

COPPER-CLAD LAMINATE

TECHNICAL FIELD

[0001]

5 The present invention relates to a copper-clad laminate.

BACKGROUND ART

[0002]

Printed wiring boards are widely used in electronic equipment such as portable electronic
10 equipment. Particularly, with higher functionality of portable electronic equipment and the
like in recent years, the frequencies of signals have become higher, and printed wiring
boards suitable for such high frequency applications have been required. For these high
frequency printed wiring boards, those having low transmission loss are desired in order to
allow transmission without deteriorating the quality of high frequency signals. A printed
15 wiring board comprises a copper foil processed into a wiring pattern and an insulating resin
substrate, and the transmission loss is mainly composed of the conductor loss due to the
copper foil and the dielectric loss due to the insulating resin substrate. Therefore, in a
resin layer-attached copper foil applied to high frequency applications, the dielectric loss
due to the resin layer is desirably suppressed. For this, excellent dielectric characteristics,
20 particularly a low dielectric loss tangent, are required of the resin layer.

[0003]

As a copper foil used for the manufacture of a copper-clad laminate or a printed wiring board,
a resin-attached copper foil comprising a resin layer on one surface in order to enhance
adhesion to a resin substrate such as a prepreg is known. A prepreg is a generic name
25 for a composite material in which a substrate such as a synthetic resin plate, a glass plate,
a glass woven fabric, a glass nonwoven fabric, or paper is impregnated with a synthetic
resin. For example, Patent Literature 1 (JP5118469B) discloses a resin layer-attached
copper foil comprising a filler particle-containing resin layer on a surface of a copper foil,
and it is disclosed that the filler particle-containing resin layer is a semi-cured resin layer
30 comprising an aromatic polyamide resin polymer, an epoxy resin, and a curing accelerator

and comprising filler particles treated with phenylaminosilane, which is an amino silane coupling agent.

[0004]

Patent Literature 2 (JP2009-518208A) discloses a method for manufacturing a high
5 frequency printed circuit board laminate, and this manufacturing method allegedly
comprises providing a low profile copper foil sheet, applying a low dielectric loss resin layer,
partially curing the low dielectric loss resin to form a low profile copper sheet coated with
the resin, and laminating the low profile copper sheet coated with the resin on a prepreg to
form a copper-clad laminate. Patent Literature 3 (JP2016-028885A) discloses a metal-
10 clad laminate with which a printed wiring board having reduced loss during signal
transmission can be manufactured, and describes a metal-clad laminate comprising an
insulating layer comprising a polyphenylene ether compound, a metal layer attached to the
insulating layer, and an intermediate layer comprising a silane compound interposed
between the insulating layer and the metal layer, wherein the ten-point average roughness
15 Rz of the attachment surface of the metal layer is 0.5 μm or more and 4 μm or less.

CITATION LIST

PATENT LITERATURE

[0005]

20 Patent Literature 1: JP5118469B

Patent Literature 2: JP2009-518208A

Patent Literature 3: JP2016-028885A

SUMMARY OF INVENTION

25 [0006]

It has been considered that in a copper-clad laminate or a printed wiring board, a resin
substrate such as a prepreg occupies a large portion in the thickness direction, and
therefore the dielectric loss tangent of an superthin adhesive layer (also referred to as a
primer layer) interposed between the resin substrate and a copper foil and the transmission
30 loss due to the dielectric loss tangent are at negligible levels. Therefore, in the present

circumstances, attempts to reduce a dielectric loss tangent and transmission loss in a copper-clad laminate have been directed exclusively to the improvement of the copper foil and the resin substrate. In other words, it has been considered that even if the dielectric loss tangent of the adhesive layer is somewhat large, it is offset by the dielectric characteristics of the resin substrate because of the thinness of the adhesive layer and, as a result, hardly influences the entire dielectric characteristics. However, it has become clear that when evaluation is performed in a much higher frequency band (for example, such as 50 GHz) rather than at the previous 10 GHz level, with the need for even higher frequencies in recent years, the dielectric loss tangent of even the superthin adhesive layer (primer layer) and the transmission loss due to the dielectric loss tangent are unexpectedly largely reflected in the dielectric characteristics of the copper-clad laminate or the printed wiring board. On the other hand, in terms of the function as the adhesive layer, high adhesion (peel strength) to the copper foil is desired.

[0007]

The present inventors have now found that when in a copper-clad laminate comprising a copper foil, an adhesive layer, and a resin layer in order, a specific resin is selected as the adhesive layer and the surface roughness of the copper foil on the adhesive layer side is specified, it is possible to provide a copper-clad laminate in which transmission characteristics exhibited by a resin layer can be further improved while sufficient peel strength between a copper foil and the resin layer is ensured.

[0008]

Therefore, it is an object of the present invention to provide a copper-clad laminate in which transmission characteristics exhibited by a resin layer can be further improved while sufficient peel strength between a copper foil and the resin layer is ensured.

[0009]

According to an aspect of the present invention, there is provided a copper-clad laminate comprising:

a copper foil;

an adhesive layer provided on a surface of the copper foil and comprising one or more selected from the group consisting of a polyphenylene ether resin, a polyimide resin,

an olefin-based resin, a liquid crystal polymer, a polyester resin, a polystyrene resin, a hydrocarbon elastomer, a benzoxazine resin, an active ester resin, a cyanate ester resin, a bismaleimide resin, a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, a fluororesin, a resin having a vinyl group, and copolymers thereof; and

a resin layer provided on a surface of the adhesive layer,

wherein the surface of the copper foil on the adhesive layer side has a maximum height S_z of 6.8 μm or less as measured in accordance with ISO 25178, and the adhesive layer has a dielectric loss tangent value at a frequency of 1 GHz, δ_a , which is equal to or less than a dielectric loss tangent value of the resin layer at a frequency of 1 GHz, δ_r .

