Title: PEELABLE COPPER FOILS, MANUFACTURING METHOD OF CORELESS SUBSTRATE, AND CORELESS SUBSTRATE OBTAINED BY THE MANUFACTURING METHOD

Abstract: The present invention provides a ultrathin pealable copper foil for manufacturing coreless substrate, comprising a chemical treatment layer, an ultrathin functional copper layer provided below the chemical treatment layer, a metallic release layer provided below the ultrathin functional copper layer, a carrier copper layer provided below the metallic release layer, and a roughening and chemical treatment layers provided below the carrier copper layer. The present invention also provides a pealable copper foil comprising a chemical treatment layer, a carrier copper layer provided below the chemical treatment layer, a metallic release layer provided below the carrier copper layer, an ultrathin functional copper layer provided below the metallic release layer, a smooth roughening and chemical treatment layers provided below the ultrathin functional copper layer, and a primer layer provided below the smooth roughening and chemical treatment layers. The present invention also provides a method of manufacturing a coreless substrate, comprising: (a) forming the ultrathin pealable copper foil of the exemplary embodiment of the present invention as a first ultrathin pealable copper foil; (b) laminating the first ultrathin pealable copper foil on each side of a central prepreg to form a primary central core, (c) forming the ultrathin pealable copper foil of another exemplary embodiment of the present invention as the second pealable copper foil, (d) laminating the second pealable copper foil on a build-up film, (e) combining the primary central core obtained in (b) with a laminate obtained in (d), or laminating the laminate on one or both sides of the primary central core, (f) separating the metallic release layer on the carrier copper layer and the functional copper layer of the second pealable copper foil from the structure obtained in (e), and (g) removing the primary central core except for the ultrathin functional copper layer and the chemical treatment layer from the structure obtained in (f).
PEELABLE COPPER FOILS, MANUFACTURING METHOD OF CORELESS SUBSTRATE, AND CORELESS SUBSTRATE OBTAINED BY THE MANUFACTURING METHOD

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TECHNICAL FIELD OF THE INVENTION

The present invention relates to a peelable copper foil for manufacturing coreless substrate, a method of manufacturing the coreless substrate, and a coreless substrate obtained by the manufacturing method.

DISCUSSION OF BACKGROUND ART

Recently, in printed wiring boards, multilayer structures have been widely employed for miniaturization increased wiring density of printed wiring boards. Multilayer printed wiring boards are mainly used in mobile electronic devices to achieve downsizing. Then, multilayer printed wiring boards are required both further thickness reduction in interlayer insulating layers and further weight reduction.

In order to satisfy such requirements, the coreless build-up method disclosed in JP 2007-165513 has been used. This method is for forming a multilayer structure without using the so-called core substrate. In the market, utilization of a copper foil with a peelable-type carrier in the coreless build-up method has been introduced to make separation between the multilayer printed wiring board and the supporting substrate easy.

In this regard, WO 2012/133637 teaches a multilayer printed wiring board manufacturing method, which is a coreless build-up method, and a multilayer printed wiring board obtained by said method. US 2013/0043060 also discloses a method for
forming coreless flip chip ball grid array (FCBGA) substrate. In the two literatures, an organic agent is used as a release layer with a not fine-tunable release force. The foil obtained has a very low release force (below 10 N/m) and thus, is too easily peelable. The foil obtained has high risk of chemical degradation if blisters are present during coreless laminate manufacturing.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a peelable copper foil for manufacturing coreless substrate with an appropriate release force.

Another object of the present invention is to provide a method of manufacturing the coreless substrate, which does not cause any warpage during the peeling and any delamination during the coreless substrate manufacturing process.

The other object of the present invention is to provide a coreless substrate obtained by the manufacturing method, with very low L/S which can be achieved with modified semi-additive process (MSAP).

In order to achieve the objects above, an exemplary embodiment of the present invention provides an ultrathin peelable copper foil for manufacturing coreless substrate, comprising: a chemical treatment layer, an ultrathin functional copper layer provided below the chemical treatment layer, a metallic release layer provided below the ultrathin functional copper layer, a carrier copper layer provided below the metallic release layer, and a roughening and chemical treatment layers provided below the carrier copper layer.

