[DESCRIPTION]

[Title of Invention]

POLISHING PAD

[Technical Field]

[0001]

The present invention relates to polishing pads, and particularly relates to a polishing pad for polishing a semiconductor wafer, a semiconductor device, a silicon wafer, a hard disk, a glass substrate, an optical product, various metals, or the like.

[Background Art]

[0002]

Chemical mechanical polishing (hereinafter also referred to as "CMP") is known as a polishing method used for mirror finishing a semiconductor wafer used as a substrate for forming an integrated circuit, and planarizing irregularities of an insulating film and a conductor film of a semiconductor device. CMP is a method in which the surface of a substrate to be polished, such as a semiconductor wafer, is polished with a polishing pad using a polishing slurry (hereinafter also simply referred to as a "slurry") containing abrasive grains and a reaction liquid.

[0003]

In CMP, polishing results change significantly depending on the characteristics of the polishing layer of the polishing pad. For example, a soft polishing layer reduces the generation of scratches, which are polishing defects generated on the surface to be polished, but lowering the local planarization performance and the polishing rate for the surface to be polished. A hard polishing layer enhances the local planarization performance for the surface to be polished, but increases scratches generated on the surface to be polished.

[0004]

Various polishing pads have been proposed in order to reduce the generation of scratches on the surface to be polished, enhance the planarization performance of the surface to be polished, or increase the polishing rate.

[0005]

For example, PTL 1 below discloses a polishing pad including a polishing layer in which a polymer containing an ether bond in the main chain, such as polyoxyethylene, and water-soluble particles such as cyclodextrin are dispersed in a polymer matrix material such as a conjugated diene copolymer. Also, PTL 1 discloses that such a polishing pad provides a high polishing rate, can sufficiently suppress the generation of scratches on the surface to be polished, and can achieve a high uniformity of the polishing rate in the surface to be polished.

[0006]

PTL 2 below discloses a chemical mechanical polishing pad including a polishing layer formed from a composition containing 80 parts by mass or more and 99 parts by mass or less of a thermoplastic polyurethane, and 1 parts by mass or more and 20 parts by mass or less of a polymer compound, such as polyoxyethylene, having a water absorption ratio of 3% or more and 3000% or less. PTL 2 discloses that, with such a polishing pad, the water-soluble particles in contact with a slurry are liberated to form pores, and the slurry is retained in the formed pores, thus maintaining the high planarization performance, and also reducing the generation of scratches.

[0007]

PTL 3 below discloses a polishing pad including a polishing layer containing resin and first particles such as calcium carbonate particles, wherein the first particles have an average particle size D_{50} of 1.0 to less than 5.0 μm, and the content of the first particles relative to the total amount of the polishing layer is 6.0 to 18.0 vol%, and the first particles have a Mohs hardness that is less than the Mohs hardness of a substrate to be polished.

[0008]

Usually, for example, concentric, radial, or grid-like grooves or holes (hereinafter also simply collectively referred to as "recesses") that are useful for uniformly and

sufficiently supplying a slurry onto the surface to be polished of a substrate to be polished, are formed in the polishing surface of a polishing layer of a polishing pad used for CMP. Such recesses are also useful for discharging polishing debris that may cause generation of scratches and preventing damage to a wafer as a result of absorption of the polishing pad.

[0009]

In the case where recesses are formed in the polishing surface, burrs may be generated at corner portions of the recesses when the polishing layer wears out as a result of a dresser used for dressing for optimizing the surface roughness or a substrate to be polished repeatedly coming into contact with the polishing surface. Then, if the generated burrs clog the recesses, the supply of the polishing slurry is reduced, which may result in a lower polishing rate, or reduced polishing uniformity. In addition, large burrs may generate scratches.

[0010]

To solve the above-described problems, PTL 4 below discloses a polishing pad including a polishing layer containing a thermoplastic polyurethane (A) and a polymer (B) other than the thermoplastic polyurethane (A), wherein the thermoplastic polyurethane (A) is obtained by reacting a polymer diol, an organic diisocyanate, and a chain extender, the polymer (B) is an amorphous polymer having a glass

transition temperature of 60 to 120°C and is dispersed in the thermoplastic polyurethane (A), and the polishing layer has a maximum value of a loss tangent in the range of -80 to -50°C of 8.00×10^{-2} or less. Also, as the polymer (B), a polymer including a structural unit derived from at least one monomer selected from the group consisting of acrylic acid, acrylic acid ester, methacrylic acid, methacrylic acid ester, acrylonitrile, methacrylonitrile, and styrene is disclosed. PTL 4 describes that with such a polishing pad, it is possible to reduce the burrs generated at the corner portions of the recesses.

[Citation List]

[Patent Literatures]

[0011]

[PTL 1] WO 2007/089004

[PTL 2] Japanese Laid-Open Patent Publication No. 2011-151373

[PTL 3] Japanese Laid-Open Patent Publication No. 2019-155507

[PTL 4] Japanese Laid-Open Patent Publication No. 2015-226940

[Summary of Invention]

[Technical Problem]

[0012]

It is difficult for the polishing pads disclosed PTL 1 and PTL 2 to be provided with a reduction in the amount of burrs generated at the corner portions of the recesses, a high

polishing rate, high planarization performance, and scratch resistance to suppress generation of scratches at the same time.

[0013]

With the polishing pad disclosed in PTL 3, there is concern that scratches are likely to be generated due to a relatively large particle diameter of the first particles.

[0014]

In the polishing pad disclosed in PTL 4, the polymer (B), other than the thermoplastic polyurethane serving as a matrix, is dispersed in the thermoplastic polyurethane with a substantially incompatible state. Therefore, the generation of burrs cannot be sufficiently suppressed without relatively increasing the content ratio of the polymer (B). When the content ratio of the polymer (B) is increased, the characteristics of the polishing layer composed mainly of the thermoplastic polyurethane may be reduced.

[0015]

In particular, when recesses are formed in the polishing surface of a polishing layer having a moderate hardness of about 60 to 75, as measured with a type-D durometer compliant with JIS K 7215, burrs are likely to be generated at corner portions of the recesses as a result of coming into contact the corner portion for a long period and repeatedly with a dresser for dressing or with a substrate to be polished. Then, the generated burrs gradually clog the

recesses, which may cause a gradual reduction in the amount of the slurry supplied to the polishing surface. This results in the problems of a gradual reduction in the polishing rate and the planarization performance, a reduction in the polishing uniformity, an increase in the amount of scratches generated on the surface to be polished, etc.

[0016]

It is an object of the present invention to provide a polishing pad in which burrs are less likely to be generated at corner portions of recesses formed in a polishing surface of a polishing layer having a moderate hardness and being well-balanced in a high polishing rate, scratch resistance, and high planarization performance.

[Solution to Problem]

[0017]

An aspect of the present invention relates to a polishing pad including a polishing layer that is a molded body of a polyurethane composition, wherein the polyurethane composition contains 90 to 99.9 mass% of a thermoplastic polyurethane including a non-alicyclic diisocyanate unit as an organic diisocyanate unit, and 0.1 to 10 mass% of a hygroscopic polymer having a moisture absorption rate of 0.1% or more. The molded body has a D hardness of 60 or more and less than 75, as measured with a type-D durometer compliant with JIS K 7215 for a load holding time of 5 seconds. Such a

polishing pad can provide a polishing pad in which burrs are less likely to be generated at corner portions of recesses formed in a polishing surface of a polishing layer having a moderate hardness and being well-balanced in a high polishing rate, scratch resistance, and high planarization performance.

[0018]

Preferably, the thermoplastic polyurethane includes, in a total amount of the organic diisocyanate unit, 90 to 100 mol% of 4,4'-diphenylmethane diisocyanate unit serving as the non-alicyclic diisocyanate unit. In such a case, the hygroscopic polymer is dispersed in the thermoplastic polyurethane with particularly good compatibility.

[0019]

Preferably, the polyurethane composition contains 99 to 99.9 mass% of the thermoplastic polyurethane, and 0.1 to 1 mass% of the hygroscopic polymer. In such a case, the polishing layer is likely to maintain a higher type-D durometer hardness, and thus is likely to maintain higher planarization performance.

[0020]

Examples of the hygroscopic polymer include a polyethylene oxide and a polyethylene oxide-propylene oxide block copolymer.

[0021]

Preferably, the hygroscopic polymer has an weight-average molecular weight of 70,000 to 4,000,000. In such a

case, the hygroscopic polymer has particularly good compatibility with the thermoplastic polyurethane.

[0022]

Preferably, the molded body has a saturated swollen state-breaking elongation of 250 to 400% when swollen to saturation with water at 50°C. In such a case, a polishing pad having a higher polishing rate can be easily obtained.

[0023]

Preferably, the molded body has a dry state-breaking elongation of 150 to 250% at a humidity of 48 RH% and 23°C. In such a case, a polishing pad exhibiting a higher polishing rate can be easily obtained.

[0024]

Preferably, the molded body has a ratio of S_1/S_2 of 1.0 to 2.0, where S_1 represents the above-described saturated swollen state-breaking elongation and S_2 represents the above-described dry state-breaking elongation. In such a case, a polishing pad exhibiting a higher polishing rate can be easily obtained.

