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(54) POLISHING PAD AND METHOD FOR MANUFACTURING THE POLISHING PAD

(57) A polishing pad is disclosed which is less likely to cause scratches, and has an excellent planarization performance and polishing stability. In one aspect, the invention provides a polishing pad comprising an ultrafine fiber-entangled body formed of ultrafine fibers having an average fineness of 0.01 to 0.8 dtex, and a polymeric elastomer. The polymeric elastomer has a glass transition temperature of-10˚C or below, storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

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Description

Technical Field

[0001] The present invention relates to a polishing pad, and more particularly to a polishing pad for polishing various devices, substrates and other products on which planarization or mirror polishing are carried out, examples of which include semiconductor substrates, semiconductor devices, compound semiconductor devices, compound semiconductor substrates, compound semiconductor products, LED substrates, LED products, bare silicon wafers, silicon wafers, hard disk substrates, glass substrates, glass products, metal substrates, metal products, plastic substrates, plastic products, ceramic substrates and ceramic products, and to a method for manufacturing the polishing pad.

Background Art

[0002] In recent years, with the increasing levels of integration and multilayer interconnection in integrated circuits, there has existed a need for high-precision flatness on the semiconductor wafers where the integrated circuits are formed.

[0003] One known process for polishing semiconductor wafers is chemical mechanical polishing (CMP). CMP is a process for polishing a substrate surface to be polished with a polishing pad while slowly dispensing a slurry of abrasive grains onto the surface.

[0004] Patent Documents 1 to 4 below disclose polishing pads adapted for use in CMP which are composed of a polymer foam having a closed cell structure and being produced by foam molding a two-component curing polyurethane. Because such polishing pads have a high stiffness compared with the nonwoven fabric-type polishing pads described below, they are advantageously used in, for example, the polishing of semiconductor wafers requiring high-precision flatness.

[0005] Polishing pads composed of a polymer foam having a closed cell structure are produced by, for example, subjecting a two-component curing polyurethane to a cast-foam-molding. Because such polishing pads have a relatively high stiffness, convex parts on the substrate being polished tend to incur selective loading during polishing, resulting in a relative high polishing rate. However, when clumped abrasive grains are present on the polishing surface, because such clumped abrasive grains also selectively incur loading, scratches are readily formed on the surface being polished. In particular, as described in Non-Patent Document 1, when a substrate having copper wiring that is scratched easily or a material with a low dielectric constant and with weak interfacial adhesion is polished, there is a particular tendency for scratches and interfacial separation to occur. Moreover, in a cast-foam-molding, because it is difficult to uniformly foam a polymeric elastomer, variability tends to arise in the flatness of the substrate being polished and in the polishing rate during the polishing operation. Moreover, in a polishing pad having closed cells, the voids that originate from the closed cells become clogged with abrasive particles and abrasion debris. As a result, when the polishing pad is used for an extended period of time, the polishing rate decreases as abrasion proceeds (this characteristic is also referred to as polishing stability).

[0006] Patent Documents 5 to 14 disclose, as a different type of polishing pad, nonwoven fabric-type polishing pads obtained by impregnating a nonwoven fabric with a polyurethane resin and wet-coagulating the resin. Nonwoven fabric-type polishing pads have an excellent flexibility. For this reason, when clumped abrasive grains are present on the polishing surface of a substrate being polished, the polishing pad deforms, thereby suppressing the selective loading at the clumped abrasive grains. However, the polishing characteristics of nonwoven fabric-type polishing pads have a tendency to change readily over time, making such pads difficult to use for a precise planarization treatment. Also, because the polishing pad is too flexible and deforms so as to follow the surface shape of the substrate being polished, it is difficult to obtain a high planarization performance (the ability to render the substrate being polished flat). In addition, the fibers have a fineness of 2 to 10 dtex and are thus large, making it difficult to avoid local stress concentration.

