

ROUGHENED COPPER FOIL, COPPER-CLADDED LAMINATE BOARD, AND PRINTED WIRING BOARD

TECHNICAL FIELD

5 [0001]

The present invention relates to a roughened copper foil, a copper-clad laminate, and a printed wiring board.

BACKGROUND ART

10 [0002]

In a manufacturing process of a printed wiring board, a copper foil is widely used in the form of a copper-clad laminate obtained by bonding the copper foil to an insulating resin substrate. In this respect, the copper foil and the insulating resin substrate are desired to have high adhesion to each other in order to prevent occurrence of peeling of wiring during the manufacture of the printed wiring board. Therefore, in an ordinary copper foil for manufacturing a printed wiring board, the bonding surface of the copper foil is subjected to roughening treatment to form irregularities composed of fine copper particles, and these irregularities are allowed to bite into an insulating resin substrate by pressing to exhibit an anchor effect to improve the adhesion.

20 [0003]

With high-functionalization of portable electronic devices and the like in recent years, frequencies of signals, irrespective of digital or analog signals, have been increased for the purpose of high-speed processing of large-capacity data, and printed wiring boards suitable for high-frequency applications are required. In such printed wiring boards for high frequencies, transmission loss is desirably reduced in order to enable transmission without deteriorating high-frequency signals. A printed wiring board comprises a copper foil processed into a wiring pattern and an insulating substrate, and main losses in the transmission loss include conductor loss caused by the copper foil and dielectric loss caused by the insulating substrate.

30 [0004]

The conductor loss can be increased by a skin effect of a copper foil that appears more remarkably as the frequency increases. Thus, in order to suppress transmission loss in high-frequency applications, micronization of roughening particles is required for the purpose of reducing the skin effect of a copper foil. As a copper foil having such fine roughening particles, Patent Literature 1 (WO2014/133164) for example discloses a surface-treated copper foil comprising a black-roughened surface roughened by fixing copper particles (for example, approximately spherical copper particles) having a particle size of 10 nm or larger and 250 nm or smaller. Further, Patent Literature 2 (JP2011-168887A) discloses, as a copper foil excellent in transmission characteristics in a high-frequency region, a roughened copper foil having a roughened surface having a surface roughness Rz after roughened treatment of 1.1 μm or less.

CITATION LIST

PATENT LITERATURE

15 [0005]

Patent Literature 1: WO2014/133164

Patent Literature 2: JP2011-168887A

SUMMARY OF INVENTION

20 [0006]

As described above, in order to improve transmission characteristics (high-frequency characteristics), fine roughening treatments have been attempted on the bonding surface of a copper foil to an insulating resin substrate. However, when a copper foil merely subjected to micro-roughening treatment is used to process a copper-clad laminate or manufacture a printed wiring board, there may occur a problem that the peel strength between the copper foil and the substrate is generally low, in particular the copper-clad laminate or the printed wiring board deteriorates in heat-resistant reliability (heat-resistant peel strength).

[0007]

30 The present inventors have now discovered that by controlling, in the surface of a

roughened copper foil, a roughness slope $\tan \theta$ and a small projected area, each calculated based on a mean height R_c and a mean width R_{Sm} of profile elements, in predetermined ranges, both excellent transmission characteristics and high peel strength can be achieved in a copper-clad laminate or a printed wiring board manufactured using the roughened copper foil.

[0008]

Therefore, it is an object of the present invention to provide a roughened copper foil that, when used for a copper-clad laminate or a printed wiring board, can provide both excellent transmission characteristics and high peel strength.

[0009]

According to an aspect of the present invention, there is provided a roughened copper foil comprising a roughened surface on at least one side,

wherein the roughened surface has a roughness slope $\tan \theta$ of 0.58 or less as calculated based on a mean height R_c (μm) and a mean width R_{Sm} (μm) of profile elements by formula $R_c/(0.5 \times R_{Sm})$, and

wherein the roughened surface has a small projected area $R_c \times R_{Sm}$ of $0.45 \mu\text{m}^2$ or more and $2.00 \mu\text{m}^2$ or less that is a product of the mean height R_c (μm) and the mean width R_{Sm} (μm) of the profile elements,

wherein R_c and R_{Sm} are values measured in accordance with JIS B0601-2013 under a condition of not performing a cutoff by a cutoff value λ_s and a cutoff value λ_c .

[0010]

According to another aspect of the present invention, there is provided a copper-clad laminate comprising the roughened copper foil.

[0011]

According to another aspect of the present invention, there is provided a printed wiring board comprising the roughened copper foil.

BRIEF DESCRIPTION OF DRAWINGS

[0012]

Figure 1 is a diagram for explaining roughness slope $\tan \theta$ calculated by a trigonometric

function.

DESCRIPTION OF EMBODIMENTS

[0013]

5 Definitions

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

[0014]

As used herein, "mean height Rc" or "Rc" is a parameter that represents the mean of
10 heights of profile elements in a sampling length, measured in accordance with JIS B0601-2013.

[0015]

As used herein, "mean width RSm" or "RSm" is a parameter that represents the mean of widths of profile elements in a sampling length, measured in accordance with JIS B0601-
15 2013. The mean width RSm is a parameter for evaluating the size of streaks or particles in a transverse direction, rather than the height of irregularities of the surface.

[0016]

Regarding the Rc and the RSm, the minimum height and the minimum width are specified for a ridge or dale that constitutes a profile element, and the ridge or dale whose height is
20 10% or less of the maximum height Rz or whose width is 1% or less of the sampling length is regarded as noise and as a part of a dale or ridge that precedes or follows.