Another exemplary embodiment of the present invention provides a peelable copper foil comprising: a chemical treatment layer, a carrier copper layer provided below the chemical treatment layer, a metallic release layer provided below the carrier copper layer, an ultrathin functional copper layer provided below the metallic release
layer, a smooth roughening and chemical treatment layers provided below the ultrathin functional copper layer, and a primer layer provided below the smooth roughening and chemical treatment layers.

The other exemplary embodiment of the present invention provides a method of manufacturing a coreless substrate, comprising: (a) forming the ultrathin peelable copper foil of the exemplary embodiment of the present invention as mentioned in the first ultrathin peelable copper foil, (b) laminating the first ultrathin peelable copper foil on each side of the central prepreg to form a primary central core, (c) forming the ultrathin peelable copper foil of another embodiment of the present invention as the second peelable copper foil, (d) laminating the second peelable copper foil on a build-up film, (e) combining the primary central core obtained in (b) with a laminate obtained in (d), or laminating the laminate on one or both sides of the primary central core, (f) separating the metallic release layer on the carrier copper layer and the functional copper layer of the second peelable copper foil from the structure obtained in (e), and (g) removing the primary central core by separating the carrier core from the structure obtained in (f). According to the exemplary embodiments of the present invention, the release force must be fine-tuned, and thus, there would be no risk of blister or delamination and no warpage after (g) removing the central core by separating the carrier core from the structure obtained in (f). There is no need for routing or heating for removing the top and bottom coreless substrate from the sacrificial core. There would be no residues from the release layer left on the ultrathin functional foil after peeling. According to the exemplary embodiments of the present invention, very narrow L/S may be obtained. Neither seeder process nor full additive processes are needed allowing a MSAP process with differential flash etching.
BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents the first ultrathin peelable copper foil 120 according to an exemplary embodiment of the present invention.

FIG. 2 shows the relation between the release force and the metal content from the release layer.

FIG. 3 represents a primary center core 100 according to an exemplary embodiment of the present invention, of which the first ultrathin peelable copper foil 120 is laminated on both side of the central prepreg 110.

FIG. 4 represents the second ultrathin peelable copper foil 210 according to an exemplary embodiment of the present invention.

FIG. 5 represents a laminate 200 of second ultrathin peelable copper foil 210 on build-up film 220 according to an exemplary embodiment of the present invention.

FIG. 6 represents a lamination of the laminate 200 on one side of the central core 100, according to an exemplary embodiment of the present invention.

FIG. 7 represents a lamination of the laminate 200 on both sides of the central core 100, according to an exemplary embodiment of the present invention.

FIGS. 8 and 10 represent the structure of which the treated top carrier copper layer 212 is stripped with the release layer 215 from the stack, according to an exemplary embodiment of the present invention.

FIGS. 9 and 11 represent the structure of which another laminate 200 is relaminated on the top of the structures of FIGs. 7 and 9, respectively, according to an exemplary embodiment of the present invention.

FIG. 12 represents the coreless construction according to an exemplary embodiment of the present invention.

FIG. 13 represents the central sacrificial core 300 separated from the coreless
substrates according to an exemplary embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, the present invention will be described with reference to the drawings.

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Step A: Formation of the first ultrathin peelable copper foil 120

As shown in Fig. 1, a first ultrathin peelable copper foil 120 is first made. The first ultrathin peelable copper foil 120 comprises a roughening treatment layer 123, a carrier copper layer 122, a release layer 125, a functional copper layer 121, and a chemical treatment layer 124.

1. Carrier copper layer 122

A copper layer is used as a carrier. In the first peelable copper foil 120, the thickness of the carrier copper layer 122 is from 5 to 140 µm. The thickness of the carrier copper layer 122 is preferably 7 to 120 µm, more preferably 70 to 105 µm, in view of the warpage control during processing.

2. Roughening treatment layer 123

On the surface of the carrier copper layer 122, specific mechanical and chemical bonding treatments are conducted to form a roughening treatment layer 123.

