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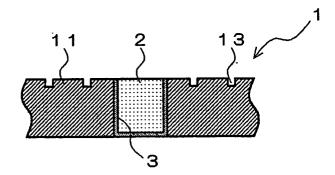
## (54) Polishing pad and method of polishing a semiconductor wafer

(57) A polishing pad, a polishing laminated pad and a semiconductor wafer polishing method all of which prevent a leak of slurry from the gap between a polishing substrate and a reduction in polishing efficiency caused by a scratched and a window member and enable the optical detection of the polishing end point to be carried out efficiently.

The polishing pad comprises a polishing substrate

having a through hole extending from the front side to the rear side and a light transmitting member arranged in the through hole, and the outer wall of the above light transmitting member and the inner wall of the though hole opposite to the outer wall are bonded together with a photocurable adhesive such as a polyurethane (meth) acrylate to fix the above light transmitting member in the through hole.





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#### Description

#### Field of the Invention

**[0001]** The present invention relates to a polishing pad and a method of polishing a semiconductor wafer. More specifically, it relates to a polishing pad comprising a window member for optical end-point detection, which prevents a leak of slurry from the gap between a polishing pad substrate and the window member and which enables the optical detection of the polishing end point to be carried out efficiently without a reduction in polishing efficiency caused by a scratched surface to be polished and to a method of polishing a semiconductor wafer with the polishing pad.

#### Description of the Prior Art

[0002] In the polishing of a semiconductor wafer, after the purpose of polishing is accomplished, the determination of the polishing end point for terminating polishing can be made based on a time obtained empirically. However, various materials are used to form surfaces to be polished and the polishing time differs by each material. It is conceivable that the material forming the surface to be polished will change in the future. Further, the same can be said of slurry used for polishing and a polishing machine. Therefore, it is extremely inefficient to obtain the polishing time from these. To cope with this, researches into optical end-point detection devices and processes using an optical method capable of directly observing the state of the surface to be polished are now under way as disclosed by JP-A 9-7985 and JP-A 2000-326220 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). [0003] In the above optical end-point detection devices and processes, a window which is made of a hard and homogeneous resin capable of transmitting light for end-point detection and having no essential property of absorbing and carrying abrasive grains contained in slurry is formed in a polishing pad, and the surface to be polished is observed only from this window (JP-A 11-512977).

**[0004]** The polishing pad having this window is manufactured by pushing a window member into a hole formed in a polishing substrate. This polishing pad has a problem that optical end-point detection may become unsatisfactory due to a leak of slurry from the gap between the window member and the polishing pad substrate because the window member becomes loose during polishing.

**[0005]** To solve the above problem, USP 6045439 discloses a method of bonding a window member to a polishing pad substrate with an adhesive and enumerates polyurethane elastomers, rubber cement and epoxybased adhesives as preferred examples of the adhesive. The polyurethane elastomer adhesive has great adhesive force and excellent durability and fills the gap

between the window member and the polishing pad substrate by swelling after curing, thereby contributing to the prevention of a leak of the slurry. However, it involves the following problems: (1) the curing of the adhesive takes long, thereby reducing the production yield, and (2) the window member is distorted by the swelling of the adhesive at the time of curing, whereby part of the window member may project from the surface of the polishing pad substrate and accordingly, a polishing pad having a smooth surface may not be obtained. Meanwhile, when rubber cement or a commonly used adhesive such as an epoxy-based adhesive is used, part of the adhesive may be solidified while it overflows into the polishing surface of the polishing pad or part of the adhesive solidified during polishing may fall off as a fragment, thereby scratching the surface to be polished.

#### Summary of the Invention

**[0006]** It is an object of the present invention which has been made to solve the above problems to provide a polishing pad comprising a window member for optical end-point detection, which prevents a leak of slurry from the gap between the window member and a polishing pad substrate and which enables the optical detection of the polishing end point to be carried out efficiently without a reduction in polishing efficiency caused by a scratched surface to be polished, as well as a polishing laminated pad and a method of polishing a semiconductor wafer.

**[0007]** Other objects and advantages of the present invention will become apparent from the following description.

[0008] The inventors of the present invention have conducted intensive studies on a polishing pad used for polishing, making use of an optical end-point detection device, specifically a method of fixing a window member to a polishing pad and have found that efficient polishing can be carried out through optical end-point detection by bonding and fixing a light transmitting member as the window member in a polishing pad substrate without a gap between them with a photocurable adhesive to prevent a leak of slurry from the gap during polishing and a bad phenomenon such as scratching. The present invention has been accomplished based on this finding. [0009] That is, according to the present invention, firstly, the above objects and advantages of the present invention are attained by a polishing pad comprising a polishing substrate having a through hole extending from its polishing surface to the opposite surface and a light transmitting member arranged in the through hole, said outer wall of the light transmitting member being bonded to the inner wall of the through hole opposed to the outer wall with a photocured adhesive layer so that the light transmitting member is fixed in the through hole. **[0010]** According to the present invention, secondly, the above objects and advantages of the present invention are attained by a polishing laminated pad compris-

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ing the polishing pad of the present invention and a base layer having light transmission properties formed on the surface opposite to the polishing surface of the polishing pad.

**[0011]** According to the present invention, thirdly, the above objects and advantages of the present invention are attained by a method of polishing a semiconductor wafer with a polishing pad, wherein the polishing pad or the polishing laminated pad of the present invention is used and the polishing end point of the semiconductor wafer is detected by an optical end-point detection device through the light transmitting member of the polishing pad or the polishing laminate pad.

### Brief Description of the Drawings

#### [0012]

Fig. 1 is a sectional view of an example of a polishing pad of the present invention;

Fig. 2 is a sectional view of an example of a through hole formed in a polishing substrate;

Fig. 3 is a sectional view of another example of the through hole formed in the polishing substrate;

Fig. 4 is a sectional view of still another example of the through hole formed in the polishing substrate; Fig. 5 is a sectional view of a further example of the through hole formed in the polishing substrate;

Fig. 6 is a sectional view of a still further example of the through hole formed in the polishing substrate:

Fig. 7 is a sectional view of a still further example of the through hole formed in the polishing substrate:

Fig. 8 is a sectional view of another example of the polishing pad of the present invention;

Fig. 9 is a sectional view of still another example of the polishing pad of the present invention;

Fig. 10 is a sectional view of a further example of the polishing pad of the present invention;

Fig. 11 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 12 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 13 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 14 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 15 is a sectional view of a still further example of the polishing pad of the present invention;

Fug. 16 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 17 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 18 is an image diagram of part of the polishing pad shown in Fig. 17;

Fig. 19 is a sectional view of a still further example of the polishing pad of the present invention;

Fig. 20 is a plan view of an example of the polishing pad having a light transmitting member fixed in a through hole formed in the polishing substrate;

Fig. 21 is a plan view of another example of the polishing pad having light transmitting members fixed in through holes formed in the polishing substrate; Fig. 22 is a sectional view of an example of a polishing pad comprising a fixing layer;

Fig. 23 is a sectional view of another example of the polishing pad comprising a fixing layer;

Fig. 24 is a sectional view of still another example of the polishing pad comprising a fixing layer;

Fig. 25 is a sectional view of a further example of the polishing pad comprising a fixing layer;

Fig. 26 is a sectional view of an example of a polishing laminated pad of the present invention; and Fig. 27 is a diagram for explaining a polishing machine using the polishing pad or polishing laminated pad of the present invention.

## Detailed Description of the Preferred Embodiment

[0013] The present invention will be described in detail hereinunder.

**[0014]** The polishing pad of the present invention comprises a polishing substrate having a through hole extending from its polishing surface to the opposite surface and a light transmitting member arranged in this through hole.

[0015] The above polishing substrate has a polishing function by itself, preferably can hold slurry on the polishing surface and can retain the residual dust after polishing temporarily. More preferably, it can maintain its shape even when the light transmitting member is arranged in the through hole. It doesn't matter whether this polishing substrate has light transmission properties or not. The planar shape of the polishing substrate is not particularly limited and may be circular or polygonal such as quadrangular. The size of the polishing substrate is not particularly limited as well. The thickness of the polishing substrate may vary according to application purpose but 0.5 mm or more, preferably 1 to 3 mm, for example. The thickness may be totally constant or partially different.

**[0016]** Preferably, the polishing surface of the above polishing substrate has a structure that at least microholes (to be referred to as "pores" hereinafter), grooves, depressions or fluff is formed during polishing in order to hold slurry and retain the residual dust after polishing temporarily. They may have a predetermined shape such as a dot pattern or random shape. They may be formed in advance or formed during polishing. Fluff may be formed by surface renewal.

[0017] The polishing substrate is selected from (1) a polishing substrate which comprises a water-insoluble matrix material (A) and a water-soluble substance (B) (in a form of particle or fiber) dispersed in the water-insoluble matrix material (A) and forms pores or grooves

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during polishing, (2) a polishing substrate such as a foamed material which comprises a water-insoluble matrix material (A) and pores dispersed in the water-insoluble matrix material (A), and (3) a polishing substrate which consists only of a water-insoluble matrix (A) and can be fluffed by surface renewal.

**[0018]** Various material may be used as the above water-insoluble matrix material (A). An organic material is preferably used because it can be easily molded to have a predetermined shape or properties easily and can provide suitable elasticity. As the organic material may be used a thermoplastic resin, thermosetting resin, elastomer or rubber. They may be used alone or in combination of two or more. It doesn't matter whether the above water-insoluble matrix material (A) has light transmission properties or not.

**[0019]** Examples of the above thermoplastic resin include polyolefin resin, polystyrene resin, polyacrylic resin such as (meth)acrylate resin, vinyl ester resin excluding polyacrylic resin, polyester resin, polyamide resin, fluororesin, polycarbonate resin and polyacetal resin. They may be used alone or in combination of two or more.