[0007] In such nonwoven fabric-type polishing pads, there has come to be known, more recently, a nonwoven fabric-type polishing pad which is obtained by using a nonwoven fabric formed of bundles of ultrafine fibers, which is intended to achieve a higher planarization performance (e.g., see Patent Documents 15 to 18). Specifically, Patent Document 15 describes a polishing pad in the form of a sheet composed of both a nonwoven fabric formed of entangled bundles of ultrafine polyester fibers having an average fineness of from 0.0001 to 0.01 dtex and a polymeric elastomer made primarily of a polyurethane present in spaces at the interior of the nonwoven fabric. This publication states that a polishing treatment at a higher precision than before is achieved with such a polishing pad.

[0008] However, because the polishing pads like those described in Patent Documents 15 to 18 make use of a nonwoven fabric obtained by needlepunching ultrafine staple fibers having a low fineness, such pads have a low apparent density and a high void volume. Hence, only soft polishing pads with low stiffness can be obtained. Because these polishing pads deform so as to follow the surface shape, a sufficiently high planarization performance cannot be achieved.

[0009] Also, none of these documents provide details concerning the polymeric elastomer used in such nonwoven fabric-type polishing pads. Nor do these documents sufficiently describe the stability of the polishing pads over time.

[0010]

Patent Document 1: Japanese Patent Application Laid-open No. 2000-178374
Patent Document 2: Japanese Patent Application Laid-open No. 2000-248034
Patent Document 3: Japanese Patent Application Laid-open No. 2001-89548
Patent Document 4: Japanese Patent Application Laid-open No. H11-322878
Patent Document 5: Japanese Patent Application Laid-open No. 2002-9026
Patent Document 6: Japanese Patent Application Laid-open No. H11-99479
Patent Document 7: Japanese Patent Application Laid-open No. 2005-212055
Patent Document 8: Japanese Patent Application Laid-open No. H3-234475
Patent Document 9: Japanese Patent Application Laid-open No. H10-128674
Patent Document 10: Japanese Patent Application Laid-open No. 2004-311731
Patent Document 11: Japanese Patent Application Laid-open No. H10-225864
Patent Document 12: Japanese Translation of PCT Application No. 2005-518286
Patent Document 13: Japanese Patent Application Laid-open No. 2003-201676
Patent Document 14: Japanese Patent Application Laid-open No. 2005-334997
Patent Document 15: Japanese Patent Application Laid-open No. 2007-54910
Patent Document 16: Japanese Patent Application Laid-open No. 2003-170347
Patent Document 17: Japanese Patent Application Laid-open No. 2004-130395
Patent Document 18: Japanese Patent Application Laid-open No. 2002-172555

[0011] Non-Patent Document 1: M. Kashiwagi et al., "CMP no saiensu [The science of CMP]", Science Forum KK; August 20, 1997, pp. 113-119

Summary of the Invention

[0012] It is an object of the present invention to provide a polishing pad which is less likely to cause scratches and has both an excellent planarization performance and polishing efficiency.

[0013] In one aspect, the invention relates to a polishing pad which comprises an ultrafine fiber-entangled body formed of ultrafine fibers having an average fineness of 0.01 to 0.8 dtex, and a polymeric elastomer, wherein the polymeric elastomer has a glass transition temperature of -10˚C or below, storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

[0014] The objects, features, aspects and advantages of the inventions will become more apparent from the following detailed description.

Mode for Carrying Out the Invention

[0015] Backing materials made of ultrafine fibers generally have a large surface area and a low flexural modulus. For this reason, hitherto known polishing pads of a type obtained by impregnating a polymeric elastomer into a nonwoven fabric composed of ultrafine fibers have a large contact surface area with the substrate being polished, enabling to carry out a soft polishing. However, it has been possible to obtain in this way only the polishing pads having a low stiffness and falling short in terms of their planarizing characteristics and polishing stability over time. Because the voids in the nonwoven fabric become slurry reservoirs, thus giving the nonwoven fabric a high ability to retain the abrasive slurry, the polishing rate is easily increased. Yet, given that voids account for more than one-half of the apparent volume, polishing pads of a type obtained by impregnating hitherto known nonwoven fabrics with a polymeric elastomer, while capable of carrying out a highly efficient polishing, have a low stiffness and thus leave something to be desired in terms of the planarizing ability and the polishing stability over time.

