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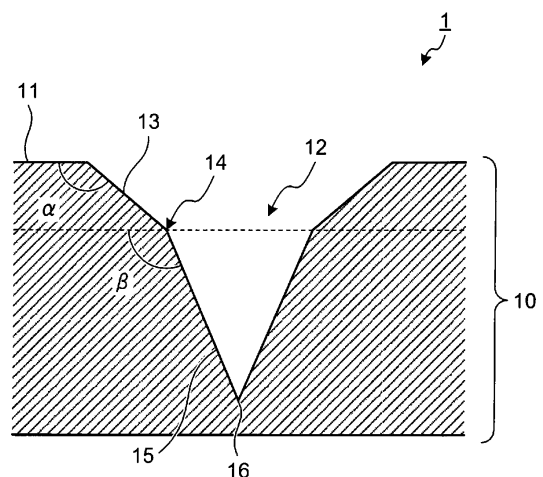
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(54) **POLISHING PAD**

(57) A polishing pad includes at least a polishing layer including a groove, on a polishing surface, having side surfaces, wherein at least one of the side surfaces includes a first side surface that extends continuously to the polishing surface and forms an angle α with the polishing surface, and a second side surface that extends continuously to the first side surface and forms an angle β with a plane parallel to the polishing surface, the angle α formed with the polishing surface is larger than 95 degrees, the angle β formed with the plane parallel to the polishing surface is larger than 95 degrees, and the angle β formed with the plane parallel to the polishing surface is smaller than the angle α formed with the polishing surface, and a bending point depth from the polishing surface to a bending point between the first side surface and the second side surface is more than 0.2 mm and not more than 3.0 mm.

FIG.1



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Description

Field

5 **[0001]** The present invention relates to a polishing pad. More particularly, the present invention relates to a polishing pad preferably used in order to form a flat surface in a semiconductor, a dielectric/metallic composite, an integrated circuit, and the like.

Background

10 **[0002]** As the density of a semiconductor device becomes higher, the importance of technologies such as multilayer wiring, and formation of interlayer insulating films and electrodes (such as a plug and a damascene structure) associated with the multilayer wiring is increasing. At the same time, the importance of planarization processes of the interlayer insulating films and the electrode metal films is increasing. As an efficient technology for the planarization processes, a polishing technology called CMP (Chemical Mechanical Polishing) is widespread.

15 **[0003]** The CMP apparatus generally includes a polishing head that holds a semiconductor wafer as a subject to be processed, a polishing pad for performing a polishing process of a subject to be processed, and a polishing platen that holds the polishing pad. In a polishing process of a semiconductor wafer using a slurry, a semiconductor wafer and a polishing pad move relative to each other, so that projections of a semiconductor wafer surface layer are removed to planarize the wafer surface layer. A pad surface is updated by dressing with a diamond dresser and the like for clogging prevention and setting.

20 **[0004]** Conventionally, there is known a technology to improve wafer flatness and a polishing rate by providing a groove that is arranged on a polishing layer surface and has a concentric circular pattern and a substantially rectangular cross-sectional shape (for example, see Patent Literature 1).

25 **[0005]** However, in this technology, corners in a cross-sectional shape of a groove and burr-like materials formed in the corners caused by dressings performed prior to, following to, or during polishing may sometimes cause generation of scratches. To solve this problem, there is disclosed a technology of providing an inclined surface at a boundary between a polishing surface and a groove (for example, see Patent Literatures 2 and 3).

Citation List

Patent Literature

[0006]

35 Patent Literature 1: Japanese Patent Application Laid-Open No. 2002-144219
 Patent Literature 2: Japanese Patent Application Laid-Open No. 2004-186392
 Patent Literature 3: Japanese Patent Application Laid-Open No. 2010-45306

Summary

Technical Problem

45 **[0007]** Here, the inventors have found that an inclined surface is provided at a boundary between a polishing surface and a groove, so that not only scratches are reduced, but also improvement in suction and slurry flow between a wafer and a polishing pad is developed to increase the polishing rate. However, the inventors have also found that variation of a polishing rate cannot be suppressed at some angle of the inclined surface. Furthermore, the inventors have also found that provision of such an inclined surface reduces a polishing surface area to increase a pad cut rate, resulting in shortened pad life.

50 **[0008]** In view of the above problems associated with conventional technologies, an object of the present invention is to provide a polishing pad that, among other polishing properties, has a long life and can suppress variation of a polishing rate while maintaining a high polishing rate.

Solution to Problem

55 **[0009]** The inventors considered that an inclination from a polishing surface to a groove bottom influences a pad cut rate, and that an angle at a boundary between a polishing surface and a groove influences a polishing rate. To balance them, the inventors considered that the problems could be solved by combining an angle at which a pad cut rate decreases

and an angle at which variation of a polishing rate decreases.

[0010] Therefore, the present invention employs the following means to solve the above problems. That is, a polishing pad includes at least a polishing layer, wherein the polishing layer includes a groove on a polishing surface, the groove having side surfaces, at least one of the side surfaces includes a first side surface that extends continuously to the polishing surface and forms an angle α with the polishing surface, and a second side surface that extends continuously to the first side surface and forms an angle β with a plane parallel to the polishing surface, the angle α formed with the polishing surface is larger than 95 degrees, the angle β formed with the plane parallel to the polishing surface is larger than 95 degrees, and the angle β formed with the plane parallel to the polishing surface is smaller than the angle α formed with the polishing surface, and a bending point depth from the polishing surface to a bending point between the first side surface and the second side surface is more than 0.2 mm and not more than 3.0 mm.

Advantageous Effects of Invention

[0011] According to the present invention, a polishing pad that has a long life and can suppress variation of a polishing rate while maintaining a high polishing rate can be provided.

Brief Description of Drawings

[0012]

FIG. 1 is a partial cross-sectional view illustrating a configuration of a main part of a polishing pad according to an embodiment of the present invention.

FIG. 2 is a partial cross-sectional view illustrating the configuration (second example) of a main part of a polishing pad according to an embodiment of the present invention.

FIG. 3 is a partial cross-sectional view illustrating the configuration (third example) of a main part of a polishing pad according to an embodiment of the present invention.

FIG. 4 is a partial cross-sectional view illustrating the configuration (fourth example) of a main part of a polishing pad according to an embodiment of the present invention.

Description of Embodiments

[0013] Embodiments for carrying out the present invention will be described below.