[0010]

According to another aspect of the present invention, there is provided a method for manufacturing the copper-clad laminate, comprising the steps of:

providing a copper foil having a surface having a maximum height S_z of 6.8 μm or less as measured in accordance with ISO 25178;

applying a resin varnish comprising an adhesive to a surface of the copper foil and drying the resin varnish to obtain an adhesive-attached copper foil, the adhesive comprising one or more selected from the group consisting of a polyphenylene ether resin, a polyimide resin, an olefin-based resin, a liquid crystal polymer, a polyester resin, a polystyrene resin, a hydrocarbon elastomer, a benzoxazine resin, an active ester resin, a cyanate ester resin, a bismaleimide resin, a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, a fluororesin, a resin having a vinyl group, and copolymers thereof, and, having a dielectric loss tangent value at a frequency of 1 GHz of δ_a after curing; and

bonding the adhesive-attached copper foil to a resin layer having a dielectric loss tangent value at a frequency of 1 GHz of δ_r to form a copper-clad laminate, wherein the δ_a is equal to or less than the δ_r .

BRIEF DESCRIPTION OF DRAWINGS

[0011]

Figure 1 is a diagram showing the procedure for fabricating an adhesive layer sample for dielectric characteristic evaluation in Examples 1 to 10.

Figure 2 is a diagram showing the procedure for fabricating a copper-clad laminate sample in Examples 1 to 10.

5

DESCRIPTION OF EMBODIMENTS

[0012]

Embodiments of the present invention will be described below.

[0013]

10 Definitions

The definitions of parameters used for specifying the present invention are shown below.

[0014]

As used herein, "maximum height Sz" is a parameter that represents the distance from the highest point to the lowest point of a surface measured in accordance with ISO 25178.

15 The maximum height Sz can be calculated by measuring the surface profile of a predetermined measurement area (for example, a region of 10000 μm^2) at a copper foil surface by a commercially available laser microscope.

[0015]

20 In the present invention, "kurtosis Sku" is a parameter that represents the sharpness of height distribution measured in accordance with ISO 25178, and is also referred to as peakedness. Sku = 3 means that the height distribution is a normal distribution. Sku > 3 means that there are many sharp peaks and valleys at a surface. Sku < 3 means that the surface is flat. The kurtosis Sku can be calculated by measuring the surface profile of a predetermined measurement area (for example, a region of 10000 μm^2) at a copper foil
25 surface by a commercially available laser microscope.

[0016]

As used herein, a "dielectric loss tangent value at a frequency of 1 GHz" is a dielectric loss tangent value measured by the SPDR dielectric resonator method in accordance with ASTM D2520 (JIS C2565: 1992). This dielectric loss tangent value can be measured using
30 a commercially available network analyzer.

[0017]

Copper-Clad Laminate

The copper-clad laminate of the present invention comprises a copper foil, an adhesive layer, and a resin layer. The adhesive layer comprises one or more selected from the group consisting of a polyphenylene ether resin, a polyimide resin, an olefin-based resin, a liquid crystal polymer, a polyester resin, a polystyrene resin, a hydrocarbon elastomer, a benzoxazine resin, an active ester resin, a cyanate ester resin, a bismaleimide resin, a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, a fluororesin, a resin having a vinyl group, and copolymers thereof and is provided on a surface of the copper foil. The resin layer is provided on the surface of the adhesive layer. In the copper-clad laminate, the maximum height S_z at the surface of the copper foil on the adhesive layer side is 6.8 μm or less. The dielectric loss tangent value of the adhesive layer at a frequency of 1 GHz, δ_a , is equal to or less than the dielectric loss tangent value of the resin layer at a frequency of 1 GHz, δ_r . When in this manner, in a copper-clad laminate comprising a copper foil, an adhesive layer, and a resin layer in order, a specific resin is selected as the adhesive layer and the surface roughness of the copper foil on the adhesive layer side is specified, it is possible to provide a copper-clad laminate in which transmission characteristics exhibited by a resin layer can be further improved while sufficient peel strength between a copper foil and the resin layer is ensured. Therefore, the copper-clad laminate of the present invention can be preferably applied to applications used in a high frequency band, for example, with signal frequencies of 10 GHz or more, such as high frequency boards used in automobile antennae, cellular phone base station antennae, high performance servers, anti-collision radars, or the like, or printed wiring boards for high frequency digital communication in network equipment. Examples of such network equipment include (i) base station servers, routers, and the like, (ii) office networks, and (iii) the basic systems of high speed portable communication.

[0018]

As described above, it has been considered that in a copper-clad laminate or a printed wiring board, a resin substrate such as a prepreg occupies a large portion in the thickness direction, and therefore the dielectric loss tangent of an superthin adhesive layer (also

referred to as a primer layer) interposed between the resin substrate and a copper foil, and the transmission loss due to the dielectric loss tangent are at negligible levels. However, it has become clear that when evaluation is performed in a much higher frequency band (for example, such as 50 GHz) rather than at the previous 10 GHz level, with the need for even higher frequencies in recent years, the dielectric loss tangent of even the superthin adhesive layer (primer layer) and the transmission loss due to the dielectric loss tangent are unexpectedly largely reflected in the dielectric characteristics of the copper-clad laminate or the printed wiring board. In this respect, in the copper-clad laminate of the present invention, by selectively using, as the adhesive layer, the above-described one, more improved transmission characteristics (more reduced transmission loss) than those of a laminate consisting of a copper foil and a resin layer (adhesive layer-free laminate) can be achieved. Moreover, as the adhesive layer, high adhesion (peel strength) between the copper foil and the resin layer can also be achieved.

[0019]

Specifically, in a state in which the adhesive layer is cured, the peel strength of the copper foil from the adhesive layer measured in accordance with JIS C 6481-1996 is preferably 0.3 kN/m or more, more preferably 0.4 kN/m or more, further preferably 0.5 kN/m or more, and most preferably 0.6 kN/m or more. Higher peel strength is generally preferable, but the product typically has a value of 1.4 kN/m or less, more typically 1.2 kN/m or less.

[0020]

The copper foil may be a metal foil as electrodeposited or rolled (so-called raw foil) or may be in the form of a surface-treated foil in which at least either one surface has been subjected to surface treatment, as long as the surface on the adhesive layer side satisfies the above-described maximum height S_z . The surface treatment can be various types of surface treatments performed for enhancing or providing some properties (for example, rustproofing properties, humidity resistance, chemical resistance, acid resistance, heat resistance, and adhesion to a substrate) on the surface of the metal foil. The surface treatment may be performed on at least one surface of the metal foil or on both surfaces of the metal foil. Examples of the surface treatment performed on the copper foil include

rustproofing treatment, silane treatment, roughening treatment, and barrier forming treatment.