[0025]

Preferably, the molded body, in a form of a sheet having a thickness of 0.5 mm, has a laser light transmittance of 60% or more for 550-nm wavelength when swollen to saturation with water at 50°C. In such a case, optical detection means for determining an end point of polishing can be easily adopted when polishing a surface to be polished of a

substrate to be polished, such as a wafer.

[0026]

Preferably, the molded body has a Vickers hardness of 5 or more and less than 21. In such a case, a polishing pad exhibiting enhanced scratch resistance can be easily obtained.

[0027]

Preferably, the molded body has a storage modulus of 0.1 to 1.0 GPa when swollen to saturation with water at 50°C. In such a case, a polishing layer that can be easily allowed to maintain higher planarization performance can be easily obtained.

[0028]

Preferably, the molded body is an unfoamed molded body. In such a case, the hardness of the polishing layer is more likely to be increased, which makes it possible to more easily achieve higher planarization performance and a higher polishing rate. In addition, an abrasive grain agglomerate, which is formed as a result of the abrasive grains contained in the slurry penetrating into the pores, is less likely to be generated, so that scratches generated as a result of such an agglomerate scratching the wafer surface are less likely to be generated.

[Advantageous Effects of Invention]

[0029]

According to the present invention, it is possible to obtain a polishing pad in which burrs are less likely to be generated at corner portions of recesses formed in a polishing surface of a polishing layer having a moderate hardness and being well-balanced in a high polishing rate, scratch resistance, and high planarization performance.

[Brief Description of Drawings]

[0030]

[FIG. 1] FIG. 1 is an explanatory diagram for illustrating CMP using a polishing pad 10 according to an embodiment.

[FIG. 2] FIG. 2 shows SEM photographs taken in burr tests in examples.

[Description of Embodiment]

[0031]

In the following, an embodiment of a polishing pad will be described in detail.

[0032]

The polishing pad according to the present embodiment includes a polishing layer that is a molded body of a polyurethane composition. The polyurethane composition contains 90 to 99.9 mass% of a thermoplastic polyurethane including a non-alicyclic diisocyanate unit as an organic diisocyanate unit (hereinafter also referred to as a non-alicyclic thermoplastic polyurethane), and 0.1 to 10 mass% of

a hygroscopic polymer. The molded body has a durometer D hardness of 60 or more and less than 75, as measured with a type-D durometer compliant with JIS K 7215 for a load holding time of 5 seconds.

[0033]

The non-alicyclic thermoplastic polyurethane is a thermoplastic polyurethane obtained by reacting a polyurethane raw material containing an organic diisocyanate, a polymer diol, and a chain extender. Also, the non-alicyclic thermoplastic polyurethane is a thermoplastic polyurethane obtained using an organic diisocyanate containing a non-alicyclic diisocyanate. The content ratio of the non-alicyclic diisocyanate unit contained in a total amount of the organic diisocyanate units contained in the non-alicyclic thermoplastic polyurethane is preferably 60 to 100 mol%, more preferably 90 to 100 mol%, particularly preferably 95 to 100 mol%, quite particularly preferably 99 to 100 mol%. When the content ratio of the non-alicyclic diisocyanate units is too low, the compatibility between the non-alicyclic thermoplastic polyurethane and the hygroscopic polymer tends to be reduced.

[0034]

By using such a molded body of a polyurethane composition as a polishing layer of a polishing pad, it is possible to obtain a polishing pad including a polishing layer in which burrs are less likely to be generated at corner portions of recesses formed in a polishing surface of a

polishing layer having a moderate hardness and being well-balanced in the high polishing rate, the scratch resistance, and the high planarization performance.

[0035]

In such a molded body of a polyurethane composition, the dispersibility of the hygroscopic polymer contained in the molded body is increased due to an increased compatibility between the non-alicyclic thermoplastic polyurethane and the hygroscopic polymer. More specifically, a soft segment derived from the polymer diol in the non-alicyclic thermoplastic polyurethane and the hygroscopic polymer become more compatible. Then, the surface stretchability of the molded body is appropriately enhanced when the polishing layer that is the molded body is moistened with a slurry. Also, due to appropriately enhanced surface stretchability of the polishing layer, fuzz generated as a result of the polishing surface being scraped by the dresser during dressing is more likely to be caught by the dresser, so that burrs can be more easily scraped off. As a result, the clogging of the recesses by burrs can be more easily suppressed. Due to the high stretchability of the hygroscopic polymer, the dressing performance is also enhanced. Moreover, due to the hydrophilicity of the hygroscopic polymer, the generation of scratches can be more easily reduced.

[0036]

On the other hand, a crystalline hard segment

derived from the chain extender and contained in the non-alicyclic thermoplastic polyurethane has low compatibility with the hygroscopic polymer. Therefore, the crystalline hard segment is likely to be retained. As a result, the hardness of the non-alicyclic thermoplastic polyurethane is less likely to be reduced. That is, the hygroscopic polymer has high compatibility with the soft segment, and has a low compatibility with the hard segment.

[0037]

The soft segment contained in the non-alicyclic thermoplastic polyurethane has high compatibility with the hygroscopic polymer, and thus increases the surface stretchability of the polishing layer. Accordingly, the fuzz on the polishing pad surface generated by dressing is more likely to be caught by the dresser, so that burrs can be more easily scraped off. Accordingly, the clogging of the recesses by burrs can be suppressed.

[0038]

The non-alicyclic diisocyanate used for the production of the non-alicyclic thermoplastic polyurethane refers to a diisocyanate other than an alicyclic diisocyanate, and more specifically, refers to an aromatic diisocyanate or linear aliphatic diisocyanate having no aliphatic ring structure.

[0039]

The aromatic diisocyanate is a diisocyanate compound

containing an aromatic ring in the molecular structure. Specific examples thereof include 2,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate, 1,5-naphthylene diisocyanate, 4,4'-diisocyanatobiphenyl, 3,3'-dimethyl- 4,4'-diisocyanatobiphenyl, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane, chlorophenylene-2,4-diisocyanate, and tetramethylxylylene diisocyanate.

[0040]

The linear aliphatic diisocyanate is a diisocyanate compound having a linear aliphatic skeleton having no ring structure in the molecular structure. Specific examples thereof include ethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, isophorone diisocyanate, lysine diisocyanate, 2,6-diisocyanatomethyl caproate, bis(2-isocyanatoethyl)fumarate, bis(2-isocyanatoethyl)carbonate, and 2-isocyanatoethyl-2,6-diisocyanatohexanoate.

[0041]

The non-alicyclic thermoplastic polyurethane is obtained using, as an organic diisocyanate used as a raw material, an organic diisocyanate containing, for example, 60

mol% or more, preferably 90 mol% or more, more preferably 95 mol% or more, particularly preferably 99 mol% or more, quite particularly preferably 100 mol% of a non-alicyclic diisocyanate.

[0042]

The non-alicyclic diisocyanates may be used alone or in combination of two or more thereof. Among these, it is particularly preferable to use an organic diisocyanate including preferably an aromatic diisocyanate, more preferably 4,4'-diphenylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, and isophorone diisocyanate, particularly preferably 100 mol% of 4,4'-diphenylmethane diisocyanate, from the viewpoint of obtaining a polishing pad having particularly good planarization performance.

[0043]

Note that the non-alicyclic diisocyanate may be used in combination with an alicyclic diisocyanate as long as the effects of the present invention are not impaired. The alicyclic diisocyanate is a diisocyanate compound containing an aliphatic ring structure. Specific examples thereof include isopropylidene bis(4-cyclohexyl isocyanate), cyclohexylmethane diisocyanate, methylcyclohexane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, cyclohexylene diisocyanate, methylcyclohexylene diisocyanate, and bis(2-isocyanatoethyl)-4-cyclohexylene. When the content ratio of the alicyclic diisocyanate is too high, the

compatibility with the hygroscopic polymer is reduced, and the planarization performance also tend to be reduced.

[0044]

The polymer diol is a diol having a number-average molecular weight of 300 or more, and examples thereof include polyether diol, polyester diol, polycarbonate diol, and a polymer diol including any combination thereof.

[0045]

Specific examples of the polyether diol include poly(ethylene glycol), poly(propylene glycol), poly(tetramethylene glycol), poly(methyl tetramethylene glycol), poly(oxypropylene glycol), and a glycerin-based polyalkylene ether glycol. These may be used alone or in combination of two or more thereof. Among these, poly(ethylene glycol) and poly(tetramethylene glycol) are preferable because of their particularly good compatibility with the hard segment of the non-alicyclic thermoplastic polyurethane.

[0046]

A polyester diol refers to a polymer diol having an ester structure in the main chain, produced by a direct esterification reaction or transesterification reaction between dicarboxylic acid or an ester-forming derivative thereof (e.g., an ester, anhydride, etc.) and a low-molecular weight diol.