[0017]

As used herein, "roughness slope $\tan \theta$ " means a parameter calculated based on the mean height Rc (μm) and the mean width RSm (μm) of the profile elements by formula
25 $Rc/(0.5 \times RSm)$. Further, as used herein, "small projected area" or "SPA" means a parameter calculated by a product of the mean height Rc (μm) and the mean width RSm (μm) of the profile elements (specifically, $Rc \times RSm$).

[0018]

As used herein, "developed interfacial area ratio Sdr" is a parameter that indicates how
30 much the developed area (surface area) of a defined region increases compared to the

area of the defined region, measured in accordance with ISO 25178 and expressed in percentage. A smaller value thereof indicates that the surface profile is closer to a flat surface, and the Sdr of a completely flat surface is 0%. On the other hand, a larger value thereof indicates a rougher surface profile.

5 [0019]

As used herein, "arithmetic mean height Sa" or "Sa" is a parameter that represents the mean of absolute values of differences in height at respective points with respect to the average surface of a surface, measured in accordance with ISO 25178. In other words, the "arithmetic mean height Sa" or "Sa" corresponds to a parameter obtained by
10 expanding the arithmetic mean height Ra of a profile to a surface.

[0020]

As used herein, "root mean square height Sq" or "Sq" is a parameter corresponding to the standard deviation of distances from the mean surface, measured in accordance with ISO 25178. In other words, the "root mean square height Sq" or "Sq" corresponds to a
15 parameter obtained by expanding a root mean square height Rq of a profile to a surface.

[0021]

RSm and Rc can be calculated respectively by measuring a surface profile of a predetermined measurement length in a roughened surface by a commercially available laser microscope. Sdr, Sa, and Sq can be calculated respectively by measuring a
20 surface profile of a predetermined measurement area in a roughened surface by a commercially available laser microscope. Herein, the parameters Sdr, Sa, and Sq are measured under a condition of not performing a cutoff using an S filter and an L filter, and the parameters RSm and Rc are measured under a condition of not performing a cutoff by a cutoff value λ_s and a cutoff value λ_c . Besides, preferred conditions in measuring and
25 analyzing a surface profile by a laser microscope will be described later in EXAMPLES.

[0022]

As used herein, the "electrode surface" of an electrodeposited copper foil refers to the surface on the side in contact with a cathode during the manufacture of the electrodeposited copper foil.

30 [0023]

As used herein, the "deposited surface" of an electrodeposited copper foil refers to the surface on the side on which electrolytic copper is deposited during the manufacture of the electrodeposited copper foil, in other words, the surface on the side not in contact with a cathode.

5 [0024]

Roughened Copper Foil

The copper foil of the present invention is a roughened copper foil. This roughened copper foil comprises a roughened surface on at least one side thereof. This roughened surface has a roughness slope $\tan \theta$ of 0.58 or less as calculated based on a mean height R_c (μm) and a mean width R_{Sm} (μm) of profile elements by formula $R_c/(0.5 \times R_{Sm})$. Further, the roughened surface has a small projected area $R_c \times R_{Sm}$ of $0.45 \mu\text{m}^2$ or more and $2.00 \mu\text{m}^2$ or less that is a product of the mean height R_c (μm) and the mean width R_{Sm} (μm) of the profile elements. By controlling the roughness slope $\tan \theta$ and the small projected area, each calculated based on the mean height R_c and the mean width R_{Sm} of the profile elements, in predetermined ranges in this manner in the surface of the roughened copper foil, both excellent transmission characteristics and high peel strength can be achieved in a copper-clad laminate or a printed wiring board manufactured using this roughened copper foil.

[0025]

20 As described above, in order to improve transmission characteristics (high-frequency characteristics), fine roughening treatments have been attempted on the bonding surface of a copper foil to an insulating resin substrate. However, when a copper foil merely subjected to micro-roughening treatment is used to process a copper-clad laminate or manufacture a printed wiring board, there may occur a problem that the peel strength between the copper foil and the substrate is generally low, in particular the copper-clad laminate or the printed wiring board deteriorates in heat-resistant reliability (heat-resistant peel strength).

[0026]

30 Facing this problem, the present inventors have conducted studies to find that the transmission characteristics relate to the roughness slope $\tan \theta$ of the roughened surface

and the peel strength (heat-resistant peel strength in particular) between the copper foil and the substrate relates to the small projected area (SPA) of the roughened surface. These mechanisms are not necessarily certain, but it is conceivable as follows. Here, Figure 1 shows the roughness slope $\tan \theta$ calculated by a trigonometric function. As shown in Figure 1, the roughness slope $\tan \theta$ is calculated by formula $Rc/(0.5 \times RSm)$, in other words, corresponds to angles of ridges or dales in the roughened surface. Specifically, as the roughness slope $\tan \theta$ is smaller, these angles are smaller (in other words, ridges or dales slope more gently), and therefore a current flows more smoothly. To the contrary, as the roughness slope $\tan \theta$ is larger, these angles are larger, and therefore the resistance is larger (in other words, the current resistance increases). Thus, it is conceivable that by controlling the roughness slope $\tan \theta$ in small values of 0.58 or less, excellent transmission characteristics can be achieved. The SPA indicates the size (projected area) of nodules in the roughened surface, and by increasing the value of the SPA, an anchor effect (specifically, an effect of improving physical adhesion utilizing the irregularities of the copper foil surface) to a substrate can be increased. On the other hand, when the SPA in the roughened surface is too large, the nodules are coarse, so that the copper-clad laminate or the printed wiring board is likely to deteriorate in transmission characteristics. Thus, by controlling the SPA in $0.45 \mu\text{m}^2$ or more and $2.00 \mu\text{m}^2$ or less, high adhesion reliability to a substrate can be ensured while the roughened surface has fine nodules which are advantageous in view of transmission characteristics. As a result, according to the roughened copper foil of the present invention, both excellent transmission characteristics and adhesion reliability due to high peel strength (heat-resistant peel strength in particular) can be achieved in a copper-clad laminate or a printed wiring board manufactured using the roughened copper foil.