[0016] The inventors have arrived at the present invention after discovering that: (1) a polishing pad having a high stiffness can be obtained by using an ultrafine fiber-entangled body of ultrafine fibers and a polymeric elastomer having a specific glass transition temperature, specific storage moduli and a specific water absorption ratio, and the structure of such a polishing pad is maintained even during polishing, enhancing the polishing stability over time; (2) the fibers readily form fibrils at the surface of the polishing pad during polishing, thereby increasing the contact surface area with the substrate being polished and concurrently the wettability, which in turn increases the retention of the abrasive slurry, resulting in an increased polishing rate; and (3) on account of the ultrafine fibers, the surface of the polishing pad makes soft contact to the substrate, minimizing stress concentration during polishing treatment, and making it less likely for scratches to form on the substrate being polished. The inventors have also found that, by setting the void volume of the polishing pad to 50% or more, it is possible to provide the pad with both an increased retention of the abrasive slurry and a high stiffness, which is particularly ideal for polishing bare silicon wafers.

[0017] Thus, the polishing pad of the present embodiment is composed of an ultrafine fiber-entangled body formed of ultrafine fibers having an average fineness of 0.01 to 0.8 dtex, and a polymeric elastomer, wherein the polymeric elastomer has a glass transition temperature of - 10˚C or below, storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

[0018] The composition, method of manufacture and method of use of the polishing pad according to the present embodiment are described below.

Composition of Polishing Pad

[0019] The ultrafine fiber-entangled body is formed of ultrafine fibers having an average fineness in a range of from 0.01 to 0.8 dtex, and preferably from 0.05 to 0.5 dtex. When the ultrafine fibers have an average fineness below 0.01 dtex, the ultrafine fiber bundles near the surface of the polishing pad do not fully fibrillate, as a result of which the abrasive slurry retention will decrease, which may result in decreases in the polishing efficiency and the polishing uniformity. On the other hand, when the ultrafine fibers have an average fineness greater than 0.8 dtex, the surface of the polishing pad becomes too coarse, lowering the polishing rate. In addition, the stress in polishing with the fibers increases, making scratches more likely to arise.

[0020] The ultrafine fiber-entangled body is composed of bundles of preferably 5 to 70 ultrafine fibers, and more preferably 10 to 50 ultrafine fibers. When the number of ultrafine fibers collected into a bundle exceeds 70, the fibers near the surface of the polishing pad may not fully fibrillate, as a result of which the retention of abrasive slurry may decrease. On the other hand, when the number of ultrafine fibers collected into a bundle is less than 5, the fineness becomes substantially larger or the fiber density at the surface tends to decreases, which may make the surface of the polishing pad too coarse and lower the polishing rate. In addition, the stress in polishing with the fibers increases, making scratches more likely to arise.

[0021] Examples of ultrafine fibers include aromatic polyester fibers formed of polyethylene terephthalate (PET), isophthalic acid-modified polyethylene terephthalate, sulfoisophthalic acid-modified polyethylene terephthalate, polybutylene terephthalate or polyhexamethylene terephthalate; aliphatic polyester fibers formed of polylactic acid, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate or polyhydroxybutyrate-polyhydroxyvalerate copolymer; polyamide fibers formed of polyamide 6, polyamide 66, polyamide 10, polyamide 11, polyamide 12 or polyamide 6-12; polyolefin fibers formed of polypropylene, polyethylene, polybutene, polymethylpentene or a chlorinated polyolefin; modified polyvinyl alcohol fibers formed of modified polyvinyl alcohol containing 25 to 70 mol% of ethylene units; and elastomer fibers formed of a polyurethane elastomer, polyamide elastomer or polyester elastomer. These may be used alone or as combinations of two or more types thereof. In view of enabling the formation of a compact, high-density ultrafine fiber-entangled body, it is especially preferable for the ultrafine fibers in the present embodiment to be formed of polyester fibers.

[0022] Of the above ultrafine fibers, fibers which are formed of a thermoplastic resin having a glass transition temperature (T_g) of at least 50˚C, and especially at least 60˚C, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 2 mass%, are preferred. When the glass transition temperature of the thermoplastic resin is in the above range, a higher stiffness can be maintained, thereby enabling the planarization performance to become even higher. Moreover, even during polishing, the stiffness does not decrease over time, enabling to obtain a polishing pad having excellent polishing stability and polishing uniformity. From the standpoint of industrial production, the upper limit in the glass transition temperature, although not subject to any particular limitation, is preferably 300˚C or less, and more preferably 150˚C or less.