[0014] The inventors extensively studied a polishing pad that has a long life and can suppress variation of a polishing rate while maintaining a high polishing rate. As a result, the inventors found that the problem described above can be solved once for all by configuring a polishing pad having at least a polishing layer, wherein the polishing layer includes a groove on a polishing surface, and the groove has side surfaces; at least one of the side surfaces includes a first side surface that extends continuously from the polishing surface and forms an angle α with the polishing surface and a second side surface that extends continuously from the first side surface and forms an angle β with a plane parallel to the polishing surface; the angle α formed with the polishing surface is larger than 95 degrees, the angle β formed with the plane parallel to the polishing surface is larger than 95 degrees, and the angle β formed with the plane parallel to the polishing surface is smaller than the angle α formed with the polishing surface; and a bending point depth from the polishing surface to a bending point between the first side surface and the second side surface is more than 0.2 mm and not more than 3.0 mm.

[0015] In the present invention, the polishing pad preferably has at least a cushion layer in addition to the polishing layer. When a cushion layer is not provided, distortion caused by, for example, water absorption of the polishing layer cannot be buffered. Therefore, a polishing rate and in-plane uniformity of a material to be polished unstably vary. A distortion constant of the cushion layer is preferably not lower than $7.3 \times 10^{-6} \mu\text{m}/\text{Pa}$ and not higher than $4.4 \times 10^{-4} \mu\text{m}/\text{Pa}$. From a viewpoint of polishing rate variation and local flatness of a material to be polished, the upper limit of the distortion constant is preferably not higher than $3.0 \times 10^{-4} \mu\text{m}/\text{Pa}$, and more preferably not higher than $1.5 \times 10^{-4} \mu\text{m}/\text{Pa}$. Also, the lower limit of the distortion constant is preferably not lower than $1.0 \times 10^{-5} \mu\text{m}/\text{Pa}$, and more preferably not lower than $1.2 \times 10^{-5} \mu\text{m}/\text{Pa}$. When polishing rate variation is large, a polishing amount of a material to be polished varies. As a result, a film thickness of a material to be polished varies, thereby adversely affecting performance of a semiconductor device. Therefore, the polishing rate variation is preferably not more than 20%, more preferably not more than 15%.

[0016] A distortion constant in the present invention was calculated according to the following equation:

$$\text{Distortion constant } (\mu\text{m}/\text{Pa}) = (T1 - T2) / (177 - 27) / 1000,$$

wherein T1 (μm) is a thickness when a pressure of 27 kPa is applied for 60 seconds with a dial gauge using an indenter having a leading end diameter of 5 mm, and T2 (μm) is a thickness when a pressure of 177 kPa is applied for 60 seconds thereafter.

[0017] Examples of such a cushion layer may include, but are not limited to, natural rubber, nitrile rubber, "Neoprene (registered trademark)" rubber, polybutadiene rubber, thermosetting polyurethane rubber, thermoplastic polyurethane rubber, silicone rubber, non-foamed elastomer such as "Hytrel (registered trademark)", a polyolefin foamed body such as "Toraypef (registered trademark, PEF manufactured by Toray Industries, Inc.)", and non-woven fabric such as "Suba 400" manufactured by Nitta Haas Incorporated.

[0018] The distortion constant of the cushion layer can be adjusted depending on a material thereof. For example, when the cushion layer is a foamed body, increasing a foaming degree tends to cause the foamed body to become soft. Therefore, the distortion constant tends to increase. Also, when the cushion layer is non-foamed, hardness can be controlled by adjusting a crosslinking degree in the cushion layer.

[0019] The thickness of the cushion layer is preferably 0.1 to 2 mm. From a viewpoint of in-plane uniformity on a whole surface of a semiconductor substrate, the thickness is preferably not less than 0.25 mm, and more preferably not less than 0.3 mm. Moreover, from a viewpoint of local flatness, the thickness is preferably not more than 2 mm, and more preferably not more than 1 mm.

[0020] The polishing layer surface (polishing surface) of the polishing pad according to the present invention has a groove. Examples of a shape of the groove as seen from the polishing layer surface may include, but are not limited to, lattice, radial, concentric circular, and spiral shapes. When the groove is an open-type and extends in a circumferential direction, slurry can be efficiently updated. Therefore, a lattice shape is the most preferable.

[0021] According to the present invention, at least one of the side surfaces of the groove includes a first side surface that extends continuously from a polishing surface and forms an angle α with the polishing surface, and a second side surface that extends continuously from the first side surface and forms an angle β with a plane parallel to the polishing surface. Each of the first side surface and the second side surface may be plane (linear in a cross-sectional shape of the groove) or curved (curved in a cross-sectional shape of the groove).

[0022] In the present invention, the angle α is larger than 95 degrees, the angle β is larger than 95 degrees, and the angle β is smaller than the angle α . Thus, variation of a polishing rate can be suppressed while maintaining a high polishing rate. This can be explained as below. Variation of a polishing rate is generally large in initial and middle stages of polishing. However, by providing an inclined surface having an angle larger than 95 degrees at a boundary between the polishing surface and the groove, not only a polishing rate increases, but also such variation of a polishing rate in initial and middle stages can be effectively suppressed.

[0023] On the other hand, in such a configuration, a contact area between a material to be polished and a polishing pad surface is small. Accordingly, there is a concern that a pad cut rate is high. Therefore, a configuration in which the groove provides a larger contact area when the depth of the groove is equal to or deeper than a certain depth is preferable. By adjusting the angle α and the angle β as described above, such an object can be achieved. The difference between the angle α and the angle β is more preferably not larger than 55 degrees, and further preferably not larger than 50 degrees.

[0024] From a viewpoint of retention and fluidity of slurry, the lower limit of the angle α is preferably not smaller than 105 degrees, and more preferably not smaller than 115 degrees. Also, the upper limit of the angle α is preferably not larger than 150 degrees, and more preferably not larger than 140 degrees. Both the side surfaces forming a groove and facing each other may have a similar shape. However, since slurry flows due to a centrifugal force, it is more effective that, of the side surfaces forming a groove and facing each other, at least the side surface on a circumferential side has an inclination. The angle β is not limited as long as the angle β is smaller than the angle α . However, the upper limit of the angle β is preferably smaller than 150 degrees, and further preferably smaller than 140 degrees.

[0025] Here, a side surface (side surface 3) that extends continuously from the side surface 2 in a direction opposite to the side surface 1. In such a case, an angle (angle 3) formed between the side surface 3 and the polishing surface is preferably larger than 95 degrees and smaller than the angle β .

[0026] Similarly, when n is a natural number equal to or more than 3, a side surface (side surface (n + 1)) that extends continuously in a direction opposite to a side surface (n - 1) with respect to a side surface n can be provided. In such a case, an angle (angle (n + 1)) formed between the side surface (n + 1) and the polishing surface is preferably larger than 95 degrees and smaller than an angle n.

