

(43) International Publication Date
17 November 2016 (17.11.2016)(51) International Patent Classification:
H01L 21/683 (2006.01)(21) International Application Number:
PCT/EP2015/060264(22) International Filing Date:
8 May 2015 (08.05.2015)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants: IMEC VZW [BE/BE]; Kapeldreef 75, B-3001 Leuven (BE). FUJIFILM CORPORATION [JP/JP]; 26-30, Nishiazabu 2-chome, Minato-ku, Tokyo, 1068620 (JP).

(72) Inventors: PHOMMAHAXAY, Alain; IMEC VZW, Patent department, Kapeldreef 75, B-3001 Leuven (BE). NAKAMURA, Atsushi; FUJIFILM Electronic Materials, (Europe) N.V., Keetberglaan 1A, B-2070 Zwijndrecht (BE). KAMOCHI, Yoshitaka; FUJIFILM Corporation, 4000 Kawashiri, Yoshida-cho, Haibara-gun, Shizuoka, Shizuoka 421-0396 (JP). IWAI, Yu; FUJIFILM Corporation, 4000 Kawashiri, Yoshida-cho, Haibara-gun, Shizuoka, Shizuoka 421-0396 (JP). KOYAMA, Ichiro; FUJIFILM Corporation, 4000 Kawashiri, Yoshida-cho, Haibara-gun, Shizuoka, Shizuoka 421-0396 (JP).

(74) Agents: HERTOGHE, Kris et al.; DenK ip bvba, Huidelgemsesteenweg 1114, B-9820 Merelbeke (BE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD FOR MANUFACTURING DEVICE SUBSTRATE AND SEMICONDUCTOR DEVICE

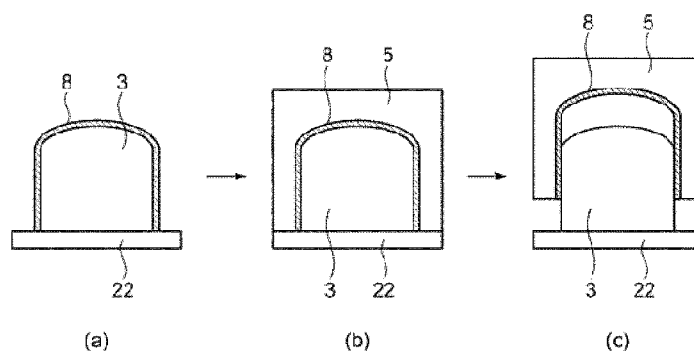


Figure 3

(57) Abstract: Provided are methods for manufacturing device substrates according to which metal oxides (8) formed on the surfaces of metallic convex parts (3) or concave parts on the surface of a wafer (22) can be readily removed; and methods for manufacturing semiconductor devices. A method for manufacturing a device substrate comprises applying a temporary bonding composition (5) comprising a thermoplastic resin and a compound containing a fluorine atom on a carrier to form a temporary bonding agent layer (5); and applying a wafer (22) having at least one of convex parts (3) and concave parts of which main component is copper on a surface of the temporary bonding agent layer on the side opposite to the carrier in such a manner that the side having the at least one of convex parts and concave parts adjoins the temporary bonding agent layer to form a laminate; and heating the laminate at a temperature higher than 170 °C, then separating the carrier from the laminate, and further peeling off the temporary bonding agent.

METHOD FOR MANUFACTURING DEVICE SUBSTRATE AND
SEMICONDUCTOR DEVICE

5 **Field of the invention**

[0001] The present invention relates to methods for manufacturing device substrates, and methods for manufacturing semiconductor devices. In particular, the present invention relates to methods for manufacturing device substrates, comprising bonding a wafer with a temporary bonding agent and thinning the wafer.

10

State of the art

[0002] Proposals have previously been made to manufacture thinned semiconductor device substrates. Wafers such as silicon wafers having a thickness of about 700 to 900 μm have widely been known for use in manufacturing processes of semiconductor devices. Recently, attempts have been made to reduce the thickness of wafers to 200 μm or less for the purpose of reducing the size of integrated circuit (IC) chips or other purposes. However, wafers having a thickness of 200 μm or less are so thin and therefore, components for manufacturing semiconductor devices using such a wafer as substrates are also so thin that such components are hard to stably support without damaging the components during further processing or simply transferring or otherwise handling such components.

[0003] To solve the problems as described above, techniques using temporary bonding agents have been proposed, as shown in JP-A2014-189731, for example. Specifically, such a method is explained with reference to Figure 4. As shown in Figure 4(A), a protective layer 71 is provided on the surface of an un-thinned wafer 60 comprising a substrate 61 and metallic convex parts 62 called bumps or pillars or the like on the surface of the substrate. Separately from the wafer 60 having the protective layer 71, a temporary bonding agent layer 11 is provided on the surface of a carrier 12 to form an adhesive carrier 100. The wafer 60 having the protective layer 71 is bonded to the adhesive carrier 100 in such a manner that the protective layer 71 faces the temporary bonding agent layer 11. In (C), the wafer 60 is thinned. The protective layer 71 is dissolved in a solvent to separate the thinned wafer 60 from the adhesive carrier 100, whereby the thinned wafer 60 is isolated. Such a method allows suitable thinning.

Summary of the invention

[0004] However, the surfaces of the metallic convex parts or concave parts of the wafer described above may lose their metallic luster by natural oxidation or the like during processing. Such oxidation of the surfaces of the convex parts or concave parts should desirably be removed because the oxidation would lower the conductivity of the wafer. However, an additional process was needed to remove metal oxides, which involved more labor.

[0005] The present invention aims to solve the problems described above, thereby providing methods for manufacturing device substrates according to which metal oxides formed on the surfaces of metallic convex parts or concave parts on the surface of a wafer can be readily removed; and methods for manufacturing semiconductor devices.

[0006] As a result of our careful studies to solve the problems described above, we found that when a temporary bonding composition comprising a thermoplastic resin and a compound containing a fluorine atom is used and heated at a temperature higher than 170 °C and then the temporary bonding agent is peeled off from the wafer, the metal oxides can be removed together with the temporary bonding agent. Specifically, the problems described above were solved by the following means <1>, preferably <2> to <16>.

[0007] <1> A method for manufacturing a device substrate comprising:

- applying a temporary bonding composition comprising a thermoplastic resin and a compound containing a fluorine atom on a carrier to form a temporary bonding agent layer; and applying a wafer having at least one of convex parts and concave parts of which main component is copper on a surface of the temporary bonding agent layer on the side opposite to the carrier in such a manner that the side having the at least one of convex parts and concave parts adjoins the temporary bonding agent layer to form a laminate; or
- applying a temporary bonding composition comprising a thermoplastic resin and a compound containing a fluorine atom on a surface of a wafer having, on its surface, at least one of convex parts and concave parts of which main component is copper on the side having the at least one of convex parts and concave parts to form a temporary

bonding agent layer; and applying a carrier on the temporary bonding agent layer on the side opposite to the surface adjoining the wafer to form a laminate; and

- heating the laminate at a temperature higher than 170 °C, then separating the carrier from the laminate, and further peeling off the temporary bonding agent.

5 **[0008]** <2> The method for manufacturing a device substrate according to <1>, wherein the thermoplastic resin is an elastomer.

[0009] <3> The method for manufacturing a device substrate according to <2>, wherein the elastomer has a 5 % mass reduction temperature of 250 °C or more when the elastomer is heated from 25 °C at a rate of 20 °C/min.

10 **[0010]** <4> The method for manufacturing a device substrate according to <2> or <3>, wherein the elastomer contains a repeating unit derived from styrene.

[0011] <5> The method for manufacturing a device substrate according to any one of <2> to <4>, wherein the elastomer is a block copolymer having a styrene block at one or both terminals.

15 **[0012]** <6> The method for manufacturing a device substrate according to any one of <1> to <5>, wherein the compound containing a fluorine atom further contains a lipophilic group.

[0013] <7> The method for manufacturing a device substrate according to any one of <1> to <6>, wherein the compound containing a fluorine atom is liquid at 25 °C.

20 **[0014]** <8> The method for manufacturing a device substrate according to any one of <1> to <7>, wherein at least one of an abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer on the side of the carrier and an abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer on the side of the wafer is 10 to 35 % when the abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer is determined using Electron Spectroscopy for Chemical Analysis by irradiating a test area of 1400 μm x 700 μm on the surface of the temporary bonding agent layer with monochromatic Al Kα rays at 25W and detecting photoelectrons at a take-off angle of 45°.

30 **[0015]** <9> The method for manufacturing a device substrate according to any one of <1> to <8>, wherein the temporary bonding agent layer is liquid at 25 °C and comprises a compound containing a silicon atom.

[0016] <10> The method for manufacturing a device substrate according to any one of <1> to <9>, wherein the carrier and the temporary bonding agent layer adjoin each other.

[0017] <11> The method for manufacturing a device substrate according to
5 any one of <1> to <10>, wherein the surface of the laminate on the side of the wafer is subjected to at least one of a mechanical process and a chemical process after the laminate has been heated.

[0018] <12> The method for manufacturing a device substrate according to
10 any one of <1> to <11>, wherein the peeled temporary bonding agent contains a copper oxide.

