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(19) **United States**(12) **Patent Application Publication**
IZUTANI et al.(10) **Pub. No.: US 2011/0259568 A1**(43) **Pub. Date: Oct. 27, 2011**(54) **THERMAL CONDUCTIVE SHEET****Publication Classification**(75) Inventors: **Seiji IZUTANI**, Osaka (JP); **Hisae UCHIYAMA**, Osaka (JP); **Takahiro FUKUOKA**, Osaka (JP); **Kazutaka HARA**, Osaka (JP); **Hitotsugu HIRANO**, Osaka (JP)(51) **Int. Cl.**
F28F 7/00 (2006.01)(52) **U.S. Cl.** 165/185(73) Assignee: **NITTO DENKO CORPORATION**, Osaka (JP)(21) Appl. No.: **13/016,726**(57) **ABSTRACT**(22) Filed: **Jan. 28, 2011**(30) **Foreign Application Priority Data**

Jan. 29, 2010	(JP)	2010-018256
Apr. 9, 2010	(JP)	2010-090908
Jul. 16, 2010	(JP)	2010-161853

A thermal conductive sheet containing a plate-like boron nitride particle, wherein the thermal conductivity in a direction perpendicular to the thickness direction of the thermal conductive sheet is 4 W/m·K or more, and a glass transition point determined as the peak value of $\tan\delta$ obtained by measuring a dynamic viscoelasticity of the thermal conductive sheet at a frequency of 10 Hz is 125° C. or more.