[0027]

Therefore, the roughened surface of the roughened copper foil has a roughness slope $\tan \theta$ of 0.58 or less and a small projected area (SPA) of $0.45 \mu\text{m}^2$ or more and $2.00 \mu\text{m}^2$ or less. The roughened surface preferably has a roughness slope $\tan \theta$ of 0.30 or less and a small projected area of $0.45 \mu\text{m}^2$ or more and $1.00 \mu\text{m}^2$ or less, more preferably has a roughness slope $\tan \theta$ of 0.25 or less and a small projected area of $0.47 \mu\text{m}^2$ or more and

0.80 μm^2 or less, further preferably has a roughness slope $\tan \theta$ of 0.05 or more and 0.20 or less and a small projected area of 0.47 μm^2 or more and 0.80 μm^2 or less, and particularly preferably has a roughness slope $\tan \theta$ of 0.10 or more and 0.15 or less and a small projected area of 0.50 μm^2 or more and 0.60 μm^2 or less.

5 [0028]

In the roughened copper foil, the roughened surface preferably has a developed interfacial area ratio Sdr of 60% or less, more preferably 1% or more and 40% or less, further preferably 2% or more and 30% or less, particularly preferably 3% or more and 20% or less, and most preferably 5% or more and 15% or less. When the roughened surface
10 has Sdr within the above ranges, the roughened surface has a shape rich in irregularities convenient for achieving higher adhesion reliability while the roughened copper foil provides excellent transmission characteristics.

[0029]

In the roughened copper foil, the roughened surface preferably has a mean height Rc of
15 0.15 μm or more and 0.80 μm or less, more preferably 0.16 μm or more and 0.60 μm or less, further preferably 0.16 μm or more and 0.50 μm or less, still further preferably 0.17 μm or more and 0.40 μm or less, particularly preferably 0.17 μm or more and 0.30 μm or less, and most preferably 0.18 μm or more and 0.25 μm or less. When the roughened surface has Rc within the above ranges, the roughness slope $\tan \theta$ and the SPA are
20 easily controlled in the above-described ranges, and more excellent transmission characteristics can be achieved while high adhesion reliability is secured.

[0030]

In the roughened copper foil, the roughened surface preferably has an arithmetic mean height Sa of 0.30 μm or less, more preferably 0.01 μm or more and 0.25 μm or less,
25 further preferably 0.02 μm or more and 0.22 μm or less, particularly preferably 0.03 μm or more and 0.17 μm or less, and most preferably 0.05 μm or more and 0.14 μm or less. When the roughened surface has Sa within the above ranges, more excellent transmission characteristics can be achieved.

[0031]

30 In the roughened copper foil, the roughened surface preferably has a root mean square

height Sq of 0.35 μm or less, more preferably 0.02 μm or more and 0.30 μm or less, further preferably 0.02 μm or more and 0.25 μm or less, particularly preferably 0.03 μm or more and 0.20 μm or less, and most preferably 0.03 μm or more and 0.17 μm or less. When the roughened surface has Sq within the above ranges, more excellent transmission characteristics can be achieved.

[0032]

In the roughened copper foil, the roughened surface preferably has a mean width RSm of the profile elements of 2.40 μm or more and 3.50 μm or less, more preferably 2.60 μm or more and 3.50 μm or less, and further preferably 2.60 μm or more and 3.30 μm or less.

When the roughened surface has RSm within the above ranges, the roughness slope $\tan \theta$ and the SPA are easily controlled in the above-described ranges, and while high adhesion reliability is secured, the shapes of ridges or dales in the roughened surface are sufficiently gentle, so that more excellent transmission characteristics can be achieved.

[0033]

The thickness of the roughened copper foil is not particularly limited but is preferably 0.1 μm or more and 210 μm or less, and more preferably 0.5 μm or more and 70 μm or less. The roughened copper foil of the present invention is not limited to one obtained by subjecting a surface of an ordinary copper foil to roughening treatment and may be one obtained by subjecting the copper foil surface of a carrier-attached copper foil to roughening treatment or micro-roughening treatment.

[0034]

The roughened copper foil of the present invention can be preferably manufactured by subjecting a smooth copper foil surface (for example, a deposited surface of an electrodeposited copper foil (smooth foil)) to roughening treatment under desired low-roughening conditions to form fine roughening particles. Therefore, according to a preferred aspect of the present invention, the roughened copper foil is an electrodeposited copper foil, and the roughened surface is present on the deposited surface side of the electrodeposited copper foil. The roughened copper foil may have roughened surfaces on both sides or may have a roughened surface only on one side. The roughened surface typically comprises a plurality of roughening particles, and these plurality of

roughening particles are each preferably a copper particle. The copper particle may be composed of metal copper or a copper alloy.

[0035]

The roughening treatment for forming the roughened surface can be preferably carried out by forming roughening particles out of copper or a copper alloy on a copper foil. The copper foil before performing the roughening treatment may be a non-roughened copper foil or may be one subjected to preliminary roughening. The surface of the copper foil to be subjected to the roughening treatment preferably has a ten-point average roughness Rz of 0.10 μm or more and 1.20 μm or less, and more preferably 0.30 μm or more and 1.00 μm or less, as measured in accordance with JIS B0601-1994. When the Rz is within the above ranges, a surface profile required for the roughened copper foil of the present invention is easily provided to the roughened surface.