[0021]

The maximum height S_z at the surface of the copper foil on the adhesive layer side is 6.8 μm or less, preferably 0.15 μm or more and 6.8 μm or less, more preferably 0.25 μm or more and 5.0 μm or less, and further preferably 0.30 μm or more and 3.0 μm or less. When the maximum height S_z is within such ranges, the transmission loss can be desirably reduced while sufficient adhesion to the resin layer via the adhesive layer is ensured. In other words, the conductor loss due to the copper foil, which can increase due to the skin effect of the copper foil, can be reduced to achieve a further reduction in transmission loss.

[0022]

The kurtosis (peakedness) S_{ku} at the surface of the copper foil on the adhesive layer side is preferably 2.0 or more and 4.0 or less, more preferably 2.2 or more and 3.8 or less, and further preferably 2.4 or more and 3.5 or less. When the kurtosis (peakedness) S_{ku} is within such ranges, the transmission loss can be desirably reduced. In other words, the conductor loss due to the copper foil, which can increase due to the skin effect of the copper foil, can be reduced to achieve a further reduction in transmission loss.

[0023]

The thickness of the copper foil is not particularly limited, but is preferably 0.1 μm or more and 100 μm or less, more preferably 0.15 μm or more and 50 μm or less, and further preferably 0.2 μm or more and 40 μm or less. When the thickness is within these ranges, processes such as a modified semi-additive process (MSAP), a semi-additive process (SAP), and a subtractive process, which are general pattern forming methods for the formation of the wiring of printed wiring boards, can be adopted. For the copper foil, a carrier-attached copper foil may be used.

[0024]

The adhesive layer is a layer that functions as a primer layer for enhancing the adhesion between the copper foil and the resin layer (for example, an insulating substrate), and comprises one or more selected from the group consisting of a polyphenylene ether resin, a polyimide resin (typically a low dielectric polyimide resin), an olefin-based resin (for

example, a polyethylene resin, a polypropylene resin, a polymethylpentene resin, or a cycloolefin resin), a liquid crystal polymer, a polyester resin, a polystyrene resin, a hydrocarbon elastomer, a benzoxazine resin, an active ester resin, a cyanate ester resin, a bismaleimide resin, a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin (for example, a dicyclopentadiene type epoxy resin), a fluororesin, a resin having a vinyl group, and copolymers thereof. All of these resins not only exert excellent adhesion performance to the resin layer and the copper foil but have a low dielectric loss tangent and therefore contribute to a reduction in transmission loss.

[0025]

Specifically, the dielectric loss tangent value of the adhesive layer at a frequency of 1 GHz, δ_a , is equal to or less than the dielectric loss tangent value of the resin layer at a frequency of 1 GHz, δ_r , preferably less than δ_r . For example, the dielectric loss tangent value of the adhesive layer at a frequency of 1 GHz, δ_a , is preferably 0.0001 or more and 0.003 or less, more preferably 0.0005 or more and 0.003 or less, further preferably 0.0008 or more and 0.0025 or less, and particularly preferably 0.001 or more and 0.002 or less. When the dielectric loss tangent value δ_a is within these ranges, the dielectric loss tangent value of the adhesive layer, δ_a , is equal to or less than the dielectric loss tangent value of the resin layer, δ_r , when the dielectric loss tangent value of the resin layer, δ_r , is 0.003 or more. In any case, by adopting an adhesive layer having a low dielectric loss tangent value δ_a as described above, the transmission characteristics exhibited by the resin layer can be unexpectedly improved.

[0026]

According to a preferred aspect of the present invention, the adhesive layer comprises at least one selected from the group consisting of an olefin-based resin, a polystyrene resin, a liquid crystal polymer, and a fluororesin in an amount of 10% by weight or more, more preferably 15% by weight or more, and further preferably 20% by weight or more based on the total weight of the adhesive layer. When the adhesive layer comprises the above resin in such ranges, advantages are that in addition to being able to exert the above-described effects much more effectively, the dielectric loss tangent can be made lower.

[0027]

According to another preferred aspect of the present invention, the adhesive layer comprises a polyphenylene ether resin in an amount of preferably 20% by weight or more, more preferably 25% by weight or more, and further preferably 30% by weight or more based on the total weight of the adhesive layer. When the adhesive layer comprises the
5 above resin in such ranges, advantages are that in addition to being able to exert the above-described effects much more effectively, the heat resistance and the chemical resistance are enhanced.

[0028]

According to yet another preferred aspect of the present invention, the adhesive layer
10 comprises a polyimide resin in an amount of preferably 10% by weight or more, more preferably 20% by weight or more, and further preferably 30% by weight or more based on the total weight of the adhesive layer. When the adhesive layer comprises the above resin in such ranges, advantages are that in addition to being able to exert the above-described effects much more effectively, the adhesion to the copper foil is enhanced.

15 [0029]

According to yet another preferred aspect of the present invention, the adhesive layer comprises at least one selected from the group consisting of a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, and a resin having a vinyl group, in an amount of preferably 1% by weight or more, more preferably 5%
20 by weight or more, and further preferably 10% by weight or more based on the total weight of the adhesive layer. When the adhesive layer comprises the above resin in such ranges, advantages are that it contributes to the enhancement of the adhesion to the copper foil and a decrease in the dielectric loss tangent of the adhesive layer, in addition to being able to exert the above-described effects much more effectively.