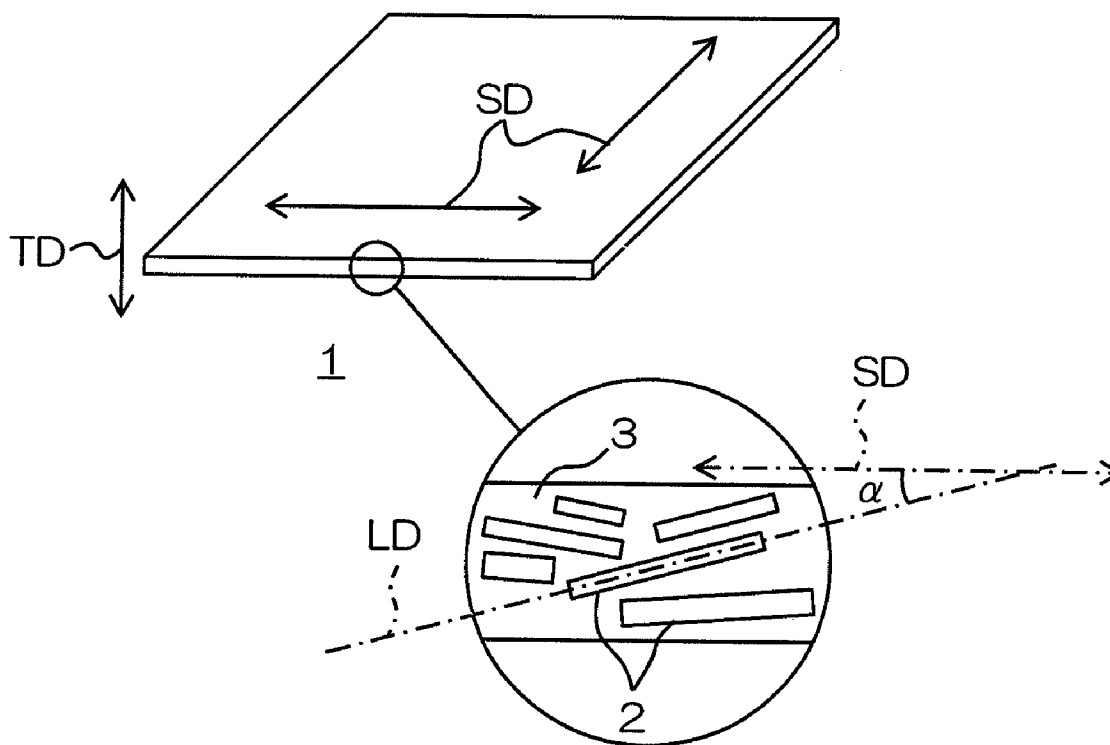


FIG. 1

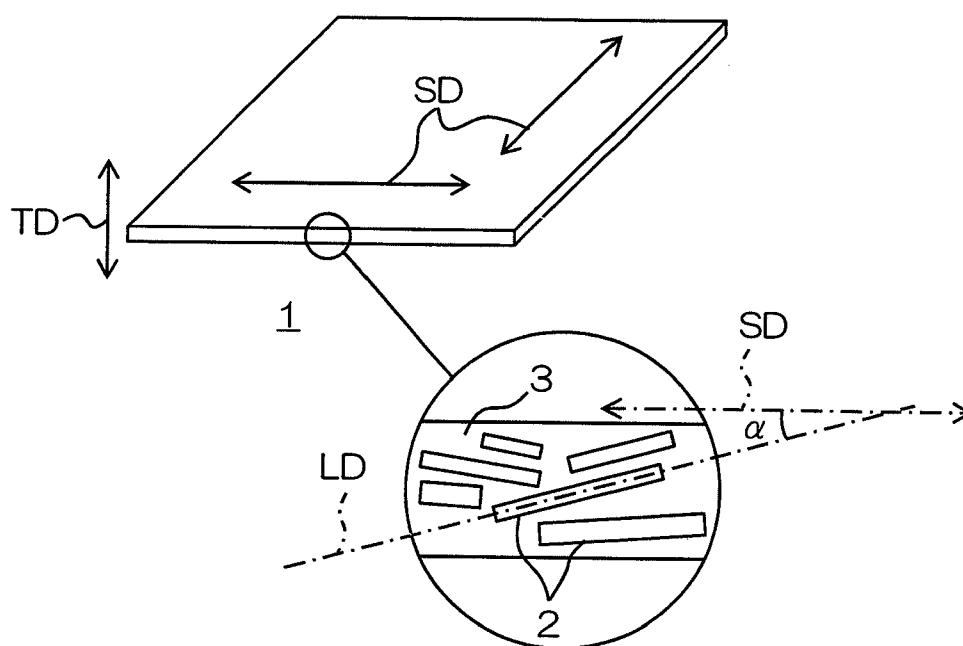


FIG. 2

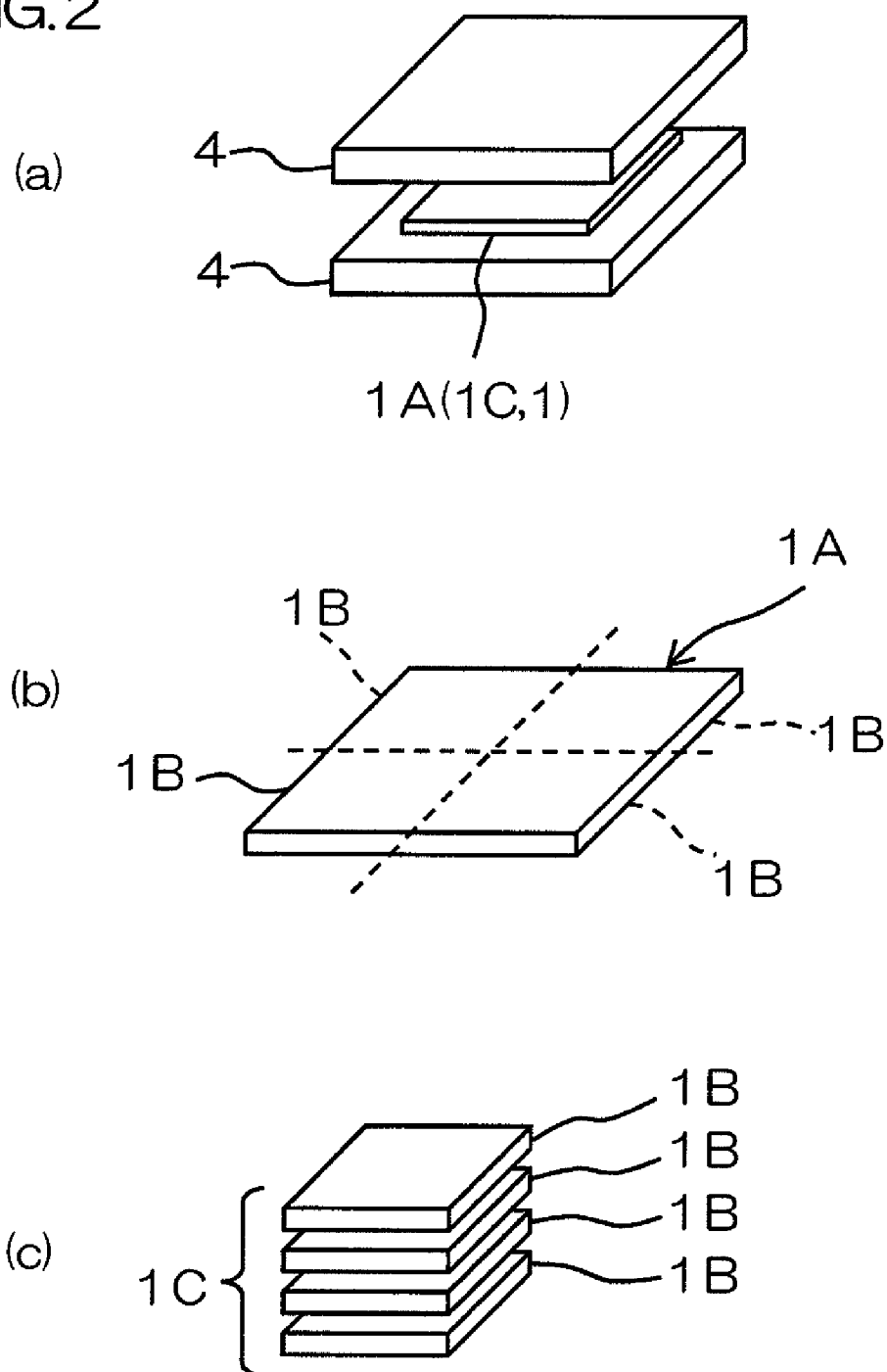


FIG.3

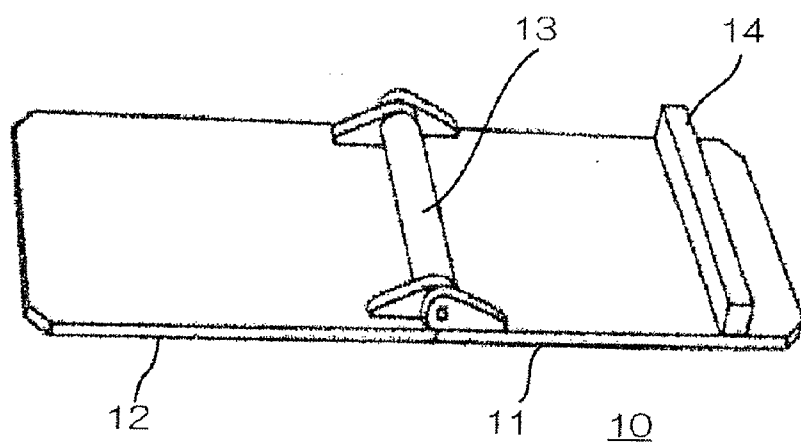
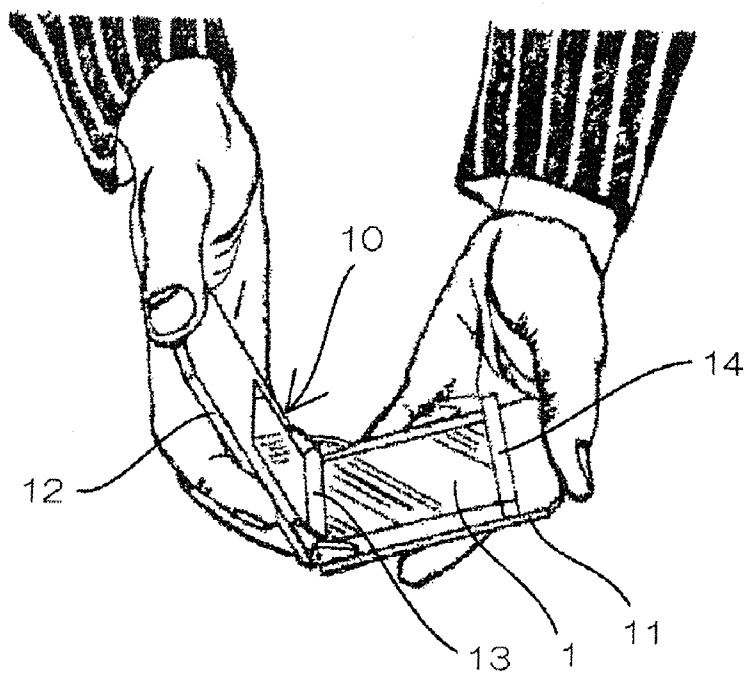


FIG.4



THERMAL CONDUCTIVE SHEET

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims priority from Japanese Patent Application No. 2010-018256 filed on Jan. 29, 2010; No. 2010-090908 filed on Apr. 9, 2010; and No. 2010-161853 filed on Jul. 16, 2010, the contents of which are hereby incorporated by reference into this application.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a thermal conductive sheet, to be specific, to a thermal conductive sheet for use in power electronics technology.

[0004] 2. Description of Related Art

[0005] In recent years, power electronics technology which uses semiconductor elements to convert and control electric power is applied in hybrid devices, high-brightness LED devices, and electromagnetic induction heating devices. In power electronics technology, a high current is converted to, for example, heat, and therefore materials that are disposed near the semiconductor element are required to have excellent heat dissipation characteristics (excellent heat conductivity).

[0006] For example, Japanese Unexamined Patent Publication No. 2008-280496 has proposed a thermal conductive sheet containing a plate-like boron nitride powder and an acrylic ester copolymer resin.

[0007] In the thermal conductive sheet of Japanese Unexamined Patent Publication No. 2008-280496, the boron nitride powder is oriented so as to orient its major axis direction (direction perpendicular to the plate thickness of the boron nitride powder) in the thickness direction of the sheet, and thermal conductivity in the thickness direction of the thermal conductive sheet is improved in this way.

SUMMARY OF THE INVENTION

[0008] However, there are cases where the thermal conductive sheet is required to have a high thermal conductivity in a direction (plane direction) perpendicular to the thickness direction depending on its use and purpose. In such a case, the thermal conductive sheet of Japanese Unexamined Patent Publication No. 2008-280496 is disadvantageous in that the major axis direction of the boron nitride powder is perpendicular to (crossing) the plane direction, and therefore the thermal conductivity in the plane direction is insufficient.

[0009] Furthermore, when such a thermal conductive sheet is used, for example, the thermal conductive sheet is bonded to various devices for conducting (dissipating) heat generated from the devices, and therefore excellent heat resistance (resistance to deformation) is required so as not to be deformed by the heat and not to be peeled off from the devices.

[0010] An object of the present invention is to provide a thermal conductive sheet that is excellent in thermal conductivity in the plane direction, and also excellent in heat resistance.

[0011] A thermal conductive sheet of the present invention contains a plate-like boron nitride particle, wherein the thermal conductivity in a direction perpendicular to the thickness direction of the thermal conductive sheet is 4 W/m·K or more, and a glass transition point determined as the peak value of

tan δ obtained by measuring a dynamic viscoelasticity of the thermal conductive sheet at a frequency of 10 Hz is 125° C. or more.

[0012] The thermal conductive sheet of the present invention is excellent in thermal conductivity in the plane direction that is perpendicular to the thickness direction, and also excellent in heat resistance.

[0013] Therefore, the thermal conductive sheet of the present invention can be applied to various heat dissipation uses as a thermal conductive sheet that allows decrease in deformation under high temperature, that suppresses peeling off, that is excellent in handleability, and that is excellent in thermal conductivity in the plane direction.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 shows a perspective view of an embodiment of a thermal conductive sheet of the present invention.

[0015] FIG. 2 shows process drawings for describing a method for producing the thermal conductive sheet shown in FIG. 1:

[0016] (a) illustrating a step of hot pressing a mixture or a laminated sheet,

[0017] (b) illustrating a step of dividing the pressed sheet into a plurality of pieces, and

[0018] (c) illustrating a step of laminating the divided sheets.

[0019] FIG. 3 shows a perspective view of a test device (Type I, before bend test) of a bend test.