[0019] <13> The method for manufacturing a device substrate according to any one of <1> to <12>, comprising peeling off the temporary bonding agent layer at an angle of 60° to 180° with respect to the substrate surface of the wafer.

[0020] <14> The method for manufacturing a device substrate according to
15 any one of <1> to <13>, wherein the wafer comprises two or more rectangular semiconductor chips having at least one of a convex part and a concave part and arranged in such a manner that two opposite sides of one of the rectangular semiconductor chips are in parallel with two opposite sides of the other rectangular semiconductor chip(s), and the temporary bonding agent layer is peeled off at an angle
20 of greater than 30° and less than 60° with respect to one side of the rectangle.

[0021] <15> A method for manufacturing a semiconductor device, comprising a method for manufacturing a device substrate according to any one of <1> to <14>.

[0022] <16> Use of a temporary bonding composition comprising a
25 thermoplastic resin and a compound containing a fluorine atom for removing copper oxides on a surface of at least one of convex parts and concave parts of which main component is copper on the surface of a wafer.

Brief description of the figures

30 [0023] Figure 1a to Figure 1g are schematic diagrams showing a method for manufacturing a device substrate according to the present invention.

[0024] Figure 2 is a schematic diagram showing the angle at which a temporary bonding agent layer is peeled off from a wafer.

[0025] Figure 3 is a conceptual diagram showing a process for removing a copper oxide when a temporary bonding agent layer is peeled off from a convex part.

5 [0026] Figure 4 is a schematic diagram showing a conventional method for manufacturing a device substrate.

Detailed description of the invention

[0027] The invention is described in detail hereunder. In this description,
10 the numerical range expressed by the wording "a number to another number" means the range that falls between the former number indicating the lowermost limit of the range and the latter number indicating the uppermost limit thereof. First described are the terms used in this description.

[0028] The angles indicated herein mean not only to include exact angles
15 in a mathematical sense but also to allow for an error of about $\pm 0.5^\circ$.

[0029] A method for manufacturing a device substrate according to the present invention comprises:

- applying a temporary bonding composition comprising a thermoplastic resin and a compound containing a fluorine atom on a carrier to form a temporary bonding agent
20 layer; and applying a wafer having at least one of convex parts and concave parts of which main component is a metal (preferably copper) on a surface of the temporary bonding agent layer on the side opposite to the carrier in such a manner that the side having the at least one of convex parts and concave parts adjoins the temporary bonding agent layer to form a laminate; or
- 25 - applying a temporary bonding composition comprising a thermoplastic resin and a compound containing a fluorine atom on a surface of a wafer having, on its surface, at least one of convex parts and concave parts of which main component is a metal (preferably copper) on the side having the at least one of convex parts and concave parts to form a temporary bonding agent layer; and applying a carrier on the temporary
30 bonding agent layer on the side opposite to the surface adjoining the wafer to form a laminate; and

- heating the laminate at a temperature higher than 170 °C, then separating the carrier from the laminate, and further peeling off the temporary bonding agent.

A temporary bonding composition comprising a thermoplastic resin and a compound containing a fluorine atom is heated at a temperature higher than 170 °C, thereby
5 producing an anchoring effect to improve the adhesion of the temporary bonding composition to a wafer. As a result, the bonding force between metal oxides (preferably copper oxides) formed by natural oxidation on the surface of at least one of convex parts and concave parts (hereinafter sometimes referred to as “convex parts and/or
10 concave parts”) of the wafer and the temporary bonding agent becomes stronger than the bonding force between the copper oxides and the convex parts and/or concave parts so that the metal oxides (preferably copper oxides) can be removed together with the temporary bonding agent when the temporary bonding agent (preferably temporary
15 bonding agent layer) is peeled off. According to the present invention, any additional process conventionally used for removing metal oxides (preferably copper oxides) can be eliminated. Further according to the present invention, the temporary bonding agent layer can be readily peeled off from the wafer without using a protective layer, separation layer, release layer or the like as in conventional methods because the temporary bonding composition comprises a compound containing a fluorine atom so
20 that the compound containing a fluorine atom is concentrated in the near-surface region of the temporary bonding agent layer.

[0030] The method of the present invention will be explained in detail below by way of example, with reference to Figures 1 to 3. However, it should be understood that the present invention is not limited to these embodiments.

[0031] In Figures 1 to 3, the reference numerals have the following
25 meanings: 1 stands for wafer; 2 stands for substrate of the wafer; 3 stands for convex parts and/or concave parts; 4 stands for carrier; 5 stands for temporary bonding agent layer; 6 stands for support; 7 stands for semiconductor chip; 8 stands for copper oxide; 22 stands for thinned wafer.

[0032] Figure 1 is a schematic diagram showing a method for
30 manufacturing a device substrate according to the present invention.

[0033] As shown in Figure 1a, a wafer 1 comprises a substrate 2 and convex parts and/or concave parts 3 of which main component is a metal (preferably

copper) on the surface of the substrate. The expression “the main component is a metal” here means that the most abundant component of the convex parts and/or concave parts is a metal, and preferably the convex parts and/or concave parts comprise 90 % by mass or more, even 95 % by mass or more of a metal (preferably copper).

5 Further, a carrier 4 supporting the wafer 1 is used in the present invention, as shown in Figure 1a.

[0034] Herein, the convex parts and/or concave parts are exemplified by bump and pillar. Of course, the convex parts and/or concave parts may be other metallic convex parts and/or concave parts without departing from the scope of the
10 present invention.

[0035] The substrate of the wafer may be made of, but not specifically limited to, silicon, a moulded resin (e.g., an epoxy resin or the like), a mixture of a moulded resin and silicon or the like. The carrier may be made of, but not specifically limited to, a silicon substrate, a ceramic substrate, a moulded substrate, a glass substrate
15 or the like.

[0036] Then, a temporary bonding composition is applied on the carrier 4 to form a temporary bonding agent layer 5, as shown in Figure 1b. The temporary bonding composition is applied on the carrier 4 by coating or forming the temporary bonding composition as a film and laminating the temporary bonding composition. A
20 more preferred coating technique is spin coating, spray coating, or roll coating. When the temporary bonding composition contains a solvent, the temporary bonding composition is preferably applied as a layer and then dried. Drying conditions depend on the type of the temporary bonding composition and the thickness of the temporary bonding agent layer. Drying conditions preferably include, for example, 60 to 220 °C
25 for 10 to 600 seconds. The drying temperature is more preferably 80 to 200 °C. The drying period is more preferably 30 to 500 seconds, even more preferably 40 to 400 seconds. Drying may take place by stepwise increasing the temperature in two steps. For example, the drying steps comprise heating at 90 to 130 °C for 30 seconds to 250 seconds, and then heating at 170 to 220 °C for 30 seconds to 250 seconds.

30 **[0037]** Although the temporary bonding composition is provided on the surface of the carrier 4 in Figure 1b, the temporary bonding agent layer 5 may be formed on the surface of an extra layer provided on the surface of the carrier 4.

Examples of extra layers include a release layer and a separation layer. In a preferred embodiment of the present invention, the temporary bonding agent layer 5 is provided on the surface of the carrier 4.

[0038] Although the temporary bonding composition is applied on the carrier in Figure 1b, the temporary bonding composition may be applied on the surface of the wafer on the side having the convex parts and/or concave parts in an alternative embodiment. In the present invention, it is preferably applied on the carrier.

[0039] Then, the wafer having the convex parts and/or concave parts 3 of which main component is a metal (preferably copper) and/or convex parts, on the surface of the wafer substrate, is applied in such a manner that the side having the convex parts and/or concave parts 3 adjoin the temporary bonding agent layer 5 to form a laminate, as shown in Figure 1c. More preferably, the laminate can be prepared by bonding the wafer, the carrier and the temporary bonding agent layer under heat and pressure. Pressure bonding conditions preferably include, for example, a temperature of 100 to 230 °C, and a pressure of 0.01 to 1 MPa for a period of 1 to 15 minutes.

[0040] If the temporary bonding agent layer has been applied on the surface of the wafer, the carrier is applied on the temporary bonding agent layer on the side opposite to the surface adjoining the wafer to form a laminate. In the latter case, the temporary bonding agent layer and the carrier may adjoin each other or may be mediated by an extra layer. Examples of extra layers include a release layer and a separation layer.

[0041] In a more preferred embodiment of the present invention, the temporary bonding agent layer 5 is provided on the surface of the carrier 4 and laminated with the wafer. Further, the temporary bonding agent layer may be provided in a single layer or two or more layers, preferably a single layer.

[0042] After heating, the substrate 2 of the wafer, i.e., the side of the wafer opposite to the side adjoining the temporary bonding agent layer 5 is thinned, as shown in Figure 1d (22 in Figure 1d). Thinning takes place by at least one of a mechanical process or a chemical process. The mechanical process and chemical process are not specifically limited, but preferably include, for example, thinning processes such as grinding and chemical mechanical polishing (CMP); high temperature vacuum processes such as chemical vapor deposition (CVD) and physical vapor deposition

(PVD); processes using chemicals such as organic solvents, and acidic or basic treatment solutions; plating; irradiation with active rays; heating/cooling processes; and the like.

[0043] The thickness of the substrate of the wafer after thinning is preferably less than 500 μm , more preferably 1 to 200 μm in average.