25 [0030]

The adhesive layer may further comprise a filler as desired. The dielectric loss tangent of the resin layer can be desirably reduced by the addition of a filler. For the filler, a known one that can be used in a resin composition can be appropriately used. The filler is preferably an inorganic filler. Examples of preferred inorganic fillers include particles of
30 silica, alumina, talc, and the like. From the viewpoint of reducing the dielectric loss tangent,

silica particles are particularly preferred. The particle diameter of the filler is not particularly limited, but in terms of maintaining the surface smoothness of the resin layer and suppressing aggregation during the mixing of a varnish, the average particle diameter D50 measured by average particle diameter laser diffraction scattering particle size distribution measurement is preferably 0.01 μm or more and 2.0 μm or less, more preferably 0.01 μm or more and 1.5 μm or less, and further preferably 0.01 μm or more and 1.0 μm or less. The content of the filler in the adhesive layer is 85% by weight or less, preferably 0% by weight or more and 75% by weight or less, more preferably 0% by weight or more and 60% by weight or less, and further preferably 0% by weight or more and 50% by weight or less based on the total weight of the adhesive layer. In the case of such content, a decrease in peel strength can also be avoided while the dielectric loss tangent is excellent. When an inorganic filler is contained, filler particles subjected to specific surface treatment are preferably used. Particularly, the filler particles are preferably surface-treated with a silane coupling agent.

[0031]

The adhesive layer may comprise imidazole as a curing accelerator. An imidazole-based curing accelerator is incorporated into a molecular structure as part of a resin without being liberated as ions, after a curing reaction with the resin components, and therefore the dielectric characteristics and insulation reliability of the resin layer can be made excellent. The content of the imidazole-based curing accelerator is not particularly limited, and the amount that provides the desired curing should be appropriately determined considering various conditions such as the composition of the resin layer.

[0032]

The thickness of the adhesive layer is preferably 0.1 μm or more and 20 μm or less, more preferably 0.3 μm or more and 18 μm or less, further preferably 0.5 μm or more and 15 μm or less, and most preferably 1 μm or more and 10 μm or less. In the copper-clad laminate of the present invention, even if the thickness of the adhesive layer is thin like these, the ensuring of sufficient peel strength between the copper foil and the resin layer, and the improvement of the transmission characteristics exhibited by the resin layer (reduction in transmission loss) can be achieved.

[0033]

The resin layer can be one generally used as a resin substrate in a copper-clad laminate and is not particularly limited. A preferred resin layer comprises a glass cloth and an insulating resin with which the glass cloth is impregnated, from the viewpoint of ensuring
5 rigidity and insulating properties, and is typically a prepreg. Preferred examples of the insulating resin used as a prepreg include an epoxy resin, a cyanate ester resin, a polyimide resin, a bismaleimide triazine resin (BT resin), a polyphenylene ether resin, a phenolic resin, a liquid crystal polymer resin, and a polytetrafluoroethylene resin (PTFE). However, the resin layer is not limited to the above one having rigidity and may be one having flexibility.

10 In this case, the resin layer is preferably free of glass cloth.

[0034]

The dielectric loss tangent value of the resin layer at a frequency of 1 GHz, δ_r , is desirably low from the viewpoint of transmission loss reduction and typically 0.0001 or more and 0.03 or less, more typically 0.0001 or more and 0.02 or less, further typically 0.0002 or more and
15 0.01 or less, and most typically 0.0003 or more and 0.005 or less.

[0035]

The thickness of the resin layer should be appropriately determined according to the application and is not particularly limited, and is preferably 5 μm or more and 5 mm or less, more preferably 10 μm or more and 3 mm or less, and further preferably 15 μm or more and
20 1 mm or less.

[0036]

The manufacture of the copper-clad laminate should be performed according to a known method and is not particularly limited. Typically, the copper-clad laminate can be manufactured by applying a resin varnish comprising an adhesive component to a copper
25 foil and drying the resin varnish, and bonding the obtained adhesive-attached copper foil to a resin layer (such as prepreg). Alternatively, the copper-clad laminate may be manufactured by previously applying an adhesive to a resin layer (such as prepreg) to form an adhesive-attached resin layer, bonding a copper foil to the surface of the adhesive layer, and curing the resin layer and the adhesive layer.

EXAMPLES

[0037]

The present invention will be more specifically described by the following Examples.

[0038]

- 5 The raw materials for resin varnishes used for the fabrication of adhesive layers in the following Examples are as follows.

<Raw Material Components for Resin Varnishes>

- polyphenylene ether resin (PPE): OPE-2St-2200 (styrene derivative of bifunctional polyphenylene ether oligomer, manufactured by MITSUBISHI GAS CHEMICAL COMPANY, INC., number average molecular weight: about 2200, viscosity at 120°C: less than 8000 Pa·s)
- cyclic olefin resin: L3PS (cycloolefin, manufactured by ZEON Corporation, dielectric constant (1 GHz): 2.2 (nominal value), dielectric loss tangent (1 GHz): 0.0018 (nominal value))
- 15 - cyclic olefin resin: TOPAS6017 (cyclic olefin copolymer, manufactured by POLYPLASTICS CO., LTD.)
- hydrogenated styrene butadiene resin: MP-10 (hydrogenated styrene-based thermoplastic elastomer, manufactured by Asahi Kasei Corporation, dielectric constant (1 GHz): 2.4, dielectric loss tangent (1 GHz): 0.0012)
- 20 - styrene butadiene resin: TR2003 (manufactured by JSR)
- low dielectric polyimide resin: PIAD-301 (terminal functional group: carboxyl group, solvent: mixed liquid of cyclohexanone, methylcyclohexane, and ethylene glycol dimethyl ether, manufactured by Arakawa Chemical Industries, Ltd., dielectric constant (1 GHz): 2.70, dielectric loss tangent (1 GHz): 0.003, softening point: 140°C)
- 25 - epoxy resin: NC-3000H (biphenyl aralkyl type, manufactured by Nippon Kayaku Co., Ltd., epoxy equivalent: 288 g/Eq)
- epoxidized polybutadiene resin: JP100 (manufactured by Nippon Soda Co., Ltd.)
- maleimide resin: MIR-3000 (biphenyl aralkyl type, manufactured by Nippon Kayaku Co., Ltd., functional group equivalent: 275 g/Eq)

- polycarbodiimide resin: CARBODILITE V-09GB (manufactured by Nisshinbo Chemical Inc.)

- imidazole-based curing accelerator: 2P4MHZ (manufactured by SHIKOKU CHEMICALS CORPORATION)

5 - polyamide resin: BPAM-155 (phenolic hydroxyl group-containing polybutadiene-modified aromatic polyamide resin, manufactured by Nippon Kayaku Co., Ltd.)