[0020] FIG. 4 shows a perspective view of a test device (Type I, during bend test) of a bend test.

DETAILED DESCRIPTION OF THE INVENTION

[0021] A thermal conductive sheet of the present invention contains boron nitride particles.

[0022] To be specific, the thermal conductive sheet contains boron nitride (BN) particles as an essential component, and further contains, for example, a resin component.

[0023] The boron nitride particles are formed into a plate-like (or flake-like) shape, and are dispersed so as to be oriented in a predetermined direction (described later) in the thermal conductive sheet.

[0024] The boron nitride particles have an average length in the longitudinal direction (maximum length in the direction perpendicular to the plate thickness direction) of, for example, 1 to 100 μm , or preferably 3 to 90 μm . The boron nitride particles have an average length in the longitudinal direction of, 5 μm or more, preferably 10 μm or more, more preferably 20 μm or more, even more preferably 30 μm or more, or most preferably 40 μm or more, and usually has an average length in the longitudinal direction of, for example, 100 μm or less, or preferably 90 μm or less.

[0025] The average thickness (the length in the thickness direction of the plate, that is, the length in the short-side direction of the particles) of the boron nitride particles is, for example, 0.01 to 20 μm , or preferably 0.1 to 15 μm .

[0026] The aspect ratio (length in the longitudinal direction/thickness) of the boron nitride particles is, for example, 2 to 10000, or preferably 10 to 5000.

[0027] The average particle size of the boron nitride particles as measured by a light scattering method is, for example, 5 μm or more, preferably 10 μm or more, more

preferably 20 μm or more, particularly preferably 30 μm or more, or most preferably 40 μm or more, and usually is 100 μm or less.

[0028] The average particle size as measured by the light scattering method is a volume average particle size measured with a dynamic light scattering type particle size distribution analyzer.

[0029] When the average particle size of the boron nitride particles as measured by the light scattering method is below the above-described range, the thermal conductive sheet may become fragile, and handleability may be reduced.

[0030] The bulk density (JIS K 5101, apparent density) of the boron nitride particles is, for example, 0.3 to 1.5 g/cm^3 , or preferably 0.5 to 1.0 g/cm^3 .

[0031] As the boron nitride particles, a commercially available product or processed goods thereof can be used. Examples of commercially available products of the boron nitride particles include the "PT" series (for example, "PT-110") manufactured by Momentive Performance Materials Inc., and the "SHOBN®UHP" series (for example, "SHOBN®UHP-1") manufactured by Showa Denko K.K.

[0032] The resin component is a component that is capable of dispersing the boron nitride particles, i.e., a dispersion medium (matrix) in which the boron nitride particles are dispersed, including, for example, resin components such as a thermosetting resin component and a thermoplastic resin component.

[0033] Examples of the thermosetting resin component include epoxy resin, thermosetting polyimide, phenol resin, urea resin, melamine resin, unsaturated polyester resin, diallyl phthalate resin, silicone resin, and thermosetting urethane resin.

[0034] Examples of the thermoplastic resin component include polyolefin (for example, polyethylene, polypropylene, and ethylene-propylene copolymer), acrylic resin (for example, polymethyl methacrylate), polyvinyl acetate, ethylene-vinyl acetate copolymer, polyvinyl chloride, polystyrene, polyacrylonitrile, polyamide (Nylon®), polycarbonate, polyacetal, polyethylene terephthalate, polyphenylene oxide, polyphenylene sulfide, polysulfone, polyether sulfone, poly ether ether ketone, polyallyl sulfone, thermoplastic polyimide, thermoplastic urethane resin, polyamino-bismaleimide, polyamide-imide, polyether-imide, bismaleimide-triazine resin, polymethylpentene, fluorine resin, liquid crystal polymer, olefin-vinyl alcohol copolymer, ionomer, polyarylate, acrylonitrile-ethylene-styrene copolymer, acrylonitrile-butadiene-styrene copolymer, and acrylonitrile-styrene copolymer.

[0035] These resin components can be used alone or in combination of two or more.

[0036] Of the thermosetting resin components, preferably, an epoxy resin is used.

[0037] The epoxy resin is in a state of liquid, semi-solid, or solid under normal temperature.

[0038] To be specific, examples of the epoxy resin include aromatic epoxy resins such as bisphenol epoxy resin (for example, bisphenol A epoxy resin, bisphenol F epoxy resin, bisphenol S epoxy resin, hydrogenated bisphenol A epoxy resin, dimer acid-modified bisphenol epoxy resin, and the like), novolak epoxy resin (for example, phenol novolak epoxy resin, cresol novolak epoxy resin, biphenyl epoxy resin, and the like), naphthalene epoxy resin, fluorene epoxy resin (for example, bisaryl fluorene epoxy resin and the like), and triphenylmethane epoxy resin (for example, trishydrox-

yphenylmethane epoxy resin and the like); nitrogen-containing-cyclic epoxy resins such as triepoxypropyl isocyanurate (triglycidyl isocyanurate) and hydantoin epoxy resin; aliphatic epoxy resin; alicyclic epoxy resin (for example, dicyclo ring-type epoxy resin and the like); glycidylether epoxy resin; and glycidylamine epoxy resin.

[0039] These epoxy resins can be used alone or in combination of two or more.

[0040] The epoxy resin has an epoxy equivalent of, for example, 100 to 1000 $\text{g}/\text{equiv.}$, or preferably 180 to 700 $\text{g}/\text{equiv.}$, and has a softening temperature (ring and ball test) of, for example, 80° C. or less (to be specific, 20 to 80° C.), or preferably 70° C. or less (to be specific, 35 to 70° C.).

[0041] The epoxy resin has a melt viscosity at 80° C. of, for example, 10 to 20,000 $\text{mPa}\cdot\text{s}$, or preferably 50 to 10,000 $\text{mPa}\cdot\text{s}$. When two or more epoxy resins are used in combination, the melt viscosity of the mixture of these epoxy resins is set within the above-described range.

[0042] When two or more epoxy resins are used in combination, for example, a combination of a liquid epoxy resin and a solid epoxy resin is used, or more preferably, a combination of a liquid aromatic epoxy resin and a solid aromatic epoxy resin is used. Examples of such a combination include, to be more specific, a combination of a liquid bisphenol epoxy resin and a solid triphenylmethane epoxy resin, and a combination of a liquid bisphenol epoxy resin and a solid bisphenol epoxy resin.

[0043] Preferably, a semi-solid epoxy resin is used alone, or more preferably, a semi-solid aromatic epoxy resin is used alone. Examples of those epoxy resins include, in particular, a semi-solid fluorene epoxy resin.

[0044] A combination of a liquid epoxy resin and a solid epoxy resin, or a semi-solid epoxy resin can improve conformability to irregularities (described later) of the thermal conductive sheet.

[0045] Furthermore, by combining a plurality of epoxy resins having different properties and condition, the glass transition point can be set to a desired range.

[0046] Furthermore, when two or more epoxy resins are used in combination, for example, a first epoxy resin having a softening temperature of, for example, below 45° C., or preferably 35° C. or less, and a second epoxy resin having a softening temperature of, for example, 45° C. or more, or preferably 55° C. or more are used in combination. In this way, the kinetic viscosity (in conformity with JIS K 7233, described later) of the resin component (mixture) can be set to a desired range, and also, conformability to irregularities of the thermal conductive sheet can be improved.

[0047] The epoxy resin can also be prepared as an epoxy resin composition containing, for example, an epoxy resin, a curing agent, and a curing accelerator.

[0048] The curing agent is a latent curing agent (epoxy resin curing agent) that can cure the epoxy resin by heating, and examples thereof include an imidazole compound, an amine compound, an acid anhydride compound, an amide compound, a hydrazide compound, and an imidazoline compound. In addition to the above-described compounds, a phenol compound, a urea compound, and a polysulfide compound can also be used.

[0049] Examples of the imidazole compound include 2-phenyl imidazole, 2-methyl imidazole, 2-ethyl-4-methyl imidazole, and 2-phenyl-4-methyl-5-hydroxymethyl imidazole.

[0050] Examples of the amine compound include aliphatic polyamines such as ethylene diamine, propylene diamine, diethylene triamine, and triethylene tetramine; and aromatic polyamines such as metha phenylenediamine, diaminodiphenyl methane, and diaminodiphenyl sulfone.