The roughening treatment may include one or more selected from the group consisting of a nodular copper treatment, formation of a rust proofing layer and an application of a silane coupling agent layer. The combination of the nodular copper treatment with the rust proofing layer applied, preferably on the nodular copper treatment is preferable. The coupling agent layer applied preferably on the rust proofing
layer is more preferable for ensuring sufficient mechanical and chemical bonding to the material used as sacrificial core 110.

A nodular copper treatment layer may be formed preferably by the electrodeposition of an arsenic-free copper layer on the bottom of the carrier copper layer 122 thereby improving/secureing its adhesiveness and bonding with respect to the materials to be used as sacrificial core in the coreless substrate industry. The roughness RzJIS measured on the roughening layer surface is not more than 10 μm.

On the surface of the nodular copper treatment layer or on the surface of the carrier copper layer 122, a rust proofing layer comprising preferably a plated nanometric zinc-chromate layer may be formed. The zinc-chromate layer is a plated layer containing at least Cr and Zn. In addition, Cr deposit and Zn deposit in the plated rust proofing layer are preferably 5 to 7 mg/m² and 7 to 9 mg/m², respectively.

A coupling agent may also be formed on the surface of the carrier copper layer, on the surface of the nodular copper treatment layer, or on the surface of the rust proofing layer for increasing the bond strength of the carrier foil to the prepreg 110. The coupling agent can be formed from sol-gels, silanes, siloxanes, thiols, phosphonic acids, titanates, zirconates or organic acid-chromium chloride coordination complexes. The silane coupling agent such as the organo-functional or non-functionalized silane coupling agent may be preferably employed. In particular, a nanometric silane coupling agent may be employed. Specifically, the silane coupling agent layer may be applied on the surface of the carrier foil, on the surface of the nodular copper treatment layer, or on the surface of the rust proofing layer by contact with an appropriate diluted silane coupling agent solution, followed by drying. The silane coupling agent used in the present invention is for example an epoxy functional silane coupling agent such as gamma-glycidoxypropyl trimethoxysilane, gamma-glycidoxypropyl triethoxysilane and
the like; an amino functional silane coupling agent such as gamma-aminopropyl triethoxysilane, gamma-aminopropyl trimethoxysilane and the like; an ureido silane functional coupling agent such as gamma-ureidopropyl trialkoxysilane and the like; and a non functionalized silane coupling agent such as tetraethoxysilane and the like.

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The nodular copper layer 123 as above gives the carrier copper layer 122 roughness. The roughness RzJIS measured on the roughening layer surface is not more than 10 μη and typically below 8μη. Due to such a combination of mechanical and chemical bonding treatment, the double side copper clad laminate 100 comprising the ultrathin peelable copper foil 121 and the carrier foil 122 with its roughening treatment layer 123 including the rust proofing layer and the coupling agent layer would exhibit sufficient bonding strength, which makes it possible to withstand several thermal and chemical process steps afterwards.

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3. Release layer 125

The release layer 125 is provided between the carrier copper layer 122 and the functional copper layer 121.

The release layer 125 is composed of a non-organic material, that is, a metal. This is different from the commonly used release layer which comprises an organic material.

20 Specifically, the release layer 125 includes at least one metal selected from the group consisting of Cr, Ni, Zn, Mo, W, Co, Pb, Ag, Ta, Cu, Al, Mn, Fe, Ti, Sn, Steel, Zn, V, their oxide, and their hydroxide, preferably, from the group consisting of Cr, Ni, Zn, Mo, Co, Pb, Ag, their oxide, and their hydroxide. Since the release layer 125 is comprised of a metal, the thickness of the release layer 125 may be fine-tunable, and then deposited metal amount in correlation with the thickness of the release layer 125 may
also be fme-tunable in the range of from 0 to 20 mg/m², preferably from 3.5 to 8 mg/m² for the coreless substrate purpose (see FIG. 2). In the prior art, organic material was used as a release layer, resulting in a unique low release force level irregardless of process conditions (in the typical range of 5-8 N/m).