[0027] When the polishing layer is scraped off as a material to be polished is polished and the polishing surface passes the bending point that is a boundary between the first side surface and the second side surface, variation of a polishing rate can occur. Furthermore, a pad cut rate differs depending on whether a groove side surface in the shallowest part

is the first side surface or the second side surface. Therefore, the depth from the polishing surface to the bending point is preferably equal to or deeper than a level of inhibiting reduction in effects of an inclined groove part on the polishing surface side. In view of this, and considering that the life of a polishing pad is preferably long, a specific depth from the polishing surface to the bending point is preferably not less than 10% and not more than 95% of the depth of the entire groove, and more preferably not less than 20% and not more than 90% thereof.

[0028] Since it is important that a pad life is long and that suppression of variation of a polishing rate is balanced with, the bending point depth from the polishing surface to the bending point between the first side surface and the second side surface is more than 0.2 mm and not more than 3.0 mm. The polishing surface described here means a polishing surface before the polishing layer is scraped off. When the bending point depth is deep, a pad life becomes short. When the bending point depth is shallow, a polishing rate varies. The upper limit of the bending point depth from the polishing surface to the bending point between the first side surface and the second side surface is preferably not more than 2.5 mm, more preferably not more than 2.0 mm, and further preferably not more than 1.8 mm. Also, the lower limit of the bending point depth from the polishing surface to the bending point between the first side surface and the second side surface is preferably not less than 0.3 mm, more preferably not less than 0.4 mm, and further preferably not less than 0.5 mm.

[0029] A specific shape of the groove according to the present invention as described above will be described with reference to the drawings. FIG. 1 is a partial cross-sectional view illustrating the configuration of a main part of a polishing pad according to an embodiment of the present invention. A polishing pad 1 illustrated in FIG. 1 has a polishing layer 10. A groove 12 is formed on a polishing surface 11 of the polishing layer 10. The groove 12 has a first side surface 13 that extends continuously to the polishing surface 11 and inclines at an angle α formed with respect to the polishing surface 11, a second side surface 15 that extends continuously to the first side surface 13 and bends with respect to the first side surface 13 at a bending point 14, and a deepest groove part 16. An angle β of the second side surface with respect to a plane parallel to the polishing surface 11 is smaller than the angle α of the first side surface 13 with respect to the polishing surface 11.

[0030] Here, a groove shape configured by the second side surfaces 15 and the deepest part 16 is not limited to the shape illustrated in FIG. 1. For example, like a groove 17 of a polishing pad 2 illustrated in FIG. 2, a deepest part 18 may have a bottom surface substantially parallel to the polishing surface 11. Also, like a groove 19 of a polishing pad 3 illustrated in FIG. 3, a boundary part between the second side surface 15 and a deepest part 20 may constitute a curved surface. Also, like a groove 21 of a polishing pad 4 shown in FIG. 4, the cross-sectional shape of second side surfaces 15 and a deepest part 22 may constitute a U-shape.

[0031] As the polishing layer constituting the polishing pad, a closed cell structure is preferable, because a flat surface is formed in a semiconductor, a dielectric/metallic composite, an integrated circuit, and the like. The hardness of the polishing layer measured by an Asker D hardness meter is preferably 45 to 65 degrees. When the Asker D hardness is less than 45 degrees, as the wafer in-plane uniformity of a polishing rate for a material to be polished decreases, the uniformity of wafer in-plane planarization properties (planarity) tends to decrease.

[0032] Examples of a material for forming such a structure may include, but are not particularly limited to, polyethylene, polypropylene, polyester, polyurethane, polyurea, polyamide, polyvinyl chloride, polyacetal, polycarbonate, polymethyl methacrylate, polytetrafluoroethylene, epoxy resin, ABS resin, AS resin, phenol resin, melamine resin, "Neoprene (registered trademark)" rubber, butadiene rubber, styrene butadiene rubber, ethylene propylene rubber, silicone rubber, fluorine rubber, and resins including these as a main component. Two or more of these may be used. Also in these resins, since a closed cell diameter can be relatively easily controlled, a material including polyurethane as a main component is more preferable.

[0033] Polyurethane is a macromolecule synthesized by a polyaddition reaction or a polymerization reaction of polyisocyanate. A compound used as a reference of polyisocyanate is an active hydrogen-containing compound that is a compound containing two or more polyhydroxy groups or an amino group-containing compound. Examples of polyisocyanate may include, but are not limited to, tolylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate. Two or more of these may be used.

[0034] A compound containing a polyhydroxy group is representatively polyol. Examples thereof may include polyether polyol, polytetramethylene ether glycol, epoxy resin-modified polyol, polyester polyol, acrylic polyol, polybutadiene polyol, and silicone polyol. Two or more of these may be used. Combination and optimum amounts of polyisocyanate and polyol, and a catalyst, a foaming agent and a foam stabilizer are preferably determined depending on hardness, a cell diameter and a foaming ratio.

[0035] As a method of forming closed cells in the polyurethane, a chemical foaming method in which various foaming agents are blended into a resin during production of polyurethane is generally used. However, a method including foaming a resin by mechanical stirring and thereafter curing the foamed resin may also preferably be used.

[0036] The average cell diameter of closed cells is preferably not less than 30 μm in order to reduce scratches. Also, in view of flatness of local unevenness of a material to be polished, the average cell diameter is preferably not more than 150 μm , more preferably not more than 140 μm , and further preferably not more than 130 μm . The average cell

diameter is obtained as follows. Of cells observed in one field of view when observing a sample section at a magnification of 400 times using an ultra-deep microscope VK-8500 manufactured by Keyence Corporation, circular cells excluding cells that are observed in a circle in a state of being deficient in the field end are measured using an image processing apparatus to obtain a circle-equivalent diameter from the cross-sectional area. Then, a number average value is calculated.

[0037] A preferred embodiment of the polishing pad according to the present invention is a pad that contains a polymer of a vinyl compound as well as polyurethane and has closed cells. With only a polymer from a vinyl compound, toughness and hardness can be improved, but a uniform polishing pad having closed cells is unlikely to be obtained. Furthermore, polyurethane becomes brittle when hardness is brought to be higher. By impregnating a vinyl compound into polyurethane, a polishing pad containing closed cells and having high toughness and hardness can be obtained.

[0038] A vinyl compound is a polymerizable compound having a carbon-carbon double bond. Specific examples of the vinyl compound may include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, n-lauryl methacrylate, 2-hydroxy ethyl methacrylate, 2-hydroxy propyl methacrylate, 2-hydroxy butyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, glycidyl methacrylate, ethylene glycol dimethacrylate, acrylic acid, methacrylic acid, fumaric acid, dimethyl fumarate, diethyl fumarate, dipropyl fumarate, maleic acid, dimethyl maleate, diethyl maleate, dipropyl maleate, phenylmaleimide, cyclohexyl maleimide, isopropyl maleimide, acrylonitrile, acrylamide, vinyl chloride, vinylidene chloride, styrene, α -methylstyrene, divinylbenzene, ethylene glycol dimethacrylate, and diethylene glycol dimethacrylate. Two or more of these may be used.