[0051] Examples of the acid anhydride compound include phthalic anhydride, maleic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 4-methyl-hexahydrophthalic anhydride, methyl nadic anhydride, pyromellitic anhydride, dodecenylsuccinic anhydride, dichloro succinic anhydride, benzophenone tetracarboxylic anhydride, and chlorendic anhydride.

[0052] Examples of the amide compound include dicyan diamide and polyamide.

[0053] An example of the hydrazide compound includes adipic acid dihydrazide.

[0054] Examples of the imidazoline compound include methylimidazoline, 2-ethyl-4-methylimidazoline, ethylimidazoline, isopropylimidazoline, 2,4-dimethylimidazoline, phenylimidazoline, undecylimidazoline, heptadecylimidazoline, and 2-phenyl-4-methylimidazoline.

[0055] These curing agents can be used alone or in combination of two or more.

[0056] A preferable example of the curing agent is an imidazole compound.

[0057] Examples of the curing accelerator include tertiary amine compounds such as triethylenediamine and tri-2,4,6-dimethylaminomethylphenol; phosphorus compounds such as triphenylphosphine, tetraphenylphosphonium tetraphenylborate, and tetra-n-butylphosphonium-o,o-diethylphosphorodithioate; a quaternary ammonium salt compound; an organic metal salt compound; and derivatives thereof. These curing accelerators can be used alone or in combination of two or more.

[0058] In the epoxy resin composition, the mixing ratio of the curing agent is, for example, 0.5 to 50 parts by mass, or preferably 1 to 10 parts by mass per 100 parts by mass of the epoxy resin, and the mixing ratio of the curing accelerator is, for example, 0.1 to 10 parts by mass, or preferably 0.2 to 5 parts by mass per 100 parts by mass of the epoxy resin.

[0059] The above-described curing agent, and/or the curing accelerator can be prepared and used, as necessary, as a solution, i.e., the curing agent and/or the curing accelerator dissolved in a solvent; and/or as a dispersion liquid, i.e., the curing agent and/or the curing accelerator dispersed in a solvent.

[0060] Examples of the solvent include organic solvents including ketones such as acetone and methyl ethyl ketone, ester such as ethyl acetate, and amide such as N,N-dimethylformamide; and water-based solvents including water, and alcohols such as methanol, ethanol, propanol, and isopropanol. A preferable example is an organic solvent, more preferable examples are ketones and amides.

[0061] Of the thermoplastic resin components, preferably, polyolefin is used.

[0062] Preferable examples of polyolefin are polyethylene and ethylene-propylene copolymer.

[0063] Examples of polyethylene include a low density polyethylene and a high density polyethylene.

[0064] Examples of ethylene-propylene copolymer include a random copolymer, a block copolymer, or a graft copolymer of ethylene and propylene.

[0065] These polyolefins can be used alone or in combination of two or more.

[0066] The polyolefins have a weight average molecular weight and/or a number average molecular weight of, for example, 1000 to 10000.

[0067] The polyolefin can be used alone, or can be used in combination.

[0068] Of the resin components, preferably, a thermosetting resin component is used, or more preferably, an epoxy resin is used.

[0069] The resin component has a kinetic viscosity as measured in conformity with the kinetic viscosity test of JIS K 7233 (bubble viscometer method) (temperature: 25° C.±0.5° C., solvent: butyl carbitol, resin component (solid content) concentration: 40 mass %) of, for example, 0.22×10^{-4} to 2.00×10^{-4} m²/s, preferably 0.3×10^{-4} to 1.9×10^{-4} m²/s, or more preferably 0.4×10^{-4} to 1.8×10^{-4} m²/s. The above-described kinetic viscosity can also be set to, for example, 0.22×10^{-4} to 1.00×10^{-4} m²/s, preferably 0.3×10^{-4} to 0.9×10^{-4} m²/s, or more preferably 0.4×10^{-4} to 0.8×10^{-4} m²/s.

[0070] When the kinetic viscosity of the resin component exceeds the above-described range, excellent flexibility and conformability to irregularities (described later) may not be given to the thermal conductive sheet. On the other hand, when the kinetic viscosity of the resin component is below the above-described range, boron nitride particles may not be oriented in a predetermined direction.

[0071] In the kinetic viscosity test in conformity with JIS K 7233 (bubble viscometer method), the kinetic viscosity of the resin component is measured by comparing the bubble rising speed of a resin component sample with the bubble rising speed of criterion samples (having a known kinetic viscosity), and determining the kinetic viscosity of the criterion sample having a matching rising speed to be the kinetic viscosity of the resin component.

[0072] In the thermal conductive sheet, the proportion of the volume-based boron nitride particle content (solid content, that is, the volume percentage of boron nitride particles relative to a total volume of the resin component and the boron nitride particles) is, for example, 35 vol % or more, preferably 60 vol % or more, or more preferably 75 vol % or more, and usually, for example, 95 vol % or less, or preferably 90 vol % or less.

[0073] When the proportion of the volume-based boron nitride particle content is below the above-described range, the boron nitride particles may not be oriented in a predetermined direction in the thermal conductive sheet. On the other hand, when the proportion of the volume-based boron nitride particle content exceeds the above-described range, the thermal conductive sheet may become fragile, and handleability and conformability to irregularities may be reduced.

[0074] The mass-based mixing ratio of the boron nitride particles relative to 100 parts by mass of the total amount (total solid content) of the components (boron nitride particles and resin component) forming the thermal conductive sheet is, for example, 40 to 95 parts by mass, or preferably 65 to 90 parts by mass, and the mass-based mixing ratio of the resin component relative to 100 parts by mass of the total amount of the components forming the thermal conductive sheet is, for example, 5 to 60 parts by mass, or preferably 10 to 35 parts by mass. The mass-based mixing ratio of the boron nitride particles relative to 100 parts by mass of the resin component is, for example, 60 to 1900 parts by mass, or preferably 185 to 900 parts by mass.

[0075] When two epoxy resins (a first epoxy resin and a second epoxy resin) are used in combination, the mass ratio

(mass of the first epoxy resin/mass of the second epoxy resin) of the first epoxy resin relative to the second epoxy resin can be set appropriately in accordance with the softening temperature and the like of the epoxy resins (the first epoxy resin and the second epoxy resin). For example, the mass ratio of the first epoxy resin relative to the second epoxy resin is 1/99 to 99/1, or preferably 10/90 to 90/10.

[0076] In the resin component, in addition to the above-described components (polymer), for example, a polymer precursor (for example, a low molecular weight polymer including oligomer), and/or a monomer are contained.

[0077] FIG. 1 shows a perspective view of an embodiment of a thermal conductive sheet of the present invention, and FIG. 2 shows process drawings for describing a method for producing the thermal conductive sheet shown in FIG. 1.

[0078] Next, a method for producing a thermal conductive sheet as an embodiment of the present invention is described with reference to FIG. 1 and FIG. 2.

[0079] In this method, first, the above-described components are blended at the above-described mixing ratio and are stirred and mixed, thereby preparing a mixture.

[0080] In the stirring and mixing, in order to mix the components efficiently, for example, the solvent may be blended therein with the above-described components, or, for example, the resin component (preferably, the thermoplastic resin component) can be melted by heating.

[0081] Examples of the solvent include the above-described organic solvents. When the above-described curing agent and/or the curing accelerator are prepared as a solvent solution and/or a solvent dispersion liquid, the solvent of the solvent solution and/or the solvent dispersion liquid can also serve as a mixing solvent for the stirring and mixing without adding a solvent during the stirring and mixing. Alternatively, in the stirring and mixing, a solvent can be further added as a mixing solvent.

[0082] In the case when the stirring and mixing is performed using a solvent, the solvent is removed after the stirring and mixing.

[0083] To remove the solvent, for example, the mixture is allowed to stand at room temperature for 1 to 48 hours; heated at 40 to 100° C. for 0.5 to 3 hours; or heated under a reduced pressure atmosphere of, for example, 0.001 to 50 kPa, at 20 to 60° C., for 0.5 to 3 hours.

[0084] When the resin component (preferably, a thermoplastic resin component) is to be melted by heating, the heating temperature is, for example, a temperature in the neighborhood of or exceeding the softening temperature of the resin component, to be specific, 40 to 150° C., or preferably 70 to 140° C.