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The release layer 125 is set to have a releasing force in such degree that the stack is not delaminated during all the manipulation or handling steps but it may be easily peelable by hand and/or by mechanic method at the end of the coreless substrate manufacturing process. In the present invention, for example, by adjusting the current density for the release layer electrodeposition and the subsequent thickness of the metallic release layer 125, for example, to 8 mg/m², a release force after thermal process between 15 N/m and 60 N/m, more preferably between 20 N/m and 55 N/m may be obtained. No residues from the metallic release layer are left on the functional copper foil 121 after peeling. There is no risk of blister or delamination and no warpage related to the high carrier bonding level. If the release force is below 15 N/m, delamination is more easily generated during the coreless process. If the release force is above 60 N/m, warpage could be generated during the peeling. The coreless as well as the peeling process (either manually or mechanically) can seriously impact the final warpage results.

The release layer 125 has a nanometric scale and preferably has a thickness of below 20 nm.

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Since the release layer 125 is provided between the carrier copper layer 122 and the ultrathin functional copper layer 121, multiple hot lamination cycles and wet chemical process steps in between and allowing an easy separation at the end of the process are possible.

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The release layer 125 is produced by the electro-deposition. In this regard,
different from the prior art, galvanic process or any other chemical and physical method may be used. For example, the electro-deposition may be conducted through a specific bath of a determined composition of from 150 to 300 g/l, preferably from 240 to 260 g/l of chromic acid, and from 1.5 to 3 g/l, preferably from 2.2 to 2.5 g/l of sulfuric acid, and under a temperature of 22°C. This allows a processing window sweeping in a range of 30 N/m release force value.

4. Functional copper layer 121

The functional copper layer 121 is an ultrathin foil electroplated on the release layer 125. The thickness of the functional copper layer 121 is typically from 0.5 to 12μm with a roughness RzJIS range from 1 to 3μm. The low roughness of the carrier foil for example, with Ra below 0.4μm generates the very low profile of the functional foil for example, with Ra below 0.4μm.

5. Chemical layer 124

A chemical layer 124 is formed on the surface of the functional copper layer 121. The chemical layer 124 is a surface protection layer and an anti-tarnishing layer. The chemical layer formed 124 comprises a plated nanometric zinc-chromate layer. The zinc-chromate layer is a plated layer containing at least Cr and Zn. In addition, Cr deposit and Zn deposit is 2 to 4 mg/m² and 8 to 10 mg/m², respectively.

The chemical layer 124 can be applied on top of the functional copper layer 121 in order to avoid any oxidation after the first lamination and allows an easy processability in the subsequent steps.

Step B: Lamination of the first ultrathin peelable copper foil 120 on each side
of the central prepreg 110 to form a primary central core 100

The two peelable copper foils 120 made in step A as shown in Fig. 1 are laminated on each side of a central prepreg 110 to form a primary central core 100, which is shown in Fig. 3.

The prepreg 110 is a kind of sheet that the reinforced fibers are beforehand impregnated by matrix. For example, glass fibers impregnated by an insulated resin can be used.

The primary central core formed 100 will become sacrificial near the end of the process. Thus, the prepreg 110 will be a part of the so-called as sacrificial central core as shown in Fig. 13.

In this process, a hot lamination cycle method is used. The method is conducted under the high temperature. For example the hot lamination cycle can be conducted under the condition of a plateau temperature of 200°C during 100 minute.

After hot lamination, a primary central core 100 is formed. As shown in Fig. 3, the primary central core 100 is a double sided clad core with the ultrathin peelable copper foil 120 on their outsides.

Step C: Formation of the second peelable copper foil 210

As shown in Fig. 4, the second peelable copper foil 210 is made. The foil 210 is composed of a carrier copper layer 212 with a chemical treatment layer 214, a release layer 215 and a treated functional copper layer 211 on top of which a thin resin coating so called primer layer 216 is coated.

1. Functional copper layer 211
For this second ultrathin peelable copper foil 210, the ultrathin foil 211 is electroplated on the release layer 215. The thickness of the functional copper layer 211 is typically from 0.5 to 12 μm. The roughness Ra of the functional copper layer is fixed by the carrier foil profile and is typically below 0.4 μm.