- inorganic filler: SC-2050MTX (manufactured by Admatechs Company Limited, average particle diameter D50 = 0.5 μm , surface-phenylaminosilane-treated product)

[0039]

10 Examples 1 to 3

(1) Fabrication of Electrodeposited Copper Foils

Three types of electrodeposited copper foils A to C were fabricated by the following methods.

[0040]

<Electrodeposited Copper Foil A>

15 Electrolysis was performed in a copper sulfate solution at a solution temperature of 45°C and a current density of 55 A/dm² using a rotating electrode made of titanium (surface roughness Ra = 0.20 μm) for a cathode and DSA for an anode, thereby fabricating a raw foil. The composition of this copper sulfate solution was a copper concentration of 80 g/L, a free sulfuric acid concentration of 140 g/L, a bis(3-sulfopropyl) disulfide concentration of

20 30 mg/L, a diallyldimethylammonium chloride polymer concentration of 50 mg/L, and a chlorine concentration of 40 mg/L. Then, the surface treatments of the following (a) to (c) were sequentially performed on the electrolytic solution surface of the raw foil.

(a) Zinc-Nickel Film Formation

- potassium pyrophosphate concentration: 80 g/L

25 - zinc concentration: 0.2 g/L

- nickel concentration: 2 g/L

- solution temperature: 40°C

- current density: 0.5 A/dm²

(b) Chromate Layer Formation

30 - chromic acid concentration: 1 g/L, pH 11

- solution temperature: 25°C

- current density: 1 A/dm²

(c) Silane Layer Formation

- silane coupling agent: 3-aminopropyltrimethoxysilane (3 g/L aqueous solution)

5 - liquid treatment method: shower treatment

[0041]

The surface-treated surface of the electrodeposited copper foil A thus obtained had a ten-point average roughness Rzjis of 0.5 μm (measured in accordance with JIS B0601-2001) and a maximum height Sz of 0.35 μm and had no particulate protrusions. The thickness
10 of the electrodeposited copper foil A was 18 μm.

[0042]

<Electrodeposited Copper Foil B>

Particulate protrusions were formed on the surface of the raw foil of the electrodeposited copper foil A on the electrolytic solution surface side, and then the same surface treatment
15 as the electrodeposited copper foil A was performed. The formation of particulate protrusions was performed by the following three-stage electrolysis treatment. The first-stage electrolysis treatment was performed in a copper sulfate solution (copper concentration: 10.5 g/L, free sulfuric acid concentration: 220 g/L) under the conditions of a solution temperature of 30°C and a current density of 28 A/dm². The second-stage
20 electrolysis treatment was performed in a copper sulfate solution (copper concentration: 10.5 g/L, free sulfuric acid concentration: 220 g/L) under the conditions of a solution temperature of 30°C and a current density of 16 A/dm². The third-stage electrolysis treatment was performed in a copper sulfate solution (copper concentration: 70 g/L, free sulfuric acid concentration: 220 g/L) under the conditions of a solution temperature of 52°C
25 and a current density of 21 A/dm².

[0043]

The surface-treated surface of the electrodeposited copper foil B thus obtained had a ten-point average roughness Rzjis of 1.8 μm (in accordance with JIS B0601-2001) and a maximum height Sz of 3.30 μm. The thickness of the electrodeposited copper foil B was
30 18 μm.

[0044]

<Electrodeposited Copper Foil C>

Using an electrodeposited copper foil in which the surface roughness on the electrode surface side was $R_{zjs} = 1.4 \mu\text{m}$, roughening treatment was performed such that fine copper particles were deposited on the electrode surface side. Specifically, the above electrodeposited copper foil was immersed in a copper electrolytic solution at a liquid temperature of 25°C having a copper concentration of 8 g/L and a free sulfuric acid concentration of 150 g/L and containing an additive (glue), and a current was passed for 10 seconds using an amount of electricity of 200 C/dm^2 , thereby depositing and fixing fine copper particles on the surface on the electrode surface side. Then, "covering plating" was performed to anchor the fine copper particles to the electrode surface. This covering plating was performed under smooth plating conditions in which the copper concentration was 70 g/L, the free sulfuric acid concentration was 120 g/L, the liquid temperature was 45°C , and the current density was 25 A/dm^2 .

[0045]

After the roughening treatment, both surfaces of the electrodeposited copper foil were subjected to rustproofing treatment. Specifically, the electrodeposited copper foil was immersed in a solution having a potassium pyrophosphate concentration of 80 g/L, a zinc concentration of 0.2 g/L, a nickel concentration of 2 g/L, and a liquid temperature of 40°C , anode stainless steel (SUS) plates were disposed on both sides of the electrodeposited copper foil as a cathode, and electrolysis was performed at a current density of 0.5 A/dm^2 to form zinc-nickel alloy layers on both surfaces of the electrodeposited copper foil. Further, chromate layers were formed by an electrolysis method. Specifically, the electrodeposited copper foil was immersed in a solution having a chromic acid concentration of 1 g/L, a pH of 11, and a liquid temperature of 25°C , stainless steel (SUS) plates as anodes were disposed on both sides of the electrodeposited copper foil as a cathode, and electrolysis was performed at a current density of 1 A/dm^2 to form chromate layers on the surfaces of the zinc-nickel alloy layers to form rustproofing-treated layers.

[0046]

The electrodeposited copper foil on which the rustproofing-treated layers were formed was rinsed with water, and the surface of the rustproofing-treated layer on the roughening-treated surface was immediately subjected to silane coupling agent treatment. This silane coupling agent treatment was performed by dissolving γ -glycidoxypyrtrimethoxysilane in ion-exchanged water to prepare an aqueous solution having a concentration of 3 g/L, showering the entire surface of the rustproofing-treated layer on the roughening-treated surface with this aqueous solution, and then bringing the surface into contact with a roll to make the liquid film thickness uniform. The electrodeposited copper foil after the silane coupling agent treatment was held for 4 seconds in a drying furnace set to an atmosphere in which the copper foil temperature was 150°C, to dissipate moisture to obtain an electrodeposited copper foil C as a surface-treated copper foil.

[0047]

For the electrodeposited copper foil C thus obtained, the ten-point average roughness Rz of the roughening-treated surface was 3.0 μm (in accordance with JIS B0601-2001), and the maximum height Sz was 6.63 μm . The thickness of the electrodeposited copper foil C was 18 μm .

