	5.0	-	-	6.40	0.41	9	-	73.9	15	66.8
Example 6	Smecton SA	8.0	-	-	7.09	0.78	8	86	72.9	15	65.6
Example 7	Kunipia G	5.0	-	-	7.04	0.36	-	-	54.5	17	49.0
Example 8	Kunipia G	8.0	-	-	7.68	0.69	15	63	46.4	20	46.4
Comparative Example 1	-	0	0.8	8.7	4.40	0.23	13	313	78.2	21	79.1
Comparative Example 5	S-BEN NX	2.5	-	-	5.69	0.07	-	-	53.1	16	45.3
Comparative Example 6	S-BEN NX	5.0	-	-	5.70	0.05	-	-	26.2	18	22.6
Comparative Example 7	S-BEN NX	8.0	-	-	5.96	0.07	12	505	14.5	20	14.5

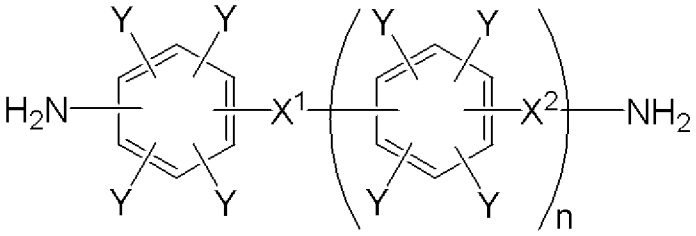
Claims

[1] A circuit substrate comprising an insulating resin layer,
wherein said insulating resin layer contains polyimide and a clay mineral,
said insulating resin layer has an elastic modulus of not less than 0.3 GPa and not more than 30 GPa at 450 degrees C, and
said insulating resin layer with a thickness of 20 micrometers has a light transmittance of not less than 40 % at a wavelength of 650 nm.

[2] The circuit substrate according to claim 1,
wherein said insulating resin layer has a hygroscopic expansion coefficient of not less than 5 ppm/% RH and not more than 20 ppm/% RH at a relative humidity of 20 to 60 %.

[3] The circuit substrate according to claim 1 or 2,
wherein said insulating resin layer has a water absorption of not more than 2 %.

[4] The circuit substrate according to any of claims 1 to 3,
wherein a precursor of said polyimide is synthesized by using diamine compounds and
at least one of said diamine compounds is a compound represented by the following general formula (1)
[Chem.3]

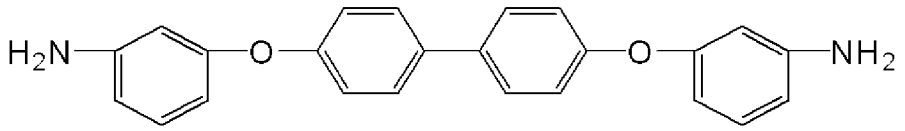


(1)

(in the formula (1), X^1 and X^2 are each independently selected from the group consisting of a single bond, an oxygen atom, a sulfur atom, a carbonyl group, a sulfonyl group and a hydrocarbon group which may have been substituted with a halogen atom, Ys are each independently selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, a nitro group and a hydrocarbon group which may have been substituted with a halogen atom, and n represents an integer of 0 to 8).

[5] The circuit substrate according to claim 4,
wherein at least one of said diamine compounds is a compound represented by the following general formula (2).

[Chem.4]



(2)

[6] The circuit substrate according to any of claims 1 to 5, wherein said clay mineral contained in said insulating resin layer is smectite group clay minerals or at least one kind selected from the group of swelling mica, vermiculite and halloysite.

[7] The circuit substrate according to any of claims 1 to 6, wherein said circuit substrate is a flexible circuit substrate which further contains a metal layer.

[8] The circuit substrate according to any of claims 1 to 6, wherein said circuit substrate is a chip-on-film substrate using said insulating resin layer.