[0044] Then, the laminate shown in Figure 1d is heated at a temperature higher than 170 °C. The lower limit of the heating temperature is preferably 175 °C or more, more preferably 180 °C or more, even more preferably more than 180 °C, further more preferably 185 °C or more. The upper limit of the heating temperature is more preferably 300 °C or less. Metal oxides (preferably copper oxides) formed on the surfaces of the convex parts can be removed more effectively by selecting such ranges.

[0045] The heating period is preferably 30 seconds or more, more preferably 1 minute or more, even more preferably 30 minutes or more after the heating temperature has been reached. The upper limit of the heating period is not specifically limited, but preferably 5 hours or less, more preferably 1 hour or less after the heating temperature has been reached.

[0046] Although this embodiment comprises thinning the substrate of the wafer followed by heating at the temperature higher than 170 °C, an alternative embodiment comprises heating at the temperature higher than 170 °C followed by thinning the substrate of the wafer.

[0047] After heating, the carrier 4 is separated from the laminate, as shown in Figure 1e. Separation may take place by applying a force or by using a release layer or a separation layer as described above. Examples of release layers and separation layers include layers that are dissolved in solvents, layers that are separated by irradiation and the like. In the present invention, separation preferably takes place by applying a force. In other words, separation preferably takes place by pulling up an edge of the carrier 4 in a direction perpendicular to the thinned wafer 22 without any additional process. In this case, separation also preferably takes place after making a slit between the carrier 4 and the temporary bonding agent layer 5 with a knife or the like. In the present invention, the carrier 4 and the temporary bonding agent layer 5 are preferably separated at the interface there between. Specifically, the separation strength A at the interface between the carrier 4 and the temporary bonding agent layer 5 and the

separation strength B between the surface of the wafer having the convex parts and/or concave parts and the temporary bonding agent layer 5 preferably satisfy the following relation:

$$A < B \quad \cdots \cdots \text{formula (1)}.$$

- 5 The separation speed is preferably 30 to 70 mm/min, more preferably 40 to 60 mm/min. Separation preferably takes place at 40 °C or less, more preferably in the range of 10 to 40 °C.

[0048] After the carrier 4 has been separated from the laminate, the thinned wafer 22 having the temporary bonding agent layer 5 on the surface of the
10 thinned wafer is preferably transferred to a support 6, as shown in Figure 1f. Examples of the support 6 include a dicing tape, a back grinding tape and the like. However, it should be understood that it may be subjected to subsequent steps without being transferred to the support 6 or the like.

[0049] Then, the temporary bonding agent layer 5 is peeled off from the
15 thinned wafer 22 having the temporary bonding agent layer 5 on the surface of the thinned wafer, as shown in Figure 1g. It may be peeled off by any means not specifically limited, e.g., mechanically or by hand. Peeling preferably takes place at 40 °C or less, more preferably in the range of 10 to 40 °C.

[0050] Although the temporary bonding agent is shown as a layer in
20 Figure 1g, it should be understood that the temporary bonding agent may not necessarily be peeled off in the form of a layer within the scope of the present invention.

[0051] Preferably, the temporary bonding agent layer 5 is peeled off at an angle of 60° to 180° with respect to the surface of the substrate of the wafer (the angle α in Figure 1g). At such an angle, it can be successfully peeled off with a smaller force.
25 This also helps the temporary bonding agent layer to be peeled off while it remains in the form of a layer. Examples of peeling means include peeling by hand, mechanical peeling and the like. The peeling force depends on the bonding conditions and the like, but can be 10 to 135 N, for example. The lower limit of the peel angle α is preferably 90° or more. The upper limit of the angle α is preferably 150° or less.

30 **[0052]** Typically, the thinned wafer 22 used in the present invention comprises two or more rectangular semiconductor chips 7 having at least one of a convex part and a concave part, as shown in Figure 2. Thus, the convex parts exist

within the semiconductor chips 7. Further, the rectangular semiconductor chips are preferably arranged in such a manner that two opposite sides of one of the rectangular semiconductor chips are in parallel with two opposite sides of the other rectangular semiconductor chip(s). In the present invention, the temporary bonding agent layer is preferably peeled off at an angle of greater than 30° and less than 60° with respect to one side of the rectangle. Thus, it is preferably peeled off in the direction of angle β in Figure 2. The arrow in the figure indicates the direction in which the temporary bonding agent layer is peeled off. In such a direction, the temporary bonding agent can be peeled off with a smaller peeling force. This also helps the temporary bonding agent layer to be peeled off while it remains in the form of a layer.

[0053] More preferably, the peel angle is 40° or more and 50° or less with respect to one side of the rectangle of the rectangular semiconductor chips. The rectangle herein means not only to include a rectangle in a mathematical sense but also to allow for an error within an acceptable range in the technical field of the present invention. Further, the rectangle includes a square, and it is more preferably a square.

[0054] Figure 3 is a schematic diagram showing how a copper oxide is removed, in which Figure 3(a) shows that a film of a copper oxide 8 has been formed on the surface of a convex part 3 of a thinned wafer 22. Although the copper oxide 8 is shown as a film in Figure 3(a), it need not be in the form of a perfect film and may be partially oxidized copper. Then, a temporary bonding agent layer 5 is formed on the surface of the convex part 3 already having a film of the copper oxide 8 formed thereon in the present invention, as shown in Figure 3(b). Then, the temporary bonding agent layer 5 is heated at a temperature higher than 170°C , thereby producing an anchoring effect to improve the bonding force between the convex part 3 and the film of the copper oxide 8. The temporary bonding agent penetrates into fine irregularities of copper oxide by applying heat, the bonding force between the copper oxide and the temporary bonding agent layer is greater than the bonding force between the copper oxide and the convex parts. It is what is called an anchoring effect. As a result, the copper oxide 8 can be effectively removed when the temporary bonding agent layer 5 is peeled off (Figure 3(c)).

[0055] The device substrate obtained by the method described above is then diced into, for example, the individual rectangular semiconductor chips and

incorporated into semiconductor devices. Thus, the present invention also discloses a method for manufacturing a semiconductor device, comprising the method for manufacturing a device substrate described above.

5 [0056] Next, the temporary bonding composition used in the present invention is explained.

[0057] The temporary bonding composition used in the present invention comprises a thermoplastic resin and a compound containing a fluorine atom.

10 [0058] The temporary bonding composition used in the present invention comprises a compound containing a fluorine atom so that the compound containing a fluorine atom is readily concentrated in the near-surface region of the temporary bonding agent layer, whereby the concentration of the compound containing a fluorine atom near surface of the temporary bonding agent layer can be increased. As a result, the temporary bonding agent layer can be formed so that it is readily peelable from the wafer. Further, the heating step allows the temporary bonding agent layer to follow
15 even minute irregularities on the carrier or the wafer and to have high adhesiveness thanks to an appropriate anchoring effect.

[0059] Specifically, at least one of the abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer on the side of the carrier and the abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer
20 on the side of the wafer is preferably 10 to 35 %, more preferably 15 to 30 % when the abundance ratio of fluorine atoms on the surface is determined by irradiating a test area of 1400 μm x 700 μm on the surface of the temporary bonding agent layer with monochromatic Al K α rays at 25W and detecting photoelectrons at a take-off angle of 45°.

25 [0060] <<Compound containing a fluorine atom>>

The temporary bonding composition used in the present invention comprises a compound containing a fluorine atom. The compound containing a fluorine atom is preferably a fluorine-based liquid form compound, herein defined as a compound that is in liquid form at 25°C. According to an embodiment, the fluorine-based liquid form
30 compound has a viscosity between 1 mPa·s and 100.000 mPa·s at 25°C. The viscosity at 25°C of the compound containing a fluorine atom is more preferably 10 mPa·s to 20.000 mPa·s, and even more preferably 100 mPa·s to 15.000 mPa·s.

[0061] The compound containing a fluorine atom that can preferably be used in the present invention may be either an oligomer or a polymer. Further, it may be a mixture of an oligomer and a polymer. Such a mixture may further comprise a monomer. Further, the compound containing a fluorine atom may also be a monomer.

5 [0062] The compound containing a fluorine atom is preferably an oligomer, a polymer or a mixture thereof to improve heat resistance or the like. Oligomers and polymers include, for example, radical polymers, cationic polymers, anionic polymers and the like, any of which can preferably be used. Vinyl polymers are especially preferred.

10 [0063] In the present invention, the compound containing a fluorine atom is preferably a compound that is not denatured during processing the wafer or the carrier to be temporarily bonded. For example, it is preferably a compound that can exist as a liquid after heating at 250 °C or more or after the wafer has been treated with various chemicals. As a specific example, it preferably has a viscosity of 1 to 100.000 mPa.s,
15 more preferably 10 to 20.000 mPa.s, even more preferably 100 to 15.000 mPa.s at 25 °C after heating from 25 °C to 250 °C under heating conditions of 10 °C/min and then cooling to 25 °C.

[0064] Preferably, the compound containing a fluorine atom having such properties is a non-thermosetting compound containing no reactive group. The reactive
20 group here refers to a group that reacts upon heating at 250 °C in general, including polymerizable groups, hydrolysable groups and the like. Specifically, they include, for example, meth(acryl), epoxy, isocyanato and the like groups.