**[0020]** Examples of the above thermosetting resin include phenolic resin, epoxy resin, unsaturated polyester resin, polyurethane resin, polyurethane resin, urea resin and silicon resin. They may be used alone or in combination of two or more.

[0021] Examples of the above elastomer include styrene elastomers such as styrene-butadiene-styrene block copolymer (SBS) and hydrogenated block copolymer thereof (SEBS), thermoplastic elastomers such as polyolefin elastomer (TPO), thermoplastic polyurethane elastomer (TPU), thermoplastic polyester elastomer (TPEE), polyamide elastomer (TPAE) and diene elastomer such as 1,2-polybutadiene, silicone resin elastomer and fluororesin elastomer. They may be used alone or in combination of two or more.

**[0022]** Examples of the above rubber include butadiene rubber, styrene-butadiene rubber, isoprene rubber, isobutylene-isoprene rubber, acrylic rubber, acrylonitrile·butadiene rubber, ethylene-propylene rubber, ethylene-propylene-diene rubber, silicone rubber and fluorine rubber. They may be used alone or in combination of two or more.

**[0023]** These materials may be modified by an acid anhydride group, carboxyl group, hydroxyl group, epoxy or amino group. The hydrophilic nature with the watersoluble material (B), abrasive grains and an aqueous medium contained in the slurry used for polishing of these materials can be adjusted by modification. The modified materials may be used in combination of two or more.

**[0024]** The above water-insoluble matrix material (A) may be a crosslinked polymer or non-crosslinked polymer. At least part of the matrix material (A) is preferably a crosslinked polymer. For example, when the water-insoluble matrix material (A) is a mixture of two or more

materials, at least part of at least one of the materials is a crosslinked polymer.

[0025] When at least part of the above water-insoluble matrix material (A) has a crosslinked structure, elastic recovery force can be provided to the polishing pad. Therefore, as displacement caused by shear stress applied to the polishing pad at the time of polishing can be suppressed, it is possible to prevent the pores formed by the dissolution or elimination of the water-soluble substance (B) from being filled by the plastic deformation of the water-insoluble matrix material (A) when it is excessively stretched at the time of polishing and surface renewal. It is also possible to prevent the surface of the polishing pad from being fluffed excessively. Consequently, the retainability of the slurry at the time of polishing is high, the retainability of the slurry is easily recovered by surface renewal, and further the scratching on the surface of the material to be polished can be prevented.

[0026] Examples of the above crosslinked polymer include polymers obtained by crosslinking resins such as polyurethane resin, epoxy resin, polyacrylic resin, unsaturated polyester resin and vinyl ester resin (excluding polyacrylic resin), diene-based elastomer (1,2-polybutadiene), butadiene rubber, isoprene rubber, acrylic rubber, acrylonitrile-butadiene rubber, styrene-butadiene rubber, ethylene-propylene rubber, silicone rubber, fluorine rubber and styrene-isoprene rubber, out of the above thermoplastic resins, thermosetting resins, elastomers and rubbers, and polymers obtained by crosslinking polyethylene or polyvinylidene fluoride in the presence of a crosslinking agent or through exposure to ultraviolet radiation or electron beam. Ionomers may also be used.

[0027] Out of these crosslinked polymers, crosslinked 1,2-polybutadiene is particularly preferred because it can provide sufficiently high light transmission properties, is stable to a strong acid or strong alkali contained in many kinds of slurry and further is rarely softened by water absorption. This crosslinked 1,2-polybutadiene may be used alone or mixed with other rubber such as butadiene rubber or isoprene rubber.

**[0028]** The above water-insoluble matrix material (A) may contain a material having a functional group. This material may be hydrophilic or hydrophobic. To improve compatibility with slurry, it is preferably hydrophilic. Examples of the hydrophilic material include the above materials modified by at least one selected from polar groups such as acid anhydride group, carboxyl group, hydroxyl group, epoxy group and amino group and (co) polymers comprising monomers having a functional group.

**[0029]** The (co)polymers comprising monomers having a functional group include copolymers comprising (i) an aliphatic conjugated diene monomer (to be referred to as "monomer (a)" hereinafter) as a polymerization unit, (ii) a monomer having at least one polymerizable unsaturated group and at least one functional group se-

lected from the group consisting of carboxyl group, amino group, hydroxyl group, epoxy group, sulfonic acid group and phosphoric acid group (to be referred to as "monomer (b)" hereinafter) as a polymerization unit and copolymers comprising (i), (ii) and (iii) a monomer having at least two polymerizable unsaturated groups (to be referred to as "monomer (c)" hereinafter) as polymerization units.

**[0030]** Examples of the above monomer (a) include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene and chloroprene. They may be used alone or in combination of two or more.

[0031] Out of the above monomers (b), monomers having a carboxyl group include unsaturated carboxylic acids such as (meth) acrylic acid, maleic acid, fumaric acid, itaconic acid, tetraconic acid and cinnamic acid; free carboxyl group-containing esters such as monoesters of a nonpolymerizable polycarboxylic acid such as phthalic acid, succinic acid or adipic acid and a hydroxyl group-containing unsaturated compound such as (meth)allyl alcohol or 2-hydroxyethyl (meth)acrylate, and salt compounds thereof. Out of these, unsaturated carboxylic acids are preferred. They may be used alone or in combination of two or more.

[0032] The monomer having an amino group is preferably a monomer having a tertiary amino group. Examples of the monomer having a tertiary amino group include dialkylaminoalkyl (meth)acrylates such as dimethylaminomethyl (meth)acrylate, diethylaminomethyl (meth)acrylate, 2-dimethylaminoethyl (meth)acrylate, 2-diethylaminoethyl (meth)acrylate, 2-(di-n-propylamino)ethyl (meth)acrylate, 2-dimethylaminopropyl (meth) acrylate, 2-diethylaminopropyl (meth)acrylate, 2-(di-npropylamino)propyl (meth)acrylate, 3-dimethylaminopropyl (meth)acrylate, 3-diethylaminopropyl (meth)acrylate and 3-(di-n-propylamino)propyl (meth)acrylate; Ndialkylaminoalkyl group-containing unsaturated amides such as N-dimethylaminomethyl (meth)acrylamide, Ndiethylaminomethyl (meth)acrylamide, N-(2-dimethylaminoethyl) (meth)acrylamide, N-(2-diethylaminoethyl) (meth)acrylamide, N-(2-dimethylaminopropyl) (meth) acrylamide, N-(2-diethylaminopropyl) (meth)acrylamide, N-(3-dimethylaminopropyl) (meth)acrylamide and N-(3-diethylaminopropyl) (meth)acrylamide; and tertiary amino group-containing vinyl aromatic compounds such as N,N-dimethyl-p-aminostyrene, N,N-diethyl-paminostyrene, dimethyl(p-vinylbenzyl)amine, diethyl(pvinylbenzyl)amine, dimethyl(p-vinylphenethyl)amine, diethyl(p-vinylphenethyl)amine, dimethyl(p-vinylbenzyloxymethyl)amine, dimethyl[2-(p-vinylbenzyloxy)ethyl] amine, diethyl(p-vinylbenzyloxymethyl)amine, diethyl [2-(p-vinylbenzyloxy)ethyl]amine, dimethyl (p-vinylphenethyloxymethyl) amine, dimethyl[2-(p-vinylphenethyloxy)ethyl]amine, diethyl(p-vinylphenethyloxymethyl)amine, diethyl[2-(p-vinylphenethyloxy)ethyl] amine, 2-vinylpyridine, 3-vinylpyridine and 4-vinylpyridine. Out of these, dialkylaminoalkyl (meth)acrylates and tertiary amino group-containing vinyl aromatic compounds are preferred. They may be used alone or in combination of two or more.

[0033] Examples of the monomer having a hydroxyl group include hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth) acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate; mono(meth)acrylates of a polyalkylene glycol (the number of alkylene glycol units is preferably 2 to 23) such as polyethylene glycol and polypropylene glycol; hydroxyl group-containing unsaturated amides such as N-hydroxymethyl (meth) acrylamide, N-(2-hydroxyethyl) (meth)acrylamide and N,N-bis(2-hydroxyethyl) (meth)acrylamide; hydroxyl group-containing vinyl aromatic compounds such as ohydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, o-hydroxy- $\alpha$ -methylstyrene, m-hydroxy- $\alpha$ -methylstyrene, p-hydroxy-α-methylstyrene and p-vinylbenzyl alcohol; and (meth)allyl alcohols. Out of these, hydroxylalkyl (meth)acrylates and hydroxyl group-containing vinyl aromatic compounds are preferred. They may be used alone or in combination of two or more.

**[0034]** Examples of the monomer having an epoxy group include (meth)allyl glycidyl ethers, glycidyl (meth) acrylates and 3,4-oxycyclohexyl (meth)acrylates. They may be used alone or in combination of two or more.

[0035] Examples of the monomer having a sulfonic acid group include (meth)acrylamide monomers such as 2-(meth)acrylamidoethanesulfonic acid, 2-(meth) acrylamidopropanesulfonic acid, 3-(meth)acrylamidopropanesulfonic acid, 2-(meth)acrylamido-2-methylpropanesulfonic acid and 3-(meth)acrylamido-2-methylpropanesulfonic acid; (meth)acrylate monomers such as ethyl (meth)acrylate 2-sulfonate, propyl (meth)acrylate 2-sulfonate, propyl (meth)acrylate 2-sulfonate; vinyl aromatic compounds monomers such as p-vinylbenzenesulfonic acid and p-isopropenylbenzenesulfonic acid; and salt compounds thereof. They may be used alone or in combination of two or more.