[0047]

Specific examples of the dicarboxylic acid include C2-C12 aliphatic dicarboxylic acids such as oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, 2-methyl succinic acid, 2-methyl adipic acid, 3-methyl adipic acid, 3-methyl pentanedioic acid, 2-methyloctanedioic acid, 3,8-dimethyldecanedioic acid, and 3,7-dimethyldecanedioic acid; C14-C48 dimerized aliphatic dicarboxylic acids (dimer acids) obtained by dimerization of unsaturated fatty acids obtained by fractional distillation of triglycerides, as well as hydrogenated products (hydrogenated dimer acid) from these C14-C48 dimerized aliphatic dicarboxylic acids; alicyclic dicarboxylic acids such as 1,4-cyclohexane dicarboxylic acid; and aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, and ortho-phthalic acid. These may be used alone or in combination of two or more thereof.

[0048]

Specific examples of the low-molecular weight diol include aliphatic diols such as ethylene glycol, 1,3-propanediol, 1,2-propane diol, 2-methyl-1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 2-methyl-1,8-octanediol, 1,9-nonanediol, and 1,10-decanediol; and alicyclic diols such as cyclohexane dimethanol (e.g., 1,4-cyclohexane dimethanol) and cyclohexanediol (e.g., 1,4-

cyclohexanediol). These may be used alone or in combination of two or more thereof. Among these, low-molecular weight diols having 3 to 12 carbon atoms are preferable, and low-molecular weight diols having 4 to 9 carbon atoms are more preferable.

[0049]

A polycarbonate diol is obtained by reaction of a low-molecular weight diol and a carbonate compound such as dialkyl carbonate, alkylene carbonate, and diaryl carbonate. Examples of the low-molecular weight diol include the same low-molecular weight diols as those described above. Specific examples of the dialkyl carbonate include dimethyl carbonate and diethyl carbonate. Specific examples of the alkylene carbonate include ethylene carbonate. Specific examples of the diaryl carbonate include diphenyl carbonate.

[0050]

Among the polymer diols, polyether diols such as poly(ethylene glycol) and poly(tetramethylene glycol), and polyester diols such as poly(nonamethylene adipate)diol, poly(2-methyl-1,8-octamethylene adipate)diol, poly(2-methyl-1,8-octamethylene-co-nonamethylene adipate)diol, and poly(methylpentane adipate)diol are preferable, and polyester diols including a low-molecular weight diol unit having 6 to 12 carbon atoms are particularly preferable because of their particularly good compatibility with the hard segment derived from the chain extender unit of the non-alicyclic

thermoplastic polyurethane.

[0051]

The number-average molecular weight of the polymer diol is 300 or more, preferably from greater than 300 to 2,000, more preferably 350 to 2000, even more preferably 500 to 1,500, particularly preferably 600 to 1,000, because high compatibility with the hard segment in the non-alicyclic thermoplastic polyurethane can be maintained, particularly, which makes it possible to more easily suppress the generation of scratches on the surface to be polished. Note that the number-average molecular weight of the polymer diol refers to a number-average molecular weight calculated based on the hydroxyl value measured in accordance with JIS K 1557.

[0052]

As the chain extender, chain extenders conventionally used for the production of polyurethane, which are compounds including, in the molecule, two or more active hydrogen atoms capable of reacting with an isocyanate group, and having a molecular weight of 300 or less, can be used.

[0053]

Specific examples of the chain extender include diols such as ethylene glycol, diethylene glycol, propylene glycol, 2,2-diethyl-1,3-propanediol, 1,2-, 1,3-, 2,3- or 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,4-bis(β-hydroxyethoxy)benzene, 1,4-cyclohexanediol, bis-(β-hydroxyethyl)terephthalate, 1,9-

nonanediol, and m- or p-xylylene glycol; and diamines such as ethylenediamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, nonamethylene diamine, decamethylene diamine, undecamethylene diamine, dodecamethylene diamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, 3-methylpentamethylenediamine, 1,2-cyclohexanediamine, 1,3-cyclohexanediamine, 1,4-cyclohexanediamine, 1,2-diaminopropane, 1,3-diaminopropane, hydrazine, xylylene diamine, isophoronediamine, piperazine, o-, m- or p-phenylenediamine, tolylenediamine, xylenediamine, adipic acid dihydrazide, isophthalic acid dihydrazide, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 4,4'-bis(4-aminophenoxy)biphenyl, 4,4'-bis(3-aminophenoxy)biphenyl, 1,4'-bis(4-aminophenoxy)benzene, 1,3'-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 3,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulfone, 3,4-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, 4,4'-methylene-bis(2-chloroaniline), 3,3'-dimethyl-4,4'-diaminobiphenyl, 4,4'-diaminodiphenylsulfide, 2,6'-diaminotoluene, 2,4-diaminochlorobenzene, 1,2-diaminoanthraquinone, 1,4-diaminoanthraquinone, 3,3'-diaminobenzophenone, 3,4-diaminobenzophenone, 4,4'-diaminobenzophenone, 4,4'-diaminobibenzyl, R(+)-2,2'-diamino-1,1'-binaphthalene, S(+)-2,2'-diamino-1,1'-binaphthalene, 1,n-bis(4-aminophenoxy) C3-10 alkane (n is 3 to 10) (e.g., 1,3-bis(4-aminophenoxy) C3-10

alkane, 1,4-bis(4-aminophenoxy) C3-10 alkane, 1,5-bis(4-aminophenoxy) C3-10 alkane, etc.)) 1,2-bis[2-(4-aminophenoxy)ethoxy]ethane, 9,9-bis(4-aminophenyl)fluorene, and 4,4'-diaminobenzanilide. These may be used alone or in combination of two or more thereof.

[0054]

Among the chain extenders, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, and 1,4-cyclohexane dimethanol are particularly preferable because of their good compatibility with the soft segment derived from the polymer diol unit.

[0055]

The molecular weight of the chain extender is 300 or less, and is particularly preferably 60 to 300, from the viewpoint of good compatibility between the soft segment and the hard segment.

[0056]

As described above, the non-alicyclic thermoplastic polyurethane is obtained by reacting a polyurethane raw material containing an organic diisocyanate containing a non-alicyclic diisocyanate, a polymer diol, and a chain extender. For the production of the non-alicyclic thermoplastic polyurethane, any known polyurethane synthesis method using a prepolymer method or one-shot method involving a urethanation reaction can be used without any particular limitation. Among these, a method in which the polyurethane raw material is

subjected to melt-polymerization substantially in the absence of a solvent is preferable, and a method in which the polyurethane raw material is subjected to continuous melt-polymerization using a multi-screw extruder is particularly preferable because of the excellent continuous productivity.

[0057]

The mixing ratio of the polymer diol, the organic diisocyanate, and the chain extender in the polyurethane raw material can be adjusted as appropriate. However, it is preferable to mix the components such that the isocyanate group contained in the organic diisocyanate is in an amount of preferably 0.95 to 1.30 moles, more preferably 0.96 to 1.10 moles, particularly preferably 0.97 to 1.05 moles, per mole of the active hydrogen atoms contained in the polymer diol and the chain extender.

[0058]

The mass ratio of the polymer diol, the organic diisocyanate, and the chain extender in the polyurethane raw material (mass of polymer diol: total mass of organic diisocyanate and chain extender) is preferably 10:90 to 50:50, more preferably 15:85 to 40:60, particularly preferably 20:80 to 30:70.

[0059]

The content ratio of nitrogen atoms derived from the isocyanate group in the non-alicyclic thermoplastic polyurethane is preferably 4.5 to 7.5 mass%, more preferably

5.0 to 7.3 mass%, particularly preferably 5.3 to 7.0 mass%, because a polishing layer having a moderate hardness and being well-balanced in a high polishing rate, scratch resistance, and high planarization performance can be easily obtained.

[0060]

Preferred among non-alicyclic thermoplastic polyurethanes obtained in this manner is a thermoplastic polyurethane obtained by reacting a polymer diol such as poly(ethylene glycol), poly(tetramethylene glycol), poly(nonamethylene adipate)diol, poly(2-methyl-1,8-octamethylene adipate)diol, poly(2-methyl-1,8-octamethylene-co-nonamethylene adipate)diol, and poly(methylpentane adipate)diol; an organic diisocyanate including a non-alicyclic diisocyanate such as 4,4'-diphenylmethane diisocyanate, 2,4-tolylene diisocyanate, and 2,6-tolylene diisocyanate; and at least one chain extender selected from the group consisting of 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol, and 1,4-cyclohexane dimethanol, because such a non-alicyclic thermoplastic polyurethane has excellent optical transmission, so that means for optically detecting the polishing amount can be easily adopted in CMP.

[0061]

The weight-average molecular weight of the non-alicyclic thermoplastic polyurethane is preferably 80,000 to 200,000, more preferably 120,000 to 180,000, from the

viewpoint of the particularly good compatibility with the hygroscopic polymer. Note that the weight-average molecular weight is a weight-average molecular weight in terms of polystyrene measured by gel permeation chromatography.