[0085] Next, in this method, the obtained mixture is hot-pressed.

[0086] To be specific, as shown in FIG. 2 (a), as necessary, for example, the mixture is hot-pressed with two releasing films 4 sandwiching the mixture, thereby producing a pressed sheet 1A. Conditions for the hot-pressing are as follows: a temperature of, for example, 50 to 150° C., or preferably 60 to 140° C.; a pressure of, for example, 1 to 100 MPa, or preferably 5 to 50 MPa; and a duration of, for example, 0.1 to 100 minutes, or preferably 1 to 30 minutes.

[0087] More preferably, the mixture is hot-pressed under vacuum. The degree of vacuum in the vacuum hot-pressing is, for example, 1 to 100 Pa, or preferably 5 to 50 Pa, and the temperature, the pressure, and the duration are the same as those described above for the hot-pressing.

[0088] When the temperature, the pressure, and/or the duration in the hot-pressing is outside the above-described range, there is a case where a porosity P (described later) of the thermal conductive sheet 1 cannot be adjusted to a desired value.

[0089] The pressed sheet 1A obtained by the hot-pressing has a thickness of, for example, 50 to 1000 μ m, or preferably 100 to 800 μ m.

[0090] Next, in this method, as shown in FIG. 2 (b), the pressed sheet 1A is divided into a plurality of pieces (for example, four pieces), thereby producing a divided sheet 1B (dividing step). In the division of the pressed sheet 1A, the pressed sheet 1A is cut along the thickness direction so that the pressed sheet 1A is divided into a plurality of pieces when the pressed sheet 1A is projected in the thickness direction. The pressed sheet 1A is cut so that the respective divided sheets 1B have the same shape when the divided sheets 1B are projected in the thickness direction.

[0091] Next, in this method, as shown in FIG. 2 (c), the respective divided sheets 1B are laminated in the thickness direction, thereby producing a laminated sheet 1C (laminating step).

[0092] Thereafter, in this method, as shown in FIG. 2 (a), the laminated sheet 1C is hot-pressed (preferably hot-pressed under vacuum) (hot-pressing step). The conditions for the hot-pressing are the same as the conditions for the hot-pressing of the above-described mixture.

[0093] The thickness of the hot-pressed laminated sheet 1C is, for example, 1 mm or less, or preferably 0.8 mm or less, and usually is, for example, 0.05 mm or more, or preferably 0.1 mm or more.

[0094] Thereafter, the series of the steps of the above-described dividing step (FIG. 2 (b)), laminating step (FIG. 2 (c)), and hot-pressing step (FIG. 2 (a)) are performed repeatedly, so as to allow boron nitride particles 2 to be efficiently oriented in a predetermined direction in the resin component 3 in the thermal conductive sheet 1. The number of the repetition is not particularly limited, and can be set appropriately according to the charging state of the boron nitride particles. The number of the repetition is, for example, 1 to 10 times, or preferably 2 to 7 times.

[0095] The thermal conductive sheet 1 can be obtained in this manner.

[0096] The thickness of the obtained thermal conductive sheet 1 is, for example, 1 mm or less, or preferably 0.8 mm or less, and usually, for example, 0.05 mm or more, or preferably 0.1 mm or more.

[0097] In the thermal conductive sheet 1, the proportion of the volume-based boron nitride particle content (solid content, that is, volume percentage of boron nitride particles relative to the total volume of the resin component and the boron nitride particles) is, as described above, for example, 35 vol % or more (preferably 60 vol % or more, or more preferably 75 vol % or more), and usually 95 vol % or less (preferably 90 vol % or less).

[0098] When the proportion of the boron nitride particle content is below the above-described range, the boron nitride particles may not be oriented in a predetermined direction in the thermal conductive sheet.

[0099] When the resin component 3 is the thermosetting resin component, for example, the series of the steps of the above-described dividing step (FIG. 2 (b)), laminating step (FIG. 2 (c)), and hot-pressing step (FIG. 2 (a)) are performed repeatedly for an uncured thermal conductive sheet 1, and

then the uncured (or semi-cured (in B-stage)) thermal conductive sheet **1** is cured by heat after the hot-pressing step (FIG. 2 (a)), i.e., after the final step, thereby producing a cured thermal conductive sheet **1**.

[0100] To cure the thermal conductive sheet **1** by heat, the above-described hot press or a dryer is used. Preferably, a dryer is used. Conditions for the curing by heat are as follows: a heating temperature of, for example, 60 to 250° C., or preferably 80 to 200° C., and a pressure of, for example, 100 MPa or less, or preferably 50 MPa or less.

[0101] In the thus obtained thermal conductive sheet **1**, as shown in FIG. 1 and its partially enlarged schematic view, the longitudinal direction LD of the boron nitride particle **2** is oriented along a plane (surface) direction SD that crosses (is perpendicular to) the thickness direction TD of the thermal conductive sheet **1**.

[0102] The calculated average of the angle formed between the longitudinal direction LD of the boron nitride particle **2** and the plane direction SD of the thermal conductive sheet **1** (orientation angle α of the boron nitride particles **2** relative to the thermal conductive sheet **1**) is, for example, 25 degrees or less, or preferably 20 degrees or less, and usually 0 degree or more.

[0103] The orientation angle α of the boron nitride particle **2** relative to the thermal conductive sheet **1** is obtained as follows: the thermal conductive sheet **1** is cut along the thickness direction with a cross section polisher (CP); the cross section thus appeared is photographed with a scanning electron microscope (SEM) at a magnification that enables observation of 200 or more boron nitride particles **2** in the field of view; a tilt angle α between the longitudinal direction LD of the boron nitride particle **2** and the plane direction SD (direction perpendicular to the thickness direction TD) of the thermal conductive sheet **1** is obtained from the obtained SEM photograph; and the average value of the tilt angles α is calculated.

[0104] The thus obtained thermal conductivity in the plane direction SD of the thermal conductive sheet **1** is 4 W/m·K or more, preferably 5 W/m·K or more, more preferably 10 W/m·K or more, even more preferably 15 W/m·K or more, or particularly preferably 25 W/m·K or more, and usually 200 W/m·K or less.

[0105] The thermal conductivity in the plane direction SD of the thermal conductive sheet **1** is substantially the same before and after the curing by heat when the resin component **3** is the thermosetting resin component.

[0106] When the thermal conductivity in the plane direction SD of the thermal conductive sheet **1** is below the above-described range, thermal conductivity in the plane direction SD is insufficient, and therefore there is a case where the thermal conductive sheet **1** cannot be used for heat dissipation that requires thermal conductivity in such a plane direction SD.

[0107] The thermal conductivity in the plane direction SD of the thermal conductive sheet **1** is measured by a pulse heating method. In the pulse heating method, the xenon flash analyzer "LFA-447" (manufactured by Erich NETZSCH GmbH & Co. Holding KG) is used.

[0108] The thermal conductivity in the thickness direction TD of the thermal conductive sheet **1** is, for example, 0.5 to 15 W/m·K, or preferably 1 to 10 W/m·K.

[0109] The thermal conductivity in the thickness direction TD of the thermal conductive sheet **1** is measured by a pulse heating method, a laser flash method, or a TWA method. In

the pulse heating method, the above-described device is used, in the laser flash method, "TC-9000" (manufactured by Ulvac, Inc.) is used, and in the TWA method, "ai-Phase mobile" (manufactured by ai-Phase Co., Ltd) is used.

[0110] Thus, the ratio of the thermal conductivity in the plane direction SD of the thermal conductive sheet **1** relative to the thermal conductivity in the thickness direction TD of the thermal conductive sheet **1** (thermal conductivity in the plane direction SD/thermal conductivity in the thickness direction TD) is, for example, 1.5 or more, preferably 3 or more, or more preferably 4 or more, and usually 20 or less.

[0111] Although not shown in FIG. 1, for example, pores (gaps) are formed in the thermal conductive sheet **1**.

[0112] The proportion of the pores in the thermal conductive sheet **1**, that is, a porosity P, can be adjusted by setting the proportion of the boron nitride particle **2** content (volume-based), and further setting the temperature, the pressure, and/or the duration at the time of hot pressing the mixture of the boron nitride particle **2** and the resin component **3** (FIG. 2 (a)). To be specific, the porosity P can be adjusted by setting the temperature, the pressure, and/or the duration of the hot pressing (FIG. 2 (a)) within the above-described range.