[0065] Further, the compound containing a fluorine atom preferably has a
10 % mass reduction temperature of 250 °C or more, more preferably 280 °C or more
25 when it is heated from 25 °C at a rate of 20 °C/min. The upper limit is not specifically limited, but preferably 1000 °C or less, more preferably 800 °C or less, for example. According to this embodiment, a temporary bonding agent layer having high heat resistance is readily formed. As used herein, the mass loss temperature refers to the value measured by a thermogravimetric analyzer (TGA) in a stream of nitrogen gas
30 under the heating conditions indicated above.

[0066] Preferably, the compound containing a fluorine atom used in the present invention contains a lipophilic group. The lipophilic group may be a straight-chain or branched alkyl group, a cycloalkyl group, an aromatic group or the like.

[0067] The compound containing a fluorine atom may be a compound
5 containing only one lipophilic group or two or more lipophilic groups. Further, the lipophilic group may contain a fluorine atom. Thus, the compound containing a fluorine atom in the present invention may be a compound containing a fluorine atom only in a lipophilic group. Alternatively, it may be a compound further comprising a group containing elemental fluorine (also referred to as a fluorine group) in addition to a
10 lipophilic group. Preferably, it is a compound containing a lipophilic group and a fluorine group. When the compound containing a fluorine atom is a compound containing a lipophilic group and a fluorine group, the lipophilic group may or may not contain a fluorine atom, but preferably does not contain a fluorine atom.

[0068] The compound containing a fluorine atom contains one or more
15 lipophilic groups, preferably 2 to 100 lipophilic groups, especially preferably 6 to 80 lipophilic groups in one molecule.

[0069] Fluorine groups that can be used include known fluorine groups. For example, they include fluorine-containing alkyl groups, fluorine-containing alkylene groups and the like. It should be noted that fluorine groups that function as
20 lipophilic groups are included in lipophilic groups.

[0070] The compound containing a fluorine atom preferably contains 1 to 90 % by mass, more preferably 2 to 80 % by mass, even more preferably 5 to 70 % by mass of fluorine atoms. If the fluorine content is in the ranges indicated above, high peelability is achieved.

25 [0071] The content of fluorine atoms is defined as “{(the number of fluorine atoms in one molecule x the mass of a fluorine atom) / the mass of all atoms in one molecule} x 100”.

[0072] Suitable examples of commercially available compounds containing a fluorine atom include F-251, F-281, F-477, F-552, F-553, F-554, F-555, F-
30 556, F-557, F-558, F-559, F-560, F-561, F-562, F-563, F-565, F-567, F-568, F-569, F-571, R-40, R-41, R-43, and R-94 of the Megaface® series manufactured by DIC Corporation.

[0073] The amount of the compound containing a fluorine atom in the temporary bonding composition used in the present invention is preferably 0.01 to 10 % by mass, more preferably 0.02 to 5 % by mass based on the mass of the temporary bonding composition excluding the solvent. When the amount of the compound
5 containing a fluorine atom is in the ranges indicated above, high adhesiveness and peelability are achieved. Only one compound containing a fluorine atom or a combination of two or more compounds containing a fluorine atom may be used. When two or more such compounds are used in combination, the total amount should preferably be in the ranges indicated above.

10 [0074] <<Elastomer>>

The thermoplastic resin contained in the temporary bonding composition used in the present invention is preferably an elastomer. The use of an elastomer allows the temporary bonding agent layer to follow even convex parts and/or concave parts in the wafer and to have high adhesiveness thanks to an appropriate anchoring effect. Further,
15 the carrier can be suitably separated from the thinned wafer or the temporary bonding agent can be suitably peeled off from the thinned wafer without any stress on the thinned wafer, whereby the semiconductor chips or the like on the wafer can be prevented from breakage or dropping.

[0075] As used herein, the elastomer refers to a polymer compound that
20 exhibits elastic deformation. In other words, it is defined as a polymer compound having the property of instantaneously deforming in response to an external force once the external force is applied and rapidly restoring the original shape when the external force is removed.

[0076] The elastomer preferably has a weight average molecular weight of
25 2.000 to 200.000, more preferably 10.000 to 200.000, even more preferably 50.000 to 100.000. When it is in the ranges indicated above, the elastomer has high solubility in solvents, thereby improving coatability.

[0077] In the present invention, the elastomer is not specifically limited, and examples include block copolymers, random copolymers, and graft copolymers,
30 among which block copolymers are preferred.

[0078] Types of elastomers that can be used include elastomers containing a repeating unit derived from styrene (polystyrene elastomers), polyester elastomers,

polyolefin elastomers, polyurethane elastomers, polyamide elastomers, polyacrylate elastomers, silicone elastomers, polyimide elastomers and the like. Especially, polystyrene elastomers, polyester elastomers, and polyamide elastomers are preferred, among which polystyrene elastomers are most preferred because of heat resistance and peelability.

[0079] In the present invention, the elastomer is preferably a hydrogenated product. Especially, it is preferably a hydrogenated product of a polystyrene elastomer. If the elastomer is a hydrogenated product, heat stability and storage stability improve. Moreover, peelability improves. The hydrogenated product here refers to a polymer consisting of a hydrogenated elastomer.

[0080] Preferably, the elastomer has a 5 % mass reduction temperature of 250 °C or more, more preferably 300 °C or more, even more preferably 350 °C or more, most preferably 400 °C or more when it is heated from 25 °C at a rate of 20 °C/min. The upper limit is not specifically limited, but preferably 1000 °C or less, more preferably 800 °C or less, for example. According to this embodiment, a temporary bonding agent layer having high heat resistance is readily formed.

[0081] Assuming that the initial size is 100 %, the elastomer used in the present invention preferably has the property of deforming to up to 200 % with a small external force at room temperature (20 °C) and rapidly returning to 130 % or less when the external force is removed.

[0082] <<<Polystyrene elastomer>>>

The polystyrene elastomer is not specifically limited, and can be appropriately selected depending on the purpose. For example, such elastomers include styrene-butadiene-styrene (SBS) block copolymers, styrene-isoprene-styrene (SIS) block copolymers, styrene-ethylene-butylene-styrene (SEBS) block copolymers, styrene-butadiene-butylene-styrene (SBBS) copolymers and hydrogenated products thereof; styrene-ethylene-butylene-styrene (SEBS) block copolymers, styrene-ethylene-propylene-styrene (SEPS) block copolymers, styrene-ethylene-ethylene-propylene-styrene block copolymers and the like.

[0083] The amount of the repeating unit derived from styrene contained in the polystyrene elastomer is preferably 10 to 90 % by mass. To improve peelability, the lower limit is preferably 25 % by mass or more, more preferably 51 % by mass or more.

[0084] The polystyrene elastomer is preferably a block copolymer of styrene and another resin, more preferably a block copolymer having a styrene block at one or both terminals, especially preferably a block copolymer having a styrene block at both terminals. If the polystyrene elastomer is a block copolymer having a styrene
5 block (a repeating unit derived from styrene) at one or both terminals, heat stability tends to further improve. This is because a repeating unit derived from styrene having high heat resistance is present at a terminal. Especially, block moieties of the repeating unit derived from styrene are preferably reactive hard polystyrene blocks because heat resistance and chemical resistance tend to be better. Block copolymers comprising
10 these blocks seem to undergo phase separation into hard and soft blocks at 200 °C or more. The morphology of the phase-separated block copolymers seems to contribute to reduced surface roughness of substrates of wafers. In addition, such resins are also more preferred in terms of solubility in solvents and resistance to resist solvents.

[0085] If the polystyrene elastomer is a hydrogenated product, stability to
15 heat improves and denaturation such as degradation or polymerization or the like is less likely to occur. Further, this is also more preferred in terms of solubility in solvents and resistance to resist solvents.

[0086] The amount of unsaturated double bonds in the polystyrene elastomer is preferably less than 15 mmol, more preferably less than 5 mmol, most
20 preferably less than 0.5 mmol per gram of the polystyrene elastomer to improve peelability after the heating step. It should be noted that the amount of unsaturated double bonds here does not include unsaturated double bonds in benzene rings derived from styrene. The amount of unsaturated double bonds can be calculated by nuclear magnetic resonance (NMR) spectroscopy.

[0087] As used herein, the “repeating unit derived from styrene” refers to a structural unit derived from styrene contained in a polymer obtained by polymerizing styrene or a styrene derivative and optionally substituted. Examples of the styrene derivative include -methylstyrene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, and the like. Examples of the substituent include an alkyl group
25 having 1 to 5 carbon atoms, an alkoxy group having 1 to 5 carbon atoms, an alkoxyalkyl group having 1 to 5 carbon atoms, an acetoxyl group, a carboxyl group, and the like.

[0088] Suitable polystyrene based elastomers which are commercially available are TufpreneTM A, TufpreneTM 125, TufpreneTM 126S, SolpreneTM T, AsapreneTM T-411, AsapreneTM T-432, AsapreneTM T-437, AsapreneTM T-438, AsapreneTM T-439, TuftecTM H1272, TuftecTM P1500, TuftecTM H1043, TuftecTM H1052, TuftecTM H1062, TuftecTM M1943, TuftecTM P2000, SeptonTM 1001, SeptonTM 8004, SeptonTM 4033, SeptonTM S2104.