[0048]

The methods for measuring the maximum height Sz and kurtosis (peakedness) Sku , which represent a surface shape, on the side (roughening-treated surface) of the electrodeposited copper foils A to C on which an adhesive layer was to be provided were as follows.

[0049]

<Maximum Height Sz >

The measurement of the maximum height Sz at a copper foil surface was performed in accordance with ISO 25178 by surface texture analysis using a laser microscope (VK-X100 manufactured by KEYENCE CORPORATION). Specifically, the surface profile of a two-dimensional region in a measurement field of view of 100 μm x 100 μm at a copper foil surface was measured by a laser method. The average value when measurement was performed in three places for the same sample was adopted as the value of the maximum height Sz . The results were as shown in Table 1.

[0050]

<Kurtosis (Peakedness) Sku>

The measurement of the kurtosis (peakedness) Sku at a copper foil surface was performed in accordance with ISO 25178 by surface texture analysis using a laser microscope (VK-X100 manufactured by KEYENCE CORPORATION). Specifically, the surface profile of a two-dimensional region in a measurement field of view of 100 μm x 100 μm at a copper foil surface was measured by a laser method. The average value when measurement was performed in 10 places for the same sample was adopted as the kurtosis (peakedness) Sku. The results were as shown in Table 1.

[0051]

10 [Table 1]

Table 1

		Ex. 1	Ex. 2	Ex. 3
Type of electrodeposited copper foil		A	B	C
Surface texture of copper foil	Sz(μm)	0.35	3.30	6.63
	Sku	3.01	3.11	2.40

[0052]

(2) Preparation of Resin Varnish

15 The above raw material components for a resin varnish and an organic solvent (mixed solvent of 50% of toluene and 50% of methyl ethyl ketone) were weighed so that a blending ratio (mass ratio) shown in Table 2 was attained and the proportion of solids was 10 parts by weight. The weighed raw material components for a resin varnish and solvent were placed into a flask and stirred by a propeller type stirring apparatus at 60°C for 30 minutes to dissolve the resin components in the solvent, and the resin varnish was collected.

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[0053]

(3) Fabrication and Evaluation of Adhesive Layer Single Body

The surfaces of the copper foils A (Example 1), the copper foils B (Example 2), or the copper foils C (Example 3) having the above Sz and Sku were coated with the resin varnish obtained in the above (1) so that the coating thickness after drying was 50 μm . The coating resin varnish was dried in an oven to a semi-cured (B stage) state. Thus, two adhesive-attached copper foils 10 each comprising an adhesive layer 14 on one surface of a copper

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foil 12 as shown in Figure 1 were fabricated. As shown in Figure 1, the two adhesive-attached copper foils 10 were laminated so that the adhesive layers 14 were stacked to each other, and vacuum pressing was performed under the conditions of a pressing temperature of 190°C, a temperature holding time of 90 minutes, and a pressure of 400 N to bring the adhesive layer 14 into a cured state. The thickness of the cured adhesive layer 14 was 100 μm . The copper foils were etched away from the laminate after the pressing to obtain a resin film composed of the adhesive layer 14 alone.

[0054]

<Dielectric Characteristic Evaluation-Dielectric Loss Tangent>

For the above-obtained resin film composed of the adhesive layer 14 alone, the dielectric loss tangent value at 1 GHz, δ_a , was measured by the SPDR dielectric resonator method using a network analyzer (PNA-L N5234A manufactured by Keysight). This measurement was performed in accordance with ASTM D2520 (JIS C2565: 1992). The results were as shown in Table 2. In Table 2, the magnitude relationship with the dielectric loss tangent value of the prepreg used as the resin layer in (4) and (5) described later at 1 GHz, δ_r , is also shown together. As seen from Table 2, it is seen that the dielectric loss tangent value of the adhesive layer at a frequency of 1 GHz, δ_a , is equal to or less than the dielectric loss tangent value of the resin layer (prepreg) at a frequency of 1 GHz, δ_r (= 0.003).

[0055]

(4) Fabrication of Copper-Clad Laminate and Measurement of Peel Strength R

According to the same procedure as the above (3), as shown in Figure 2, adhesive layers 24 were formed on the surfaces of copper foils 22, that is, the copper foils A (Example 1), the copper foils B (Example 2), or the copper foils C (Example 3), having the above S_z and S_{ku} so that the coating thickness after drying was 4 μm , thereby fabricating adhesive-attached copper foils 20. Then, the adhesive-attached copper foils 20 as outermost layers were laminated together with two prepregs (MEGTRON-6 manufactured by Panasonic Corporation, actual thickness: 200 μm , dielectric constant D_k : 3.9 and dielectric loss tangent D_f : 0.003 at 1 GHz by SPDR method), which were resin layers 26, to obtain a resin substrate having a thickness of 0.25 mm. As shown in Figure 2, vacuum pressing was performed under the conditions of a pressing temperature of 190°C, a temperature holding time of 120

minutes, and a pressure of 300 N to bring the adhesive layers 24 into a cured state to obtain a copper-clad laminate 28. Peel strength measurement test circuits were formed on the obtained copper-clad laminate 28. Specifically, dry films were bonded to both surfaces of the copper-clad laminate 28 to form etching resist layers. Then, the etching resist layers on both surfaces were exposed and developed for peel strength measurement test circuits having a width of 10 mm to form etching patterns. Then, circuit etching was performed with a copper etchant, and the etching resists were stripped to obtain circuits 22a. The circuit 22a thus formed was peeled off from the adhesive layer 24 to measure the peel strength R (kN/m) between the circuit 22a and the adhesive layer 24. The measurement of this peel strength R was performed in accordance with JIS C 6481-1996. The results were as shown in Table 2.