[0039] Among the above-described vinyl compounds, $\text{CH}_2=\text{CR}^1\text{COOR}^2$ (R^1 : a methyl group or an ethyl group, R^2 : a methyl group, an ethyl group, a propyl group, or a butyl group) is preferable. Especially, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, and isobutyl methacrylate are preferable. This is because closed cells can be easily formed into polyurethane; monomers can be favorably impregnated; polymerization curing can be easily performed; and a foaming structure containing a polymer of a polymerization-cured vinyl compound and polyurethane has high hardness and favorable planarization properties.

[0040] Examples of a polymerization initiator preferably used for obtaining these polymers of vinyl compounds may include a radical initiator such as azobisisobutyronitrile, azobis(2,4-dimethylvaleronitrile), azobis cyclohexane carbonitrile, benzoyl peroxide, lauroyl peroxide, and isopropyl peroxy dicarbonate. Two or more of these may be used. Also, a redox-based polymerization initiator, for example, a combination of peroxide and amines can be used.

[0041] A method of impregnating a vinyl compound into polyurethane may include a method including immersing polyurethane in a vessel containing a vinyl compound. At that time, treatments such as heating, pressurizing, pressure-reducing, stirring, shaking, and ultrasonic vibration are preferably performed in order to increase an impregnation speed.

[0042] The impregnation amount of the vinyl compound into polyurethane should be determined depending on types of the vinyl compound and polyurethane to be used and properties of a polishing pad to be manufactured. Therefore, the impregnation amount cannot be completely defined. However, for example, the content ratio of the polymer obtained from the vinyl compound and polyurethane in a polymerization-cured foamed structure is preferably 30/70 to 80/20 in terms of weight. When the content ratio of the polymer obtained from the vinyl compound is not less than 30/70 in terms of weight, hardness of the polishing pad can be made sufficiently high. Also, when the content ratio is not more than 80/20, elasticity of the polishing layer can be made sufficiently high.

[0043] Here, the content ratio of the polymer obtained from the polymerization-cured vinyl compound in polyurethane can be measured by a pyrolysis gas chromatography/mass spectrometry technique. An apparatus that can be used in this technique may include a double-shot pyrolyzer "PY-2010D" (manufactured by Frontier Laboratories Ltd.) as a thermal decomposition apparatus and "TRIO-1" (manufactured by VG) as a gas chromatography and mass spectrometry apparatus.

[0044] In the present invention, from a viewpoint of flatness of local unevenness of a semiconductor substrate, a phase of the polymer obtained from the vinyl compound and a phase of polyurethane are preferably contained without being separated from each other. When expressed quantitatively, it is preferable that an infrared spectrum obtained when the polishing pad be observed using an infrared microspectrometer with a spot size of 50 μm have an infrared absorption peak of the polymer polymerized from the vinyl compound and an infrared absorption peak of polyurethane, and that infrared spectra in various locations be approximately the same. An infrared microspectrometer to be used here may include IR μs manufactured by SPECTRA-TEC.

[0045] In order to improve properties, the polishing pad may contain various additives such as an abrasive, an antistatic agent, a lubricant, a stabilizer, and a dye.

[0046] In the present invention, in order to reduce poor local flatness and global steps, the density of the polishing layer is preferably not less than 0.3 g/cm³, more preferably not less than 0.6 g/cm³, and further preferably not less than 0.65 g/cm³. On the other hand, in order to reduce scratches, the density is preferably not more than 1.1 g/cm³, more preferably not more than 0.9 g/cm³, and further preferably not more than 0.85 g/cm³. Here, the density of the polishing layer in the present invention is a value measured using a Harvard-type pycnometer (in accordance with JIS R-3503

standard) with water as a medium.

[0047] Examples of a material to be polished in the present invention may include a surface of an insulating layer or a metal wiring formed on a semiconductor wafer. The insulating layer may include an interlayer insulating film of a metal wiring, a lower-layer insulating film of a metal wiring, and a shallow trench isolation layer used for element isolation. The metal wiring may be made from aluminum, tungsten, copper, or an alloy thereof. Examples of a structure of the metal wiring may include damascene, dual damascene, and a plug. When copper is used as the metal wiring, barrier metal such as silicon nitride also becomes a subject to be polished. Currently, silicon oxide is mainly used as the insulating film. However, a low dielectric constant insulating film is also used. In addition to a semiconductor wafer, a magnetic head, a hard disk, sapphire, SiC, MEMS (Micro Electro Mechanical Systems), and the like may be used as a subject to be polished.

[0048] The polishing method according to the present invention is suitably used in order to form a flat surface of glass, a semiconductor, a dielectric/metallic composite, an integrated circuit, and the like.

Examples

[0049] The present invention will be further described in detail by examples. However, the present invention should not be interpreted to be limited by the examples. Measurement was performed as below.

<Measurement of cell diameter>

[0050] Of cells observed in one field of view when observing a sample section at a magnification of 400 times using an ultra-deep microscope VK-8500 manufactured by Keyence Corporation, circular cells excluding cells that are observed in a circle in a state of being deficient in the field end are measured using an image processing apparatus to obtain a circle-equivalent diameter from the cross-sectional area. A number average value is calculated to serve as an average cell diameter.

<Measurement of hardness>

[0051] Measurement was performed in accordance with JIS K6253-1997. The produced polyurethane resin was cut out into a piece having a size of 2 cm × 2 cm (thickness: optional). The piece was used as a hardness measurement sample, and left to stand for 16 hours in an environment of a temperature of 23°C ± 2°C and a humidity of 50% ± 5%. During measurement, samples were superimposed on each other to have a thickness of not less than 6 mm. Hardness was measured using a hardness meter (manufactured by Kobunshi Keiki Co., Ltd., Asker D-type hardness meter).

<Measurement of micro rubber A hardness>

[0052] A cushion layer was cut out into a piece having a size of 3 cm × 3 cm. The piece was used as a hardness measurement sample, and left to stand for 16 hours in an environment of a temperature of 23°C ± 2°C and a humidity of 50% ± 5%. Different three points in one piece of sample were measured using a micro rubber hardness meter MD-1 manufactured by Kobunshi Keiki Co., Ltd. An average value was calculated to serve as a micro rubber A hardness.

<Measurement of inclination angle>

[0053] A pad having a groove formed on a polishing layer surface was disposed so that a razor blade was vertical to a groove direction. Then, the pad was sliced in a groove depth direction. The obtained groove section was observed by an ultra-deep microscope VK-8500 manufactured by Keyence Corporation. An angle (angle α) formed between a polishing surface and a side surface extending continuously to the groove polishing surface was measured. At locations of 1/3 and 2/3 of a radius from a pad center, the closest grooves were measured. An average of one each location, two locations in total, was calculated to serve as an inclination angle. An angle β was measured in a similar manner thereto.