[0089] The amount of the thermoplastic resin (preferably elastomer) contained in the temporary bonding composition used in the present invention is preferably 50,00 to 99,99 % by mass, more preferably 70,00 to 99,99 % by mass, especially preferably 88,00 to 99,99 % by mass based on the mass of the temporary bonding composition excluding the solvent. When the thermoplastic resin (preferably elastomer) is contained in an amount in the ranges indicated above, high adhesiveness and peelability are achieved.

[0090] Further, a combination of multiple types of elastomers may be contained in the temporary bonding composition used in the present invention.

[0091] Further, the temporary bonding composition used in the present invention preferably comprises a compound containing a fluorine atom and a thermoplastic resin (preferably elastomer) in a mass ratio of the compound containing a fluorine atom to the thermoplastic resin (preferably elastomer) of 0,001:99,999 to 10:90,00, more preferably 0,001:99,999 to 5:95,00, even more preferably 0,010:99,99 to 5:95,00.

[0092] Preferably, the temporary bonding composition of the present invention contains a solvent. When a bonding layer is formed from the temporary bonding composition of the present invention by coating, a solvent is preferably contained. Known solvents can be used without limitation, among which organic solvents are preferred. Suitable solvents are for example esters such as ethyl acetate, acetic acid-n-butyl, isobutyl acetate, amyl formate, ethers such as diethylene glycol dimethyl ether, tetrahydrofuran, ethylene glycol monomethyl ether, or hydrocarbon such as mesitylene. In addition to those listed above, other organic solvents can be found in paragraphs 0122 and 0123 of JP-A2014-189731, the disclosure of which is incorporated herein by reference.

[0093] When the temporary bonding composition contains a solvent, the amount of the solvent contained in the temporary bonding composition should preferably be selected in such a manner that the total solids content of the temporary bonding composition equals 5 to 80 % by mass, more preferably 5 to 70 % by mass, especially preferably 10 to 60 % by mass to improve coatability.

[0094] A single solvent may be used or two or more solvents may be used. When two or more solvents are used, the total amount should preferably be in the ranges indicated above.

[0095] In addition to the compound containing a fluorine atom or in place of the compound containing a fluorine atom, the temporary bonding composition used in the present invention may comprise a compound containing a silicon atom. The compound containing a silicon atom is preferably liquid at 25 °C.

[0096] Further, the temporary bonding composition used in the present invention may contain antioxidants, surfactants, polymerizable compounds, solvents and the like. Detailed information about these components can be found in JP-A2014-189731, the disclosure of which is incorporated herein by reference.

[0097] Example
The present invention will further be detailed below referring to Examples. Materials, amount of use, ratio, details of processes, procedures of process and so forth described in Examples below may be modified arbitrarily, without departing from the spirit of the present invention. Accordingly, the scope of the present invention should not be construed to be limited by Examples below.

[0098] <Preparation of temporary bonding compositions>
The following components were mixed into homogeneous solutions and then filtered through a polytetrafluoroethylene filter having a pore size of 5 µm to prepare compositions of Examples and Comparative examples.

[Table 1]

	Resin		Compound containing a fluorine atom		Solvent		Heating temperature	Peel angle (α)	Peel angle (β)
	Kind	Parts by mass	Kind	Parts by mass	Kind	Parts by mass	Unit : °C	Unit : °	Unit : °
Example 1	P-1	27.9	F-1	0.1	Mesitylene	72	200	90	45
Example 2	P-2	29.9	F-4	0.1	Mesitylene	70	200	90	45
Example 3	P-3	29.9	F-3	0.1	Mesitylene	70	200	90	45
Example 4	P-1	27.9	F-1	0.1	Mesitylene	72	200	75	45
Example 5	P-1	27.9	F-1	0.1	Mesitylene	72	200	160	45
Example 6	P-1	27.9	F-1	0.1	Mesitylene	72	200	90	35
Example 7	P-1	27.9	F-1	0.1	Mesitylene	72	200	90	55
Example 8	P-1	27.9	F-1	0.1	Mesitylene	72	180	90	45
Example 9	P-1	28.0	F-1	0.05	Mesitylene	72	200	90	45
Example 10	P-1	28.0	F-1	0.03	Mesitylene	72	200	90	45
Example 11	P-1	27.9	F-2	0.1	Mesitylene	72	200	90	45
Example 12	P-1	27.9	F-3	0.1	Mesitylene	72	200	90	45
Example 13	P-1	27.9	F-4	0.1	Mesitylene	72	200	90	45
Example 14	P-1	27.9	F-5	0.1	Mesitylene	72	200	90	45
Example 15	P-1	27.9	F-1	0.1	Mesitylene	72	200	45	45
Example 16	P-1	27.9	F-1	0.1	Mesitylene	72	200	200	45
Example 17	P-1	27.9	F-1	0.1	Mesitylene	72	200	90	25
Example 18	P-1	27.9	F-1	0.1	Mesitylene	72	200	90	70
Comparative Example 1	P-1	27.9	F-1	0.1	Mesitylene	72	170	90	45
Comparative Example 2	P-1	28.0	F-1	0	Mesitylene	72	200	90	45
Comparative Example 3	P-4	59.9	F-1	0.1	Mesitylene	40	200	90	45

<<Make-up of temporary bonding compositions>>

- Each resin shown in Table 1: each amount in parts by mass shown in Table 1;
- Each compound containing a fluorine atom shown in Table 1: each amount in parts by mass shown in Table 1;

- 5 - Each solvent shown in Table 1: each amount in parts by mass shown in table 1. The compounds shown in Table 1 are as follows:

<Resins> as shown in Table 2.

[Table 2]

Resin			
Symbol	Product name	Manufacturer	Type
P-1	Septon S2104	Kuraray Co., Ltd.	Thermoplastic
P-2	Tuftec P2000	Asahi Kasei Chemicals Corporation	Thermoplastic
P-3	Tuftec H1043	Asahi Kasei Chemicals Corporation	Thermoplastic
P-4	JEK 871	Mitsubishi Chemical Corporation	Thermosetting

- 10 The resins P-1 to P-3 above exhibit a 5 % mass reduction temperature of 250 °C or more when they are heated from 25 °C at a rate of 20 °C/min.

<Compounds containing a fluorine atom> as shown in Table 3.

[Table 3]

Symbol	Product name	Manufacturer	Hydrolysable groups	Lipophilic group	Appearance (25°C)
F-1	Megafac F-553	DIC Corporation	Having	Having	Liquid
F-2	Megafac F-569	DIC Corporation	Not having	Having	Liquid
F-3	Megafac R-41	DIC Corporation	Having	Not having	Liquid
F-4	Megafac F-552	DIC Corporation	Not having	Having	Wax state
F-5	Megafac F-562	DIC Corporation	Having	Having	Powder

- 15 <Formation of a laminate>

On a 12-inch silicon wafer (a first wafer) having on its surface multiple rectangular semiconductor chips containing bumps therein was dripped 15 mL of each temporary bonding composition shown in Table 1 over 30 seconds while the wafer was spun at 50 rpm using a wafer bonder (XBS300 from SUSS MicroTec). The spin speed was

20 increased to 800 rpm and kept for 80 seconds. Then, the wafer was heated at 110 °C for 3 minutes, and further heated at 190 °C for 3 minutes to give a laminate 1 having a temporary bonding agent layer formed on the surface of the first wafer.

<Bonding of the laminate 1>

- A 12-inch silicon wafer (a second wafer) was bonded to the surface of the laminate 1 on
- 25 the side having the temporary bonding agent layer using a wafer bonder (XBS300 from

SUSS MicroTec) under vacuum at 190 °C and a pressure of 0.11 MPa for 3 minutes to give a laminate 2.

<Grinding of the laminate 2>

The surface of the first wafer of the laminate 2 on the side having no temporary bonding agent layer was grinded, to reduce the thickness, to 50 µm using the back grinder DFG 8540 (from DISCO Corporation) to give a laminate 3.

<Heating test of the laminate 3>

The laminate was heated on a hot plate for 60 minutes at each temperature shown in Table 1.

10 <Peeling after grinding>

The laminate 3 was bonded at the centre of a dicing tape together with a dicing frame using a dicing tape mounter with the grinded surface of the first wafer facing downward. Then, the second wafer was peeled off by pulling it up in a direction perpendicular to the substrate surface of the first wafer with a force of 50 mm/min at 25 °C using a wafer debonder (XBC300 Gen2 from SUSS MicroTec) to give a laminate 4 having the temporary bonding agent layer left on the surface of the first wafer.

[0099] Evaluation

<Determination of the abundance ratio of fluorine atoms>

The abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer was determined by Electron Spectroscopy for Chemical Analysis (ESCA).

After the second wafer was separated from the laminate 1, the abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer on the side deprived of the second wafer was determined by irradiating a test area of 1400 µm x 700 µm on the surface of the temporary bonding agent layer with monochromatic Al Kα rays at 25W and detecting photoelectrons at a take-off angle of 45°. The results were reported in %.

<Evaluation of the peeling force>

The temporary bonding agent layer left on the laminate 4 was pulled up at a rate of 50 mm/min while keeping the peel angle (α) and the peel angle (β) shown in Table 1, and the maximum value of the force imparted during then was measured using a force gauge (DS2-200N from IMADA CO., LTD.), and evaluated according to the following criteria.