[0056]

(5) Fabrication of Copper-Clad Laminate and Measurement of Transmission Loss

According to the same procedure as the above (3), as shown in Figure 2, adhesive layers 24 were formed on the surfaces of copper foils 22, that is, the copper foils A (Example 1), the copper foils B (Example 2), or the copper foils C (Example 3), having the above S_z and S_{ku} so that the coating thickness after drying was 4 μm , thereby fabricating adhesive-attached copper foils 20. Then, the adhesive-attached copper foils 20 as outermost layers were laminated together with two prepregs (MEGTRON-6 manufactured by Panasonic Corporation, actual thickness: 68 μm , dielectric constant D_k : 3.9 and dielectric loss tangent D_f : 0.003 at 1 GHz by SPDR method), which were resin layers 26, to obtain a both-surface copper-clad laminate 28 having a thickness of 0.14 mm. Then, the copper foil was pattern-etched to make a microstrip circuit. A pattern in which the characteristic impedance of the circuit was 50 Ω was selected, and the transmission loss S_{21} (db/cm) at 50 GHz was measured. The results were as shown in Table 2. Table 2 also shows together the relative proportions (%) to the transmission loss S_{21} (db/cm), at 50 GHz, of reference samples fabricated in the same manner as above except that the copper foils A, B, or C were directly laminated on prepregs without using adhesive layers (see Examples 11 to 13 described later). It is meant that the lower this relative proportion is, the larger the effect of reducing the transmission loss due to the adhesive layers is.

[0057]

Example 4

The above raw material components for a resin varnish and an organic solvent (cyclopentanone) were weighed so that a blending ratio (mass ratio) shown in Table 2 was attained and the proportion of solids was 30 parts by weight. The weighed raw material components for a resin varnish and solvent were placed into a flask and stirred by a propeller type stirring apparatus at ordinary temperature for 30 minutes to dissolve the resin components in the solvent, and the resin varnish was collected. The fabrication and evaluation of an adhesive layer and a copper-clad laminate were performed in the same manner as in Example 1 except that the resin varnish thus obtained was used. The results were as shown in Table 2.

[0058]

Examples 5 to 7

The above raw material components for a resin varnish and an organic solvent (toluene) were weighed so that a blending ratio (mass ratio) shown in Table 2 was attained and the proportion of solids was 10 parts by weight. The weighed raw material components for a resin varnish and solvent were placed into a flask and stirred by a propeller type stirring apparatus at 60°C for 30 minutes to dissolve the resin components in the solvent, and the resin varnish was collected. The fabrication and evaluation of an adhesive layer and a copper-clad laminate were performed in the same manner as in Example 1 except that the resin varnish thus obtained was used. The results were as shown in Table 2.

[0059]

Example 8 (Comparison)

The above raw material components for a resin varnish and an organic solvent (mixed solvent of 50% of toluene and 50% of methyl ethyl ketone) were weighed so that a blending ratio (mass ratio) shown in Table 3 was attained and the proportion of solids was 10 parts by weight. The weighed raw material components for a resin varnish and solvent were placed into a flask and stirred by a propeller type stirring apparatus at 60°C for 30 minutes to dissolve the resin components in the solvent, and the resin varnish was collected. The fabrication and evaluation of an adhesive layer and a copper-clad laminate were performed

in the same manner as in Example 1 except that the resin varnish thus obtained was used. The results were as shown in Table 3.

[0060]

Examples 9 and 10 (Comparison)

- 5 The above raw material components for a resin varnish and an organic solvent (mixed solution of 25% of dimethylacetamide and 75% of cyclopentanone) were weighed so that a blending ratio (mass ratio) shown in Table 3 was attained and the proportion of solids was 10 parts by weight. The weighed raw material components for a resin varnish and solvent were placed into a flask and stirred by a propeller type stirring apparatus at 60°C for 30
- 10 minutes to dissolve the resin components in the solvent, and the resin varnish was collected. The fabrication and evaluation of an adhesive layer and a copper-clad laminate were performed in the same manner as in Example 1 except that the resin varnish thus obtained was used. The results were as shown in Table 3.

[0061]

15 Example 11 (Comparison)

The fabrication of a copper foil laminate and the measurement of transmission loss were performed in the same manner as in Example 1 except that adhesive layers were not formed. The results were as shown in Table 3.

[0062]

20 Example 12 (Comparison)

The fabrication of a copper foil laminate and the measurement of transmission loss were performed in the same manner as in Example 2 except that adhesive layers were not formed. The results were as shown in Table 3.

[0063]

25 Example 13 (Comparison)

The fabrication of a copper foil laminate and the measurement of transmission loss were performed in the same manner as in Example 3 except that adhesive layers were not formed. The results were as shown in Table 3.

[0064]

[Table 2]

Table 2

		Product name	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Adhesive layer (parts weight) by	Polyphenylene ether resin (PPE)	OPE-2St-2200	50						
	Cyclic olefin resin	L3PS					100		
	Cyclic olefin resin	TOPAS6017						100	
	Hydrogenated styrene butadiene resin	MP-10				10			100
	Styrene butadiene resin	TR2003	20						
	Low dielectric polyimide resin	PIAD-301				30.5			
	Epoxy resin	NC-3000H				3			
	Epoxidized polybutadiene resin	JP100							
	Maleimide resin	MIR-3000				8			
	Polycarbodiimide resin	V-09GB				3			
	Imidazole	2P4MHZ				0.5			
	Polyamide resin	BPAM-155							
	Inorganic filler	SC-2050MTX	30			45			
	Total			100			100	100	100
Type of electrodeposited copper foil			A	B	C	A	A	A	A
Evaluation with adhesive layer single body (@1GHz)		Dielectric loss tangent value δa	0.0019			0.003	0.0018	0.0001	0.0012
		Relationship with dielectric loss tangent value of resin layer, δr	$\delta a \leq \delta r (= 0.003)$						
Evaluation of adhesive layer as primer layer		Peel strength (kN/m)	0.53	0.65	0.81	0.72	0.51	0.95	0.63
Evaluation of microstrip circuit (@50GHz)		Transmission loss (db/cm)	-0.46	-0.55	-0.68	-0.50	-0.46	-0.47	-0.46
		Relative proportion (%) of transmission loss to reference value*	89	93	96	96	89	90	89

* The reference value of transmission loss is the value shown in Example 11 for one using copper foils A, the value shown in Example 12 for one using copper foils B, and the value shown in Example 13 for one using copper foils C.