<Measurement of bending point depth>

[0054] A pad having a groove formed on a polishing layer surface was disposed so that a razor blade was vertical to a groove direction. Then, the pad was sliced in a groove depth direction. The obtained groove section was observed by an ultra-deep microscope VK-8500 manufactured by Keyence Corporation. A vertical distance from the polishing surface, to a midpoint between two bending points each including a first side surface and a second side surface and both facing each other, was measured. At locations of 1/3 and 2/3 of a radius from a pad center, the closest grooves were measured. An average of one each location, two locations in total, was calculated to serve as a bending point depth.

<Measurement of initial inter-bending point distance>

[0055] A pad having a groove formed on a polishing layer surface was disposed so that a razor blade was vertical to a groove direction. Then, the pad was sliced in a groove depth direction. The obtained groove section was observed by an ultra-deep microscope VK-8500 manufactured by Keyence Corporation. A distance between two bending points each having an angle α and including a polishing surface and a first side surface and both facing each other was measured to obtain a bending point distance. Also, the inter-bending point distance in the initial stage of polishing was determined as an initial inter-bending point distance.

<Calculation of distortion constant>

[0056] A distortion constant was calculated according to the following equation:

$$\text{Distortion constant } (\mu\text{m}/\text{Pa}) = (T1 - T2) / (177 - 27) / 1000,$$

wherein T1 (μm) is a thickness when a pressure of 27 kPa was applied for 60 seconds with a dial gauge using an indenter having a leading end diameter of 5 mm, and T2 (μm) is a thickness when a pressure of 177 kPa was applied for 60 seconds thereafter.

<Calculation of average polishing rate>

[0057] Using Mirra 3400 manufactured by Applied Materials, Inc., polishing was performed while performing end point detection under a given polishing condition. Polishing properties were measured in a diameter direction, excluding a region of 10 mm from the outermost circumference of an 8-inch wafer. Measurement was performed at 37 points per 5 mm on a surface within a radius of 90 mm from the center. Then, an average polishing rate (nm/minute) was calculated.

<Calculation of polishing rate variation>

[0058] After 1000 wafers were polished and an average polishing rate was measured wafer by wafer, a polishing rate variation of the first to 700th wafers was calculated according to the following equation:

$$\text{Polishing rate variation } (\%) = \{(\text{Maximum wafer average polishing rate}) - (\text{minimum wafer average polishing rate})\} / (\text{1000th wafer average polishing rate}).$$

[0059] When the variation of a polishing rate is large, insufficient polishing or excess polishing can cause device failure. Therefore, the polishing rate variation is suitably low, preferably not more than 30%, and more preferably not more than 20%.

<Measurement of average pad cut rate>

[0060] Using Mirra 3400 manufactured by Applied Materials, Inc., polishing was performed while performing end point detection under a given polishing condition. With a depth gauge, a groove depth (D1) mm after polishing 30 workpieces and a groove depth (D2) mm after polishing 1000 workpieces were measured. Calculation was made from dress time (t_d) minutes by a dresser.

$$\text{Average pad cut rate } (\mu\text{m}/\text{minute}) = (D1 - D2) \times 1000 / t_d$$

[0061] The average pad cut rate depends on the inter-bending point distance as well as the angle α and the angle β . The inter-bending point distance changes as polishing proceeds. When the average inter-bending point distance from the initial stage to the final stage of polishing is smaller, the average pad cut rate is lower.

Average inter-bending point distance (mm) =
 {(Polishing initial stage cross-sectional area) -
 (Polishing final stage cross-sectional area)} / {(Polishing
 initial stage deepest part groove depth) - (Polishing final
 stage deepest part groove depth)}

<Calculation of polishing pad life>

[0062] A groove depth in the polishing initial stage was measured. Then, an effective groove depth (D3) mm that is shallower by 0.3 mm from the deepest part was calculated. Calculation was made from a time (t_p) minute during which a wafer was polished and the average pad cut rate.

Polishing pad life (time) = $D3 \times 1000 / (\text{Average pad cut rate}) \times t_p / 60$

[0063] The polishing pad life is preferably not less than 15 hours.

[0064] Examples 1 to 12 and Comparative Examples 1 to 4 will be described below.

(Example 1)

[0065] In a RIM molding machine, 30 parts by weight of polypropylene glycol, 40 parts by weight of diphenylmethane diisocyanate, 0.5 parts by weight of water, 0.3 parts by weight of triethylamine, 1.7 parts by weight of a silicone foam stabilizer, and 0.09 parts by weight of tin octylate were mixed. The mixture was discharged into a mold and subjected to pressure molding. Thus, a foamed polyurethane sheet containing closed cells was produced.

[0066] The foamed polyurethane sheet was immersed in methyl methacrylate added with 0.2 parts by weight of azobisisobutyronitrile for 60 minutes. Next, the foamed polyurethane sheet was immersed in a solution including 15 parts by weight of polyvinyl alcohol "CP" (polymerization degree: about 500, manufactured by Nacalai Tesque Inc.), 35 parts by weight of ethyl alcohol (special grade chemical, manufactured by Katayama Chemical Co., Ltd.), and 50 parts by weight of water, and then dried. Thus, a surface layer of the foamed polyurethane sheet was coated with polyvinyl alcohol.

[0067] Next, the foamed polyurethane sheet was placed between two glass plates via vinyl chloride gaskets, and then heated for 6 hours at 65°C and for 3 hours at 120°C to be polymerization-cured. The sheet was released from between the glass plates, washed with water, and then vacuum-dried at 50°C. The hard foamed sheet obtained as above was subjected to a slicing process into a piece having a thickness of 2.00 mm. Thus, a polishing layer was produced. The content ratio of methyl methacrylate in the polishing layer was 66% by weight. The polishing layer had a D hardness of 54 degrees and a density of 0.81 g/cm³. An average cell diameter of closed cells was 45 μm.

[0068] Both surfaces of the obtained hard foamed sheet were ground. Thus, a polishing layer having a thickness of 2.4 mm was produced.

[0069] Thermoplastic polyurethane (cushion layer thickness: 0.3 μm) manufactured by Nihon Matai Co., Ltd. having a distortion constant of 0.15×10^{-4} μm/Pa (micro rubber A hardness 89) as a cushion layer was laminated on the polishing layer obtained by the above method via an MA-6203 adhesive layer manufactured by Mitsui Chemicals Polyurethanes, Inc. using a roll coater. Furthermore, a double-sided tape 5604TDM manufactured by Sekisui Chemical Co., Ltd. as a rear surface tape was bonded to the rear surface thereof. This laminate was punched into a circle having a diameter of 508 mm. A groove having a groove pitch of 15 mm, an angle α of 135 degrees, an angle β of 120 degrees, and a groove depth of 1.9 mm was formed in an XY grid pattern on the polishing layer surface. Thus, a polishing pad was obtained. At this time, the bending point depth was 0.69 mm, and the initial stage inter-bending point distance was 3 mm.