2. Treatment layer 213

A very smooth, preferably arsenic free copper based layer 213 is formed by electro-deposition on the surface of the functional copper layer 211. The layer formed 213 is very smooth compared to a regular nodular or dendritic copper treatment layer. Thus, the treated functional copper layer 213 is so-called 'Almost no profile' (ANP) layer. The profile of the ANP layer 213 is below 1.3 μm in Rz JIS (Japanese Industry Standard) and measured by contactless profilometry.

On the surface of the ANP copper layer 213, a rust proofing layer comprising a plated nanometric chromate layer may be formed. The zinc-chromate layer is preferably a plated layer containing at least Cr and Zn. The contents of Cr deposit and Zn deposit in the plated rust proofing layer is 2 to 3 mg/m² and 3 to 5 mg/m², respectively.

A coupling agent may also preferably be formed on the surface of the rust proofing layer for increasing the bond strength of the carrier foil to the prepreg. The coupling agent can be formed from sol-gels, silanes, siloxanes, thiols, phosphonic acids, titanates, zirconates or organic acid-chromium chloride coordination complexes. Specifically, the organo-fucntionnal or non-functionalized silane coupling agent may be used in combination with the ANP layer 213. The silane coupling agent layer may be preferably applied on the surface of the ultrathin functional foil 211 with its ANP profile.
by contact with an appropriate diluted silane coupling agent solution, followed by drying. The silane coupling agent used in the present invention is, for example, an epoxy functional silane coupling agent such as gamma-glycidoxypropyl trimethoxysilane, gamma-glycidoxypropyl triethoxysilane and the like; an amino functional silane coupling agent such as gamma-aminopropyl triethoxysilane, gamma-aminopropyl trimethoxysilane and the like; an ureido functional silane coupling agent such as gamma-ureidopropyl trialkoxysilane and the like; and a non functionalized silane such as tetraethoxysilane and the like.

The combination of the ANP layer, the rust proofing layer preferably applied on the ANP layer and the silane coupling agent preferably applied on the rust proofing layer is used for enhancing the peel strength to the primer layer 216, and is applied on the surface of the functional copper foil 211. In addition, the combination of the three layers with the primer layer is for ensuring sufficient mechanical and chemical bonding to the insulating build-up film 220.

The ANP layer 213 with the rust proofing layer, the silane coupling agent layer and the primer layer 216 allows a fast and precise flash etching during the further patterning according to the typical MSAP process, resulting in a better line definition and allowing line/space (L/S) to be narrowed, for example, to 5 μm. Improved signal speed and lower conductor losses are also positive consequences of this almost no profile ultrathin foil. The very low roughness of the functional copper foil 213 enables a very narrow L/S (Line/Space) with a straight etched track side and allowing the well-defined subsequent electrolytic copper plating on top of the track line.

3. Primer layer 216
The ANP layer is coated with primer resin 216 by appropriate equipment for coating copper rolls. For example, chemical or physical vapor deposition, spraying or roll to roll coating processes like air knife coating, knife-over-roll 'gap coating', slot-die coating, kiss coating, metering rod (Meyer bar) coating, curtain coating, silk screen coating, curtain coating, spin coating and slot die coating may be used. The very thin primer layer 216 is coated preferably with a slot die head coater.

As the primer resin, for example, a halogen free epoxy-polyamide based resin may be used. The thickness of the dried primer layer 216 is generally from 1 to 10 μm, preferably from 3 to 5 μm. The primer layer is cured and dried such a way to reach an advanced B-stage curing level. The curing level and the thickness of the primer layer 216 combined with the functional foil 213 with a reduced profile, allow securing a high bonding strength with the build-up film 220 above 0.9 N/mm over the several different processes afterwards and avoid delamination.

4. Release layer 215

In the second ultrathin peelable copper foil 210, the electroplated release layer 215 between the ultrathin functional foil 211 and the carrier foil 212 is composed of a metal. This is different from the conventional release layer which comprises an organic compound. Specifically, the electroplated layer includes at least one selected from the group consisting of Cr, Ni, Zn, Mo, W, Co, Pb, Ag, Ta, Cu, Al, Mn, Fe, Ti, Sn, Steel, Zn, V, their oxide, and their hydroxide, preferably, from the group consisting of Cr, Ni, Zn, Mo, Co, Pb, Ag, their oxide, and their hydroxide.