The peel angle (α) here refers to the peel angle of the temporary bonding agent layer with respect to the substrate surface of the first wafer (the angle α in Figure 1g). On the other hand, the peel angle (β) refers to the peel angle with respect to one side of each rectangle on the surface of the first wafer (the angle β in Figure 2).

- 5 A: 62.5 N or more and 100 or less;
 B: 10 N or more and less than 62.5 N, or greater than 100 N and 135 N or less;
 C: less than 10 N, or greater than 135 N.

<Evaluation of the removal of copper oxides>

- 10 The surfaces of bumps after peeling in the evaluation of the peeling force described above were observed using a light microscope (model MX51, magnification 100x from Olympus Corporation), and the removal of copper oxides was evaluated according to the following criteria.

- A: Copper oxides have been removed, and metallic luster could be observed on the bumps on the entire surface of the wafer.
- 15 B: Copper oxides have been removed but incompletely, and metallic luster was not observed on some bumps on the wafer.
- C: Copper oxides have not been removed, and metallic luster was not observed on any bumps on the entire surface of the wafer.
- D: Copper oxides have not been removed, and residues of the temporary bonding agent
- 20 were rather observed in parts of the wafer

The evaluation results are summarized in Table 4.

[Table4]

	Abundance ratio of fluorine atoms	Peeling force	Removability of copper oxides
	Unit %		
Example 1	30	A	A
Example 2	26	B	B
Example 3	27	B	B
Example 4	29	B	A
Example 5	30	B	A
Example 6	30	B	A
Example 7	30	B	A
Example 8	30	A	B
Example 9	26	A	A
Example 10	14	B	A
Example 11	28	A	A
Example 12	22	B	B
Example 13	24	B	B
Example 14	23	B	B
Example 15	29	B	A
Example 16	30	B	A
Example 17	31	B	A
Example 18	31	B	A
Comparative Example 1	30	A	D
Comparative Example 2	0	C	D
Comparative Example 3	27	C	D

It was shown from the results described above that copper oxides can be removed by the peeling method of the present invention (Examples 1 to 18). Moreover, peeling could be achieved with a reasonable peeling force. However, copper oxides could not be removed when the heating temperature was 170 °C or less (Comparative example 1). Copper oxides could not be removed, either, when the temporary bonding composition did not comprise a compound containing a fluorine atom (Comparative example 2) or a thermoplastic resin (Comparative example 3). Moreover, peelability was also insufficient.

[00100] While the invention has been illustrated and described in detail in the drawings and foregoing description, such illustration and description are to be considered illustrative or exemplary and not restrictive. Other variations to the disclosed embodiments can be understood and effected by those skilled in the art in practicing the claimed invention, from a study of the drawings, the disclosure and the appended claims. In the claims, the word “comprising” does not exclude other elements or steps, and the indefinite article “a” or “an” does not exclude a plurality. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage. Any reference signs in the claims should not be construed as limiting the scope.

CLAIMS

1. A method for manufacturing a device substrate, comprising:
 - applying a temporary bonding composition comprising a thermoplastic resin and a
5 compound containing a fluorine atom on a carrier to form a temporary bonding
agent layer; and applying a wafer having at least one of convex parts and concave
parts of which main component is copper on a surface of the temporary bonding
agent layer on the side opposite to the carrier in such a manner that the side having
the at least one of convex parts and concave parts adjoins the temporary bonding
10 agent layer to form a laminate; or
 - applying a temporary bonding composition comprising a thermoplastic resin and a
compound containing a fluorine atom on a surface of a wafer having, on its surface,
at least one of convex parts and concave parts of which main component is copper
on the side having the at least one of convex parts and concave parts to form a
15 temporary bonding agent layer; and applying a carrier on the temporary bonding
agent layer on the side opposite to the surface adjoining the wafer to form a
laminate; and
 - heating the laminate at a temperature higher than 170 °C, then separating the
carrier from the laminate, and further peeling off the temporary bonding agent.
- 20 2. The method for manufacturing a device substrate according to claim 1, wherein the
thermoplastic resin is an elastomer.
3. The method for manufacturing a device substrate according to claim 2, wherein the
elastomer has a 5 % mass reduction temperature of 250 °C or more when the
elastomer is heated from 25 °C at a rate of 20 °C/min.
- 25 4. The method for manufacturing a device substrate according to claim 2 or 3, wherein
the elastomer contains a repeating unit derived from styrene.
5. The method for manufacturing a device substrate according to any one of claims 2
to 4, wherein the elastomer is a block copolymer having a styrene block at one or
both terminals.
- 30 6. The method for manufacturing a device substrate according to any one of claims 1
to 5, wherein the compound containing a fluorine atom further contains a lipophilic
group.

7. The method for manufacturing a device substrate according to any one of claims 1 to 6, wherein the compound containing a fluorine atom is liquid at 25 °C.
8. The method for manufacturing a device substrate according to any one of claims 1 to 7, wherein at least one of an abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer on the side of the carrier and an abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer on the side of the wafer is 10 to 35 % when the abundance ratio of fluorine atoms on the surface of the temporary bonding agent layer is determined using Electron Spectroscopy for Chemical Analysis by irradiating a test area of 1400 μm x 700 μm on the surface of the temporary bonding agent layer with monochromatic Al K α rays at 25W and detecting photoelectrons at a take-off angle of 45°.
9. The method for manufacturing a device substrate according to any one of claims 1 to 8, wherein the temporary bonding agent layer is liquid at 25 °C and comprises a compound containing a silicon atom.
10. The method for manufacturing a device substrate according to any one of claims 1 to 9, wherein the carrier and the temporary bonding agent layer adjoin each other.
11. The method for manufacturing a device substrate according to any one of claims 1 to 10, wherein the surface of the laminate on the side of the wafer is subjected to at least one of a mechanical process and a chemical process after the laminate has been heated.
12. The method for manufacturing a device substrate according to any one of claims 1 to 11, wherein the peeled temporary bonding agent contains a copper oxide.
13. The method for manufacturing a device substrate according to any one of claims 1 to 12, comprising peeling off the temporary bonding agent layer at an angle of 60° to 180° with respect to the substrate surface of the wafer.
14. The method for manufacturing a device substrate according to any one of claims 1 to 13, wherein the wafer comprises two or more rectangular semiconductor chips having at least one of a convex part and a concave part and arranged in such a manner that two opposite sides of one of the rectangular semiconductor chips are in parallel with two opposite sides of the other rectangular semiconductor chip(s), and the temporary bonding agent layer is peeled off at an angle of greater than 30° and less than 60° with respect to one side of the rectangle.

15. A method for manufacturing a semiconductor device, comprising a method for manufacturing a device substrate according to any one of claims 1 to 14.