[0062]

Note that the polyurethane composition according to the present embodiment may contain a thermoplastic polyurethane that does not contain a non-alicyclic diisocyanate in the organic diisocyanate unit (hereinafter also referred to as an alicyclic thermoplastic polyurethane) as long as the effects of the present invention are not impaired. In the case of containing an alicyclic thermoplastic polyurethane, the content ratio of the alicyclic thermoplastic polyurethane in the polyurethane composition is preferably 0 to 9.9 mass%, more preferably 0 to 5 mass%.

[0063]

The polyurethane composition according to the present embodiment contains a hygroscopic polymer. The hygroscopic polymer acts to suppress the generation of burrs in the recesses of a polishing layer that is a molded body of a polyurethane composition, and further enhance the dressing performance thereof.

[0064]

A hygroscopic polymer is defined as a polymer having a moisture absorption rate of 0.1% or more, and the polymer having a moisture absorption rate of preferably 0.1 to 5.0%,

more preferably 0.1 to 3.0%, particularly preferably 0.5 to 3.0%, quite particularly preferably 0.7 to 2.5%. Note that the moisture absorption rate of a hygroscopic polymer is calculated as follows. On a plate made of glass, 5.0 g of particles of a hygroscopic polymer to be mixed are thinly spread, then dried by being allowed to stand in a hot-air dryer at 50°C for 48 hours, and subsequently allowed to stand under constant temperature and humidity conditions of 23°C and 50% RH for 24 hours. Then, the moisture absorption rate is calculated based on the change in mass. Specifically, a weight (W1) immediately before the treatment under constant temperature and humidity conditions of 23°C and 50% RH, and a weight (W2) after the treatment under the under constant temperature and humidity conditions of 23°C and 50% RH are measured, and the moisture absorption rate is determined from the following mathematical expression:

$$\text{Moisture absorption rate (\%)} = \{(W2-W1)/W1\} \times 100$$

[0065]

Examples of such a hygroscopic polymer include polymers including a polyalkylene oxide structure such as a polymethylene oxide structure, a polyethylene oxide structure, a polypropylene oxide structure, a polytetramethylene oxide structure, and a polybutylene oxide structure.

[0066]

Specific examples of such a hygroscopic polymer include ether-based hygroscopic polymers such as polyethylene

oxide (PEO), polypropylene oxide (PPO), a PEO-PPO block copolymer, a polyester-based thermoplastic elastomer (TPEE), polymethylene oxide alkyl ether, polyethylene oxide alkyl ether, polyethylene oxide alkylphenyl ether, polyethylene oxide sterol ether, a polyethylene oxide lanolin derivative, a polyethylene oxide‐polypropylene oxide copolymer, and polyethylene oxide‐polypropylene alkyl ether; and ether ester-based hygroscopic polymers such as polyethylene oxide glycerin fatty acid ester, polyethylene oxide sorbitan fatty acid ester, polyethylene oxide sorbitol fatty acid ester, polyethylene oxide fatty acid alkanol amide sulfate, polyethylene glycol fatty acid ester, and ethylene glycol fatty acid ester.

[0067]

The weight-average molecular weight of the hygroscopic polymer is preferably 5,000 to 10,000,000, more preferably 10,000 to 10,000,000, even more preferably 30,000 to 7,000,000, particularly preferably 50,000 to 7,000,000, quite particularly preferably 70,000 to 4,000,000, from the viewpoint of the particularly good compatibility with the non-alicyclic thermoplastic polyurethane. Note that the weight-average molecular weight of the hygroscopic polymer is a value measured by gel permeation chromatography (in terms of polystyrene).

[0068]

The hygroscopic polymer has high compatibility with

the hydrophilic soft segment of the non-alicyclic thermoplastic polyurethane. On the other hand, the hygroscopic polymer has low compatibility with the hard segment of the non-alicyclic thermoplastic polyurethane.

[0069]

The content ratio of the non-alicyclic thermoplastic polyurethane in the polyurethane composition is 90 to 99.9 mass%, preferably 95 to 99.5 mass%, more preferably 95 to 99.0 mass%. When the content ratio of the non-alicyclic thermoplastic polyurethane is less than 90 mass%, the planarization performance and the polishing rate of the polishing pad are reduced. When the content ratio of the non-alicyclic thermoplastic polyurethane is greater than 99.9 mass%, the content ratio of the hygroscopic polymer becomes less than 0.1 mass%, which results in a reduction in the effect of sufficiently suppressing the generation of burrs in the recesses.

[0070]

The content ratio of the hygroscopic polymer in the polyurethane composition is 0.1 to 10 mass%, preferably 0.5 to 10 mass%, more preferably 0.5 to 5 mass%. When the content ratio of the hygroscopic polymer is less than 0.1 mass%, the effect of suppressing the generation of burrs in the recesses is reduced. When the content ratio of the hygroscopic polymer is greater than 10 mass%, the planarization performance and the polishing rate of the polishing pad are reduced.

[0071]

The polyurethane composition according to the present embodiment may contain, as necessary, additives such as a crosslinking agent, a filler, a crosslinking accelerator, a crosslinking auxiliary, a softening agent, a tackifier, an aging inhibitor, a processing auxiliary, an adhesion-imparting agent, an inorganic filler, an organic filler, a crystal nucleating agent, a heat stabilizer, a weathering stabilizer, an antistatic agent, a colorant, a lubricant, a flame retardant, a flame retardant accelerator (e.g., antimony oxide), a blooming inhibitor, a release agent, a thickener, an antioxidant, and a conductive agent, as long as the effects of the present invention are not impaired. Note that the molded body of the polyurethane composition according to the present embodiment is preferably an unfoamed molded body, and therefore preferably contains no foaming agent.

[0072]

The polyurethane composition is prepared by melt-kneading a blend containing the non-alicyclic thermoplastic polyurethane, the hygroscopic polymer, and other thermoplastic polyurethanes and additives that are mixed as necessary. More specifically, the polyurethane composition is prepared by melt-kneading, using a single- or multi-screw extruder, a roll, a Banbury mixer, a Labo Plastomill (registered trademark), a Brabender, or the like, a blend prepared by uniformly mixing, using a Henschel mixer, a ribbon blender, a

V-type blender, a tumbler, or the like, the non-alicyclic thermoplastic polyurethane, the hygroscopic polymer, and other thermoplastic polyurethanes and additives that are mixed as necessary. The temperature and kneading time during melt-kneading are selected as appropriate according to the type of the non-alicyclic thermoplastic polyurethane, components, ratio, the type of the melt-kneading machine, etc. For example, the melting temperature is preferably in the range of 200 to 300°C.

[0073]

The polyurethane composition is molded into a molded body for polishing layers. The molding method is not particularly limited, and examples thereof include methods in which a molten mixture extrusion-molded using a T-die or injection-molded. In particular, extrusion molding using a T-die is preferable because a molded body for polishing layers having a uniform thickness can be easily obtained. In this manner, a molded body for polishing layers is obtained.

[0074]

It is preferable that a molded body for polishing layers is an unfoamed molded body in that an increased hardness results in particularly good planarization performance, that the surface without pores prevent accumulation of polishing debris and thus reduces the generation of scratches, and that the polishing layer has a low ware rate and thus can be used for a long period of time.

[0075]

The molded body has a durometer D hardness of 60 or more and less than 75, preferably 65 or more and less than 75, as measured with a type-D durometer compliant with JIS K 7215 for a load holding time of 5 seconds. When the molded body has such a moderate hardness, a polishing layer well-balanced in a high polishing rate, scratch resistance, and high planarization performance can be obtained. When the durometer D hardness is less than 60, the polishing layer becomes too soft, resulting in a reduction in the polishing rate and degradation in the planarization performance. When the durometer D hardness is greater than 75, scratches are likely to be generated, or burrs are likely to be generated at corner portions of the recesses.

[0076]

It is preferable that the molded body has a Vickers hardness of 5 or more and less than 21, because the generation of scratches is particularly reduced. Here, the Vickers hardness is defined as a hardness measured by a Vickers indenter compliant with JIS Z 2244. When the Vickers hardness is too high, burrs tend to be generated.

[0077]

When the stretchability of the molded body, in particular, the stretchability when the molded body has absorbed a slurry is high, the dressing performance of the polishing surface is enhanced, and the fuzz generated on the

polishing surface roughened by the dresser can be easily removed during dressing. Accordingly, burrs tend not to remain. In order to allow burrs to be easily removed, the saturated swollen state-breaking elongation S_1 of the molded body when swollen to saturation with water at 50°C is preferably 250 to 400%, more preferably 250 to 350%, particularly preferably 250 to 330%. The dry state-breaking elongation S_2 of the molded body at a humidity of 48 RH% and 23°C is preferably 130 to 250%, more preferably 150 to 250%. The ratio of S_1/S_2 of the saturated swollen state-breaking elongation S_1 and the dry state-breaking elongation S_2 is preferably 1.0 to 2.0, because a polishing pad having a higher polishing rate can be easily obtained.

[0078]

It is preferable that the molded body, in the form of a sheet having a thickness of 0.5 mm, has a laser light transmittance of 60% or more for 550-nm laser wavelength when swollen to saturation with water at 50°C, because a detection method using optical means for determining an end point of polishing while polishing a surface to be polished of a substrate to be polished such as a wafer can be more easily adopted.