[0113] The porosity P of the thermal conductive sheet **1** is, for example, 30 vol % or less, or preferably 10 vol % or less.

[0114] The porosity P is measured by, for example, as follows: the thermal conductive sheet **1** is cut along the thickness direction with a cross section polisher (CP); the cross section thus appeared is observed with a scanning electron microscope (SEM) at a magnification of 200 to obtain an image; the obtained image is binarized based on the pore portion and the non-pore portion; and the area ratio, i.e., the ratio of the pore portion area to the total area of the cross section of the thermal conductive sheet **1** is determined by calculation.

[0115] The thermal conductive sheet **1** has a porosity P2 after curing of, relative to a porosity P1 before curing, for example, 100% or less, or preferably 50% or less.

[0116] For the measurement of the porosity P(P1), when the resin component **3** is a thermosetting resin component, the thermal conductive sheet **1** before being cured by heat is used.

[0117] When the porosity P of the thermal conductive sheet **1** is within the above-described range, the conformability to irregularities (described later) of the thermal conductive sheet **1** can be improved.

[0118] The glass transition point of the thermal conductive sheet **1** is 125° C. or more, preferably 130° C. or more, more preferably 140° C. or more, more preferably 150° C. or more, more preferably 170° C. or more, more preferably 190° C. or more, or more preferably 210° C. or more, and usually 300° C. or less.

[0119] When the glass transition point is the above-described lower limit or more, a thermal conductive sheet with excellent heat resistance can be ensured, and therefore deformation under high temperature can be reduced, and peeling off can be suppressed.

[0120] That is, when the thermal conductive sheet **1** is bonded to a device of various types and the temperature of the device rises to exceed the glass transition point of the thermal conductive sheet **1**, the thermal conductive sheet **1** may be peeled off from the device depending on the changes in the linear expansion coefficient. However, because the glass transition point of this thermal conductive sheet **1** is equal to or more than the above-described upper limit, even if the device temperature rises, the temperature can be prevented from exceeding the glass transition point of the thermal conductive

sheet 1, and as a result, deformation of the thermal conductive sheet 1 can be reduced, and the peeling off can be suppressed.

[0121] The glass transition point is obtained by measuring a dynamic viscoelasticity at a frequency of 10 Hz, and determining the peak value of $\tan\delta$ (loss tangent).

[0122] When the thermal conductive sheet 1 is evaluated in the bend test in conformity with the cylindrical mandrel method of JIS K 5600-5-1 under the test conditions shown below, preferably, no fracture is observed.

Test Conditions:

[0123] Test Device: Type I

[0124] Mandrel: diameter 10 mm

[0125] Bending Angle: 90 degrees or more

[0126] Thickness of the thermal conductive sheet 1: 0.3 mm

[0127] FIGS. 3 and 4 show perspective views of the Type I test device. In the following, the Type I test device is described.

[0128] In FIGS. 3 and 4, a Type I test device 10 includes a first flat plate 11; a second flat plate 12 disposed in parallel with the first flat plate 11; and a mandrel (rotation axis) 13 provided for allowing the first flat plate 11 and the second flat plate 12 to rotate relatively.

[0129] The first flat plate 11 is formed into a generally rectangular flat plate. A stopper 14 is provided at one end portion (free end portion) of the first flat plate 11. The stopper 14 is formed on the surface of the second flat plate 12 so as to extend along the one end portion of the second flat plate 12.

[0130] The second flat plate 12 is formed into a generally rectangular flat plate, and one side thereof is disposed so as to be adjacent to one side (the other end portion (proximal end portion) that is opposite to the one end portion where the stopper 14 is provided) of the first flat plate 11.

[0131] The mandrel 13 is formed so as to extend along one side of the first flat plate 11 and one side of the second flat plate 12 that are adjacent to each other.

[0132] In the Type I test device 10, as shown in FIG. 3, the surface of the first flat plate 11 is flush with the surface of the second flat plate 12 before the start of the bend test.

[0133] To perform the bend test, the thermal conductive sheet 1 is placed on the surface of the first flat plate 11 and the surface of the second flat plate 12. The thermal conductive sheet 1 is placed so that one side of the thermal conductive sheet 1 is in contact with the stopper 14.

[0134] Then, as shown in FIG. 4, the first flat plate 11 and the second flat plate 12 are rotated relatively. In particular, the free end portion of the first flat plate 11 and the free end portion of the second flat plate 12 are rotated to a predetermined angle with the mandrel 13 as the center. To be specific, the first flat plate 11 and the second flat plate 12 are rotated so as to bring the surface of the free end portions thereof closer (oppose each other).

[0135] In this way, the thermal conductive sheet 1 is bent with the mandrel 13 as the center, conforming to the rotation of the first flat plate 11 and the second flat plate 12.

[0136] More preferably, no fracture is observed in the thermal conductive sheet 1 even when the bending angle is set to 180 degrees under the above-described test conditions.

[0137] When the resin component 3 is the thermosetting resin component, a semi-cured (in B-stage) thermal conductive sheet 1 (that is, the thermal conductive sheet 1 before being cured by heat) is tested in the bend test.

[0138] When the fracture is observed in the bend test at the above bending angle in the thermal conductive sheet 1, there is a case where excellent flexibility cannot be given to the thermal conductive sheet 1.

[0139] Furthermore, for example, when the thermal conductive sheet 1 is evaluated in the 3-point bending test in conformity with JIS K 7171 (2008) under the test conditions shown below, no fracture is observed.

Test Conditions:

[0140] Test piece: size 20 mm×15 mm

[0141] Distance between supporting points: 5 mm

[0142] Testing speed: 20 mm/min (indenter depressing speed)

[0143] Bending angle: 120 degrees

[0144] Evaluation method: Presence or absence of fracture such as cracks at the center of the test piece is observed visually when tested under the above-described test conditions.

[0145] In the 3-point bending test, when the resin component 3 is a thermosetting resin component, the thermal conductive sheet 1 before being cured by heat is used.

[0146] Thus, the thermal conductive sheet 1 is excellent in conformability to irregularities because no fracture is observed in the above-described 3-point bending test. The conformability to irregularities is, when the thermal conductive sheet 1 is provided on an object with irregularities, a property of the thermal conductive sheet 1 that conforms to be in close contact with the irregularities.

[0147] A mark such as, for example, letters and symbols can be given to the thermal conductive sheet 1. That is, the thermal conductive sheet 1 is excellent in mark adhesion. The mark adhesion is a property of the thermal conductive sheet 1 that allows reliable adhesion of the above-described mark thereon.

[0148] The mark can be adhered (applied, fixed, or firmly fixed) to the thermal conductive sheet 1, to be specific, by printing, engraving, or the like.

[0149] Examples of printing include, for example, inkjet printing, relief printing, intaglio printing, and laser printing.

[0150] When the mark is to be printed by inkjet printing, relief printing, or intaglio printing, for example, an ink fixing layer for improving mark's fixed state can be provided on the surface (printing side) of the thermal conductive sheet 1.

[0151] When the mark is to be printed by laser printing, for example, a toner fixing layer for improving mark's fixed state can be provided on the surface (printing side) of the thermal conductive sheet 1.

[0152] Examples of engraving include laser engraving and punching.

[0153] The thermal conductive sheet 1 is excellent in thermal conductivity in the plane direction that is perpendicular to the thickness direction, and also excellent in heat resistance.

[0154] Thus, as a thermal conductive sheet that allows decrease in deformation under high temperature, that suppresses peeling off, that is excellent in handleability, and that has excellent thermal conductivity in the plane direction, the thermal conductive sheet can be used for various heat dissipation applications, to be specific, as a thermal conductive sheet applied in power electronics technology, to be more specific, as a thermal conductive sheet used, for example, as an LED heat dissipation substrate, or as a heat dissipation material for batteries.

[0155] In the above-described hot-pressing step (FIG. 2 (a)), for example, a plurality of calendering rolls and the like can also be used for rolling the mixture and the laminated sheet 1C.

[0156] When the resin component 3 is the thermosetting resin component, without curing by heat as described above, the thermal conductive sheet of the present invention can also be obtained as the uncured thermal conductive sheet 1.