[0023] The ultrafine fibers of the present embodiment are preferably formed of a thermoplastic resin having a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 2 mass%. In other words, it is preferable that the thermoplastic resin used to form the ultrafine fibers has a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 2 mass%. By setting the water absorption ratio to at least 0.2 mass%, the abrasive slurry is easily retained and the polishing efficiency and polishing uniformity are readily enhanced. By setting the water absorption ratio to 2 mass% or less, the polishing pad does not absorb too much abrasive slurry, thereby better suppressing a decrease in the stiffness over time. In such cases, there can be obtained a polishing pad in which the decrease in planarization performance over time is suppressed and the polishing rate and polishing uniformity do not readily fluctuate. Owing to ready availability or good manufacturability in addition to the water absorption, it is preferable that the thermoplastic resin from which the ultrafine fibers in the embodiment are formed is a polyester polymer, and especially a semi-aromatic polyester polymer in which an aromatic ingredient is used as one of the starting components.

[0024] Illustrative examples of the thermoplastic resin include aromatic polyester fibers formed of polyethylene terephthalate (PET; T_g, 77˚C; water absorption ratio when saturated with water at 50˚C (referred to below as simply the "water absorption ratio"), 1 mass%), isophthalic acid-modified polyethylene terephthalate (T_g, 67 to 77˚C; water absorption ratio, 1 masst%), sulfoisophthalic acid-modified polyethylene terephthalate (T_g, 67 to 77˚C; water absorption ratio, 1 to 3 mass%), polybutylene naphthalate (T_g, 85˚C; water absorption ratio, 1 mass%) or polyethylene naphthalate (T_g, 124˚C;

water absorption ratio, 1 mass%); and semi-aromatic polyamide fibers formed of a copolymeric polyamide of terephthalic acid with nonanediol and methyloctanediol (T_g, 125 to 140˚C; water absorption ratio, 1 to 3 mass%). PET and modified PET such as isophthalic acid-modified PET are especially preferred, for example, in that they undergo considerable crimping in the below-described wet heat treatment operation in which the ultrafine fibers are formed from an entangled web sheet composed of islands-in-the-sea type composite fibers, thus enabling a compact and high-density fiber-entangled body web of entangled fibers to be formed, in that the stiffness of the polishing sheet is easily increased, and in that changes over time owing to moisture during polishing do not readily arise.

[0025] The polishing pad according to the embodiment is preferably composed of an ultrafine fiber-entangled body formed of preferably fiber bundles into which the above-described ultrafine fibers are collected together, and a polymeric elastomer.

[0026] The polymeric elastomers which may be used in the embodiment are not specifically limited as long as they satisfy the below-described glass transition temperature, storage moduli and water absorption ratio conditions. Illustrative examples of such polymeric elastomers include elastomers which are composed of polyurethane resins, polyamide resins, (meth)acrylate resins, (meth)acrylate-styrene resins, (meth)acrylate-acrylonitrile resins, (meth)acrylate-olefin resins, (meth)acrylate-(hydrogenated) isoprene resins, (meth)acrylate-butadiene resins, styrenebutadiene resins, styrene-hydrogenated isoprene resins, acrylonitrile-butadiene resins, acrylonitrile-butadiene-styrene resins, vinyl acetate resins, (meth)acrylate-vinyl acetate resins, ethylene-vinyl acetate resins, ethylene-olefin resins, silicone resins, fluororesins and polyester resins.

[0027] As the polymeric elastomer of the embodiment, hydrogen-bonding polymeric elastomers are preferred because of their good ability to have ultrafine fibers converge as bundles and to restrain and bind the ultrafine fiber bundles. Examples of resins which form the hydrogen-bonding polymeric elastomers include polymeric elastomer resins that crystallize or aggregate under hydrogen bonding, such as polyurethane resins, polyamide resins, polyvinyl alcohol resins. The hydrogen-bonding polymeric elastomer has a high adhesion, a high fiber bundle restraining ability, and minimizes the loss of fibers.