Since the release layer 215 is comprised of a metal, the thickness of the release layer 215 may be fine-tunable, and then the deposited metal amount in correlation with the thickness of the release layer 215 may also be fine-tunable in the range of from 0 to
20 mg/m², preferably from 1.5 to 6 mg/m² to have a releasing force from 0 to 150 N/m, preferably from 10 to 40 N/m in such degree that the stack is not delaminated during all the manipulation step or handling steps prior to the hot lamination step but it may be easily peelable by hand and/or by mechanic method after the lamination on a build-up film 220. Preferably, the release layer 215 has a thickness of below 20 nm.

The release layer 215 is set to have a releasing force in such degree that the laminate 210 produced is not delaminated during all the manipulation or handling steps but it may be easily peelable by hand and/or by mechanic method after lamination on the laminate 100.

The release layer 215 is produced by the electro-deposition method. In this regard, different from the prior art, galvanic process, or any other chemical and physical method can be used. For example, the electro-deposition may be conducted through a specific bath of a determined composition of 150 to 300 g/l, preferably from 240 to 260 g/l of chromic acid, and 1.5 to 3 g/l, preferably from 2.2 to 2.5 g/l of sulfuric acid, and under a temperature of 22°C. This allows the tuning to a preferable process window range of 10 to 40 N/m release force value.

5. Carrier copper layer 212

The thickness of the electrodeposited carrier copper foil 212 is generally is from 5 to 140 μm. The thickness of the carrier copper layer 122 is preferably 7 to 120 μm, more preferably 70 to 105 μm, in view of the warpage control during processing.

6. Chemical treatment layer 214

A chemical layer 214 as a surface protection layer is preferably applied on top of the carrier copper layer 212. A chemical anti-tarnishing metallic layer 214 is preferably
applied on top of the carrier foil 212 in order to avoid any oxidation during vacuum lamination and allows easy process ability in the subsequent steps. The anti-tarnishing layer is preferably plated on the carrier foil and mainly contains chromium and zinc. The chromium content of the anti-tarnishing layer is in the range of 3 to 4 mg/m² and the zinc content is in the range of 30 to 40 mg/m².

Step D: Vacuum lamination of the peelable copper foil 210 on the build-up film 220

As shown in Fig. 5, a build-up film 220 is provided below the second ultrathin supported copper foil 210 to form a laminate 200 of second ultrathin peelable copper foil 210 on build-up film 220. The laminate produced 200 is composed of a very low CTE pre-cured build-up film 220 (for example, Ajinomoto ABF Build-Up Film) together with the second ultrathin peelable copper foil 210. The build-up film 220 can be optionally cured. The build-up film 220 insulated has a thickness of 10 to 100 µm generally.

Step E: Combination of laminates 200 with sacrificial central core 100

Thereafter, as shown in figures 5 and 6, one or two laminate(s) 200 composed of the second ultrathin peelable copper foil 210 with a cured insulated build-up film 220 is further laminated on one side or both sides of the central core 100. Fig. 6 represents a lamination of the laminate 200 on one side of the central core 100, and Fig. 7 represents a lamination of the laminate 200 on both sides of the central core 100.

The following steps will describe the different process stages which will happen on one side or in a symmetrical way on each side of the core. For simplification reasons,
only the process on one side will be described but of course these are applicable on each side the same way.

**Step F: Peeling the carrier copper layer 212**

As shown in Fig. 6, after a lamination of the laminate 200 on one side of the central core 100, the treated top carrier copper layer 212 can be stripped together with the release layer 215 from the structure obtained in STEP E. The release layer 215 allows an easy separation of the carrier copper layer 212. Almost no residues from the metallic release layer are left on the functional copper foil 121 after peeling. Table 1 as shown below represents release layer surface analysis by XPS (analysis depth: 10 nm).

<table>
<thead>
<tr>
<th></th>
<th>Metal relative atomic percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peeled carrier foil side</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>Peeled functional foil side</td>
<td>0 ± 0.5</td>
</tr>
</tbody>
</table>

There are no needs for routing or heat for releasing the top and bottom coreless surface from the sacrificial core.