[0157] That is, with the thermal conductive sheet of the present invention, when the resin component is the thermosetting resin component, there is no particular limitation as to whether or not curing by heat is carried out or when curing by heat is carried out. For example, the curing by heat can be performed after the laminating step (FIG. 2 (c)) as described above, or can be performed after the elapse of a predetermined period from the above-described hot-pressing step (FIG. 2 (a)), hot-pressing of the mixture but the hot-pressing does not allow curing by heat). To be specific, the curing by heat can be performed at the time when the sheet is applied in power electronics technology, or after the elapse of a predetermined period after such application.

EXAMPLES

[0158] Hereinafter, the present invention is described in further detail with reference to Examples. However, the present invention is not limited to Examples.

Example 1

[0159] The components described below were blended, stirred, and allowed to stand at room temperature (23° C.) for one night, thereby allowing methyl ethyl ketone (dispersion medium for the curing agent) to volatilize, and preparing a semi-solid mixture. The details of the components are as follows: 13.42 g of PT-110 (trade name, plate-like boron nitride particles, average particle size (light scattering method) 45 μ m, manufactured by Momentive Performance Materials Inc.), 1.0 g of jER®828 (trade name, bisphenol A epoxy resin, liquid, epoxy equivalent 184 to 194 g/eqv., softening temperature (ring and ball method) below 25° C., melt viscosity (80° C.) 70 mPa·s, manufactured by Japan Epoxy Resins Co., Ltd.), 2.0 g of EPPN-501HY (trade name, triphenylmethane epoxy resin, solid, epoxy equivalent 163 to 175 g/eqv., softening temperature (ring and ball method) 57 to 63° C., manufactured by NIPPON KAYAKU Co., Ltd), and 3.0 g (solid content 0.15 g) (5 mass % per total amount of epoxy resins of jER®828 and EPPN-501HY) of a curing agent (a solution of 5 mass % Curezol® 2PZ (trade name, manufactured by Shikoku Chemicals Corporation.) in methyl ethyl ketone).

[0160] In the above-described blending, the volume percentage (vol %) of the boron nitride particles relative to the total volume of the solid content excluding the curing agent (that is, solid content of the boron nitride particle and epoxy resin) was 70 vol %.

[0161] Then, the obtained mixture was sandwiched by two silicone-treated releasing films, and then these were hot-pressed with a vacuum hot-press at 80° C. under an atmosphere (vacuum atmosphere) of 10 Pa with a load of 5 tons (20 MPa) for 2 minutes. A pressed sheet having a thickness of 0.3 mm was thus obtained (ref: FIG. 2 (a)).

[0162] Thereafter, the obtained pressed sheet was cut so as to be divided into a plurality of pieces when projected in the thickness direction of the pressed sheet. Divided sheets were thus obtained (ref: FIG. 2 (b)). Next, the divided sheets were laminated in the thickness direction. A laminated sheet was thus obtained (ref: FIG. 2 (c)).

[0163] Then, the obtained laminated sheet was hot-pressed under the same conditions as described above with the above-described vacuum hot-press (ref: FIG. 2 (a)).

[0164] Then, a series of the above-described operations of cutting, laminating, and hot-pressing (ref: FIG. 2) was repeated four times. A thermal conductive sheet (in B-stage) having a thickness of 0.3 mm was thus obtained.

[0165] Thereafter, the obtained thermal conductive sheet was introduced into a dryer, and heated at 150° C. for 120 minutes so as to be cured by heat.

Examples 2 to 14

[0166] Thermal conductive sheets were obtained in the same manner as in Example 1 in accordance with the mixing formulation and production conditions of Tables 1 to 3.

(Evaluation)

1. Thermal Conductivity

[0167] The thermal conductivity of the thermal conductive sheets obtained in Examples 1 to 14 was measured.

[0168] That is, the thermal conductivity in the plane direction (SD) was measured by a pulse heating method using a xenon flash analyzer "LFA-447" (manufactured by Erich NETZSCH GmbH & Co. Holding KG).

[0169] The results are shown in Tables 1 to 3.

2. Glass Transition Point

[0170] The glass transition point of the thermal conductive sheets obtained in Examples 1 to 14 was measured.

[0171] That is, the thermal conductive sheet was measured with a temperature rising speed of 1° C./min and a frequency of 10 Hz using a dynamic viscoelasticity measuring apparatus (model number: DMS 6100, manufactured by Seiko Instruments Inc.).

[0172] The glass transition point was determined by the obtained data, i.e., the peak value of $\tan\delta$.

[0173] The results are shown in Tables 1 to 3.

3. Porosity (P)

[0174] The porosity (P1) of the thermal conductive sheets before being cured by heat in Examples 1 to 14 was measured by the following measurement method.

[0175] Measurement method of porosity: The thermal conductive sheet was cut along the thickness direction with a cross section polisher (CP); and the cross section thus appeared was observed with a scanning electron microscope (SEM) at a magnification of 200. The obtained image was binarized based on the pore portion and the non-pore portion; and the area ratio, i.e., the ratio of the pore portion area to the total area of the cross section of the thermal conductive sheet was calculated.

[0176] The results are shown in Tables 1 to 3.

4. Conformability to Irregularities (3-Point Bending Test)

[0177] The 3-point bending test in conformity with JIS K 7171 (2010) was carried out for the thermal conductive sheets before being cured by heat of Examples 1 to 14 with the following test conditions, thus evaluating conformability to irregularities with the following evaluation criteria. The results are shown in Tables 1 to 3.

Test Conditions:

[0178] Test Piece: size 20 mm×15 mm

[0179] Distance Between Supporting Points: 5 mm

[0180] Testing Speed: 20 mm/min (indenter depressing speed)

[0181] Bending Angle: 120 degrees

(Evaluation Criteria)

[0182] Excellent: No fracture was observed.

[0183] Good: Almost no fracture was observed.

[0184] Bad: Fracture was clearly observed.

5. Printed Mark Visibility (Mark Adhesion by Printing: Mark Adhesion by Inkjet Printing or Laser Printing)

[0185] Marks were printed on the thermal conductive sheets of Examples 1 to 14 by inkjet printing and laser printing, and the marks were observed.

[0186] As a result, it was confirmed that the marks were excellently visible in both cases of inkjet printing and laser printing, and that mark adhesion by printing was excellent in any of the thermal conductive sheets of Examples 1 to 14.

TABLE 1

				Average Particle Size (μm)	Example							
					Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6		
Mixing Formulation of Components	Boron Nitride Particle/g ^{*A} / [vol %] ^{*B} / [vol %] ^{*C}	PT-110 ^{*1}		45	13.42 [70] [69]	3.83 [40] [38.8]	5.75 [50] [48.8]	12.22 [68] [66.9]	23 [80] [79.2]	—		
		UHP-1 ^{*2}		9	—	—	—	—	—	12.22 [68] [66.9]		
	Polymer	Thermosetting Resin	Epoxy Resin Composition	Epoxy Resin A ^{*3} (Semi-solid)	—	3	3	3	3	3		
				Epoxy Resin B ^{*4} (Liquid)	1	—	—	—	—	—		
				Epoxy Resin C ^{*5} (Solid)	—	—	—	—	—	—		
				Epoxy Resin ID ^{*6} (Solid)	2	—	—	—	—	—		
				Curing Agent ^{*7} (Solid Content in Grams)	—	3 (0.15)	3 (0.15)	3 (0.15)	3 (0.15)	3 (0.15)		
				Curing Agent ^{*8} (Solid Content in Grams)	3 (0.15)	—	—	—	—	—		
				Production Conditions	Hot-pressing	Temperature (° C.)	80	80	80	80	80	80
				Number of Time (times) ^{*D}		5	5	5	5	5	5	
Evaluation	Thermal Conductive Sheet	Thermal Conductivity (W/m · K)	Plane Direction (SD)	Load (MPa)/(tons)	20/5	20/5	20/5	20/5	20/5	20/5		
				Thickness Direction (TD)	30	4.5	6.0	30.0	32.5	17.0		
				Ratio (SD/TD)	2.0	1.3	3.3	5.0	5.5	5.8		
				Glass Transition Point (° C.)	15.0	3.5	1.8	6.0	5.9	2.9		
				Porosity (vol %)	216	139	140	139	138	140		
				Conformability to Irregularities/3-point bending test JIS K 7171 (2008)	4	0	0	5	12	6		
				Boron Nitride Particle	Orientation Angle (α)(degrees)	Good	Good	Good	Good	Good	Good	
						18	18	18	15	13	20	

g^{*A}: Blended Weight

[vol %]^{*B}: Percentage relative to the total volume of the thermal conductive sheet (excluding curing agent)