[0036] Examples of the monomer having a phosphoric acid group include ethylene (meth)acrylate phosphate, trimethylene (meth)acrylate phosphate, tetramethylene (meth)acrylate phosphate, propylene (meth) acrylate phosphate, bis(ethylene (meth)acrylate)phosphate, bis(trimethylene (meth)acrylate)phosphate, bis (tetramethylene (meth)acrylate)phosphate, diethylene glycol (meth)acrylate phosphate, triethylene glycol (meth)acrylate phosphate, bis(diethylene glycol (meth)acrylate)phosphate, bis(diethylene glycol (meth)acrylate)phosphate, bis(triethylene glycol (meth)acrylate)phosphate, bis(polyethylene glycol (meth)acrylate)phosphate and salt compounds thereof. They may be used alone or in combination of two or more.

[0037] Examples of the above monomer (c) include ethylene glycol di(meth)acrylate, propylene glycol di (meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane di

(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra (meth)acrylate, divinylbenzene, diisopropenylbenzene and trivinylbenzene. They may be used alone or in combination of two or more.

**[0038]** The above (co)polymer comprising monomers having a functional group can be manufactured by the radical polymerization, anion polymerization or cation polymerization of the above monomers (a), (b) and (c) as hydrophilic substances. In the case of a copolymer, it may be a random copolymer, block copolymer or graft copolymer.

**[0039]** When the material having a functional group is contained in the water-insoluble matrix material (A), the content of the material is preferably 90 % or less by mass, more preferably 0.1 to 80 % by mass, much more preferably 0.2 to 50 % by mass based on 100 % by mass of the water-insoluble matrix material (A).

[0040] The residual elongation after breakage (to be simply referred to as "residual elongation at break" hereinafter) of the above water-insoluble matrix material (A) is preferably 100 % or less when a specimen of the above water-insoluble matrix material (A) is broken at 80°C in accordance with JIS K 6251. This means that the total distance between bench marks of the specimen after breakage is preferably 2 times or less the distance between the bench marks before breakage. This residual elongation at break is preferably 30 % or less, more preferably 10 % or less, particularly preferably 5 % or less. It is generally 0 % or more. As the above residual elongation at break becomes higher than 100 %, fine pieces scraped off from the surface of the polishing substrate or stretched at the time of polishing and surface renewal tend to fill the pores.

[0041] The "residual elongation at break" is an elongation obtained by subtracting the distance between bench marks before the test from the total distance between each bench mark and the broken portion of the broken and divided specimen in a tensile test in which a dumbbell-shaped specimen No. 3 is broken at a tensile rate of 500 mm/min and a test temperature of 80°C in accordance with the "vulcanized rubber tensile test method" specified in JIS K 6251. The test temperature is 80°C as the temperature reached by slide contact at the time of actual polishing is about 80°C.

[0042] The water-soluble substance (B) in the above polishing substrate (1) can form pores which can hold the slurry and retain the residual dust after polishing temporarily at a position where it is eliminated from the surface of the polishing substrate when it is dissolved or swollen by its contact with the slurry or the like supplied from the outside at the time of polishing. Various materials may be used to form this water-soluble substance (B). It may be an organic water-soluble substance or inorganic water-soluble substance. Or it may be a water-absorptive substance if it has the above functions

[0043] Examples of the organic water-soluble sub-

stance include dextrin, cyclodextrin, mannitol, saccharides such as lactose, celluloses such as hydroxypropyl cellulose and methyl cellulose, starch, protein, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid, polyethylene oxide, water-soluble photosensitive resin, sulfonated polyisoprene and sulfonated polyisoprene copolymer.

**[0044]** Examples of the inorganic water-soluble substance include potassium sulfate, potassium acetate, potassium nitrate, potassium carbonate, potassium bydrogencarbonate, potassium chloride, potassium bromide, potassium phosphate and magnesium nitrate.

**[0045]** Out of these, cyclodextrin and potassium sulfate are preferred. They may be used alone or in combination of two or more. Organic and inorganic watersoluble substances may be used in combination.

**[0046]** Preferably, the water-soluble substance (B) dissolves in water only when it is exposed to the surface of the polishing substrate and does not absorb moisture or gel when it does not surface and stays in the interior of the polishing substrate. Therefore, an outer shell for suppressing moisture absorption made of epoxy resin, polyimide, polyamide, polypeptide or polysilicate may be formed on at least part of the outermost portion of the water-soluble substance (B).

[0047] The water-soluble substance (B) is preferably solid but may be liquid. The liquid water-soluble substance (B) includes a water-soluble substance which is liquid itself and also a water-soluble substance which is not liquid but solid at normal temperature and dissolves in a medium, mainly water, to become an aqueous solution. The liquid water-soluble substance (B) preferably has no bad influence upon polishing efficiency by dissolution into the slurry during polishing. Examples of the liquid water-soluble substance (B) include organic acids such as formic acid, acetic acid, an aqueous solution of tartaric acid, aqueous solution of succinic acid and aqueous solution of malonic acid, and oxidizing aqueous solutions such as aqueous solution of hydrogen peroxide, aqueous solution of peracetic acid and nitric acid. [0048] The solid water-soluble substance (B) is not limited to a particular shape and may be particulate, i. e., globular, angular, odd-shaped (tetrapod-shaped, star-shaped, etc.) or fibrous. The water-soluble substance (B) is preferably almost globular, particularly preferably spherical. When the water-soluble substance (B) is liquid, it does not have a shape.

[0049] The size of the above water-soluble substance (B) is preferably uniform. The average particle diameter of the water-soluble substance (B) is preferably 0.1 to 500  $\mu m$ , more preferably 0.5 to 200  $\mu m$ , particularly preferably 1 to 150  $\mu m$ . When this average particle diameter is smaller than 0.1  $\mu m$ , the pores formed during polishing may be smaller than the abrasive grains contained in the slurry so that the abrasive grains may not be held in the pores disadvantageously. When the average particle diameter is larger than 500  $\mu m$ , the formed pores become too large, whereby the mechanical strength and

polishing rate of the obtained polishing pad may lower. [0050] When the above polishing substrate is the above polishing substrate (1), the content of the watersoluble substance (B) is preferably 0.1 to 90 vol%, more preferably 10 to 90 vol%, much more preferably 12 to 60 vol%, particularly preferably 15 to 45 vol% based on 100 vol% of the total of the water-insoluble matrix material (A) and the water-soluble substance (B). When the content of the water-soluble substance (B) is lower than 0.1 vol%, the pores are not fully formed in the polishing surface of the polishing substrate during polishing and the polishing rate may lower. When the content of the water-soluble substance (B) is higher than 90 vol%, it may be difficult to completely prevent the water-soluble substance (B) dispersed in the water-insoluble matrix material (A) from being gelled or dissolved one after another during polishing and therefore to maintain the hardness and mechanical strength of the polishing substrate at appropriate values.

**[0051]** The above through hole extends from the front to rear surfaces, i.e., from the polishing surface to the opposite surface of the polishing substrate and is formed to fix the light transmitting member. The above through hole may be formed at any position, center portion or end portion of the polishing substrate. When it is formed in the end portion, the end of the polishing substrate may be a cut-away portion. The through hole may be formed in the polishing substrate vertically or obliquely.

[0052] The shape of the above through hole is not particularly limited and its planar shape in a direction perpendicular to the polishing surface may be polygonal such as square, rectangular or trapezoidal, circular, fanshaped or annular. Out of these, square, rectangular and circular shapes are preferred from the viewpoints of the permeability and adhesion of a photocurable adhesive used to fix the light transmitting member. The sectional form of the above through hole may be, for example, T-shaped, inverted T-shaped, quadrangular or other shape. Figs. 2 to 6 show examples of the through hole. The edge portions of the polishing substrate corresponding to the openings of the above through hole may be chamfered as shown in Fig. 7. In Figs. 2 to 7, the top side is the polishing surface side. In Figs. 2 to 7, reference numeral 11 denotes the polishing substrate and 12 the through hole.

**[0053]** The size of the above through hole is not particularly limited. However, when its opening is circular, the opening preferably has a diameter of 20 mm or more (which is generally 2/3 or less the radius of the polishing pad), when the opening is annular, its width is 20 mm or more which is generally 2/3 or less the radius of the polishing pad, and when the opening is quadrangular, it preferably has a length of 30 mm or more which is generally 2/3 or less the radius of the polishing pad and a width of 10 mm or more which is generally 2/3 or less the radius of the polishing pad. When the above through hole is shorter than the above length, it may be difficult

for the through hole to transmit light such as light for end-point detection. The number of the through holes is not particularly limited.

**[0054]** The above through hole may be formed by cutting, for example, with a punching blade, a laser cutter, a fret saw or end mill. The through hole may be formed by using a mold at the time of molding.

[0055] The above light transmitting member is arranged in the above through hole and has light transmission properties to facilitate the detection of the polishing end point. The term "light transmission properties" as used herein means the ability of transmitting light. The degree of the light transmission properties is not particularly limited. Preferably, when the thickness of the above light transmitting member is 2 mm, it has a transmittance at a wavelength between 100 and 3,000 nm of 0.1 % or more or an integrated transmittance at a wavelength between 100 to 3,000 nm of 0.1 % or more. This transmittance or integrated transmittance is preferably 1 % or more, more preferably 2 % or more. The transmittance or integrated transmittance does not need to be higher than required, and may be 50 % or less, preferably 30 % or less, particularly preferably 20 % or less.