[0070] The polishing pad obtained by the above method was pasted on a platen of a polishing machine ("Mirra 3400" manufactured by Applied Materials, Inc.). Under a retainer ring pressure = 41 kPa (6 psi), an inner tube pressure = 28 kPa (4 psi), a membrane pressure = 28 kPa (4 psi), a platen revolution = 76 rpm, a polishing head revolution = 75 rpm, and a slurry (manufactured by Cabot Corporation, SS-25) flow of 150 mL/minute, 1000 8-inch wafers as oxide films were polished using a dresser manufactured by Saesol at a load of 17.6 N (4 lbf), a polishing time of 1 minute, and an in-situ dressing time of 30 seconds after polishing started.

[0071] The average polishing rate of the 1000th oxide film was 192.2 nm/minute. The polishing rate variation for 1000 oxide films was 8.5%. The average pad cut rate was 1.22 $\mu\text{m}/\text{minute}$, and the polishing pad life was 22 hours. Thus, the results were favorable.

(Example 2)

[0072] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 145 degrees, the polishing layer thickness was changed to 2.25 mm, and the groove depth was changed to 1.75 mm. At this time, the bending point depth was 0.46 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 195.2 nm/minute, and the polishing rate variation was 13.2%. The average pad cut rate was 1.15 $\mu\text{m}/\text{minute}$, and the polishing pad life was 21 hours. Thus, the results were favorable.

(Example 3)

[0073] Polishing was performed in the same manner as that in Example 1, except that the angle β of the groove on the polishing layer surface was changed to 100 degrees, the polishing layer thickness was changed to 3.15 mm, and the groove depth was changed to 2.65 mm. At this time, the bending point depth was 1.37 mm, and the initial stage inter-bending point distance was 3.4 mm. The average polishing rate was 184.1 nm/minute, and the polishing rate variation was 17.2%. The average pad cut rate was 1.22 $\mu\text{m}/\text{minute}$, and the polishing pad life was 32 hours. Thus, the results were favorable.

(Example 4)

[0074] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 100 degrees, the angle β was changed to 98 degrees, the polishing layer thickness was changed to 2.0 mm, and the groove depth was changed to 1.5 mm. At this time, the bending point depth was 0.3 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 187.8 nm/minute, and the polishing rate variation was 17.8%. The average pad cut rate was 1.20 $\mu\text{m}/\text{minute}$, and the polishing pad life was 16 hours. Thus, the results were favorable.

(Example 5)

[0075] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 150 degrees, the angle β was changed to 145 degrees, the polishing layer thickness was changed to 2.0 mm, and the groove depth was changed to 1.5 mm. At this time, the bending point depth was 0.27 mm, and the initial stage inter-bending point distance was 5 mm. The average polishing rate was 201.9 nm/minute, and the polishing rate variation was 18.9%. The average pad cut rate was 1.24 $\mu\text{m}/\text{minute}$, and the polishing pad life was 16 hours. Thus, the results were favorable.

(Example 6)

[0076] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 160 degrees, the angle β was changed to 110 degrees, the polishing layer thickness was changed to 2.5 mm, and the groove depth was changed to 2.05 mm. At this time, the bending point depth was 0.79 mm, and the initial stage inter-bending point distance was 5 mm. The average polishing rate was 183.8 nm/minute, and the polishing rate variation was 16.4%. The average pad cut rate was 1.35 $\mu\text{m}/\text{minute}$, and the polishing pad life was 21 hours. Thus, the results were favorable.

(Example 7)

[0077] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 115 degrees, the angle β was changed to 100 degrees, the polishing layer thickness was changed to 2.0 mm, and the groove depth was changed to 1.5 mm. At this time, the bending point depth was 0.27 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 182.5 nm/minute, and the polishing rate variation was 17.5%. The average pad cut rate was 1.22 $\mu\text{m}/\text{minute}$, and the polishing pad life was 16 hours. Thus, the results were favorable.

(Example 8)

[0078] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 165 degrees, the angle β was changed to 155 degrees, the polishing layer thickness was changed to 2.2 mm, and the groove depth was changed to 1.7 mm. At this time, the bending point depth was 0.5 mm, and the initial stage inter-bending point distance was 5 mm. The average polishing rate was 190.2 nm/minute, and the polishing rate variation was 15.6%. The average pad cut rate was 1.36 $\mu\text{m}/\text{minute}$, and the polishing pad life was 17 hours. Thus, the results were favorable.

(Example 9)

[0079] Polishing was performed in the same manner as that in Example 1, except that the polishing layer thickness was changed to 2.9 mm, and the groove depth was changed to 2.4 mm. At this time, the bending point depth was 2.1 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 185.7 nm/minute, and the polishing rate variation was 14.4%. The average pad cut rate was 1.23 $\mu\text{m}/\text{minute}$, and the polishing pad life was 28 hours. Thus, the results were favorable.

(Example 10)

[0080] Polishing was performed in the same manner as that in Example 1, except that the polishing layer thickness was changed to 3.5 mm, and the groove depth was changed to 3.0 mm. At this time, the bending point depth was 2.6 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 183.3 nm/minute, and the polishing rate variation was 15.1%. The average pad cut rate was 1.24 $\mu\text{m}/\text{minute}$, and the polishing pad life was 36 hours. Thus, the results were favorable.

(Example 11)

[0081] Polishing was performed in the same manner as that in Example 1, except that two angles α that face each other via the groove on the polishing layer surface were changed to 135 degrees and 130 degrees so that the two angles facing each other differ from each other. At this time, the bending point depth was 0.69 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 191.8 nm/minute, and the polishing rate variation was 9.0%. The average pad cut rate was 1.20 $\mu\text{m}/\text{minute}$, and the polishing pad life was 22 hours. Thus, the results were favorable.

(Example 12)

[0082] Polishing was performed in the same manner as that in Example 1, except that a polyester film having a thickness of 188 μm was bonded to the rear surface of the polishing layer via an adhesive, and a cushion layer was bonded to the polyester film surface. At this time, the bending point depth was 0.69 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 192.8 nm/minute, and the polishing rate variation was 9.3%. The average pad cut rate was 1.22 $\mu\text{m}/\text{minute}$, and the polishing pad life was 22 hours. Thus, the results were favorable.