[vol %]^{*C}: Percentage relative to the total volume of the thermal conductive sheet

Number of Time^{*D}: Number of times of hot-pressing of laminated sheet

TABLE 2

				Average Particle Size (μm)	Example		
					Ex. 7	Ex. 8	Ex. 9
Mixing Formulation of Components	Boron Nitride Particle/g ^{*A} / [vol %] ^{*B} / [vol %] ^{*C}	PT-110* ¹		45	12.22 [68] [66.9]	12.22 [68] [66.9]	13.42 [70] [69]
		UHP-1* ²		9	—	—	—
	Thermosetting Resin	Epoxy Resin Composition	Epoxy Resin A* ³ (Semi-solid)	—	—	—	
			Epoxy Resin B* ⁴ (Liquid)	1.5	3	—	
			Epoxy Resin C* ⁵ (Solid)	1.5	—	—	

TABLE 2-continued

				Average Particle Size			Example		
				(μm)	Ex. 7	Ex. 8	Ex. 9		
Production Conditions	Hot-pressing	Temperature ($^{\circ}\text{C}.$)	Number of Time (times)* ^D	Epoxy Resin D* ⁶ (Solid)	—	—	3		
				Curing Agent* ⁷ (Solid Content in Grams)	3 (0.15)	3 (0.15)	3 (0.15)		
				Curing Agent* ⁸ (Solid Content in Grams)	—	—	—		
				Load (MPa)/(tons)	20/5	20/5	20/5		
				Plane Direction (SD)	30.0	30.0	24.5		
				Thickness Direction (TD)	5.0	5.0	2.1		
				Ratio (SD/TD)	6.0	6.0	11.7		
				Glass Transition Point ($^{\circ}\text{C}.$)	130	168	217		
				Porosity (vol %)	4	2	10		
				Conformability to Irregularities/3-point bending test JIS K 7171 (2008)	Good	Good	Bad		
Evaluation	Thermal Conductive Sheet	Thermal Conductivity (W/m · K)	Orientation Angle (α)(degrees)		15	16	16		

g*^A: Blended Weight[vol %]*^B: Percentage relative to the total volume of the thermal conductive sheet (excluding curing agent)[vol %]*^C: Percentage relative to the total volume of the thermal conductive sheetNumber of Time*^D: Number of times of hot-pressing of laminated sheet

TABLE 3

				Average Particle Size	Example							
				(μm)	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14			
Mixing Formulation of Components	Boron Nitride Particle/g* ^A / [vol %]* ^B / [vol %]* ^C Polymer	PT-110* ¹		45	3.83 [40] [37.7]	13.42 [70] [69]	13.42 [70] [69]	13.42 [70] [69]	13.42 [70] [69]			
		UHP-1* ²		9	—	—	—	—	—			
		Thermosetting Resin	Epoxy Resin Composition	Epoxy Resin A* ³ (Semi-solid)	3	3	3	3	3			
				Epoxy Resin B* ⁴ (Liquid)	—	—	—	—	—			
				Epoxy Resin C* ⁵ (Solid)	—	—	—	—	—			
				Epoxy Resin D* ⁶ (Solid)	—	—	—	—	—			
				Curing Agent* ⁷ (Solid Content in Grams)	6 (0.3)	3 (0.15)	3 (0.15)	3 (0.15)	3 (0.15)			
				Curing Agent* ⁸ (Solid Content in Grams)	—	—	—	—	—			
				Production Conditions		Hot-pressing	Temperature (° C.)	80	60	70	80	80
							Number of Time (times)* ^D	5	5	5	5	5
			Load (MPa)/(tons)	20/5	20/5	20/5	20/5	40/10				
Evaluation	Thermal Conductive Sheet	Thermal Conductivity (W/m · K)	Plane Direction (SD)	4.1	10.5	11.2	32.5	50.7				
			Thickness Direction (TD)	1.1	2.2	3.0	5.5	7.3				
			Ratio (SD/TD)	3.7	4.8	3.7	5.9	6.9				
			Glass Transition Point (° C.)	145	138	138	139	139				
			Porosity (vol %)	0	29	26	8	3				
			Conformability to Irregularities/3-point bending test JIS K 7171 (2008)	Excellent	Excellent	Excellent	Excellent	Good				

TABLE 3-continued

	Average Particle Size (μm)	Example				
		Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
Boron Nitride Particle	Orientation Angle (α)(degrees)	20	17	15	15	13

g^{*d}: Blended Weight[vol %]^{*B}: Percentage relative to the total volume of the thermal conductive sheet (excluding curing agent)[vol %]^{*C}: Percentage relative to the total volume of the thermal conductive sheetNumber of Time^{*D}: Number of times of hot-pressing of laminated sheet

[0187] In Tables 1 to 3, values for the components are in grams unless otherwise specified.

[0188] In the rows of “boron nitride particles” in Tables 1 to 3, values on the top represent the Blended Weight (g) of the boron nitride particles; values in the middle represent the volume percentage (vol %) of the boron nitride particles relative to the total volume of the solid content excluding the curing agent in the thermal conductive sheet (that is, solid content of the boron nitride particles and epoxy resin); and values at the bottom represent the volume percentage (vol %) of the boron nitride particles relative to the total volume of the solid content in the thermal conductive sheet (that is, solid content of boron nitride particles, epoxy resin, and curing agent).

[0189] For the components with “*” added in Tables 1 to 3, details are given below.

PT-110^{*1}: trade name, plate-like boron nitride particles, average particle size (light scattering method) 45 μm , manufactured by Momenve Performance Materials Inc.

UHP-1^{*2}: trade name: SHOBN®UHP-1, plate-like boron nitride particles, average particle size (light scattering method) 9 μm , manufactured by Showa Denko K. K.

Epoxy Resin A^{*3}: OGSOL EG (trade name), bisarylfluorene epoxy resin, semi-solid, epoxy equivalent 294 g/eqv., softening temperature (ring and ball test) 47° C., melt viscosity (80° C.) 1360 mPa·s, manufactured by Osaka Gas Chemicals Co., Ltd.

Epoxy Resin B^{*4}: jER® 828 (trade name), bisphenol A epoxy resin, liquid, epoxy equivalent 184 to 194 g/eqv., softening temperature (ring and ball test) below 25° C., melt viscosity (80° C.) 70 mPa·s, manufactured by Japan Epoxy Resins Co., Ltd.

Epoxy Resin C^{*5}: jER® 1002 (trade name), bisphenol A epoxy resin, solid, epoxy equivalent 600 to 700 g/eqv., softening temperature (ring and ball test) 78° C., melt viscosity (80° C.) 10000 mPa·s or more (measurement limit or more), manufactured by Japan Epoxy Resins Co., Ltd.

Epoxy Resin D^{*6}: EPPN-501HY (trade name), triphenylmethane epoxy resin, solid, epoxy equivalent 163 to 175 g/eqv., softening temperature (ring and ball test) 57 to 63° C., manufactured by NIPPON KAYAKU Co., Ltd.

Curing Agent^{*7}: a solution of 5 mass % Curezol® 2PZ (trade name, manufactured by Shikoku Chemicals Corporation) in methyl ethyl ketone.

Curing Agent^{*8}: a dispersion liquid of 5 mass % Curezol® 2P4 MHZ-PW (trade name, manufactured by Shikoku Chemicals Corporation) in methyl ethyl ketone.

[0190] While the illustrative embodiments of the present invention are provided in the above description, such is for illustrative purpose only and it is not to be construed as limiting the scope of the present invention. Modification and variation of the present invention that will be obvious to those skilled in the art is to be covered by the following claims.

What is claimed is:

1. A thermal conductive sheet comprising a plate-like boron nitride particle, wherein
 - the thermal conductivity in a direction perpendicular to the thickness direction of the thermal conductive sheet is 4 W/m·K or more, and
 - a glass transition point determined as the peak value of $\tan\delta$ obtained by measuring a dynamic viscoelasticity of the thermal conductive sheet at a frequency of 10 Hz is 125° C. or more.

* * * * *