[Table 3]

Table 3

		Product name	Ex. 8*	Ex. 9*	Ex. 10*	Ex. 11*	Ex. 12*	Ex. 13*	
Adhesive layer (parts weight)	by	Polyphenylene ether resin (PPE)	OPE-2St-2200	44.5			No adhesive layer		
		Cyclic olefin resin	L3PS						
		Cyclic olefin resin	TOPAS6017						
		Hydrogenated styrene butadiene resin	MP-10						
		Styrene butadiene resin	TR2003	10					
		Low dielectric polyimide resin	PIAD-301		39.5	42.5			
		Epoxy resin	NC-3000H	5	10	17			
		Epoxidized polybutadiene resin	JP100	10					
		Maleimide resin	MIR-3000						
		Polycarbodiimide resin	V-09GB						
		Imidazole	2P4MHZ	0.5	0.5	0.5			
		Polyamide resin	BPAM-155		20	10			
		Inorganic filler	SC-2050MTX	30	30	30			
Total			100	100	100	0	0	0	
Type of electrodeposited copper foil			A	A	A	A	B	C	
Evaluation with adhesive layer single body (@1GHz)		Dielectric loss tangent value δa	0.0100	0.009	0.008	No adhesive layer			
		Relationship with dielectric loss tangent value of resin layer, δr	δa > δr (= 0.003)						
Evaluation of adhesive layer as primer layer		Peel strength (kN/m)	0.5	0.74	0.75	-	-	-	
Evaluation of microstrip circuit (@50GHz)		Transmission loss (db/cm)	-0.59	-0.56	-0.55	-0.52	-0.59	-0.71	
		Relative proportion (%) of transmission loss to reference value*	114	108	106	100	100	100	

* indicates a comparative example.

* The reference value of transmission loss is the value shown in Example 11 for one using copper foils A, the value shown in Example 12 for one using copper foils B, and the value shown in Example 13 for one using copper foils C.

CLAIMS

1. A copper-clad laminate comprising:
 - a copper foil;
 - an adhesive layer provided on a surface of the copper foil and comprising one or more selected from the group consisting of a polyphenylene ether resin, a polyimide resin, an olefin-based resin, a liquid crystal polymer, a polyester resin, a polystyrene resin, a hydrocarbon elastomer, a benzoxazine resin, an active ester resin, a cyanate ester resin, a bismaleimide resin, a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, a fluororesin, a resin having a vinyl group, and copolymers thereof; and
 - a resin layer provided on a surface of the adhesive layer,wherein the surface of the copper foil on the adhesive layer side has a maximum height S_z of 6.8 μm or less as measured in accordance with ISO 25178, and the adhesive layer has a dielectric loss tangent value at a frequency of 1 GHz, δ_a , which is equal to or less than a dielectric loss tangent value of the resin layer at a frequency of 1 GHz, δ_r .
2. The copper-clad laminate according to claim 1, wherein the maximum height S_z at the surface of the copper foil on the adhesive layer side is 0.15 μm or more and 6.8 μm or less.
3. The copper-clad laminate according to claim 1 or 2, wherein the dielectric loss tangent value of the adhesive layer at a frequency of 1 GHz, δ_a , is 0.0001 or more and 0.003 or less.
4. The copper-clad laminate according to any one of claims 1 to 3, wherein the dielectric loss tangent value of the resin layer at a frequency of 1 GHz, δ_r , is 0.0001 or more and 0.03 or less.

5. The copper-clad laminate according to any one of claims 1 to 4, wherein the surface of the copper foil on the adhesive layer side has a kurtosis S_{ku} of 2.0 or more and 4.0 or less as measured in accordance with ISO 25178 at the surface of the copper foil on the adhesive layer side.
6. The copper-clad laminate according to any one of claims 1 to 5, wherein the adhesive layer comprises at least one selected from the group consisting of an olefin-based resin, a polystyrene resin, a liquid crystal polymer, and a fluoro resin in an amount of 10% by weight or more based on a total weight of the adhesive layer.
7. The copper-clad laminate according to any one of claims 1 to 6, wherein the adhesive layer comprises a polyphenylene ether resin in an amount of 20% by weight or more based on the total weight of the adhesive layer.
8. The copper-clad laminate according to any one of claims 1 to 7, wherein the adhesive layer comprises a polyimide resin in an amount of 10% by weight or more based on the total weight of the adhesive layer.
9. The copper-clad laminate according to any one of claims 1 to 8, wherein the adhesive layer comprises at least one selected from the group consisting of a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, and a resin having a vinyl group, in an amount of 1% by weight or more based on the total weight of the adhesive layer.
10. The copper-clad laminate according to any one of claims 1 to 9, wherein the resin layer comprises a glass cloth and an insulating resin with which the glass cloth is impregnated.
11. The copper-clad laminate according to any one of claims 1 to 10, wherein the adhesive layer has a thickness of 0.1 μm or more and 20 μm or less.

12. The copper-clad laminate according to any one of claims 1 to 11, wherein the resin layer has a thickness of 5 μm or more and 5 mm or less.

13. The copper-clad laminate according to any one of claims 1 to 12, having a peel strength of the copper foil from the adhesive layer of 0.3 kN/m or more as measured in accordance with JIS C 6481-1996.

14. A method for manufacturing the copper-clad laminate according to any one of claims 1 to 13, comprising the steps of:

providing a copper foil having a surface having a maximum height S_z of 6.8 μm or less as measured in accordance with ISO 25178;

applying a resin varnish comprising an adhesive to a surface of the copper foil and drying the resin varnish to obtain an adhesive-attached copper foil, the adhesive comprising one or more selected from the group consisting of a polyphenylene ether resin, a polyimide resin, an olefin-based resin, a liquid crystal polymer, a polyester resin, a polystyrene resin, a hydrocarbon elastomer, a benzoxazine resin, an active ester resin, a cyanate ester resin, a bismaleimide resin, a butadiene resin, a hydrogenated or non-hydrogenated styrene butadiene resin, an epoxy resin, a fluororesin, a resin having a vinyl group, and copolymers thereof, and, having a dielectric loss tangent value at a frequency of 1 GHz of δ_a after curing; and

bonding the adhesive-attached copper foil to a resin layer having a dielectric loss tangent value at a frequency of 1 GHz of δ_r to form a copper-clad laminate, wherein the δ_a is equal to or less than the δ_r .