(Comparative Example 1)

[0083] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 93 degrees, the angle β was changed to 90 degrees, the polishing layer thickness was changed to 2.0 mm, and the groove depth was changed to 1.5 mm. At this time, the bending point depth was 0.27 mm, and the initial stage inter-bending point distance was 1.5 mm. The average polishing rate was 180.1 nm/minute, and the polishing rate variation was 45.1%. Thus, the polishing rate variation was large. The average pad cut rate was 1.12 $\mu\text{m}/\text{minute}$, and the polishing pad life was 18 hours. Thus, the results were favorable.

(Comparative Example 2)

[0084] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 93 degrees, the angle β was changed to 90 degrees, the polishing layer thickness was changed to 2.0 mm, and the groove depth was changed to 1.5 mm. At this time, the bending point depth was 0.27 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 189.5 nm/minute, and the polishing rate variation was 30.8%. Thus, the polishing rate variation was large. The average pad cut rate was 1.5 $\mu\text{m}/\text{minute}$, and the polishing pad life was 13 hours. Thus, the life was short.

(Comparative Example 3)

[0085] Polishing was performed in the same manner as that in Example 1, except that the angle β was changed to 98 degrees, the polishing layer thickness was changed to 2.0 mm, and the groove depth was changed to 1.5 mm. At this time, the bending point depth was 0.15 mm, and the initial stage inter-bending point distance was 3 mm. The average polishing rate was 190.1 nm/minute, and the polishing rate variation was 36.2%. Thus, the polishing rate variation was large. The average pad cut rate was 1.42 $\mu\text{m}/\text{minute}$, and the polishing pad life was 14 hours. Thus, the life was short.

(Comparative Example 4)

[0086] Polishing was performed in the same manner as that in Example 1, except that the angle α of the groove on the polishing layer surface was changed to 160 degrees, the angle β was changed to 100 degrees, the polishing layer thickness was changed to 2.5 mm, and the groove depth was changed to 2.0 mm. At this time, the bending point depth was 0.60 mm, and the initial stage inter-bending point distance was 4 mm. The average polishing rate was 184.6 nm/minute, and the polishing rate variation was 31.0%. Thus, the polishing rate variation was large. The average pad cut rate was 1.32 $\mu\text{m}/\text{minute}$, and the polishing pad life was 21 hours. Thus, the results were favorable.

[0087] The results obtained in Examples 1 to 12 and Comparative Examples 1 to 4 described above are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
α (degrees)	135	145	135	100	150	160	115	165	135	135	135, 130	135	93	93	135	160
β (degrees)	120	120	100	98	145	110	100	155	120	120	120	120	90	90	98	100
Polishing Layer Thickness (mm)	2.4	2.25	3.15	2.0	2.0	2.5	2.0	2.2	2.9	3.5	2.4	2.4	2.0	2.0	2.0	2.5
GrooveDepth (mm)	1.9	1.75	2.65	1.5	1.5	2.05	1.5	1.7	2.4	3.0	1.9	1.9	1.5	1.5	1.5	2.0
Bending Point Depth (mm)	0.69	0.46	1.37	0.3	0.27	0.79	0.27	0.5	2.1	2.6	0.69	0.69	0.27	0.27	0.15	0.60
Initial Stage Groove Inter-Bending Point Distance (mm)	3	3	3.4	3	5	5	3	5	3	3	3	3	1.5	3	3	4
Average Polishing Rate (nm/min.)	192.2	195.2	184.1	187.8	201.9	183.8	182.5	190.2	185.7	183.3	191.8	192.8	180.1	189.5	190.1	184.6
Polishing Rate Variation (%)	8.5	13.2	17.2	17.8	18.9	16.4	17.5	15.6	14.4	15.1	9.0	9.3	45.1	30.8	36.2	31.0
Average Pad Cut Rate ($\mu\text{m}/\text{min.}$)	1.22	1.15	1.22	1.20	1.24	1.35	1.22	1.36	1.23	1.24	1.20	1.22	1.12	1.5	1.42	1.32
Polishing Pad Life (hours)	22	21	32	16	16	21	16	17	28	36	22	22	18	13	14	21
Example 12 ... Polyester film having thickness of 188 μm bonded to polishing layer rear surface + cushion layer bonded to polyester film surface																

Reference Signs List

[0088]

- 5 1, 2, 3, 4 Polishing pad
 10 Polishing layer
 11 Polishing surface
 12, 17, 19, 21 Groove
 13 First side surface
 10 14 Bending point
 15 Second side surface
 16, 18, 20, 22 Deepest part

15 **Claims**

1. A polishing pad comprising at least a polishing layer, wherein
 the polishing layer comprises a groove on a polishing surface, the groove having side surfaces,
 at least one of the side surfaces comprises a first side surface that extends continuously to the polishing surface
 20 and forms an angle α with the polishing surface, and a second side surface that extends continuously to the first
 side surface and forms an angle β with a plane parallel to the polishing surface,
 the angle α formed with the polishing surface is larger than 95 degrees, the angle β formed with the plane parallel
 to the polishing surface is larger than 95 degrees, and the angle β formed with the plane parallel to the polishing
 surface is smaller than the angle α formed with the polishing surface, and
 25 a bending point depth from the polishing surface to a bending point between the first side surface and the second
 side surface is more than 0.2 mm and not more than 3.0 mm.
2. The polishing pad according to claim 1, wherein a difference between the angle α formed with the polishing surface
 and the angle β formed with the plane parallel to the polishing surface is not larger than 55 degrees.
- 30 3. The polishing pad according to claim 1 or 2, wherein the angle α formed with the polishing surface is not smaller
 than 105 degrees and not larger than 150 degrees.
4. The polishing pad according to any one of claims 1 to 3, wherein the angle β formed with the plane parallel to the
 35 polishing surface is larger than 95 degrees and smaller than 150 degrees.
5. The polishing pad according to any one of claims 1 to 4, wherein a groove pattern on the polishing surface is grid-
 shaped.