[0079]

The molded body has a storage modulus of preferably 0.1 to 1.0 GPa, more preferably 0.1 to 0.5 GPa, particularly preferably 0.1 to 0.4 GPa, when swollen to saturation with

water at 50°C, because higher planarization performance can be easily maintained. If the storage modulus when swollen to saturation with water at 50°C is too low, the polishing layer becomes soft, so that the planarization performance tends to be degraded, and the polishing rate tends to be reduced. If the storage modulus when swollen to saturation with water at 50°C is too high, the burrs generated at corner portions of the recesses may be less likely to be removed.

[0080]

The contact angle with water of the molded body is preferably 80 degrees or less, more preferably 78 degrees or less, particularly preferably 75 degrees or less, and is preferably 50 degrees or more, more preferably 60 degrees or more. When the contact angle is too high, scratches tend to be generated on the surface to be polished.

[0081]

Next, a description will be given of a polishing pad including, as a polishing layer, such a molded body for polishing layers. The polishing pad according to the present embodiment includes a polishing layer formed by cutting out a piece, such as a circular piece, from a molded body for polishing layers.

[0082]

The polishing layer is produced by adjusting the dimensions, shape, thickness, and the like of the molded body for polishing layers obtained in the above-described manner by

cutting, slicing, buffing, punching, and the like.

[0083]

In order to allow a slurry to be uniformly and sufficiently supplied onto the polishing surface of the polishing layer, it is preferable that the above-described recesses such as grooves or holes for retaining the slurry are formed in the polishing surface. Such recesses are also useful to discharge polishing debris that may cause the generation of scratches, and to prevent damage to a wafer as a result of absorption of the polishing pad.

[0084]

The shape of the grooves for retaining the slurry is not particularly limited, and concentric, spiral, grid-like, or radial grooves, grooves formed by combining two or more of the aforementioned grooves, or grooves or recesses each formed by a plurality of holes, all of which have been formed in conventional polishing pads for retaining a slurry on the polishing surface, can be used without any particular limitation. Among these, concentric or spiral grooves are preferable because of their excellent polishing characteristics such as a high polishing rate.

[0085]

The groove pitch, groove width, and groove depth of the grooves for retaining the slurry are not particularly limited. From the viewpoint of sufficiently retaining the slurry, for example, the groove pitch is preferably 1.5 to

20.0 mm, more preferably 2.5 to 15.0 mm, the groove width is preferably 0.1 to 5.0 mm, more preferably 0.3 to 3.5 mm, and the groove depth is preferably 0.1 to 1.7 mm, more preferably 0.3 to 1.5 mm.

[0086]

The thickness of the polishing layer is not particularly limited, and is, for example, preferably 0.8 to 3.0 mm, more preferably 1.0 to 2.5 mm, particularly preferably 1.2 to 2.0 mm.

[0087]

The polishing pad is a polishing pad including a polishing layer that is the above-described molded body for polishing layers, and may be either a monolayer polishing pad composed only of the polishing layer, or a multilayer polishing pad in which a cushioning layer or the like is further stacked on a back surface of the polishing layer. It is preferable that the cushioning layer is a layer having a hardness lower than the hardness of the polishing layer because this makes it possible to improve the polishing uniformity while maintaining the planarization performance.

[0088]

Specific examples of materials that can be used as the cushioning layer include composites (e.g., "Suba 400" (manufactured by Nitta Haas Incorporated)) obtained by impregnating a non-woven fabric with a polyurethane; rubbers such as a natural rubber, a nitrile rubber, a polybutadiene

rubber, and a silicone rubber; thermoplastic elastomers such as a polyester-based thermoplastic elastomer, a polyamide-based thermoplastic elastomer, and a fluorine-based thermoplastic elastomer; foamed plastics; and polyurethanes. Among these, polyurethanes having a foamed structure are particularly preferable in that the flexibility desirable for the cushioning layer can be easily achieved.

[0089]

The polishing pad according to the present embodiment described above can be preferably used for CMP. Next, an embodiment of CMP for which the polishing pad 10 of the present embodiment is used will be described.

[0090]

In CMP, a CMP apparatus 20 including a circular platen 1, a slurry supply nozzle 2 for supplying a slurry 6, a carrier 3, and a dresser 4 as shown in FIG. 1 is used, for example. A polishing pad 10 is attached to the surface of the platen 1 by means of a double-sided pressure-sensitive adhesive sheet or the like. In addition, the carrier 3 supports a substrate 5 to be polished.

[0091]

In the CMP apparatus 20, the platen 1 is rotated by a motor (not shown), for example, in the direction indicated by the arrows. The carrier 3 is rotated by a motor (not shown), for example, in the direction indicated by the arrows, while bringing a surface to be polished of the substrate 5 to

be polished into pressure contact with the polishing surface of the polishing pad 10. The dresser 4 is rotated, for example, in the direction indicated by the arrows.

[0092]

When a polishing pad is used, dressing for forming a roughness suitable for polishing by finely roughening the polishing surface of the polishing pad is performed prior to, or while polishing the substrate to be polished. Specifically, while pouring water onto the surface of the polishing pad 10 that is fixed to the platen 1 and is being rotated, the dresser 4 for CMP is pressed against the surface of the polishing pad 10 so as to condition the surface. As the dresser, it is possible to use, for example, a diamond dresser in which diamond particles are fixed onto the surface of a carrier by electrodeposition of nickel, or the like.

[0093]

As for the type of the dresser, dressers with a diamond grit of #60 to 200 are preferable, and the dresser may be selected as appropriate according to the resin composition of the polishing layer and the polishing conditions. The dresser load may vary depending on the diameter of the dresser, and is preferably about 5 to 50 N for a diameter of 150 mm or less, preferably about 10 to 250 N for a diameter of 150 to 250 mm, and preferably about 50 to 300 N for a diameter of 250 mm or more. The rotational speed of each of the dresser and the platen is preferably 10 to 200 rpm. In order

to prevent synchronization of rotations, it is preferable that the numbers of rotation of the dresser and the platen are different.

[0094]

Since the polishing pad according to the present embodiment also has excellent dressing performance, the polishing surface is sufficiently roughened by dressing, and the dressing time is also reduced. In such a polishing pad according to the present embodiment, the polishing surface of the polishing layer is preferably formed rough so as to have an arithmetic surface roughness Ra of preferably 3.0 to 8.0 μm, more preferably 4.2 to 8.0 μm, because the amount of generation of burrs and the amount of burrs removed by the dresser are likely to be brought into balance, so that the growth of burrs is likely to be suppressed. In the polishing pad according to the present embodiment, it is preferable that the polishing layer has a polishing surface having a ten-point average height (Rz) of 20 to 50 μm, more preferably 25 to 45 μm.

[0095]

After completion of dressing, or while performing dressing, the polishing of the surface to be polished of the base material to be polished is started. In polishing, the slurry 6 is supplied from the slurry supply nozzle 2 onto the surface of the rotating polishing pad. The slurry contains, for example, a liquid medium such as water or oil; an abrasive

such as silica, alumina, cerium oxide, zirconium oxide, or silicon carbide; a base; an acid; a surfactant; an oxidizing agent; a reducing agent; and a chelating agent. When performing CMP, a lubricating oil, a coolant, and the like may be used in combination with the slurry, as necessary. Then, the substrate to be polished that is fixed to the carrier and is being rotated is pressed against the polishing pad on which the slurry is evenly spread on the polishing surface. Then, the polishing treatment is continued until a predetermined flatness or polishing amount is achieved. Adjustment of the pressing force applied during polishing and the speed of relative movement between the rotation of the platen and the carrier affects the finishing quality.

[0096]

The polishing conditions are not particularly limited. To efficiently perform polishing, the rotational speed of each of the platen and the substrate to be polished is preferably as low as 300 rpm or less. The pressure applied to the substrate to be polished in order to press the substrate against the polishing surface of the polishing pad is preferably 150 kPa or less, from the viewpoint of preventing generation of scratches after polishing. During polishing, it is preferable that the slurry is continuously or discontinuously supplied to the polishing pad such that the slurry is evenly delivered onto the polishing surface.

[0097]

Then, after fully washing the substrate to be polished that has undergone polishing, the substrate to be polished is dried by removing water droplets attached thereto by using a spin drier or the like. In this manner, the surface to be polished becomes a smooth surface.

[0098]

Such CMP according to the present embodiment can be preferably used for polishing performed during the manufacturing process of various semiconductor devices, micro electro mechanical systems (MEMS), and the like. Examples of the object to be polished include semiconductor substrates such as silicon, silicon carbide, gallium nitride, gallium arsenic, zinc oxide, sapphire, germanium, and diamond; wiring materials, including, for example, an insulating film such as a silicon oxide film, a silicon nitride film, or a low-k film formed on a wiring board having predetermined wiring, and copper, aluminum, and tungsten; glass, crystal, an optical substrate, and a hard disk. In particular, the polishing pad according to the present embodiment is preferably used for polishing insulating films and wiring materials formed on semiconductor substrates.