[0028] The polymeric elastomer used in the embodiment has a glass transition temperature of -10˚C or below. At a glass transition temperature higher than -10˚C, the polymeric elastomer becomes brittle, as a result of which the polymeric elastomer sheds more readily during polishing, which tends to give rise to scratching. In addition, the ultrafine fiber bundle convergence owing to the polymeric elastomer becomes weaker, which tends to result in a decline in stability over time during polishing. The glass transition temperature is preferably -15˚C or below. Although there is no particular lower limit, in terms availability and other considerations, a lower limit of - 100˚C or above is preferred. The glass transition temperature is computed from the peak temperature of the loss modulus in the tensile mode during measurement of the dynamic viscoelasticity. Because the glass transition temperature is dependent on the peak temperature of α dispersion by the polymeric elastomer, it is preferable to suitably select the ingredients making up the polymeric elastomer so as to set the glass transition temperature of the polymeric elastomer to -10˚C or below. For example, when a polyurethane resin is used as the polymeric elastomer, the composition of the polyols serving as the soft component and the relative proportions of the hard component (isocyanate component and chain extender component) and the soft component are selected in such a way as to set the glass transition temperature to -10˚C or below. Specifically, it is desirable to select a polyol having a glass transition temperature of - 10˚C or below, preferably -20˚C or below, and to select a composition in which the mass ratio of the polyol component within the polyurethane is at least 30 wt%, and preferably at least 40 wt%.

[0029] The polymeric elastomer used in the embodiment has storage moduli at 23˚C and 50˚C of in a range from 90 to 900 MPa. The storage moduli of polyurethanes at 23˚C and 50˚C are generally less than 90 MPa. However, at storage moduli at 23˚C and 50˚C of less than 90 MPa, the polymeric elastomer which restrains the fiber bundles readily deforms, resulting in inadequate pad stiffness during polishing and thus lowering the planarizing ability. Moreover, the polymeric elastomer swells more readily due to the slurry, etc. during polishing, as a result of which the stability over time tends to decline. On the other hand, when the storage moduli at 23˚C and 50˚C exceed 900 MPa, the polymeric elastomer becomes brittle, as a result of which the polymeric elastomer sheds more readily during polishing, which tends to give rise to scratching. In addition, the ultrafine fiber bundle convergence decreases, as a result of which the stability over time during polishing readily worsens. The storage moduli at 23˚C and 50˚C are preferably from 200 to 800 MPa. Because the storage moduli of the polymeric elastomer are dependent on the composition of the polymeric elastomer, that is, on the respective elastic moduli of and the weight ratio between the hard component and the soft component making up the polymeric elastomer, it is preferable to select the composition of and the weight ratio between the hard component and the soft component in such a way as to set the storage moduli in the above range.

[0030] For example, when a polyurethane resin is used as the polymeric elastomer, illustrative examples of the soft component (polyol component) include polyether polyols such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol and poly(methyltetramethylene glycol), and copolymers thereof; polyester polyols such as polybutylene adipate diol, polybutylene sebacate diol, polyhexamethylene adipate diol, poly(3-methyl-1,5-pentylene adipate) diol, poly(3-methyl-1,5-pentylene sebacate) diol, isophthalic acid copolymeric polyol, terephthalic acid copolymeric polyol, cyclohexanol copolymeric polyol and polycaprolactone diol, and copolymers thereof; polycarbonate polyols such as polyhexamethylene carbonate diol, poly(3-methyl-1,5-pentylene carbonate) diol, polypentamethylene carbonate diol, polytetramethylene carbonate diol, poly(methyl-1,8-octamethylene carbonate) diol, polynonane methylene carbonate diol and polycyclohexane carbonate, and copolymers thereof; and polyester carbonate polyols. Also, if necessary, a polyhunctional alcohol such as a trifunctional alcohol (e.g., trimethylolpropane) or a tetrafunctional alcohol (e.g., pentaerythritol); or a short-chain alcohol such as ethylene glycol, propylene glycol, 1,4-butanediol or 1,6-hexanediol, may be concomitantly used. These may be used singly or as combinations of two or more thereof. In particular, it is preferable to include a polycarbonate polyol such as an alicyclic polycarbonate polyol, a linear polycarbonate polyol or a branched polycarbonate polyol in an amount of 60 to 100 mass% of the overall polyol component, and to include especially a noncrystalline polycarbonate polyol having a melting point of 0˚C or below in an amount of 60 to 100 mass% of the overall polyol component, because the stability over time during polishing is good on account of high resistance to the slurry used in polishing and because the water absorption and the storage moduli can easily be set within the above range of the embodiment.