Finally, a structure shown in Fig. 8 is obtained.

**Step G: MASP process**

The stripping step is followed by a patterning of the ultrathin functional copper layer according to the MSAP process, or any other methods used in the PCB manufacturing.

**Step H: Drilling and filling process**
Then, drilling, preferably, laser direct drilling and via filling process may be performed.

Others:

1. Lamination of the next layer

As shown in Fig. 9, another laminate 200 is relaminated on the top of the structure made in Fig. 8.

2. Patterning of the external layers

As shown in Fig. 9, the carrier copper layer 212 is stripped together with the release layer 215 from the stack. The release layer 215 allows easy separation of the carrier copper layer 212 from the stack. As a result, a structure shown in Fig. 10 is obtained.

Then, a patterning of the ultrathin functional copper layer through MSAP process is performed. Drilling, preferably, laser direct drilling and via filling for electrical contacts with below layer is performed.

3. Lamination of the next layer

As shown in Fig. 11, another laminate 200 is relaminated on the top of the structure made in Fig. 10.

4. Repetition of the sequence

The sequence of relamination of another laminate 200 on the top of the structure, peeling off the carrier copper layer, the MSAP patterning process and drilling and via filling process is repeated n times. That is steps D to H are to be repeated until the final number of copper layers of the PCB design is achieved. Slight variations can occur depending on the circuit layout chosen by the manufacturer.
Generally the steps are symmetric in order to obtain the same coreless laminate on both sides of the central core. Nevertheless, the process/design can be different on each side for obtaining different coreless PCB designs.

**Step I: Separation of the sacrificial core**

The release layer 125 allows separation of the functional copper layer 121 from the carrier layer 122. As shown in Fig. 11, the release layer 125 may be separated from the stack. The central core 100 can be removed by separating the treated carrier copper layer with the release layer 125 from the peelable copper foil. The central core 100 with the treated carrier copper layer becomes sacrificial as shown in Fig. 11. In the process, there is no need for routing or heating for removing the top and bottom coreless substrate from the sacrificial core. That is, it is very easy to peel the sacrificial core 100. This is because the releasing strength can be fine-tuned.

**Step J: Patterning and finishing the external layers**

As shown in Fig. 12, finally, the coreless construction can now be completed on both external sides according to print and etch and finishing processes of the state of the art. At this moment, a final process step can be applied on top of the beforehand protected functional copper foil layer 121. This step can be an etching step, a passivation layer or any other mechanical or chemical process altering the surface in such manner that the desired circuitry is obtained including the final thickness including sufficient chemical resistance for further processing. This can also include the deposition of a surface protection film including but not restricted to a solder mask and typical printed circuit board surface finish preventing surface oxidation.
Step K: Separation and final structuration

After the last process step in form of a full PCB is performed, the coreless substrates are released from the central sacrificial core (Fig. 13). The remaining central part 300 is called sacrificial core as it is, which has only a mechanical and stiffening role during processing and is removed and discarded at the end of the process.

The invention has been described using exemplary preferred embodiments. However, it is to be understood that the scope of the invention is not limited to the disclosed embodiments. On the contrary, it is intended to cover various modifications and similar arrangements. The scope of the claims, therefore, should be accorded the broadest interpretation so as to encompass all such modifications and similar arrangements.
DRAWING REFERENCE NUMBERS

100, 300: primary central core, sacrificial central core
110: central prepreg
120: first ultrathin peelable copper foil
210: second ultrathin peelable copper foil
121, 211: functional copper layer
122, 212: carrier copper layer
123, 213: roughening treatment layer
124, 214: chemical treatment layer
125, 215: release layer
200: laminate of second ultrathin peelable copper foil on build-up film
216: primer layer
220: build-up film
310: Separated layers
WHAT IS CLAIMED IS:

1. An ultrathin peelable copper foil for manufacturing coreless substrate, comprising:
   a chemical treatment layer,
   an ultrathin functional copper layer provided below the chemical treatment layer,
   a metallic release layer provided below the ultrathin functional copper layer,
   a carrier copper layer provided below the metallic release layer,
   and a roughening treatment layer provided below the carrier copper layer.