[0056] The transmittance at a wavelength between 400 nm and 800 nm which is frequently used for endpoint detection of a polishing pad used for polishing using an optical end-point detection device is preferably high. When the polishing pad has a thickness of 2 mm, it has a transmittance at a wavelength between 400 nm and 800 nm of preferably 0.1 % or more, more preferably 1 % or more, much more preferably 2 % or more, particularly preferably 3 % or more and generally 50 % or less, or an integrated transmittance at a wavelength between 400 nm and 800 nm of preferably 0.1 % or more, more preferably 1 % or more, much more preferably 2 % or more, particularly preferably 3 % or more and generally 90 % or less.

**[0057]** This transmittance or integrated transmittance does not need to be higher than required and may be 20 % or less, preferably 10 % or less, particularly preferably 5 % or less.

**[0058]** The above transmittance is a value measured at each wavelength with an UV absorptiometer which can measure the absorbance of a 2 mm-thick specimen at a predetermined wavelength. The integrated transmittance can be obtained by integrating transmittances measured similarly at a predetermined wavelength range.

[0059] The material of the light transmitting member in the present invention is not particularly limited if it provides the above light transmission properties. It may be made of a polymer material such as a resin alone or a crystalline inorganic material having light transmission properties. In the present invention, the above light transmitting member preferably contains a water-insoluble matrix material (A) and a water-soluble substance (B) dispersed in this water-insoluble matrix material (A).

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[0060] As the above water-insoluble matrix material (A), the same materials as those enumerated in the description of the water-insoluble matrix material (A) for forming the above polishing substrate may be used alone or in combination of two or more as far as they have light transmission properties even when the water-soluble substance (B) is dispersed therein. The preferred properties and shape of the material may be the same as above. The water-insoluble matrix material (A) may be the same or different from the water-insoluble matrix material (A) for forming the above polishing substrate.

[0061] At least part of the above water-insoluble matrix material (A) is preferably a crosslinked polymer, which is more preferably crosslinked 1,2-polybutadiene. [0062] As the above water-soluble substance (B), the same materials as those enumerated as the water-soluble substance (B) in the above polishing substrate (1) may be used alone or in combination of two or more. The preferred properties and shape of the substance may be the same as above. The water-soluble substance (B) may be the same or different from the water-soluble substance (B) for forming the above polishing substrate.

[0063] The above water-soluble substance (B) has the function of matching the indentation hardness of the light transmitting member with the hardness of the polishing substrate. The Shore D hardness of the entire polishing pad is preferably 35 to 100 in order to increase pressure to be applied at the time of polishing, improve the polishing rate and obtain high flatness. However, it may be difficult to obtain a desired Shore D hardness only from the above water-insoluble matrix material (A). In this case, the solid water-soluble substance (B) is dispersed into the water-insoluble matrix material (A) to increase the shore D hardness to the same level as that of the polishing substrate and the indentation hardness of the whole polishing pad to a satisfactory level, besides the formation of pores by the elimination of the solid water-soluble substance (B) during polishing.

[0064] The content of the above water-soluble substance (B) in the above light transmitting member is preferably 0.1 to 90 vol%, more preferably 0.5 to 30 vol%, much more preferably 1 to 10 volt, particularly preferably 15 to 45 volt based on 100 volt of the total of the water-insoluble matrix material (A) and the water-soluble substance (B). When the content of the water-soluble substance (B) is lower than 0.1 volt, the number of pores formed during polishing is small and a desired polishing rate is hardly obtained. When the content is larger than 90 vol%, the polishing pad may become too fragile.

**[0065]** The method of providing light transmission properties is not particularly limited. For example, it can be realized by controlling crystallinity. The above water-insoluble matrix material (A) does not need to be transparent itself (including semi-transparent) if it can provide light transmission properties (it doesn't matter whether it can transmit visible light). It preferably has higher light

transmission properties, more preferably is transparent. **[0066]** The shape of this light transmitting member is not particularly limited. The planar shape of the light transmitting member generally depends upon the shape of the through hole. Therefore, the shape of the above light transmitting member is generally the same as the shape of the through hole and may be polygonal, circular, fan-shaped or annular. The size of the above light transmitting member may be completely the same as the through hole and may be larger or smaller than the through hole in consideration of the thickness of an adhesive layer made of a photocurable adhesive formed at the interface between the light transmitting member and the inner wall of the through hole.

[0067] The sectional form of the light transmitting member is not particularly limited. Any shape is acceptable if at least part thereof can be arranged in the through hole. For example, it may have sectional forms shown in Fig. 1 and Figs. 8 to 17. Fig. 1, Fig. 8 and Fig. 9 show polishing pads in which the light transmitting member 2 having almost the same thickness and shape as the polishing substrate 11 is arranged in, bonded to and fixed in the through hole. Figs. 10 to 17 show polishing pads in which the light transmitting member 2 different from the polishing substrate 11 in thickness and shape, that is, is made thin is arranged in, bonded to and fixed in the through hole (Figs. 10 to 15), or only part of the outer wall opposed to the inner wall of the through hole of the polishing substrate of the light transmitting member is fixed with an adhesive (Fig. 16 and Fig. 17). An image showing part of the polishing pad shown in Fig. 17 is shown in Fig. 18.

[0068] When light is transmitted through the light transmitting member, the intensity of the light attenuates in proportion to the square of the thickness of the light transmitting member. Therefore, by using a light transmitting member which has been made thin, light transmission properties can be greatly improved and the polishing end point can be easily detected. The expression "made thin" means that the thickness of the light transmitting member is made smaller than the maximum thickness of the polishing substrate in a direction perpendicular to the polishing surface of the polishing pad and includes a case where a light transmitting portion of the above light transmitting member is made thin as shown in Fig. 14.

**[0069]** The thickness of the above light transmitting member is preferably 0.1 mm or more, more preferably 0.3 mm or more and generally 3 mm or less. When the thickness is smaller than 0.1 mm, it is difficult to secure sufficiently high mechanical strength for the light transmitting member.

[0070] A depressed portion, where the light transmitting member is not existent in the through hole, formed by making the light transmitting member thin (Fig. 11) or a depressed portion of the light transmitting member (Fig. 15) may be formed on either one of the front and rear sides of the polishing pad. When it is formed on the

rear side (non-polishing surface) of the polishing pad, the light transmitting member can be made thin without affecting polishing efficiency.

**[0071]** The number of the above light transmitting members is not particularly limited and may be one or more corresponding to the number of the through holes. The position (s) of the light transmitting member(s) is/ are not particularly limited. For example, when the polishing pad has one light transmitting member, it may be arranged as shown in Fig. 20. Further, when the polishing pad has two or more light transmitting members, they may be arranged concentric to one another as shown in Fig. 21.

**[0072]** The polishing pad of the present invention may have a plurality of light transmitting members which differ in light transmission properties in one through hole or in respective through holes.

**[0073]** Additives such as an abrasive grain, oxidizing agent, alkali metal hydroxide, acid, pH modifier, surfactant and scratch prevention agent all of which have been contained in slurry may be contained in the above polishing substrate forming the polishing pad of the present invention.

**[0074]** In addition to the above additives, additives such as a filler, softening agent, antioxidant, ultraviolet light absorber, antistatic agent, lubricant and plasticizer may be further contained. Examples of the filler include materials for improving stiffness such as calcium carbonate, magnesium carbonate, talc and clay, and materials having a polishing effect such as silica, alumina, ceria, zirconia, titania, manganese dioxide, dimanganese trioxide and barium carbonate. They may be used alone or in combination of two or more.

**[0075]** The above light transmitting member may also contain the above additives in limits that it can maintain light transmission properties.

[0076] A compatibilizing agent may be blended to improve compatibility between the water-insoluble matrix material (A) and the water-soluble substance (B) for forming the polishing pad substrate and the light transmitting member and the dispersibility of the water-soluble substance (B) contained in the water-insoluble matrix material (A). Examples of the compatibilizing agent include a homopolymer, block copolymer or random copolymer modified by an acid anhydride group, carboxyl group, hydroxyl group, epoxy group, oxazoline group or amino group, a nonionic surfactant, a coupling agent and the residues thereof. They may be used alone or in combination of two or more.

**[0077]** The method of dispersing the water-soluble substance (B) into the water-insoluble matrix material (A) to form the above polishing pad substrate and the light transmitting member is not particularly limited. In general, the water-insoluble matrix material (A), the water-soluble substance (B) and other additives are kneaded together. Although the water-insoluble matrix material (A) is kneaded under heating so that it can be easily processed, the water-soluble substance (B) is prefera-

bly solid at the kneading temperature. When the water-soluble substance (B) is solid, it is easily dispersed while it maintains the above preferred average particle diameter irrespective of its compatibility with the above water-insoluble matrix material (A). Therefore, the type of the water-soluble substance (B) is preferably selected according to the processing temperature of the water-insoluble matrix material (A) in use.

**[0078]** When the above components are kneaded together, reactive additives such as sulfur and peroxide may be added. The composition obtained by kneading is introduced into a metal mold having a predetermined shape and heated to obtain the polishing substrate or light transmitting member.

**[0079]** The polishing pad of the present invention is such that at least the outer wall of the above light transmitting member and the inner wall of the above through hole opposed to the outer wall are bonded together with a photocured adhesive layer so that the above light transmitting member is fixed in the above through hole. Part or all of the outer wall of the light transmitting member may be bonded with the above photocured adhesive layer.