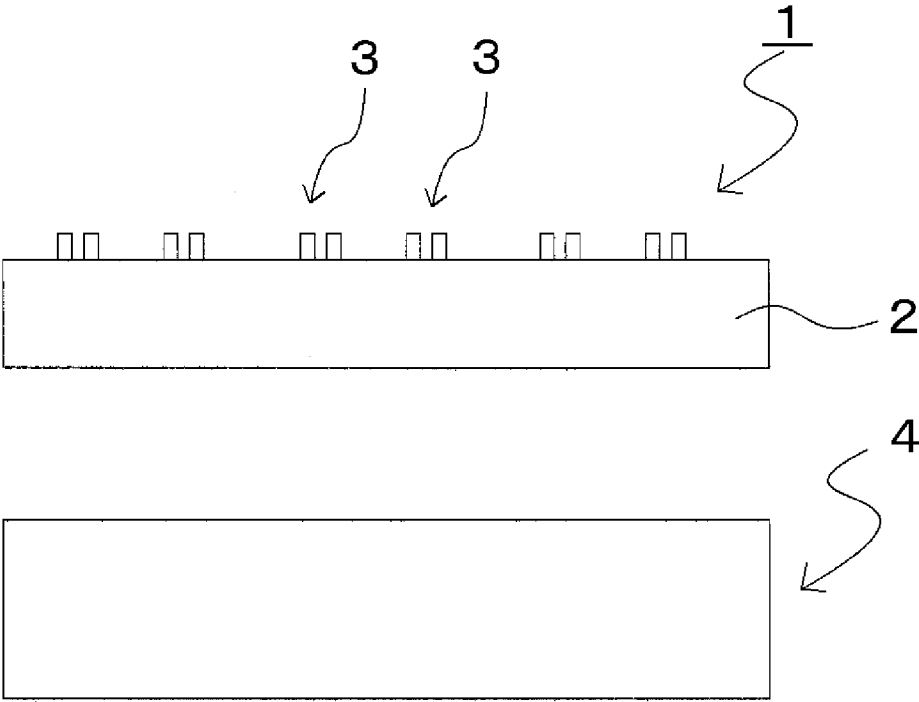


Figure 1a

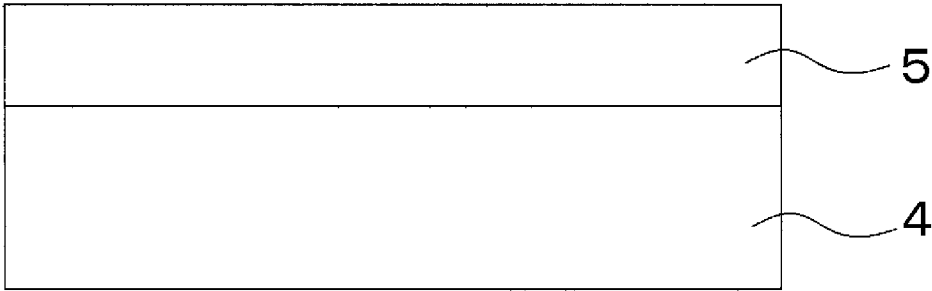


Figure 1b

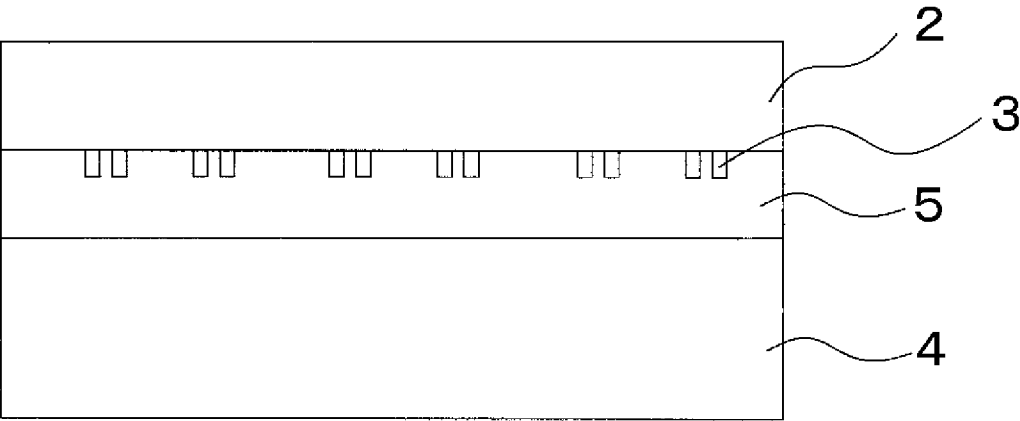


Figure 1c

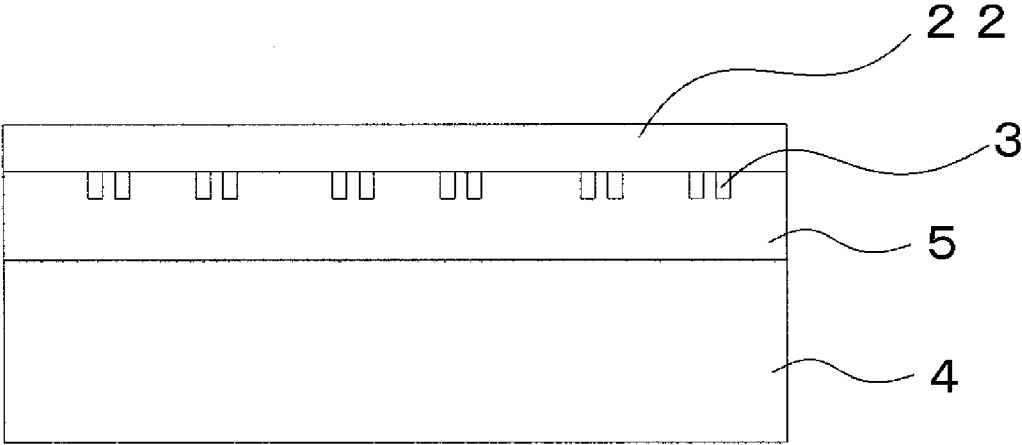


Figure 1d

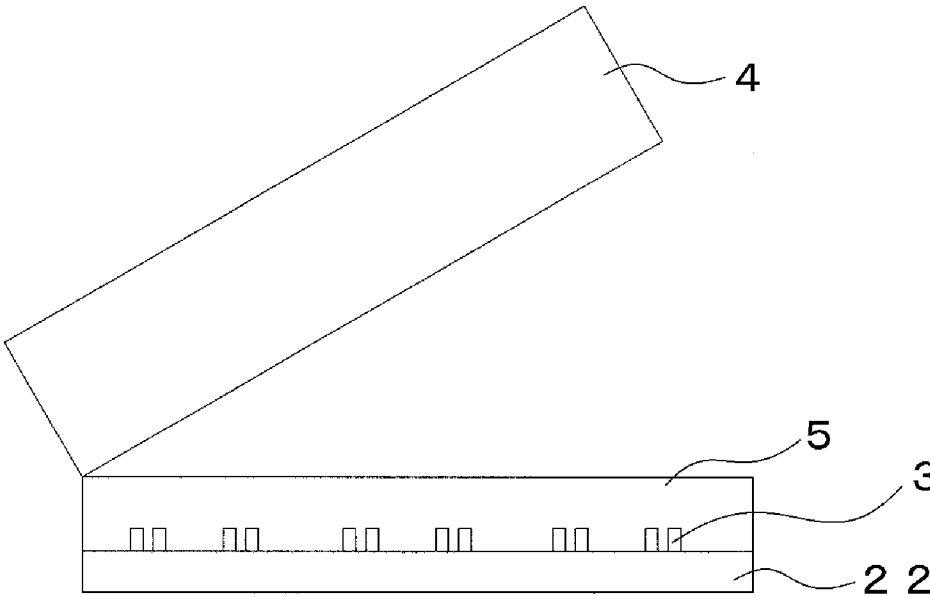


Figure 1e

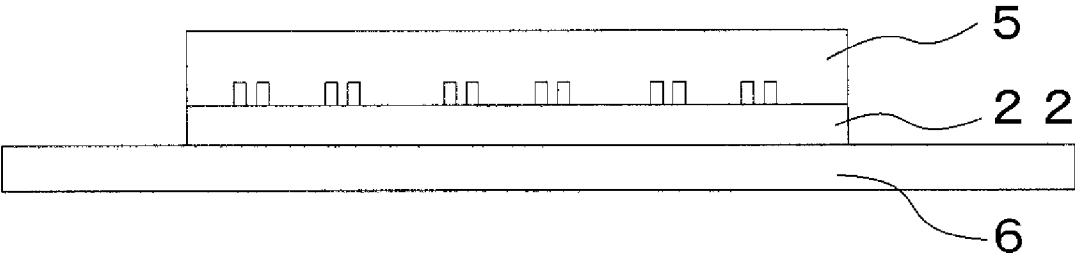


Figure 1f

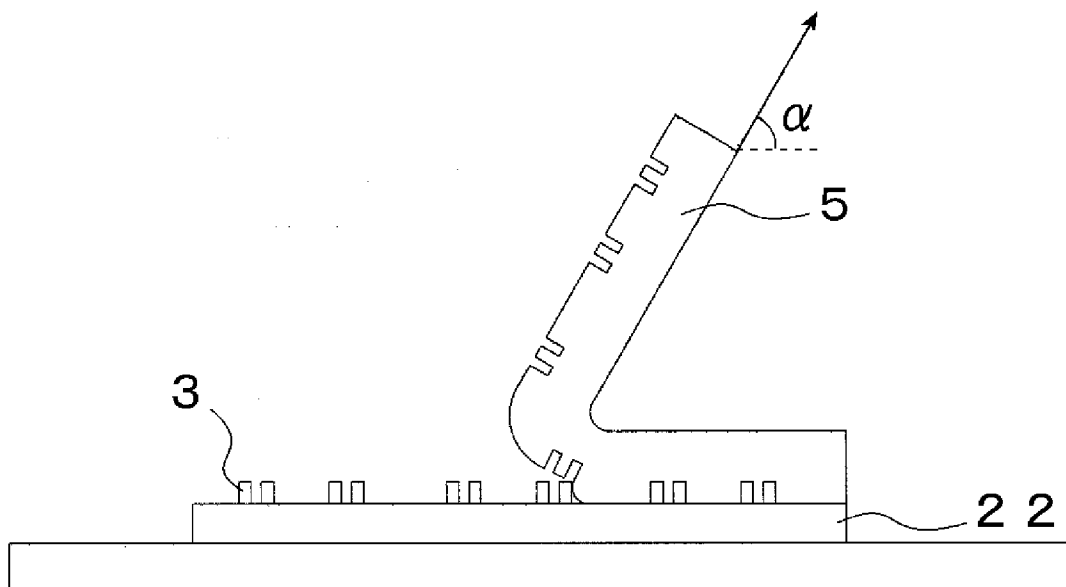


Figure 1g

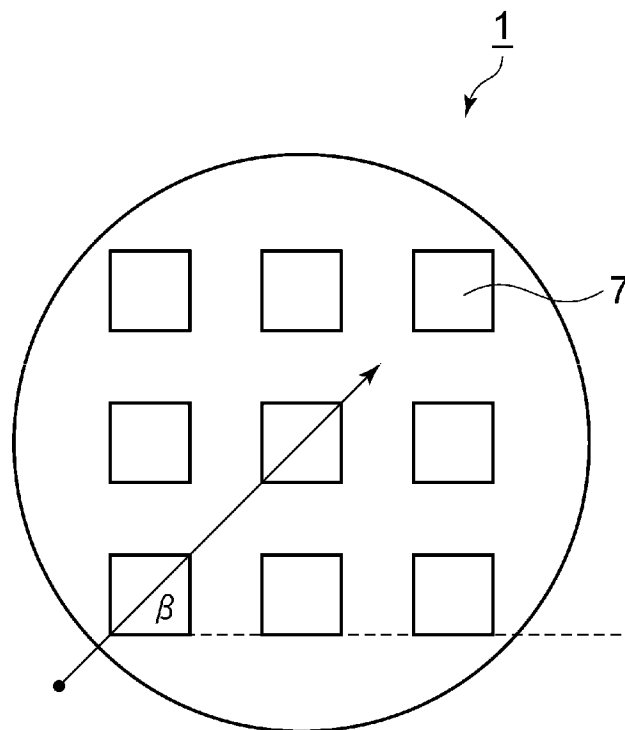


Figure 2

4/4

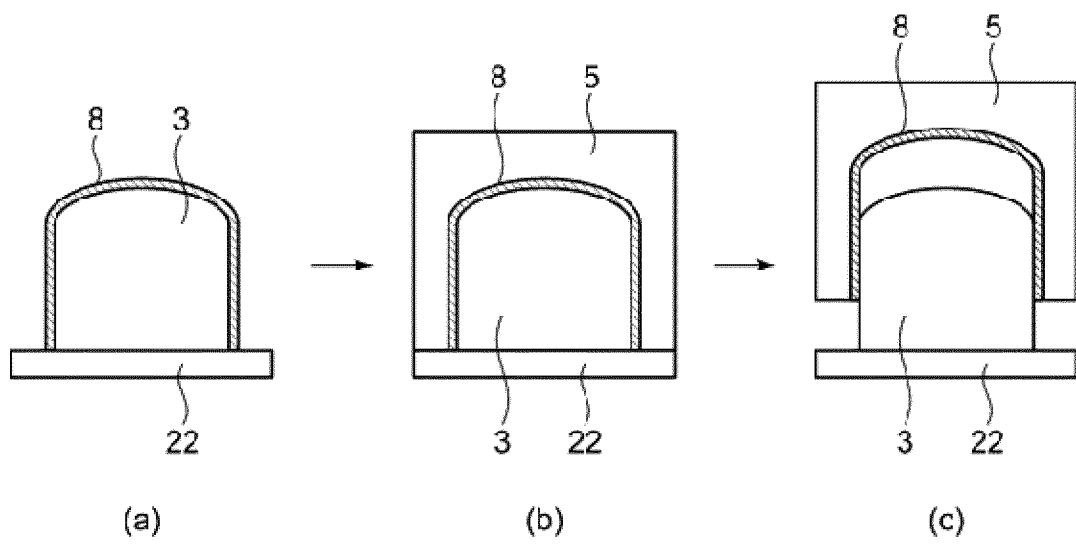


Figure 3

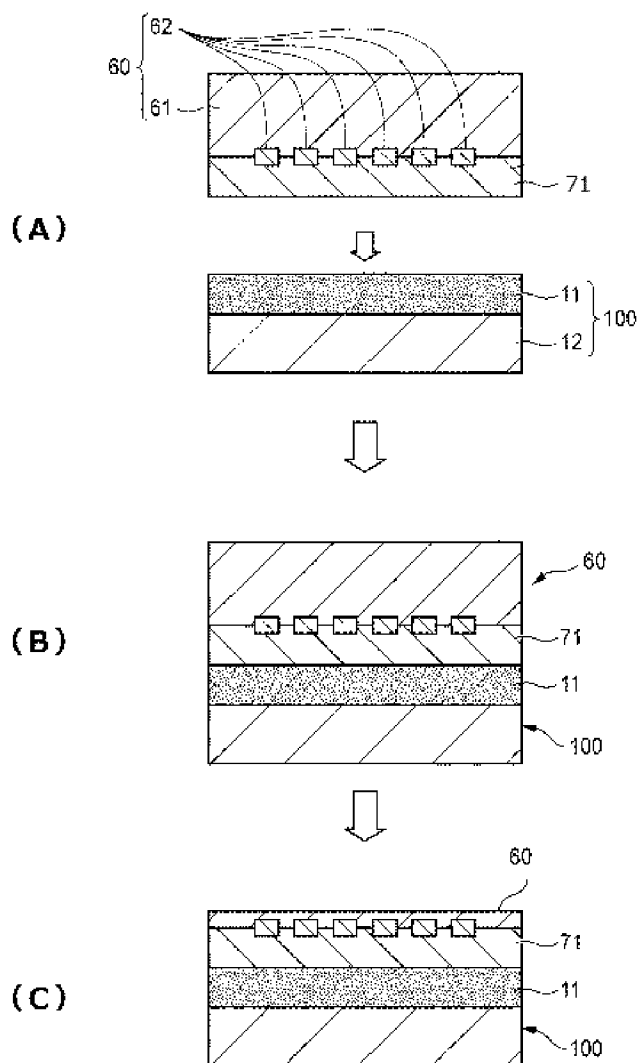


Figure 4

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/060264

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L21/683
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are 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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2014/147989 A1 (LUO SHIJIAN [US] ET AL) 29 May 2014 (2014-05-29) figures 4-6 paragraphs [0032] - [0034], [0036], [0039], [0046] - [0058] -----	1-5, 7-12, 15 6, 8
A	US 2015/122426 A1 (PULIGADDA RAMA [US] ET AL) 7 May 2015 (2015-05-07) paragraphs [0011], [0013] -----	1-15
A	US 2007/077728 A1 (KULKARNI SUDHAKAR N [US] ET AL) 5 April 2007 (2007-04-05) paragraphs [0014], [0021] -----	1-15
A	US 2011/290415 A1 (GEORGE GREGORY [US]) 1 December 2011 (2011-12-01) figure 6 paragraph [0028] -----	1-15
	- / - -	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 January 2016

Date of mailing of the international search report

18/01/2016

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

Crampin, Nicola

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/060264

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7 883 991 B1 (WU WEN-JIN [TW] ET AL) 8 February 2011 (2011-02-08) figures 2I-2J column 5, lines 4-16 -----	1-15
Y	US 2014/322893 A1 (TAN SHIRO [JP] ET AL) 30 October 2014 (2014-10-30) paragraphs [0359] - [0363] -----	6,8
A	US 2003/070517 A1 (TSUJIMOTO MASAKI [JP]) 17 April 2003 (2003-04-17) paragraphs [0032] - [0036] -----	14