[0036]

In the roughening treatment, it is preferred to perform electrolytic deposition, for example, at a temperature of 20°C or higher and 40°C or lower at 10 A/dm² or more and 200 A/dm² or less in a copper sulfate solution having a copper concentration of 3 g/L or more and 20 g/L or less and a sulfuric acid concentration of 50 g/L or more and 200 g/L or less. This electrolytic deposition is preferably performed for 0.2 seconds or longer and 30 seconds or shorter, more preferably 0.2 seconds or longer and 15 seconds or shorter, and further preferably 0.5 seconds or longer and 10 seconds or shorter. When electrolytic deposition is performed, it is preferred to set the amount of copper to be supplied between electrodes to 0.1 [(g·m)/(min·L)] or more and 15.0 [(g·m)/(min·L)] or less, wherein the amount of copper to be supplied between electrodes is defined by the following formula:

$$F_{\text{Cu}} = F_{\text{CuSO}_4} \times C_{\text{Cu}} / S$$

wherein F_{Cu} represents the amount of copper [(g·m)/(min·L)] to be supplied between electrodes, F_{CuSO_4} represents a flow rate (m³/min) of the copper sulfate solution, C_{Cu} represents the copper concentration (g/L) of the copper sulfate solution, and S represents a cross-sectional area (m²) between the anode and the cathode. Thus, a surface profile required for the roughened copper foil of the present invention is easily provided to the surface of the roughened copper foil. However, the roughened copper foil according to

the present invention may be one manufactured by any method not limited to the above method.

[0037]

The roughening treatment may further include, as desired, the second roughening
5 treatment of subjecting the surface after the above roughening treatment (first roughening treatment) to electrolytic deposition under predetermined conditions and the third roughening treatment of subjecting the surface after the second roughening treatment to electrolytic deposition under predetermined conditions. The preferred conditions described above regarding the first roughening treatment directly apply to preferred
10 conditions for the second roughening treatment.

[0038]

Meanwhile, regarding the third roughening treatment, it is preferred to perform electrolytic deposition, for example, at a temperature of 45°C or higher and 55°C or lower at 1 A/dm² or more and 5 A/dm² or less in a copper sulfate solution having a copper concentration of
15 65 g/L or more and 80 g/L or less and a sulfuric acid concentration of 200 g/L or more and 280 g/L or less. This electrolytic deposition is preferably performed for 25 seconds or longer and 35 seconds or shorter, and more preferably 27 seconds or longer and 32 seconds or shorter. Further, when electrolytic deposition is performed, it is preferred to set the amount of copper to be supplied between electrodes to 50 [(g·m)/(min·L)] or more
20 and 200 [(g·m)/(min·L)] or less.

[0039]

The roughened copper foil may be one which has been subjected to rust proofing treatment to form a rust proofing layer, optionally. The rust proofing treatment preferably comprises plating treatment using zinc. The plating treatment using zinc may be either of
25 zinc plating treatment and zinc alloy plating treatment, and for the zinc alloy plating treatment, zinc-nickel alloy treatment is particularly preferred. The zinc-nickel alloy treatment should be plating treatment including at least Ni and Zn and may further include other elements such as Sn, Cr, Co, and Mo. For example, when the rust proofing layer further comprises Mo in addition to Ni and Zn, thereby the treated surface of the
30 roughened copper foil is more excellent in adhesion to a resin, chemical resistance, and

heat resistance, and etching residues are unlikely to be left on the treated surface of the roughened copper foil. The Ni/Zn fixing ratio in the zinc-nickel alloy plating is preferably in the range of 1.2 or more and 10 or less, more preferably in the range of 2 or more and 7 or less, and further preferably 2.7 or more and 4 or less, in terms of mass ratio. The rust proofing treatment preferably further includes chromate treatment, and this chromate treatment is more preferably performed on the zinc-containing surface of plating after plating treatment using zinc. Thus, the rust proofing properties can be further improved. Particularly preferred rust proofing treatment is a combination of zinc-nickel alloy plating treatment and subsequent chromate treatment.

10 [0040]

The roughened copper foil may be one a surface of which has been subjected to silane coupling agent treatment to form a silane coupling agent layer thereon, optionally. Thus, the moisture resistance, the chemical resistance, the adhesion to an adhesive, and the like can be improved. The silane coupling agent layer can be formed by appropriately diluting a silane coupling agent, applying the diluted silane coupling agent, and drying it. Examples of the silane coupling agent include epoxy functional silane coupling agents such as 4-glycidylbutyltrimethoxysilane and 3-glycidoxypropyltrimethoxysilane, or amino functional silane coupling agents such as 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-3-(4-(3-aminopropoxy)butoxy)propyl-3-aminopropyltrimethoxysilane, and N-phenyl-3-aminopropyltrimethoxysilane, or mercapto functional silane coupling agents such as 3-mercaptopropyltrimethoxysilane, or olefin functional silane coupling agents such as vinyltrimethoxysilane and vinylphenyltrimethoxysilane, or acrylic functional silane coupling agents such as 3-methacryloxypropyltrimethoxysilane and 3-acryloxypropyltrimethoxysilane, or imidazole functional silane coupling agents such as imidazolesilane, or triazine functional silane coupling agents such as triazinesilane.

[0041]

For the above-described reasons, the roughened copper foil preferably further includes a rust proofing layer and/or a silane coupling agent layer on the roughened surface and more preferably includes both a rust proofing layer and a silane coupling agent layer.