FIG.1

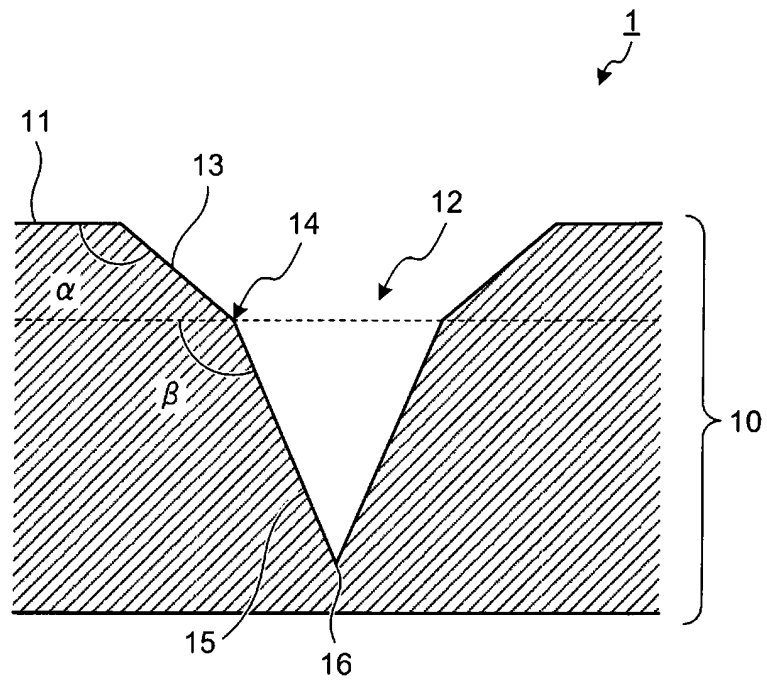


FIG.2

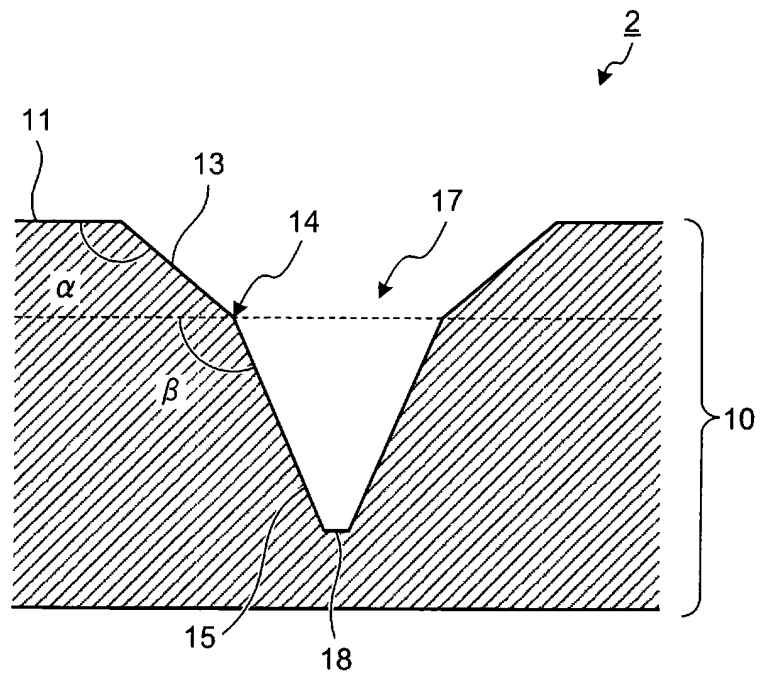


FIG.3

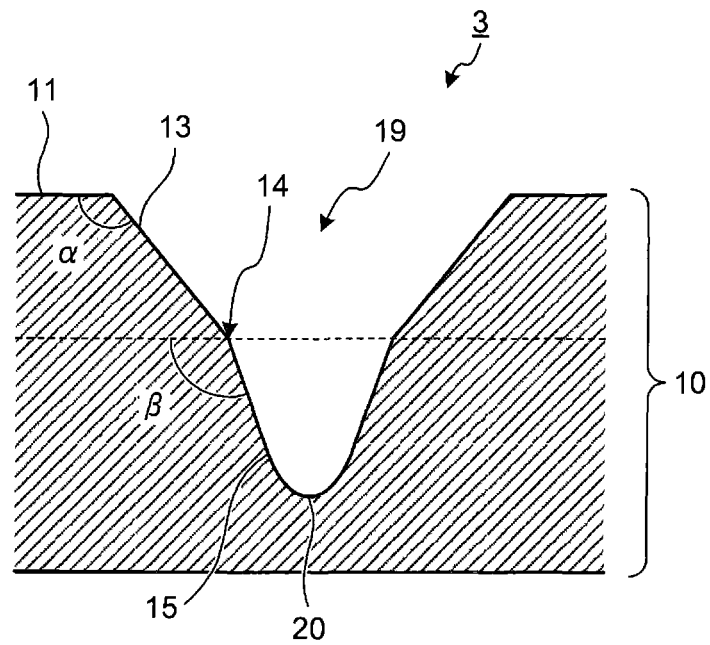
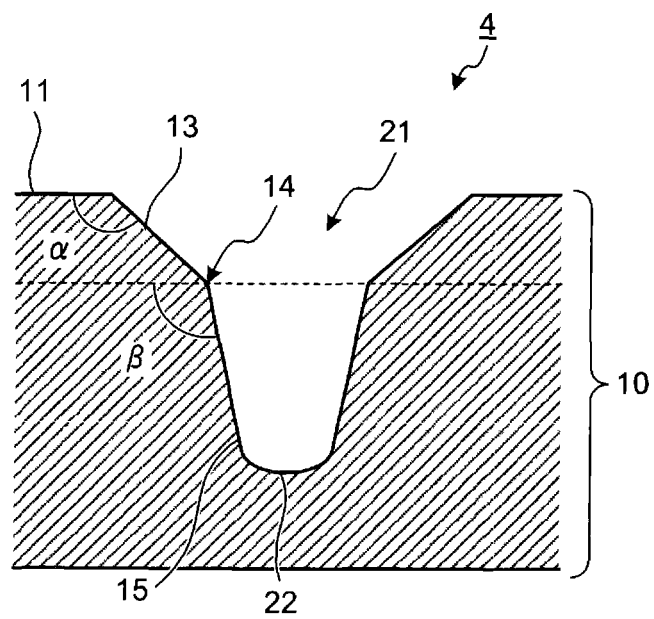


FIG.4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/067835

A. CLASSIFICATION OF SUBJECT MATTER

B24B37/26(2012.01)i, H01L21/304(2006.01)i

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)

B24B37/26, H01L21/304

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012

Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-163192 A (Shin-Etsu Handotai Co., Ltd.), 06 June 2003 (06.06.2003), paragraphs [0010] to [0012], [0034]; fig. 5 (Family: none)	1-5
A	JP 2004-186392 A (Toshiba Ceramics Co., Ltd.), 02 July 2004 (02.07.2004), paragraphs [0020] to [0029]; fig. 1, 5 (Family: none)	1-5
A	JP 2009-220265 A (JSR Corp.), 01 October 2009 (01.10.2009), entire text; all drawings & US 2009/0209185 A1 & EP 2090401 A1	1-5

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
26 July, 2012 (26.07.12)Date of mailing of the international search report
07 August, 2012 (07.08.12)Name and mailing address of the ISA/
Japanese Patent Office

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Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/067835

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-023018 A (JSR Corp.), 05 February 2009 (05.02.2009), entire text; all drawings (Family: none)	1-5

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2002144219 A [0006]
- JP 2004186392 A [0006]
- JP 2010045306 A [0006]