2. The foil of claim 1, wherein the release force between the metallic release layer and the carrier copper layer is tuned at 15 to 60 N/m.

3. The foil of claim 1, wherein the deposited metal amount of the metallic release layer is in the range of 0 to 20 mg/m.

4. The foil of claim 1, wherein the metallic release layer includes at least one selected from the group consisting of Cr, Ni, Zn, Mo, W, Co, Pb, Ag, Ta, Cu, Al, Mn, Fe, Ti, Sn, Steel, Zn, V, their oxide, and their hydroxide.

5. The foil of claim 1, wherein the ultrathin functional copper layer has a thickness of 0.5 to 12 μm.

6. The foil of claim 1, wherein the roughening treatment layer includes at least one selected from the group consisting of a nodular copper treatment layer, a rust proofing layer, and a coupling agent layer.

7. The foil of claim 1, wherein the carrier copper layer has a thickness of 5 to 140 μm.

8. A peelable copper foil comprising:
   a chemical treatment layer.
a carrier copper layer provided below the chemical treatment layer,
a metallic release layer provided below the earner copper layer,
an ultrathin functional copper layer provided below the metallic release layer,
a treatment layer with almost no profile provided below the ultrathin functional copper layer, and a primer layer provided below the almost no profile treatment layer.
9. The foil of claim 8, wherein the release force between the metallic release layer and the carrier copper layer is tuned at 10 to 40 N/m.
10. The foil of claim 8, wherein the ultrathin functional copper layer has a thickness of 0.5 to 12 μm.
11. The foil of claim 8, wherein the metallic release layer has a thickness of below 20 nm.
12. The foil of claim 8, wherein a primer layer has a thickness of 1 to 10 μm.
13. The foil of claim 8, wherein the metallic release layer includes at least one selected from the group consisting of Cr, Ni, Zn, Mo, W, Co, Pb, Ag, Ta, Cu, Al, Mn, Fe, Ti, Sn, Steel, Zn, V, their oxide, and their hydroxide.
14. The foil of claim 8, wherein the treatment layer has a profile of below 1.3 μm in Rz JIS.
15. The foil of claim 8, wherein the carrier copper layer has a thickness of 5 to 140 μm.
16. The double thin coreless substrate comprising the ultrathin peelable copper foil of claim 1 and the ultrathin peelable copper foil of claim 8.
17. A method of manufacturing a coreless substrate, comprising:
(a) forming the ultrathin peelable copper foil of claim 1 as a first ultrathin peelable copper foil,
(b) laminating the first ultrathin peelable copper foil on each side of the central prepreg to form a primary central core,
(c) forming the ultrathin peelable copper foil of claim 8 as the second peelable copper foil,
(d) laminating the second peelable copper foil on a build-up film,
(e) combining the primary central core obtained in (b) with a laminate obtained in (d),
(f) separating the metallic release layer with the carrier copper layer and the chemical treatment layer of the second peelable copper foil from the structure obtained in (e), and
(g) removing the primary central core except for the chemical treatment layer and an ultrathin functional copper layer from the structure obtained in (f).

18. The method of claim 17, further comprising:
after the step (f),
(f-1) patterning the functional copper layer through the MSAP, and
(f-2) drilling and filling the structure obtained in (f-1).

19. The method of claim 18, further comprising:
after the step (f-2),
(f-3) laminating another laminate obtained in (d), and
(f-4) stripping the carrier copper layer with the release layer from the structure obtained in (f-3).

20. A coreless substrate obtained by the method of claim 17.
FIG. 1
Fig. 2
FIG. 12
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. H05K3/02 H05K3/04 H05K3/46

ADD.

According to International Patent Classification (IPC) or both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H05K B32B C25D

Documentation searched other than minimum documentation to the extent that such documents were included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>paragraph [0009] - paragraph [0011] ;figures 1, 1A</td>
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**X** Further documents are listed in the continuation of Box C. **X** See patent family annex.

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**Date of the actual completion of the international search**

1 September 2015

**Date of mailing of the international search report**

09/09/2015

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040
Fax: (+31-70) 340-3016

**Authorized officer**

Pachol ec, Darek

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