[0080] Although only part of the outer wall of the light transmitting member may be bonded as described above, the light transmitting member must be fixed in the above through hole without the gap therebetween in a direction perpendicular to the polishing surface of the polishing pad. As far as the light transmitting member is fixed as described above, the photocured adhesive layer may be existent at any position (see Fig. 1, Figs. 8 to 17 and Fig. 19. The top side is the polishing surface side in these figures). For instance, Fig. 8, Fig. 9 and Figs. 13 to 15 show polishing pads 1 in which the inner wall of the through hole formed in the polishing substrate 11 and the outer wall of the light transmitting member 2 are totally in contact with each other and the photocured adhesive layer 3 is formed on all the contact portions. Figs. 10 to 12 show polishing pads 1 in which one or two contact portions between the inner wall of the through hole formed in the polishing substrate 11 and the outer wall of the light transmitting member 2 are perfectly bonded with the photocured adhesive layer 3. Fig. 16 and Fig. 17 shows examples in which the light transmitting member 2 smaller than the through hole in size is arranged and the adhesive layer 3 is formed on the non-polishing side of the polishing pad. Fig. 1 shows a polishing pad 1 in which the entire surface of the light transmitting member 2 on the non-polishing side of the polishing pad is covered with the same material as the photocured adhesive layer and the cover film is integrated with the adhesive layer.

[0081] As obvious from Fig. 1, Figs. 8 to 17 and Fig. 19, there is no gap which communicates from the polishing side to the non-polishing side of the polishing pad between the outer wall of the light transmitting member 2 as a window member and the inner wall of the through hole in the polishing substrate 11 due to the photocured

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adhesive layer 3, thereby making it possible to prevent the slurry from leaking to the non-polishing side of the polishing pad during polishing. In order to further enhance this effect, it is preferred to increase the area of the adhesive layer 3. As shown in Fig. 8, Fig. 9, Figs. 13 to 15 and Fig. 19, it is more preferred to form the adhesive layer at the entire interface between the outer wall of the light transmitting member and the inner wall of the through hole opposed to the outer wall. Fig. 1 shows that the non-polishing side surface of the light transmitting member 2 is also covered with the same material as the photocured adhesive layer, which makes it possible to effectively prevent a leak of the slurry. Further, as shown in Fig. 19, the photocured adhesive layer is formed to cover the entire light transmitting member 2 on the non-polishing side of the polishing pad and constitutes a continuous phase with the adhesive layer formed between the outer wall of the light transmitting member 2 and the inner wall of the through hole, which makes it possible to prevent a leak of the slurry with more certainty. In this case, the layer may perfectly cover the light transmitting member 2 and may be formed on the entire non-polishing surface of the polishing pad as shown in Fig. 19.

**[0082]** The thickness of the above layer is not particularly limited but preferably has sufficiently high strength. When the photocured adhesive layer is transparent, it preferably has a thickness that provides sufficiently high light transmission properties.

**[0083]** The photocurable adhesive for forming the above photocured adhesive layer is not particularly limited if it has photocurability and adhesion. Preferably, it has light transmission properties at a wavelength between 400 nm and 800 nm after it is photocured.

[0084] The term "light transmission properties" means that the transmittance of light having a wavelength between 400 nm and 800 nm is preferably 0.1 % or more, more preferably 1 % or more, much more preferably 2 % or more, particularly preferably 3 % or more and generally 50 % or less, or the integrated transmittance of light having a wavelength between 400 nm and 800 nm is preferably 0.1 % or more, more preferably 1 % or more, much more preferably 2 % or more, particularly preferably 3 % or more and generally 90 % or less when the thickness is 2 mm.

**[0085]** The transmittance or integrated transmittance does not need to be higher than required and generally 20 % or less and may be 10 % or less, specifically 5 % or less.

**[0086]** Preferably, the photocurable adhesive contains a resin component and an ethylenically unsaturated monomer and optionally a photopolymerization initiator and other additives.

**[0087]** Examples of the resin component include polyurethane (meth)acrylates, polyester (meth)acrylates, epoxy (meth)acrylates, polyamide (meth)acrylates, (meth)acryloyloxy group-containing siloxane polymers, glycidyl (meth)acrylates, and reactive polymers ob-

tained by reacting a polymer of other polymerizable monomer with (meth)acrylic acid. Out of these, polyurethane (meth)acrylates which have light transmission properties and provide a cured product having high strength are preferred.

**[0088]** The above polyurethane (meth)acrylates are produced by reacting a polyol compound, a polyisocyanate compound and a hydroxyl group-containing (meth)acrylate compound.

**[0089]** Specifically, they are manufactured by reacting the isocyanate group of a polyisocyanate compound with the hydroxyl group of a polyol compound and the hydroxyl group of a hydroxyl group-containing (meth) acrylate compound. For example, the following four processes may be used to manufacture the polyurethane (meth)acrylates.

Process 1: A polyol compound, a polyisocyanate compound and a hydroxyl group-containing (meth)acrylate compound are charged at the same time to be reacted with one another.

Process 2: A polyol compound and a polyisocyanate compound are first reacted with each other and then with a hydroxyl group-containing (meth)acrylate compound.

25 Process 3: A polyisocyanate compound and a hydroxyl group-containing (meth)acrylate compound are first reacted with each other and then with a polyol compound. Process 4: A polyisocyanate compound and a hydroxyl group-containing (meth)acrylate compound are first reacted with each other, then with a polyol compound and finally with a hydroxyl group-containing (meth)acrylate compound again.

**[0090]** Examples of the polyol compound as a raw material for the polyurethane (meth)acrylates include aromatic polyether polyols, aliphatic polyether polyols, alicyclic polyether polyols, polyester polyols, polycarbonate polyols and polycaprolactone polyols. Out of these, aliphatic polyether polyols are preferred.

[0091] Examples of the polyisocyanate compound include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, 1,4-hexamethylene diisocyanate, bis(2-isocyanateethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocynate, hydrogenated xylylene diisocyanate and tetramethylxylylene diisocyanate.

**[0092]** Examples of the hydroxyl group-containing (meth)acrylate compound include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypro-

pyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl (meth)acryloyl phosphate, 4-hydroxycyclohexyl (meth)acrylate, 1,6-hexanediol mono(meth) acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di (meth)acrylate, pentaerythritol tri(meth)acrylate and dipentaerythritol penta(meth)acrylate.

**[0093]** The number average molecular weight of the urethane (meth)acrylate compound thus obtained as the water-insoluble matrix material (A) of the present invention is preferably 1,000 to 40,000, more preferably 1,000 to 20,000.

[0094] Examples of the above ethylenically unsaturated monomer include acryloylmorpholine, dimethylacrylamide, diethylacrylamide, diisopropylacrylamide, isobornyl (meth)acrylate, dicyclopentenyl acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyloxyethyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, cyclohexyl methacrylate, dicyclopentadienyl (meth)acrylate, tricyclodecanyl (meth)acrylate, diacetone acrylamide, isobutoxymethyl (meth)acrylamide, Nvinylpyrrolidone, N-vinylcaprolactam, 3-hydroxycyclohexyl acrylate and 2-acryloylcyclohexylsuccinic acid. [0095] The photopolymerization initiator which may be optionally added to the photocurable adhesive used in the present invention is, for example, an ultraviolet light sensitive photopolymerization initiator. Examples of the photopolymerization initiator include 1-hydroxycyclohexylphenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one and 2,4,6-trimethylbenzoyldiphenylphosphine oxide.

**[0096]** The photocurable adhesive used in the present invention may contain a sensitizer, surfactant, etc. in addition to the above additives.

[0097] The viscosity at 25°C of the above photocurable adhesive is preferably 1,000 to 100,000 mPa·s, more preferably 2,000 to 50, 000 mPa·s, much more preferably 3,000 to 30,000 mPa·s. When this viscosity is lower than 1,000 mPa·s, the photocurable adhesive may overflow into the polishing surface of the polishing pad from the gap between the outer wall of the light transmitting member and the inner wall of the through hole at the time of use due to high flowability. When the viscosity is higher than 100,000 mPa·s, the flowability may lower and the work efficiency may deteriorate.

**[0098]** Preferably, the above photocurable adhesive has an adhesive strength under shear after curing of 5 to 9 MPa and a Young's modulus after curing of 50 to

70 MPa.

**[0099]** The method of fixing the light transmitting member in the through hole with the above photocurable adhesive is not particularly limited but the following methods may be used.

- (1) After the photocurable adhesive is applied to the bonding portion of the outer wall of the light transmitting member or the inner wall of the through hole, the light transmitting member is fitted in the through hole, and the photocurable adhesive is cured by exposure to fix the light transmitting member in the through hole.
- (2) After the light transmitting member is fitted in the through hole, the photocurable adhesive is filled in the gap between the outer wall of the light transmitting member and the inner wall of the through hole and cured by exposure to fix the light transmitting member in the through hole.
- (3) After the light transmitting member is fitted in the through hole, the photocurable adhesive is applied to the surface of the light transmitting member on the non-polishing side while it is filled into the gap between the outer wall of the light transmitting member and the inner wall of the through hole and cured by exposure to fix the light transmitting member in the through hole.

**[0100]** In all of the above methods, preferably, the photocurable adhesive does not overflow into the polishing surface of the polishing pad.

**[0101]** The photocurable adhesive is cured by exposure to visible radiation, ultraviolet radiation, far ultraviolet radiation, electron radiation, X-radiation, etc. Out of these, radiation having a wavelength of 190 to 450 nm is preferred. Exposure to the above radiation can be carried out by using a mercury lamp, etc.

[0102] The amount of exposure is preferably 10 to  $10,000 \text{ J/m}^2$ .

**[0103]** A fixing layer may be formed on the non-polishing surface of the polishing pad of the present invention to fix the polishing pad on a polishing machine, specifically the platen of a polishing machine. The fixing layer is not limited to a particular material and shape if it can fix the polishing pad.

**[0104]** The light transmission properties of the material for forming the above fixing layer are not particularly limited. When the material for forming the above fixing layer has light transmission properties, the fixing layer can be formed to cover the entire non-polishing surface of the polishing pad (See Fig. 22 and Fig. 23, numeral 4 denotes the fixing layer). When the material for forming the fixing layer does not have light transmission properties or low light transmission properties, a through hole may be formed at a position corresponding to the light transmission member (see Fig. 24). This through hole may have the same or different area from the through hole formed in the polishing substrate. When it

has a different area, it may be larger or smaller than the through hole.