[EXAMPLES]

[0099]

Hereinafter, the present invention will be described more specifically by way of examples. It should be

appreciated that the scope of the invention is by no means limited to the examples.

[0100]

First, hygroscopic polymers used in the examples will be collectively shown below.

[0101]

<Hygroscopic polymer>

· Polyethylene oxide having a weight-average molecular weight of 5,000 (PEO 5,000); moisture absorption rate 0.4% (in the range of 0.1 to 3.0%)

· Polyethylene oxide having a weight-average molecular weight of 30,000 (PEO 30,000); moisture absorption rate 0.7% (in the range of 0.1 to 3.0%)

· Polyethylene oxide having a weight-average molecular weight of 100,000 (PEO 100,000); moisture absorption rate 0.5%

· Polyethylene oxide having a weight-average molecular weight of 1,000,000 (PEO 1,000,000); moisture absorption rate 1.6% (in the range of 0.1 to 3.0%)

· Polyethylene oxide having a weight-average molecular weight of 7,000,000 (PEO 7,000,000); moisture absorption rate 2.5% (in the range of 0.1 to 3.0%)

· Polyethylene oxide-propylene oxide having a weight-average molecular weight of 100,000 (PEO-PPO 100,000); moisture absorption rate 0.7% (in the range of 0.1 to 3.0%)

· Polyethylene oxide-propylene oxide having a weight-average molecular weight of 1,000,000 (PEO-PPO 1,000,000); moisture

absorption rate 1.3% (in the range of 0.1 to 3.0%)

· Polyethylene oxide-propylene oxide having a weight-average molecular weight of 7,000,000 (PEO-PPO 7,000,000); moisture absorption rate 2.1% (in the range of 0.1 to 3.0%)

· Polyester-based thermoplastic elastomer (TPEE); moisture absorption rate 1.2% (in the range of 0.1 to 3.0%)

[0102]

<Acrylonitrile-styrene copolymer>

· Acrylonitrile-styrene copolymer; moisture absorption rate 0.08%

[0103]

Here, the moisture absorption rates of the polymers were measured in the following manner.

[0104]

On a plate made of glass, 5.0 g of particles of each of the polymers were thinly spread, and then allowed to stand in a hot-air dryer at 50°C for 48 hours to be dried. Thereafter, the particles were allowed to stand under constant temperature and humidity conditions of 23°C and 50% RH for 24 hours. Then, a weight (W1) immediately before the treatment under the constant temperature and humidity conditions of 23°C and 50% RH, and a weight (W2) after the treatment under the constant temperature and humidity conditions of 23°C and 50% RH were measured, and the moisture absorption rate was determined from the following mathematical expression:

[0105]

Moisture absorption rate (%) = {(W2-W1)/W1} × 100

[0106]

Production examples of the polyurethanes used in the present examples are shown below.

[0107]

[Production Example 1]

Poly(tetramethylene glycol) [abbreviation: PTMG] having a number-average molecular weight of 850, poly(ethylene glycol) [abbreviation: PEG] having a number-average molecular weight of 600, 1,4-butanediol [abbreviation: BD], 1,5-pentanediol [abbreviation: MPD], and 4,4'-diphenylmethane diisocyanate [abbreviation: MDI] were mixed in a mass ratio of PTMG:PEG:BD:MPD:MDI of 16.0:7.5:10.5:0.73:58.1, to prepare a blend.

[0108]

Then, the blend was continuously supplied to a coaxially rotating twin-screw extruder using a metering pump, and the molten blend was continuously extruded in the form of strands into water, and subsequently finely cut into pellets using a pelletizer. A non-alicyclic thermoplastic polyurethane I was produced by subjecting the polyurethane raw material to continuous melt-polymerization in this manner. The non-alicyclic thermoplastic polyurethane I includes, in the total amount of the organic diisocyanate unit, 100 mol% of MDI serving as a non-alicyclic diisocyanate unit. The weight-average molecular weight of the non-alicyclic thermoplastic

polyurethane I was 120,000, and the content of nitrogen atoms derived from the isocyanate group was 6.5 mass%. Then, the obtained pellets were dried through dehumidification at 70°C for 20 hours.

[0109]

[Production Example 2]

Poly(tetramethylene glycol) [abbreviation: PTMG] having a number-average molecular weight of 850, poly(ethylene glycol) [abbreviation: PEG] having a number-average molecular weight of 600, 1,4-butanediol [abbreviation: BD], and 4,4'-diphenylmethane diisocyanate [abbreviation: MDI] were mixed in a mass ratio of PTMG:PEG:BD:MDI of 16.2:7.6:18.1:58.1, to prepare a blend. Except for using this blend, a non-alicyclic thermoplastic polyurethane II was produced by subjecting the polyurethane raw material to continuous melt-polymerization in the same manner as in Production Example 1. The non-alicyclic thermoplastic polyurethane II includes, in the total amount of the organic diisocyanate unit, 100 mol% of MDI serving as a non-alicyclic diisocyanate unit. The weight-average molecular weight of the non-alicyclic thermoplastic polyurethane II was 120,000, and the content of nitrogen atoms derived from the isocyanate group was 6.5 mass%. Then, the obtained pellets were dried through dehumidification at 70°C for 20 hours.

[0110]

[Production Example 3]

Poly(tetramethylene glycol) [abbreviation: PTMG]

having a number-average molecular weight of 850, poly(ethylene glycol) [abbreviation: PEG] having a number-average molecular weight of 600, 1,4-butanediol [abbreviation: BD], 1,5-pentanediol [abbreviation: MPD], and hexamethylene diisocyanate [abbreviation: HDI] were mixed in a mass ratio of PTMG:PEG:BD:MPD:HDI of 7.9:3.7:28.2:1.9:58.1, to prepare a blend. Except for using this blend, a non-alicyclic thermoplastic polyurethane III was produced by subjecting the polyurethane raw material to continuous melt-polymerization in the same manner as in Production Example 1. The non-alicyclic thermoplastic polyurethane III includes, in the total amount of the organic diisocyanate unit, 100 mol% of HDI serving as a non-alicyclic diisocyanate unit. The weight-average molecular weight of the non-alicyclic thermoplastic polyurethane III was 120,000, and the content of nitrogen atoms derived from the isocyanate group was 6.5 mass%. Then, the obtained pellets were dried through dehumidification at 70°C for 20 hours.

[0111]

[Production Example 4]

Poly(tetramethylene glycol) [abbreviation: PTMG] having a number-average molecular weight of 850, poly(ethylene glycol) [abbreviation: PEG] having a number-average molecular weight of 600, 1,4-butanediol [abbreviation: BD], 1,5-pentanediol [abbreviation: MPD], and isophorone diisocyanate [abbreviation: IPDI] were mixed in a mass ratio of PTMG:PEG:BD:MPD:IPDI of 13.9:6.5:20.0:1.4:58.1, to prepare a

blend. Except for using this blend, an alicyclic thermoplastic polyurethane IV was produced by subjecting the polyurethane raw material to continuous melt-polymerization in the same manner as in Production Example 1. The alicyclic thermoplastic polyurethane IV includes, in the total amount of the organic diisocyanate unit, 100 mol% of IPDI serving as an alicyclic diisocyanate unit. The weight-average molecular weight of the alicyclic thermoplastic polyurethane IV was 120,000, and the content of nitrogen atoms derived from the isocyanate group was 6.5 mass%. Then, the obtained pellets were dried through dehumidification at 70°C for 20 hours.

[0112]

[Production Example 5]

Poly(tetramethylene glycol) [abbreviation: PTMG] having a number-average molecular weight of 850, poly(ethylene glycol) [abbreviation: PEG] having a number-average molecular weight of 600, 1,4-butanediol [abbreviation: BD], and cyclohexanemethyl isocyanate [abbreviation: CHI] were mixed in a mass ratio of PTMG:PEG:BD:CHI of 19.5:9.2:16.4:54.9, to prepare a blend. Except for using this blend, an alicyclic thermoplastic polyurethane V was produced by subjecting the polyurethane raw material to continuous melt-polymerization in the same manner as in Production Example 1. The alicyclic thermoplastic polyurethane V includes, in the total amount of the organic diisocyanate unit, 100 mol% of CHI serving as an alicyclic diisocyanate unit. The weight-average molecular

weight of the alicyclic thermoplastic polyurethane V was 120,000, and the content of nitrogen atoms derived from the isocyanate group was 6.5 mass%. Then, the obtained pellets were dried through dehumidification at 70°C for 20 hours. Here, 1,3-Bis(isocyanatomethyl)cyclohexane (Takenate 600 (registered trademark) from Mitsui Chemicals, Inc.) was used as the cyclohexanemethyl isocyanate.

[0113]

[Example 1]

The non-alicyclic thermoplastic polyurethane I was charged into a small-sized kneader, and melt-kneaded at a temperature of 240°C and a screw speed of 100 rpm for a kneading time of 1 minute. Then, PEO 100,000 was added into the small-sized kneader in a mass ratio of non-alicyclic thermoplastic polyurethane I:PEO 100,000 = 99.5:0.5, and the whole was further melt-kneaded at a temperature of 240°C and a screw speed of 60 rpm for a kneading time of 2 minutes. The whole was further melt-kneaded at a temperature of 240°C and a screw speed of 100 rpm for a kneading time of 4 minutes.