The rust proofing layer and the silane coupling agent layer may be formed on the roughened surface side of the roughened copper foil and may also be formed on the side on which the roughened surface is not formed.

[0042]

5 Copper-Clad Laminate

The roughened copper foil of the present invention is preferably used for the manufacture of a copper-clad laminate for a printed wiring board. In other words, according to a preferred aspect of the present invention, a copper-clad laminate comprising the above roughened copper foil is provided. By using the roughened copper foil of the present invention, both excellent transmission characteristics and high reliability can be achieved in a copper-clad laminate. This copper-clad laminate comprises the roughened copper foil of the present invention and a resin layer adhered and provided on the roughened surface of this roughened copper foil. The roughened copper foil may be provided on one surface or both surfaces of the resin layer. The resin layer comprises a resin, preferably an insulating resin. The resin layer is preferably a prepreg and/or a resin sheet. A prepreg is a generic term for a composite material obtained by impregnating a substrate such as a synthetic resin plate, a glass plate, a glass woven fabric, a glass nonwoven fabric, or paper with a synthetic resin. Preferred examples of the insulating resin include epoxy resins, cyanate resins, bismaleimide triazine resins (BT resins), polyphenylene ether resins, and phenolic resins. Examples of the insulating resin for forming the resin sheet include insulating resins such as epoxy resins, polyimide resins, and polyester resins. Filler particles composed of various inorganic particles such as silica and alumina particles may be contained in the resin layer in view of, for example, improving insulating properties. The thickness of the resin layer is not particularly limited but is preferably 1 μm or more and 1000 μm or less, more preferably 2 μm or more and 400 μm or less, and further preferably 3 μm or more and 200 μm or less. The resin layer may be composed of a plurality of layers. The resin layer such as a prepreg and/or a resin sheet may be provided on the roughened copper foil via a primer resin layer previously applied to a copper foil surface.

30 [0043]

Printed Wiring Board

The roughened copper foil of the present invention is preferably used for the manufacture of a printed wiring board. In other words, according to a preferred aspect of the present invention, a printed wiring board comprising the above roughened copper foil is provided.

- 5 By using the roughened copper foil of the present invention, both excellent transmission characteristics and high reliability can be achieved in a printed wiring board. The printed wiring board according to this aspect comprises a layer configuration in which a resin layer and a copper layer are laminated. The copper layer is a layer derived from the roughened copper foil of the present invention. The resin layer is as described above
- 10 regarding the copper-clad laminate. In any case, in the printed wiring board, a known layer configuration can be adopted. Specific examples of the printed wiring board include single-sided or double-sided printed wiring boards obtained by adhering the roughened copper foil of the present invention to one surface or both surfaces of a prepreg followed by curing to form a laminate, and then forming a circuit, and multilayer
- 15 printed wiring boards obtained by multilayering the single-sided or double-sided printed wiring boards. Other specific examples include flexible printed wiring boards, COFs, and TAB tapes obtained by forming the roughened copper foil of the present invention on a resin film and forming a circuit. Still other specific examples include: buildup wiring boards obtained by applying the above-described resin layer to the roughened copper foil
- 20 of the present invention to form a resin-attached copper foil (RCC), laminating the RCC on the above-described printed substrate using the resin layer as an insulating adhesive material layer, and then forming a circuit by a method such as a modified semi-additive process (MSAP) or a subtractive process using the roughened copper foil as all or part of a wiring layer; buildup wiring boards obtained by forming a circuit by a semi-additive
- 25 process (SAP) by removing the roughened copper foil; and direct-buildup-on-wafers obtained by alternately repeating the lamination of a resin-attached copper foil on a semiconductor integrated circuit and circuit formation.

EXAMPLES

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

[0045]

Examples 1 to 9

A roughened copper foil of the present invention was manufactured as follows.

5 [0046]

(1) Manufacture of Electrodeposited Copper Foil

In Examples 1 to 6 and 9, electrolysis was performed at a solution temperature of 45°C and a current density of 55 A/dm² using a sulfuric acidic copper sulfate solution having the composition shown below as a copper electrolytic solution, an electrode made of titanium
10 for a cathode, and a DSA (dimensionally stable anode) for an anode, to obtain an electrodeposited copper foil (smooth foil) having a thickness shown in Table 1. At this time, an electrode whose surface roughness was adjusted by polishing with a buff of #1000 was used as the cathode.

<Composition of Sulfuric Acidic Copper Sulfate Solution>

- 15 - Copper concentration: 80 g/L
- Sulfuric acid concentration: 260 g/L
- Bis(3-sulfopropyl) disulfide concentration: 30 mg/L
- Diallyldimethylammonium chloride polymer concentration: 50 mg/L
- Chlorine concentration: 40 mg/L

20 [0047]

In Examples 7 and 8, an electrodeposited copper foil (conventional foil) having a thickness shown in Table 1 was obtained using a sulfuric acidic copper sulfate solution having the composition shown below as a copper electrolytic solution. At this time, conditions other than the composition of the sulfuric acidic copper sulfate solution were the same as those
25 in Examples 1 to 6 and 9.

<Composition of Sulfuric Acidic Copper Sulfate Solution>

- Copper concentration: 80 g/L
- Sulfuric acid concentration: 300 g/L
- Glue concentration: 5 mg/L
- 30 - Chlorine concentration: 30 mg/L

[0048]

(2) Roughening Treatment

Among the electrode surface and the deposited surface included in the above-described electrodeposited copper foil, roughening treatment was performed on the deposited surface side for Examples 1 to 6 and 9 and on the electrode surface side for Examples 7 and 8. The ten-point average roughness Rz measured in accordance with JIS B0601-1994 using a contact surface roughness meter for the deposited surfaces of the electrodeposited copper foils used in Examples 1 to 6 and 9 and the electrode surfaces of the electrodeposited copper foils used in Examples 7 and 8 were as shown in Table 1.