[0105] The above fixing layer may consist of a single layer or multiple layers (see Fig. 22 and Fig. 24, the top side is a polishing side in these figures). Examples of the fixing layer include a layer composed of an adhesive material such as an adhesive double-coated tape, an adhesive layer formed by applying an adhesive, and a shear preventing layer making use of great friction with the surface of the platen of a polishing machine. When the above fixing layer is an adhesive layer composed of an adhesive material such as an adhesive double-coated layer or an adhesive layer formed by applying an adhesive, a peel layer 42 is formed as the outermost layer as required and combined with an adhesive layer 41 to form a fixing layer 4 (see Fig. 25). When this peel layer 42 is existent, the adhesive layer 41 can be protected before use and the polishing pad can be easily fixed on the polishing machine by removing this peel layer 42 at the time of use.

**[0106]** Out of the above fixing layers, the layer composed of an adhesive double-coated tape is preferred because it has a peel layer. The adhesive component which can be used in the above fixing layer may be a thermoplastic adhesive such as an acrylic or synthetic rubber adhesive, thermosetting or photocurable adhesive. Commercially available products of the adhesive include #442 of Sumitomo 3M Limited, and #5511 and #5516 of Sekisui Chemical Co., Ltd.

**[0107]** When the layer composed of an adhesive double-coated tape is used as the above fixing layer, a through hole is preferably formed at a predetermined position of the adhesive double-coated tape. The method of forming this through hole is not particularly limited. The through hole may be formed with a laser cutter or punching blade. When the laser cutter is used, the through hole may be formed after the fixing layer is formed of an adhesive double-coated tape.

**[0108]** The polishing laminated pad of the present invention comprises the above-described polishing pad and a base layer formed on the non-polishing surface (rear surface opposite to the polishing surface) of the polishing pad and has light transmission properties in the lamination direction (see Fig. 26. Reference numeral 5 denotes a polishing laminate pad and 6 denotes a base layer, and the top side is the polishing side).

**[0109]** The above base layer is formed on the rear surface opposite to the polishing surface of the polishing pad. The material for forming the base layer is not particularly limited and various materials may be used. An organic material is preferably used because it is easily molded to have a predetermined shape and predetermined properties and can provide suitable elasticity. The same materials as those used for the water-insoluble matrix material (A) of the above light transmitting member may be used as this organic material. The material for forming the base layer may be the same or different from the water-insoluble matrix material (A) of the light

transmitting member or the water-insoluble matrix material (A) of the above polishing pad substrate.

**[0110]** It doesn't matter whether the base layer has light transmission properties or not. For example, when a base layer made of a material having the same or higher light transmission properties than the above light transmitting member is used, light transmission properties can be secured for the polishing laminated pad. In this case, a cut-away may or may not be formed. Further, when a base layer having no light transmission properties is used, the light transmission properties of the polishing laminated pad can be secured by cutting away part of the base layer for transmitting light.

**[0111]** The shape of the above base layer is not particularly limited and may be circular, polygonal plate-like, for example, quadrangular, or lattice-like. In general, it has the same or larger planar size than the polishing pad. When it has a cut-away portion for securing light transmission, this portion is excluded. The thickness of the base layer is not particularly limited but generally 0.1 to 2 times the thickness of the above polishing pad substrate. It is preferably like a thin plate.

**[0112]** The above base layer may consist of a single layer or multiple layers. When it consists of two or more layers, they are made of the same component or different components.

**[0113]** The hardness of the above base layer is not particularly limited but preferably lower than that of the polishing pad substrate. Thereby, the polishing laminated pad has sufficiently high flexibility and suitable conformability to the unevenness of the surface to be polished as a whole.

**[0114]** A fixing layer may be formed on the polishing laminated pad of the present invention like the above polishing pad. It is generally formed on the rear surface of the base layer.

**[0115]** The polishing pad and polishing laminated pad of the present invention are suitably used to polish a material to be polished such as a semiconductor wafer or liquid crystal substrate.

[0116] Since the polishing pad of the present invention has transmits light through its light transmitting member, when it is set in a polishing machine equipped with an optical end-point detection device, it can be advantageously used to polish a semiconductor wafer, etc. Since the polishing laminated pad having a base layer on the rear surface of the above polishing pad has a portion for transmitting light such as a cut-away in the above base layer, it can be used with a polishing machine equipped with an optical end-point detection device as well. This optical end-point detection device detects the polishing end point by transmitting light from the rear surface of the polishing pad to the polishing surface to input it on the surface to be polished and monitoring the polishing condition of the surface to be polished with light reflected from the surface to be polished. For example, when the polishing pad or the polishing laminated pad of the present invention is disk-shaped,

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light transmitting members are arranged in a loop and concentric to the center of the disk so that polishing can be carried out while the polishing end point is always monitored. When this optical end-point detection device is used, polishing can be ended at the optimum polishing end point with certainty without polishing excessively, which is very efficient.

**[0117]** The method of polishing a semiconductor wafer of the present invention is to polish a semiconductor wafer with the polishing pad or polishing laminated pad of the present invention, using an optical end-point detection device to detect the polishing end point of the semiconductor wafer.

**[0118]** The above optical end-point detection device is as described above. In the method of polishing a semiconductor wafer of the present invention, the polishing machine as shown in Fig. 27 may be used. That is, the polishing machine comprises a polishing pad, a rotary platen for fixing the polishing pad, a pressure head which can turn and move in both vertical and horizontal directions, a slurry feed unit for dropping slurry on the platen in a predetermined amount per unit time, and an optical end-point detection device installed below the platen.

**[0119]** In this polishing machine, the polishing pad or polishing laminated pad of the present invention is fixed on the platen, and the semiconductor wafer is fixed to the lower end face of the pressure head and pressed against the polishing pad at a predetermined pressure to be brought into contact with the polishing pad. Slurry is dropped on the platen from the slurry feed unit in a predetermined amount per unit time, and the platen and the pressure head are turned to bring the semiconductor wafer in slide contact with the polishing pad for polishing.

[0120] End-point detection radiation R1 having a predetermined wavelength or wavelength range from the optical end-point detection device is applied to the surface to be polished of the semiconductor wafer through the light transmitting member from the bottom of the platen (the platen itself has light transmission properties or part of the platen is cut away to transmit end-point detection radiation). Reflected radiation R2 obtained by reflecting this end-point detection radiation R1 from the surface to be polished of the semiconductor wafer is seized by the optical end-point detection device so that polishing can be carried out while the state of the surface to be polished is monitored from this reflected radiation. [0121] The above slurry means an aqueous dispersion containing at least abrasive particles and may be slurry supplied from the outside at the time of polishing or only an aqueous medium containing no abrasive particles. When only an aqueous medium is supplied, for example, abrasive particles discharged from the inside of the polishing pad and the aqueous medium are mixed together in the polishing step to form slurry.

**[0122]** According to the method of polishing a semi-conductor wafer of the present invention, polishing can

be carried out while the state of polishing is always monitored and can be ended at the optimum polishing end point with certainty.

#### 5 Examples

**[0123]** The following examples are provided to further illustrate the present invention.

## Manufacture of polishing pad

#### (1) manufacture of light transmitting member

[0124] 97 vol% of 1,2-polybutadiene (JSR RB830 of JSR Corporation) which would be crosslinked later to become a water-insoluble matrix material (A) and 3 vol% of β-cyclodextrin having an average particle diameter of 16 μm (Dexy Pearl β-100 of Bio Research Corporation of Yokohama) as a water-soluble substance (B) were kneaded together by a kneader heated at 120°C. Thereafter, dicumyl peroxide (Percumyl D of NOF Corporation) as an organic peroxide was added in an amount of 0.8 part by mass based on 100 parts by mass of the total of 1,2-polybutadiene and β-cyclodextrin and further kneaded. Then, a crosslinking reaction was carried out in a press mold at 170°C for 20 minutes to mold a disk-like crosslinked molded product having a diameter of 600 mm and a thickness of 2.2 mm. Thereafter, a light transmitting member having a length of 57 mm, a width of 20 mm and a thickness of 2.2 mm was obtained with a dumbbell cutter.

## (2) manufacture of polishing substrate

[0125] 80 vol% of 1,2-polybutadiene (JSR RB830 of JSR Corporation) which would be crosslinked later to become a water-insoluble matrix material (A) and 20 vol% of the above β-cyclodextrin (Dexy Pearl β-100 of Bio Research Corporation of Yokohama) as a water-soluble substance (B) were kneaded together by a kneader heated at 120°C. Thereafter, dicumyl peroxide (Percumyl D of NOF Corporation) was added in an amount of 0.8 part by mass based on 100 parts by mass of the total of 1,2-polybutadiene and  $\beta$ -cyclodextrin and further kneaded. Then, a crosslinking reaction was carried out in a press mold at 170°C for 20 minutes to mold a disklike crosslinked molded product having a diameter of 51 mm and a thickness of 2.8 mm. Thereafter, concentric grooves having a width of 0.5 mm, a pitch of 2 mm and a depth of 1.4 mm were formed in one surface of the molded product with a cutting machine (of Kato Machinery Co., Ltd.). Further, a rectangular through hole having a length of 58 mm and a width of 21 mm was formed at a position 7.2 cm from the center of the disk with an end mill (of Kato Machinery Co., Ltd.) to obtain a polishing substrate.