[0114]

Then, the obtained molten mixture was allowed to stand in a vacuum drier at 70°C for 16 hours or more to be dried. Then, the dried molten mixture was sandwiched between metal plates, which were then held in a hot press molding machine (a bench-type test press from Shinto Metal Industries, Ltd.), and the molten mixture was allowed to melt at a heating

temperature of 230°C for 2 minutes. Thereafter, the molten mixture was pressurized at a gauge pressure of 40 kg/cm^2, and then allowed to stand for 1 minute. Then, the whole was cooled at room temperature, followed by removing a 2.0-mm-thick molded body held in the hot press molding machine and sandwiched between the metal plates.

[0115]

Then, the obtained 2.0-mm-thick molded body was heat-treated at 110°C for 3 hours, and subsequently subjected to cutting, to cut out a rectangular test piece measuring 30 mm × 50 mm. Then, the test piece was subjected to cutting, to form concentric striped grooves (width 1.0 mm, depth 1.0 mm, groove interval 6.5 mm). Then, a recess for housing the test piece was formed in a 2.0-mm-thick circular molded body of the same non-alicyclic thermoplastic polyurethane I, and the test piece are fitted to the recess, to obtain a unfoamed polishing layer for evaluation. Then, the polishing layer was evaluated in the following manner.

[0116]

[Durometer D hardness of molded body]

Using a type-D durometer compliant with JIS K 7215 (HARDNESS-TESTER manufactured by SHIMADZU CORPORATION), the type-D durometer hardness of the 2.0-mm-thick molded body was measured for a load holding time of 5 seconds.

[0117]

[Vickers hardness of molded body]

Using a Vickers hardness meter (HARDNESS-TESTER MVK-E2 manufactured by Akashi Seisakusho,Ltd.) compliant with JIS Z2244, the Vickers hardness of the 2.0-mm-thick molded body was measured.

[0118]

[Dry state-breaking elongation, and saturated swollen state-breaking elongation when swollen to saturation with water at 50°C, of molded body]

In place of the 2.0-mm-thick molded body, a 0.3-mm-thick molded body was produced. Then, a No. 2 test piece (JIS K 7113) was punched out from the 0.3-mm-thick molded body. Then, the No. 2 test piece was conditioned at a humidity of 48 RH% and 23°C for 48 hours. Then, using a precision universal tester (Autograph AG5000 manufactured by SHIMADZU CORPORATION), tensile testing was performed on the conditioned No. 2 test piece, to measure the breaking elongation. The tensile testing was performed under conditions of an interchuck distance of 40 mm, a tensile speed of 500 mm/min, a humidity of 48 RH%, and 23°C. The breaking elongations of five samples of the No. 2 test piece were measured, and the average value thereof was calculated as a dry state-breaking elongation S2 (%). Meanwhile, a No. 2 test piece was immersed in warm water at 50°C for 2 days, to allow the test piece to be swollen to saturation with water at 50°C. Then, the breaking elongation of the No. 2 test piece swollen to saturation was also measured in the same conditions, to obtain

a saturated swollen state-breaking elongation S1 when swollen to saturation with water at 50°C.

[0119]

[Storage modulus E' of molded body when swollen to saturation with water at 50°C]

Instead of producing the 2.0-mm-thick molded body obtained by being pressurized at a gauge pressure of 40 kg/cm^2 and allowed to stand for 1 minute, a 0.3-mm-thick molded body was produced in the same manner except that the molded body was obtained by being pressurized at a gauge pressure of 50 kg/cm^2 and allowed to stand for 1 minute. Then, the 0.3-mm-thick molded body was heat-treated at 110°C for 3 hours, and subsequently punched out into a test piece using a rectangular die measuring 30 mm × 5 mm, to punch out a test piece measuring 30 mm × 5 mm for storage modulus evaluation. Then, the test piece was immersed in warm water at 50°C for 2 days, to allow the test piece for storage modulus evaluation to be swollen to saturation with water at 50°C. Then, using a dynamic viscoelasticity measurement device [DVE Rheospectra (trade name, manufactured by Rheology Co., Ltd.)], the dynamic viscoelastic modulus at 70°C was measured in the measurement range of -100 to 180°C at a frequency of 11.0 Hz, to determine a storage modulus E' of the molded body when swollen to saturation with water at 50°C. The storage moduli E' of two samples of the test piece were measured, and the average value was calculated as a storage modulus E' (GPa).

[0120]

[Light transmittance of molded body when swollen to saturation with water at 50°C]

A 0.5-mm-thick molded body was produced in place of the 2.0-mm-thick molded body. Then, the 0.5-mm-thick molded body was heat-treated at 110°C for 3 hours, and subsequently subjected to cutting, to cut out a rectangular piece measuring 30 mm × 50 mm. Then, the test piece was immersed in warm water at 50°C for 2 days, to allow the test piece to be swollen to saturation with water at 50°C, and thereafter water droplets on the surface were wiped off. Then, using an ultraviolet-visible spectrophotometer ("UV-2450" manufactured by SHIMADZU CORPORATION), the light transmittance for a wavelength of 550 nm of the test piece of the molded body was measured under the following conditions.

· Light source: laser wavelength (550 nm)

· WI lamp: 50 W

· Distance between detection head and output head: 10 cm

· Measurement position of test piece: intermediate position between detection head and output head

[0121]

[Contact angle with water]

A press-molded sheet was obtained in the same manner as the method used for the measurement of the breaking elongation, except that the thickness was changed to 0.2 mm (200 μm). Then, the press-molded sheet was allowed to stand

at 20 °C and 65% RH for 3 days, and subsequently the contact angle of the sheet was measured using a DropMaster 500 manufactured by Kyowa Interface Science Co., Ltd. The results are shown in the tables below.

[0122]

[Evaluation of polishing characteristics]

The polishing layer for evaluation was set on a platen of a CMP apparatus (FREX 300 manufactured by EBARA CORPORATION). Then, using a diamond dresser having a diamond grit number of #100 (Asahi Diamond Industrial Co., Ltd.), a surface of a substrate to be polished was polished at a dresser rotation rate of 100 rpm, a table rotation rate of 70 rpm, and a dresser load of 40 N, while pouring a slurry (Klebosol (registered trademark) from DuPont) onto the surface at a rate of 200 mL/min. As the substrate to be polished, a "SEMATECH 764 (SKW Associates Ltd.)" obtained by laminating a TEOS film (tetraethoxysilane film) having a thickness of 3000 nm onto a silicon substrate. CMP was performed under the above-described conditions, and the difference between protrusions and recesses (hereinafter also referred to as a residual level difference) in portions in which continuous patterns each having a width of 250 μm (50% density) were formed, was measured as an indicator of the planarization performance using a precision level difference meter (Dektak XTL manufactured by Bruker Corporation). Note that when the residual level difference was 30 nm or less, or even 25 nm or

less, it was determined that the polishing layer had high planarization performance. Similarly, the polishing rate was evaluated by measuring the polishing time required until the thickness of the film having the residual protrusions became less than 100 nm. Note that when the polishing time was 180 sec or less, even 170 sec or less, particularly 160 sec or less, it was determined that the polishing layer had a high polishing rate.

[0123]

Then, using a wafer defect inspection device (SP-3 manufactured by KLA Tencor Corporation), the number of scratches larger than 0.207 μm on the entire surface of the polished substrate to be polished was counted. Note that when the number of the scratches was less than 40, even less than 30, particularly less than 25, it was determined that the generation of scratches was suppressed.

[0124]

[Burr evaluation (Evaluation of groove clogging)]

The polishing layer for evaluation was set on a platen of a CMP apparatus (FREX 300 manufactured by EBARA CORPORATION). Then, using a diamond dresser having a diamond grit number of #100 (Asahi Diamond Industrial Co., Ltd.), the surface of the polishing pad was dressed for 2 hours at a dresser rotation rate of 100 rpm, a table rotation rate of 70 rpm, and a dresser load of 40 N, while pouring distilled water onto the surface at a rate of 200 mL/min.

[0125]

Then, the grooves on the polishing layer for evaluation after completion of the polishing was photographed using a scanning electron microscope (SEM), and whether the grooves were clogged by burrs was observed. Here, it was evaluated that burrs were "Present" when the grooves were clogged by burrs larger than 50 μm, and it was evaluated that burrs were "Absent" when no burrs larger than 50 μm were present and the grooves were not clogged.

[0126]

The evaluation results are shown in Table 1 below. The SEM photographs captured in the burr evaluation are shown in FIG. 2.