[0049]

In Examples 1, 2 and 9, the roughening treatment (first roughening treatment) shown below was performed. This roughening treatment was carried out by performing electrolysis in a copper electrolytic solution for roughening treatment (copper concentration: 3 g/L or more and 20 g/L or less, sulfuric acid concentration: 50 g/L or more and 200 g/L or less, liquid temperature: 30°C) under the conditions of a current density, a time, and an amount of copper supplied between electrodes, shown in Table 1 for every example, and then rinsing with water.

[0050]

In Examples 3 to 8, the first roughening treatment, the second roughening treatment, and the third roughening treatment, shown below, were performed in the mentioned order.

- The first roughening treatment was carried out by performing electrolysis in a copper electrolytic solution for roughening treatment (copper concentration: 3 g/L or more and 20 g/L or less, sulfuric acid concentration: 50 g/L or more and 200 g/L or less, liquid temperature: 30°C) under the conditions of a current density, a time, and an amount of copper supplied between electrodes, shown in Table 1 for every example, and then rinsing with water.

- The second roughening treatment was carried out by performing electrolysis in a copper electrolytic solution for roughening treatment having the same composition as in the first roughening treatment under the conditions of a current density, a time, and an amount of copper supplied between electrodes, shown in Table 1 for every example, and then

rinsing with water.

- The third roughening treatment was carried out by performing electrolysis in a copper electrolytic solution for roughening treatment (copper concentration: 65 g/L or more and 80 g/L or less, sulfuric acid concentration: 200 g/L or more and 280 g/L or less, liquid temperature: 45°C) under the conditions of a current density, a time, and an amount of copper supplied between electrodes, shown in Table 1 for every example, and then rinsing with water.

[0051]

(3) Rust Proofing Treatment

The electrodeposited copper foil after roughening treatment was subjected to rust proofing treatment shown in Table 1. In Examples 2 and 4 to 9, both surfaces of the electrodeposited copper foil were subjected to zinc-nickel-based rust proofing treatment using a pyrophosphoric acid bath at a potassium pyrophosphate concentration of 80 g/L, a zinc concentration of 0.2 g/L, a nickel concentration of 2 g/L, a liquid temperature of 40°C, and a current density of 0.5 A/dm² as this rust proofing treatment. In contrast, in Examples 1 and 3, the surface where roughening treatment of the electrodeposited copper foil had been performed was subjected to zinc-nickel-molybdenum-based rust proofing treatment at a potassium pyrophosphate concentration of 100 g/L, a zinc concentration of 1 g/L, a nickel concentration of 2 g/L, a molybdenum concentration of 1 g/L, a liquid temperature of 40°C, and a current density of 0.5A/dm². In Examples 1 and 3, the surface where roughening treatment of the electrodeposited copper foil had not been performed was subjected to zinc-nickel-based rust proofing treatment under the same conditions as in Examples 2 and 4 to 9.

[0052]

(4) Chromate Treatment

Both surfaces of the electrodeposited copper foil that had been subjected to the above rust proofing treatment were subjected to chromate treatment to form a chromate layer on the rust proofing layer. This chromate treatment was performed under the conditions of a chromic acid concentration of 1 g/L, a pH of 11, a liquid temperature of 25°C, and a current density of 1 A/dm².

[0053]

(5) Silane Coupling Agent Treatment

The copper foil that had been subjected to the above chromate treatment was rinsed with water, and immediately after that, silane coupling agent treatment was performed to adsorb a silane coupling agent on the chromate layer on the roughened surface. This silane coupling agent treatment was carried out by spraying a silane coupling agent solution containing pure water as a solvent on the roughened surface by showering to perform adsorption treatment. As the silane coupling agent, 3-aminopropyltrimethoxysilane was used in Examples 1 to 3 and 9, 3-acryloxypropyltrimethoxysilane was used in Example 4, and 3-glycidoxypropyltrimethoxysilane was used in Examples 5 to 8. The concentration of the silane coupling agent was each set to 3 g/L. After the silane coupling agent was adsorbed, moisture was finally evaporated by a heater to obtain a roughened copper foil having a predetermined thickness.

15 [0054]

[Table 1]

Table 1

Electrodeposited copper foil			Roughening treatment									Rust proofing treatment	Si treatment	
			Treated surface	First roughening treatment			Second roughening treatment			Third roughening treatment				
Type	Thick ness (μm)	Rz (μm)		Current density (A/dm ²)	Time (s)	Amount of copper supplied between electrodes (g·m)/(min·L)	Current density (A/dm ²)	Time (s)	Amount of copper supplied between electrodes (g·m)/(min·L)	Current density (A/dm ²)	Time (s)	Amount of copper supplied between electrodes (g·m)/(min·L)	Type	Type
Ex. 1	Smooth foil	18	0.5	117.0	0.9	0.1	-	-	-	-	-	-	Zn-Ni-Mo	Amino
Ex. 2	Smooth foil	18	0.5	142.5	0.9	0.1	-	-	-	-	-	-	Zn-Ni	Amino
Ex. 3	Smooth foil	18	0.5	14.1	7.4	7.3	19.8	7.4	7.3	1.7	29.5	79.5	Zn-Ni-Mo	Amino
Ex. 4	Smooth foil	18	0.5	14.7	7.4	12.2	22.0	7.4	12.8	4.5	29.5	106.4	Zn-Ni	Acrylic
Ex. 5*	Smooth foil	18	0.5	26.8	5.4	23.3	16.9	5.4	23.3	10.4	21.6	97.2	Zn-Ni	Epoxy
Ex. 6*	Smooth foil	18	0.6	24.3	5.1	15.8	31.3	5.1	15.8	12.1	20.3	83.2	Zn-Ni	Epoxy
Ex. 7*	Conventional foil	12	0.7	29.9	3.1	21.6	21.5	3.1	21.6	10.4	12.5	82.5	Zn-Ni	Epoxy
Ex. 8*	Conventional foil	18	1.1	36.1	2.6	20.1	36.1	2.6	19.1	20.6	10.5	116.0	Zn-Ni	Epoxy
Ex. 9*	Smooth foil	18	0.5	50.0	2.2	14.8	-	-	-	-	-	-	Zn-Ni	Amino

* indicates a comparative example.