A	US 2007/004177 A1 (NAKAMURA MASARU [JP] ET AL) 4 January 2007 (2007-01-04) figure 6 paragraphs [0010], [0013], [0015], [0017], [0037], [0038] -----	14
A	US 2014/335633 A1 (OKADA SHINJI [JP] ET AL) 13 November 2014 (2014-11-13) figures 2, 11 paragraphs [0001] - [0010], [0040], [0088] - [0094], [0098], [0099] -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/060264

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2014147989	A1	29-05-2014	NONE
US 2015122426	A1	07-05-2015	CN 103155100 A 12-06-2013
		CN 104022016 A 03-09-2014	
		EP 2601676 A2 12-06-2013	
		EP 2733734 A2 21-05-2014	
		JP 2013535838 A 12-09-2013	
		JP 2014158035 A 28-08-2014	
		KR 20130136975 A 13-12-2013	
		KR 20140039330 A 01-04-2014	
		SG 187739 A1 28-03-2013	
		SG 2014014922 A 30-07-2014	
		TW 201216342 A 16-04-2012	
		TW 201440136 A 16-10-2014	
		US 2012034437 A1 09-02-2012	
		US 2014174627 A1 26-06-2014	
		US 2014239453 A1 28-08-2014	
		US 2015122426 A1 07-05-2015	
		WO 2012057893 A2 03-05-2012	
US 2007077728	A1	05-04-2007	NONE
US 2011290415	A1	01-12-2011	EP 2577720 A2 10-04-2013
		US 2011290415 A1 01-12-2011	
US 7883991	B1	08-02-2011	CN 102163559 A 24-08-2011
		TW 201130022 A 01-09-2011	
		US 7883991 B1 08-02-2011	
US 2014322893	A1	30-10-2014	JP 2013211505 A 10-10-2013
		KR 20140112562 A 23-09-2014	
		TW 201347012 A 16-11-2013	
		US 2014322893 A1 30-10-2014	
		WO 2013129704 A1 06-09-2013	
US 2003070517	A1	17-04-2003	DE 10247547 A1 17-04-2003
		JP 2003124146 A 25-04-2003	
		SG 123540 A1 26-07-2006	
		TW 559880 B 01-11-2003	
		US 2003070517 A1 17-04-2003	
		US 2003203597 A1 30-10-2003	
US 2007004177	A1	04-01-2007	JP 4705418 B2 22-06-2011
		JP 2007012751 A 18-01-2007	
		US 2007004177 A1 04-01-2007	
US 2014335633	A1	13-11-2014	JP 5617065 B2 05-11-2014
		JP 2013058711 A 28-03-2013	
		TW 201334025 A 16-08-2013	
		US 2014335633 A1 13-11-2014	
		WO 2013035590 A1 14-03-2013	