[0127]

[Table 1]

Example No.			1	2	3	4	5	6	7	8	9	10	11	12
Polyurethane composition	Non-alicyclic thermoplastic polyurethane	Type	I	I	I	I	I	I	I	I	I	II	III	I
		Diisocyanate unit	MDI	MDI	MDI	MDI	MDI	MDI	MDI	MDI	MDI	MDI	HDI	MDI
		Parts by mass	99.5	99	99	90	99	99	99	99	99	99	99	99
	Alicyclic thermoplastic polyurethane	Type	-	-	-	-	-	-	-	-	-	-	-	-
		Diisocyanate unit	-	-	-	-	-	-	-	-	-	-	-	-
		Parts by mass	-	-	-	-	-	-	-	-	-	-	-	-
	Hygroscopic polymer	Type	PEO 100,000	PEO 30,000	PEO 100,000	PEO 100,000	PEO 1,000,000	PEO 7,000,000	PEO-PPO 100,000	PEO-PPO 1,000,000	PEO-PPO 7,000,000	PEO 100,000	PEO 100,000	TPEE 100,000
		Parts by mass	0.5	1	1	10	1	10	1	10	1	10	10	1
Molded body	Durometer D hardness		72	72	71	64	72	72	73	73	73	72	71	70
	Vickers hardness		17	19	14	10	16	17	20	19	20	15	15	18
	Saturated swollen state-breaking elongation S1 (%)		255	319	280	302	287	320	313	308	300	297	320	260

	Dry state-breaking elongation S2 (%)	185	212	198	212	208	185	230	217	224	214	233	170
	S1/S2	1.4	1.5	1.4	1.4	1.4	1.7	1.4	1.4	1.3	1.4	1.4	1.5
	Light transmittance for 550 nm when swollen to saturation with water at 50°C (%)	78	70	76	73	69	63	71	64	65	68	68	77
	Storage modulus E' when swollen to saturation with water at 50°C [GPa]	0.19	0.20	0.23	0.17	0.18	0.16	0.21	0.19	0.22	0.20	0.17	0.18
	Contact angle with water (degrees)	77	76	75	78	76	77	79	75	75	76	74	73
Evaluation results	Burr evaluation	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent	Absent
	Residual level difference (nm)	20	32	21	28	24	14	18	19	18	23	20	22
	Polishing time (sec)	156	150	150	175	168	152	143	150	166	156	163	155
	Number of scratches (pcs)	10	8	8	4	5	12	7	5	13	10	17	10

[0128]

[Examples 2 to 12, Comparative Examples 1 to 8]

The characteristics of the molded bodies or the polishing layers were evaluated in the same manner as in Example 1, except that the types of the polyurethane composition were changed to the compositions shown in Table 1 or 2. The results are shown in Table 1 or 2 below. Note that an acrylonitrile-styrene copolymer having a moisture absorption rate of 0.08% was used in Comparative Example 7.

[0129]

[Table 2]

Comparative Example No.			Com. Ex. 1	Com. Ex. 2	Com. Ex. 3	Com. Ex. 4	Com. Ex. 5	Com. Ex. 6	Com. Ex. 7	Com. Ex. 8
Polyurethane composition	Non-alicyclic thermoplastic polyurethane	Type	I	I	I	I	I	I	I	III
		Diisocyanate unit	MDI	MDI	MDI	MDI	MDI	MDI	MDI	HDI
		Parts by mass	100	85	85	85	80	99	99	85
	Alicyclic thermoplastic polyurethane	Type	-	-	IV	V	-	-	-	-
		Diisocyanate unit	-	-	IPDI	CHI	-	-	-	-
		Parts by mass	-	-	14	14	-	-	-	-
	Hygroscopic polymer	Type	-	PEO 100,000	PEO 1,000,000	PEO 1,000,000	PEO 1,000,000	PEO 5,000	-	PEO 100,000
		Parts by mass	-	15	1	1	20	1	-	15
	Acrylonitrile-styrene copolymer	Parts by mass	-	-	-	-	-	-	1	-
Molded body	Durometer D hardness		73	58	74	73	57	77	72	59
	Vickers hardness		21	9	25	18	7	32	13	8

	Saturated swollen state-breaking elongation S1 (%)	219	101	96	85	213	236	192	121
	Dry state-breaking elongation S2(%)	167	88	67	56	178	153	101	90
	S1/S2	1.31	1.15	1.43	1.52	1.20	1.54	1.90	1.34
	Light transmittance for 550 nm when swollen to saturation with water at 50°C (%)	72	60	12	18	65	68	26	66
	Storage modulus E' when swollen to saturation with water at 50°C [GPa]	0.25	0.12	0.31	0.28	0.11	0.32	0.29	0.12
	Contact angle with water (degrees)	76	81	82	80	79	78	77	73
Evaluation results	Burr evaluation	Present	Present	Present	Present	Present	Present	Present	Present
	Residual level difference (nm)	32	65	35	36	68	28	45	41
	Polishing time (sec)	180	213	209	205	198	221	197	200
	Number of scratches (pcs)	17	38	27	41	27	29	47	45

[0130]

As shown in the above tables, in the polishing pads of Examples 1 to 12, no burrs were generated in the burr tests, and the grooves that were recesses were not clogged. These polishing pads also had a small residual level difference, and also exhibited excellent planarization performance. In addition, the polishing pads required a shorter polishing time, and achieved a high polishing rate. Furthermore, the polishing pads had less generation of scratches. In this manner, the polishing pads according to the present invention successfully achieved a high polishing rate, high planarization performance, and a reduction in generation of scratches, while enhancing the dressing performance. On the other hand, the polishing pads of Comparative Examples 1 to 8, which had a small breaking elongation, underwent generation of burrs in the burr tests, and the grooves were clogged.

[Reference Signs List]

[0131]

1 Platen

2 Slurry supply nozzle

3 Carrier

4 Dresser

5 Substrate to be polished

10 Polishing pad

20 CMP apparatus

[CLAIMS]

[Claim 1]

A polishing pad comprising a polishing layer that is a molded body of a polyurethane composition,

wherein the polyurethane composition contains 90 to 99.9 mass% of a thermoplastic polyurethane including a non-alicyclic diisocyanate unit as an organic diisocyanate unit, and 0.1 to 10 mass% of a hygroscopic polymer having a moisture absorption rate of 0.1% or more, and

the molded body has a D hardness of 60 or more and less than 75, as measured with a type-D durometer compliant with JIS K 7215 for a load holding time of 5 seconds.

[Claim 2]

The polishing pad according to claim 1, wherein the thermoplastic polyurethane includes, in a total amount of the organic diisocyanate unit, 90 to 100 mol% of 4,4'-diphenylmethane diisocyanate unit serving as the non-alicyclic diisocyanate unit.

[Claim 3]

The polishing pad according to claim 1 or 2, wherein the polyurethane composition contains 99 to 99.9 mass% of the thermoplastic polyurethane, and 0.1 to 1 mass% of the hygroscopic polymer.

[Claim 4]

The polishing pad according to any one of claims 1 to 3, wherein the hygroscopic polymer includes at least one selected from the group consisting of a polyethylene oxide (PEO), a polypropylene oxide (PPO), a PEO-PPO copolymer, a PEO-PPO block copolymer, and a polyester-based thermoplastic elastomer.

[Claim 5]

The polishing pad according to any one of claims 1 to 4, wherein the hygroscopic polymer has a weight-average molecular weight of 70,000 to 4,000,000.

[Claim 6]

The polishing pad according to any one of claims 1 to 5, wherein the molded body has a saturated swollen state-breaking elongation of 250 to 400% when swollen to saturation with water at 50°C.

[Claim 7]

The polishing pad according to any one of claims 1 to 6, wherein the molded body has a dry state-breaking elongation of 150 to 250% at a humidity of 48 RH% and 23°C.

[Claim 8]

The polishing pad according to claim 7, wherein the molded body has a ratio S_1/S_2 of 1.0 to 2.0, where S_1 represents the saturated swollen state-breaking elongation and S_2 represents the dry state-breaking elongation.

[Claim 9]

The polishing pad according to any one of claims 1 to 8, wherein the molded body, in a form of a sheet having a thickness of 0.5 mm, has a laser light transmittance of 60% or more for 550-nm wavelength when swollen to saturation with water at 50°C.

[Claim 10]

The polishing pad according to any one of claims 1 to 9, wherein the molded body has a Vickers hardness of 5 or more and less than 21.

[Claim 11]

The polishing pad according to any one of claims 1 to 10, wherein the molded body has a storage modulus of 0.1 to 1.0 GPa when swollen to saturation with water at 50°C.

[Claim 12]

The polishing pad according to any one of claims 1 to 11, wherein the molded body is an unfoamed molded body.

[Claim 13]

The polishing pad according to any one of claims 1 to 12, wherein a content ratio of the non-alicyclic diisocyanate unit contained in a total amount of the organic diisocyanate units contained in the thermoplastic polyurethane is 90 to 100 mol%.

[Claim 14]

The polishing pad according to any one of claims 1 to 12, wherein a content ratio of the non-alicyclic diisocyanate unit contained in a total amount of the organic diisocyanate units contained in the thermoplastic polyurethane is 95 to 100 mol%.

[Claim 15]

The polishing pad according to any one of claims 1 to 12, wherein a content ratio of the non-alicyclic diisocyanate unit contained in a total amount of the organic diisocyanate units contained in the thermoplastic polyurethane is 100 mol%.