#### (3) manufacture of polishing pad

#### Example 1

[0126] The polishing substrate 11 obtained in (2) above was set on a testing bench in such a manner that the surface (polishing surface) having the grooves 13 of the polishing substrate 11 faced down, and the light transmitting member 2 obtained in (1) above was inserted into the through hole. Thereafter, 1 ml of a photocurable adhesive essentially composed of a polyurethane acrylate and an ethylenically unsaturated monomer (Desolite Z8007 having a viscosity at 25°C of 8,000 mPa·s, manufactured by Japan Fine Coatings Co., Ltd.) was applied to the light transmitting member 2 uniformly, filled in the gap between the outer wall of the light transmitting member 2 and the inner wall of the through hole to ensure that it did not overflow into the polishing surface facing down and cured by exposure to 5,000 J/m<sup>2</sup> of light from a halogen lamp to form an adhesive layer 3, thereby obtaining the polishing pad 1 (I) shown in Fig. 1 and Fig. 20.

**[0127]** The adhesive used herein had an adhesion strength under shear after curing of 7.2 MPa and a Young's modulus of 60 MPa.

### Comparative Example 1

**[0128]** A polishing pad (II) was obtained in the same manner as in Example 1 except that a commercially available cyanoacrylate-based adhesive (Cyanobond RP-HX having a viscosity at 25°C of 1,000 mPa·s, manufactured by Taoka Chemical Co., Ltd.) was used to fix the light transmitting member in the through hole and dried by itself.

## Transmittance of light transmitting member

[0129] When the transmittance at a wavelength of 670 nm of the light transmitting member obtained in (1) above was measured with an UV absorptiometer (U-2010 of Hitachi, Ltd.), the average integrated transmittance of 5 times of measurement was 40 %. The transmittances at a position where the light transmitting members of the polishing pads (I) and (II) obtained in (3) above were existent were 41 % and 37 % under the same conditions, respectively.

## Polishing a semiconductor wafer

### Example 2

**[0130]** The polishing pad (I) obtained in Example 1 was mounted on the platen of a polishing machine equipped with an optical end-point detection device to polish a copper film wafer while slurry containing abrasive particles was supplied at a flow rate of 100 ml/min and a platen revolution of 50 rpm. As a result, the pol-

ishing rate was 7,200 Å/min. The slurry did not leak to the non-polishing surface of the polishing pad (I) from the gap between the outer wall of the light transmitting member and the inner wall of the through hole during polishing. No scratch was observed on the polished surface of the copper film wafer when seen through an optical microscope (MX50 of Olympus Co., Ltd.) at a magnification of X200 in a dark field mode.

## Comparative Example 2

**[0131]** A copper film wafer was polished in the same manner as in Example 2 except that a polishing pad obtained by fixing the light transmitting member obtained in (1) above in the through hole of a polishing substrate having a through hole of the same size was used as the light transmitting member without using an adhesive. As a result, the polishing rate was 7,100 Å/min. Although no scratch was observed on the polished surface of the copper film wafer, a large amount of the slurry leaked to the non-polishing side of the polishing pad from the gap between the outer wall of the light transmitting member and the inner wall of the through hole during polishing, thereby contaminating the platen.

## Comparative Example 3

**[0132]** A copper film wafer was polished in the same manner as in Example 2 except that the polishing pad (II) obtained in Comparative Example 1 was used. As a result, the polishing rate was 7,050 Å/min. Although the slurry did not leak to the non-polishing side of the polishing pad (II) from the gap between the outer wall of the light transmitting member and the inner wall of the through hole during polishing, the solidified product of the adhesive projected from the gap and many scratches were observed on the polished surface of the copper film wafer.

## O Comparative Example 4

**[0133]** A polishing pad (III) was manufactured in the same manner as in Example 1 except that the KR-120 vinyl urethane-based adhesive (of Koyo Sangyo Co., Ltd.) was used as an adhesive and left at room temperature to be cured.

[0134] A copper film wafer was polished with this polishing pad (III) in the same manner as in Example 2.
[0135] As a result, the polishing rate was 7,000 Å/min. A large number of scratches were observed on the polished surface of the copper film wafer.

#### Effect of the Invention

**[0136]** In Comparative Example 2, although the polishing rate was satisfactory at 7,100 Å/min, a large amount of the slurry leaked to the non-polishing side of the polishing pad from the gap between the outer wall

of the light transmitting member and the inner wall of the through hole during polishing, thereby making it difficult not only to perfect optical end-point detection but also to carry out a stable polishing step. In Comparative Example 3, the polished surface was scratched by the solidified product of the adhesive which projected from the gap between the outer wall of the light transmitting member and the inner wall of the through hole. In Example 2, the polishing rate was satisfactory at 7,200 Å/min, and the photocurable adhesive was excellent in the strength of a bonding portion which was its cured product. Therefore, stable polishing could be carried out without the collapse of the cured product during polishing.

**[0137]** As described above, since the slurry does not leak from the gap between the light transmitting member and the polishing substrate during polishing in the polishing pad of the present invention, optical end-point detection can be carried out efficiently and polishing can be carried out without causing a bad phenomenon such as scratching.

**[0138]** A film of a photocurable adhesive is formed to cover at least the above light transmitting member on the non-polishing side of the polishing pad. When this film constitutes a continuous phase with an adhesive layer formed between the outer wall of the light transmitting member and the inner wall of the through hole opposed to the outer wall, the adhesive layer is strong enough to prevent a leak of the slurry from the gap during polishing without fail, thereby making it possible to carry out polishing more efficiently.

**[0139]** The above light transmitting member contains a water-insoluble matrix material (A) and a water-soluble substance (B) dispersed in this water-insoluble matrix material (A), and when the content of the above water-soluble substance (B) is 0. 1 to 90 vol% based on 100 vol% of the total of the above water-insoluble matrix material (A) and the above water-soluble substance (B), a light transmitting member having high light transmission properties can be obtained and the detection of the polishing end point can be carried out without fail.

**[0140]** When at least part of the above water-insoluble matrix material (A) is a crosslinked polymer, it is possible to prevent pores from being filled at the time of polishing and dressing(surface renewal). It is also possible to prevent the surface of the polishing pad from being fluffed excessively. Therefore, the retainability of the slurry is high at the time of polishing, the retainability of the slurry can be easily recovered by dressing, and further scratching can be prevented.

**[0141]** When the above crosslinked polymer is crosslinked 1,2-polybutadiene, the above effect due to containing of the polymer can be fully obtained and sufficiently high light transmission properties can also be obtained. The crosslinked 1,2-polybutadiene is stable to a strong acid or strong alkali contained in many kinds of slurry and further has excellent durability as it is rarely softened by water absorption.

[0142] When the above light transmitting member has

a thickness of 2 mm and a transmittance at a wavelength between 400 nm and 800 nm of 0.1 % or more or an integrated transmittance at wavelength of 400 nm and 800 nm of 0.1 % or more, optical end-point detection using a wavelength within the above range can be easily performed.

**[0143]** When the viscosity at 25°C of the above photocurable adhesive is 1,000 to 100,000 mPa·s, the light transmitting member can be easily fixed in inner wall of the through hole. It can bond the light transmitting member without overflowing into the polishing surface of the polishing pad.

**[0144]** When the above photocurable adhesive contains a polyurethane (meth)acrylate, adhesive force to the inner wall of the through hole of the light transmitting member is high and the light transmission properties of the obtained film are high, thereby making it possible to carry out stable polishing without affecting optical endpoint detection.

**[0145]** When the sectional form of the above through hole is square, rectangular or circular, optical end-point detection can be performed efficiently.

**[0146]** The polishing laminated pad of the present invention which comprises the above polishing pad and a base layer formed on the non-polishing side of the polishing laminated pad and has light transmission properties in the lamination direction is free from a leak of the slurry from the gap during polishing and a bad phenomenon such as scratching, thereby making it possible to realize efficient polishing.

**[0147]** The method of polishing a semiconductor wafer of the present invention which uses the above polishing pad and an optical end-point detection device to detect the polishing end point of the semiconductor wafer makes it possible to polish a material to be polished efficiently by observing not only the polishing end point but also all the polishing states optically.

#### 40 Claims

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- 1. A polishing pad comprising a polishing substrate having a through hole extending from its polishing surface to the opposite surface and a light transmitting member arranged in the through hole, said light transmitting member being fixed in the through hole by bonding the outer wall of the light transmitting member to the inner wall of the through hole opposed to the outer wall with a photocured adhesive layer.
- 2. The polishing pad of claim 1, wherein a film is formed to cover the surface opposite to the polishing surface of the polishing pad of the light transmitting member, made of the same material as the photocured adhesive layer and integrated with the photocured adhesive layer.

- 3. The polishing pad of claim 1, wherein the light transmitting member comprises a water-insoluble matrix material (A) and a water-soluble substance (B) dispersed in the water-insoluble matrix material (A), and the content of the water-soluble substance (B) is 0.1 to 90 vol% based on 100 vol% of the total of the water-insoluble matrix material (A) and the water-soluble substance (B).
- **4.** The polishing pad of claim 1, wherein at least part of the water-insoluble matrix material (A) is a crosslinked polymer.
- **5.** The polishing pad of claim 4, wherein the crosslinked polymer is crosslinked 1,2-polybutadiene.
- **6.** The polishing pad of claim 1, wherein the light transmitting member has a transmittance at a wavelength between 400 nm and 800 nm of 0.1 % or more or an integrated transmittance at a wavelength between 400 nm and 800 nm of 0.1 % or more when it is 2 mm in thickness.
- 7. The polishing pad of claim 1, wherein the photocured adhesive layer comprises a photocured product of a photocured adhesive layer, and the viscosity at 25°C of the photocured adhesive layer is 1,000 to 100,000 mPa·s.
- **8.** The polishing pad of claim 1, wherein the photocurable adhesive comprises a polyurethane (meth)acrylate.
- **9.** The polishing pad of claim 1, wherein the sectional 35 form of the through hole is square, rectangular or circular.
- **10.** A polishing laminated pad comprising the polishing pad of claim 1 and a base layer having light transmission properties formed on the surface opposite to the polishing surface of the polishing pad.
- 11. A method of polishing a semiconductor wafer with a polishing pad, wherein the polishing pad of claim 1 is used and the polishing end point of a semiconductor wafer is detected by an optical end-point detection device through the light transmitting member of the polishing pad or the polishing laminated pad.
- 12. A method of polishing a semiconductor wafer with a polishing pad, wherein the polishing laminate pad of claim 10 is used and the polishing end point of a semiconductor wafer is detected by an optical endpoint detection device through the light transmitting member of the polishing pad or the polishing laminated pad.