[0055]

Evaluation

For the roughened copper foil manufactured, various evaluations shown below were performed.

5 [0056]

(a) Surface Property Parameters of Roughened Surface

The roughened surface of the roughened copper foil was measured in accordance with ISO 25178 or JIS B0601-2013 by surface roughness analysis using a laser microscope. Specific measurement conditions were as shown in Table 2. The analysis was
 10 performed for the obtained surface profile of the roughened surface following the conditions shown in Table 2 to calculate RSm, Rc, Sdr, Sa, and Sq. The values of the roughness slope $\tan \theta$ ($= Rc / (0.5 \times RSm)$) and the small projected area (SPA) ($= Rc \times RSm$) were calculated respectively based on the obtained RSm and Rc values. The results were as shown in Table 3.

15 [0057]

[Table 2]

Table 2

Measurement conditions	Model of laser microscope		Manufactured by Olympus Corporation, OLS-5000
	Objective lens magnification		100×
	Optical zoom		2×
	Direction of observation		Direction in which treatment streaks of the copper foil are perpendicular to the visual field
	Measurement method		Specify the multiple area mode; specify X = 2 and Y = 2 as "Matrix," and X = 64 μm and Y = 64 μm as "Pitch," in the lattice registering mode; and measure mutually adjacent regions of 2 × 2 (64 μm square per region)
Analysis conditions	Common conditions	Surface profile capturing region	64.419 μm in length × 64.397 μm in width (Specify a region of 1024 pixels × 1024 pixels on the region-specifying screen)
		Correction of surface slope	Perform by "Auto"
		Averaging method	Take an average of measured values of the regions of 2 × 2 simultaneously measured
	RSm Rc	Target region	Draw three lines of 64.397 μm in length perpendicularly to treatment streaks, and three lines of 64.419 μm in length in parallel with treatment streaks, and calculate profiles on respective lines to take an average
		Standard	JIS B0601-2013
		Cutoff value λs	None
		Cutoff value λc	None
	Sdr Sa Sq	Target region	Whole region specified in capturing the surface profile (the region of 1024 pixels × 1024 pixels)
		Standard	ISO 25178
		F-operation	Form-removing method is set to "multidimensional curved surface," and dimension is set to "1."
		S filter	None
		L filter	None

[0058]

(b) Peel Strength between Copper Foil and Substrate

- 5 For the roughened copper foil in a normal state and after heat load, the peel strength in a normal state and the heat-resistant peel strength were measured as follows in order to evaluate the adhesion to an insulating substrate.

[0059]

(b-1) Peel Strength in Normal State

- 10 As the insulating substrate, two sheets of prepregs (thickness 100 μm) each containing a polyphenylene ether, triallyl isocyanurate, and a bismaleimide resin as main components were prepared and stacked. The surface-treated copper foil manufactured was laminated on these stacked prepregs such that the roughened surface of the surface-

treated copper foil came into contact with the prepreg, and pressing at 32 kgf/cm² and 205°C for 120 minutes was performed to manufacture a copper-clad laminate. Subsequently, a circuit was formed on this copper-clad laminate by an etching method to manufacture a test substrate including a linear circuit having a width of 3 mm. Here, in

5 Example 7, the surface on the copper foil side of the copper-clad laminate was subjected to copper plating before forming the circuit until the thickness of the copper foil became 18 µm. The linear circuit thus obtained was peeled off from the insulating substrate in accordance with the A method (90° peel) of JIS C 5016-1994 to measure the peel strength (kgf/cm) in a normal state. Whether the obtained peel strength in a normal state

10 is good or poor was evaluated according to the following criteria. The results were as shown in Table 3.

<Evaluation Criteria for Peel Strength in Normal State>

- Good: the peel strength in a normal state is 0.54 kgf/cm or more
- Poor: the peel strength in a normal state is less than 0.54 kgf/cm

15 [0060]

(b-2) Heat-Resistant Peel Strength

The heat-resistant peel strength (kgf/cm) was measured by the same procedure as the above-described peel strength in a normal state except that the test substrate including the linear circuit was subjected to floating in a solder bath of 288°C for 300 seconds prior

20 to the measurement of the peel strength. Whether the obtained heat-resistant peel strength is good or poor was evaluated according to the following criteria. The results were as shown in Table 3.