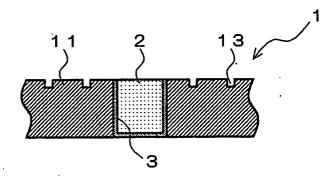


Fig. 2

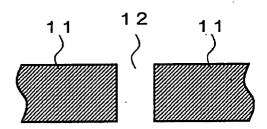


Fig. 3

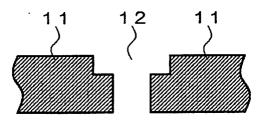
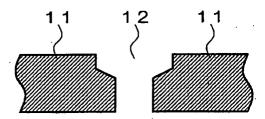


Fig. 4





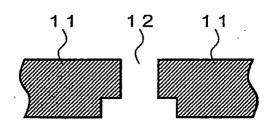


Fig. 6

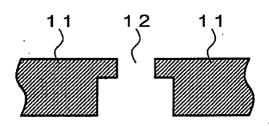


Fig. 7

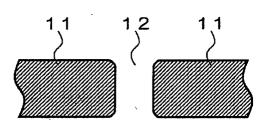


Fig. 8

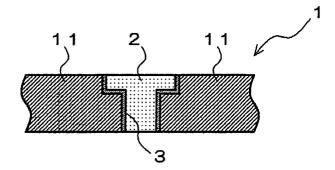


Fig. 9

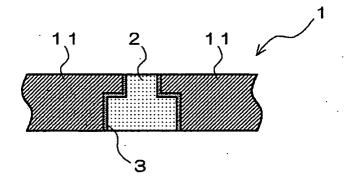


Fig. 10

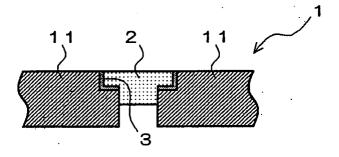


Fig. 11

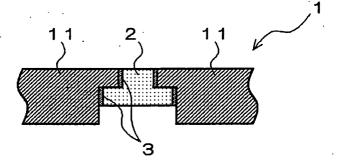


Fig. 12

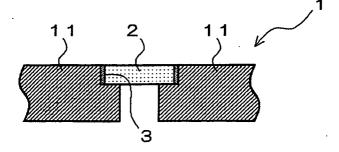


Fig. 13

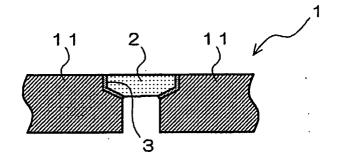


Fig. 14

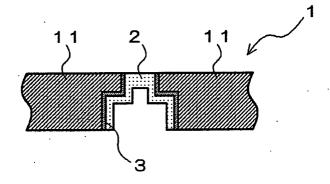


Fig. 15

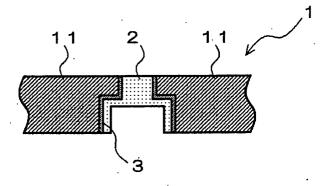
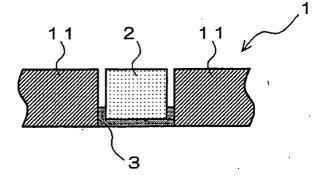


Fig. 16



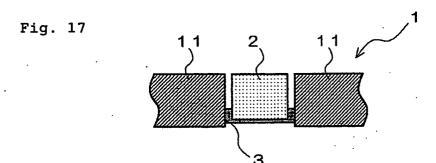
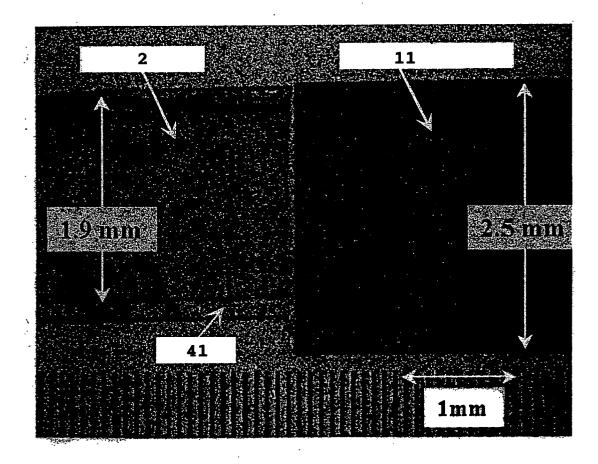
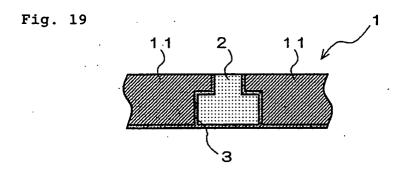


Fig. 18





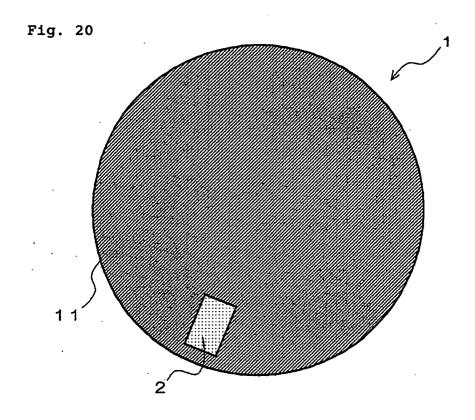
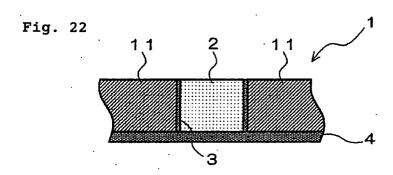
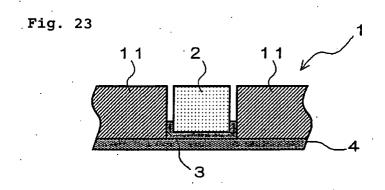
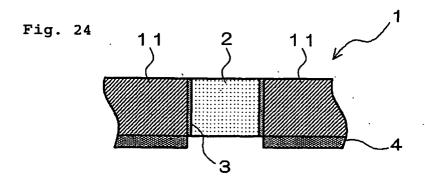


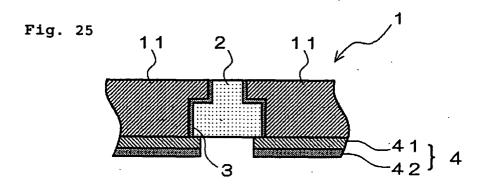
Fig. 21

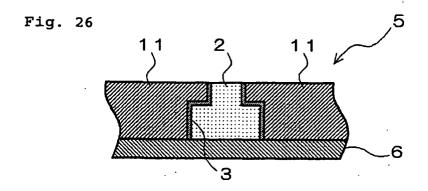
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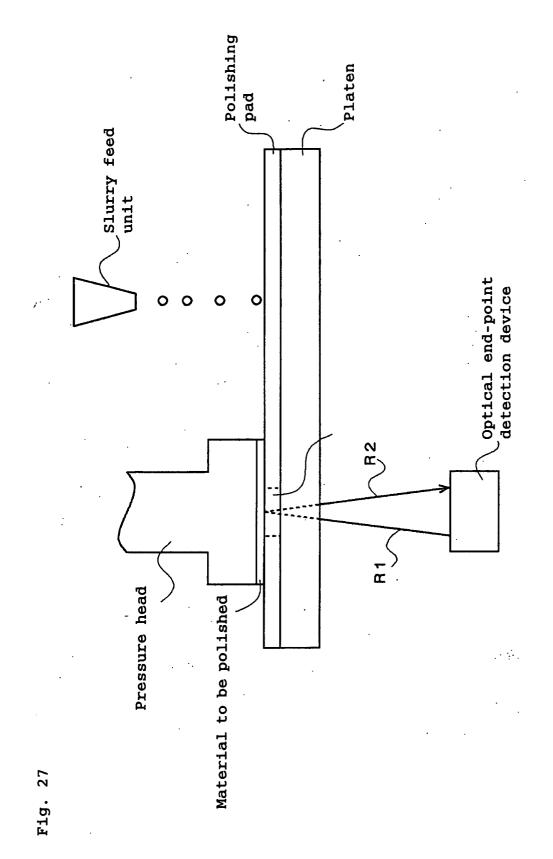














# **EUROPEAN SEARCH REPORT**

Application Number EP 04 00 9441

	DOCUMENTS CONSID	ERED TO BE RELEVANT				
Category	Citation of document with ir of relevant passa	dication, where appropriate, ges	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)		
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А	EP 0 941 806 A (LAM 15 September 1999 (					
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	The present search report has b	peen drawn up for all claims				
	Place of search	Date of completion of the search		Examiner		
	Munich	28 July 2004	Ko1	ler, S		
CATEGORY OF CITED DOCUMENTS  X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category		E : earlier patent o after the filing d O : document cite L : document citec	T: theory or principle underlying the im E: earlier patent document, but publish after the filing date D: document cited in the application L: document cited for other reasons			
A : technological background O : non-written disclosure P : intermediate document		& : member of the	a : member of the same patent family, corresponding document			

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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28-07-2004

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