<Evaluation Criteria for Heat-Resistant Peel Strength>

- Good: the heat-resistant peel strength is 0.54 kgf/cm or more
- 25 - Poor: the heat-resistant peel strength is less than 0.54 kgf/cm

[0061]

(c) Transmission Characteristics

A substrate for high frequencies (manufactured by Panasonic Corporation, MEGTRON6N) was prepared as an insulating resin substrate. The roughened copper foil was laminated

30 on both surfaces of this insulating resin substrate such that the roughened surface thereof

came into contact with the insulating resin substrate using a vacuum press machine under the conditions of a temperature of 190°C and a press time of 120 minutes to obtain a copper-clad laminate having an insulation thickness of 136 μm . Thereafter, the copper-clad laminate was etched to obtain a substrate for transmission loss measurement on which a microstrip line was formed such that the characteristic impedance was to be 50 Ω . The transmission loss (dB/cm) at 50 GHz was measured for the obtained substrate for transmission loss measurement using a network analyzer (manufactured by Keysight Technologies, N5225B). The obtained transmission loss was graded and evaluated by the following criteria. The results were as shown in Table 3.

10 <Transmission Loss Evaluation Criteria>

- Grade A (Excellent): the transmission loss is -0.57 dB/cm or more
- Grade B (Good): the transmission loss is -0.63 dB/cm or more and less than -0.57 dB/cm
- Grade C (Poor): the transmission loss is less than -0.63 dB/cm

[0062]

15 [Table 3]

Table 3

	Evaluation									
	Surface property parameters of roughened surface							Peel strength between copper foil and substrate		Transmission characteristics
	RSm (μm)	Rc (μm)	Roughness slope $\tan\theta$ Rc/0.5RSm (-)	SPA Rc $\times$ RSm (μm^2)	Sdr (%)	Sa (μm)	Sq (μm)	Peel strength (kgf/cm) in normal state	Heat-resistant peel strength (kgf/cm)	Transmission loss (dB/cm) at 50 GHz
Ex. 1	2.856	0.194	0.136	0.554	10.6	0.11	0.14	0.54 (Good)	0.55 (Good)	-0.52 (A)
Ex. 2	3.463	0.281	0.162	0.974	15.6	0.15	0.19	0.57 (Good)	0.56 (Good)	-0.57 (A)
Ex. 3	2.580	0.378	0.293	0.975	28.8	0.20	0.26	0.58 (Good)	0.58 (Good)	-0.57 (A)
Ex. 4	2.494	0.710	0.569	1.771	59.6	0.26	0.33	0.65 (Good)	0.58 (Good)	-0.61 (B)
Ex. 5*	3.534	1.223	0.692	4.323	97.7	0.49	0.60	0.70 (Good)	0.61 (Good)	-0.71 (C)
Ex. 6*	3.714	1.702	0.917	6.322	132.9	0.67	0.81	0.75 (Good)	0.64 (Good)	-0.78 (C)
Ex. 7*	3.037	0.917	0.604	2.786	72.2	0.37	0.46	0.72 (Good)	0.64 (Good)	-0.65 (C)
Ex. 8*	4.478	2.106	0.941	9.432	131.1	0.88	1.06	0.75 (Good)	0.63 (Good)	-0.80 (C)
Ex. 9*	4.401	0.097	0.044	0.427	2.2	0.06	0.07	0.52 (Poor)	0.30 (Poor)	-0.51 (A)

* indicates a comparative example.

CLAIMS

1. A roughened copper foil comprising a roughened surface on at least one side,
wherein the roughened surface has a roughness slope $\tan \theta$ of 0.58 or less as calculated based on a mean height R_c (μm) and a mean width R_{Sm} (μm) of profile elements by formula $R_c/(0.5 \times R_{Sm})$, and
wherein the roughened surface has a small projected area $R_c \times R_{Sm}$ of $0.45 \mu\text{m}^2$ or more and $2.00 \mu\text{m}^2$ or less that is a product of the mean height R_c (μm) and the mean width R_{Sm} (μm) of the profile elements,
wherein R_c and R_{Sm} are values measured in accordance with JIS B0601-2013 under a condition of not performing a cutoff by a cutoff value λ_s and a cutoff value λ_c .
2. The roughened copper foil according to claim 1, wherein the roughened surface has the roughness slope $\tan \theta$ of 0.30 or less and the small projected area $R_c \times R_{Sm}$ of $0.45 \mu\text{m}^2$ or more and $1.00 \mu\text{m}^2$ or less.
3. The roughened copper foil according to claim 1 or 2, wherein the roughened surface has a developed interfacial area ratio S_{dr} of 60% or less, wherein S_{dr} is a value measured in accordance with ISO 25178 under a condition of not performing a cutoff using an S filter and an L filter.
4. The roughened copper foil according to any one of claims 1 to 3, wherein the roughened surface has the mean height R_c of $0.15 \mu\text{m}$ or more and $0.80 \mu\text{m}$ or less.
5. The roughened copper foil according to any one of claims 1 to 4, wherein the roughened surface has an arithmetic mean height S_a of $0.30 \mu\text{m}$ or less, wherein S_a is a value measured in accordance with ISO 25178 under a condition of not performing a cutoff using an S filter and an L filter.
6. The roughened copper foil according to any one of claims 1 to 5, wherein the

roughened surface has a root mean square height S_q of 0.35 μm or less, wherein S_q is a value measured in accordance with ISO 25178 under a condition of not performing a cutoff using an S filter and an L filter.

7. The roughened copper foil according to any one of claims 1 to 6, wherein the roughened surface has the mean width R_{Sm} of the profile elements of 2.40 μm or more and 3.50 μm or less.

8. The roughened copper foil according to any one of claims 1 to 7, further comprising a rust proofing layer and/or a silane coupling agent layer on the roughened surface.

9. The roughened copper foil according to any one of claims 1 to 8, wherein the roughened copper foil is an electrodeposited copper foil, and the roughened surface is present on a deposited surface side of the electrodeposited copper foil.

10. A copper-clad laminate comprising the roughened copper foil according to any one of claims 1 to 9.

11. A printed wiring board comprising the roughened copper foil according to any one of claims 1 to 9.