[0031] Moreover, in order to set the storage moduli at 23˚C and 50˚C in a range of from 90 to 900 MPa, it is preferable to select a polyol having a glass transition temperature of -10˚C or below, and preferably -20˚C or below. Illustrative examples include the above-mentioned branched polycarbonate polyols; polyether polyols such as polypropylene glycol, polytetramethylene glycol and poly(methyltetramethylene glycol), and copolymers thereof; polyester polyols such as polybutylene sebacate diol, poly(3-methyl-1,5-pentylene adipate) diol, poly(3-methyl-1,5-pentylene sebacate) diol and polycaprolactone diol, and copolymers thereof; polycarbonate polyols such as poly(3-methyl-1,5-pentylene carbonate) diol and poly(methyl-1,8-octamethylene carbonate) diol, and copolymers thereof; and polyester carbonate polyols. In addition to the above polyols, further examples include those polyols whose glass transition temperature can be set to -10˚C or below by copolymerization.

[0032] Because polyurethane resins containing polyalkylene glycol groups with up to 5 carbons, and especially up to 3 carbons, have an especially good wettability to water, it is preferable to use a polyurethane resin containing from about 0.1 to about 10 mass% of such polyalkylene glycol groups.

[0033] By using a soft component (polyol component) having a glass transition temperature of -10˚C or below and thereby setting the glass transition temperature of the polyurethane to - 10˚C or below, and by selecting such a polyol component and adjusting the mass ratio of the polyol component in the polyurethane, the storage moduli of the polyurethane at 23˚C and 50˚C can be set in a range of from 90 to 900 MPa.

[0034] When a polyurethane resin is used as the polymeric elastomer, the isocyanate component used in the hard component (isocyanate component and chain extender component) may be a non-yellowing diisocyanate which is an aliphatic or alicyclic diisocyanate, such as hexamethylene diisocyanate, isophorone diisocyanate, norbornene diisocyanate and 4,4'-dicyclohexylmethane diisocyanate; or an aromatic diisocyanate, such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate and xylylene diisocyanate polyurethane. If necessary, concomitant use may be made of a polyfunctional isocyanate such as a trifunctional isocyanate or a tetrafunctional isocyanate. These may be used singly or as combinations of two or more thereof. Of these, 4,4'-dicyclohexylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate and xylylene diisocyanate are preferred because they have a high adhesion to ultrafine fibers and increase the ultrafine fiber bundle convergence, thereby enabling a polishing pad having a high hardness to be obtained.

[0035] As the other hard component (chain extender component), a hard component which has a high cohesiveness and a high elastic modulus and is composed of a combination of a short-chain polyol, such as a diol (e.g., ethylene glycol, propylene glycol, 1,4-butanediol, 1,4-bis(β-hydroxyethoxy)benzene, 1,4-cyclohexane diol), triol (e.g., trimethylolpropane), pentaol (e.g., pentaerythritol) or aminoalcohol (e.g., aminoethyl alcohol, aminopropyl alcohol), with a short-chain polyamine, such as a diamine (e.g., hydrazine, ethylenediamine, propylenediamine, hexamethylenediamine, xylylenediamine, isophoronediamine, piperazine and derivatives thereof, adipic acid dihydrazide, isophthalic acid dihydrazide), triamine (e.g., diethylenetriamine) or tetramine (e.g., triethylenetetramine), may be selected for use as the chain extender component. Examples which may be used together with the chain extender at the time of the chain-extending reaction include a monoamine (e.g., ethylamine, propylamine, butylamine), a carboxyl group-containing monoamine compound (e.g., 4-aminobutanoic acid, 6-aminohexanoic acid), or a monool (e.g., methanol, ethanol, propanol, butanol). By concomitantly using a carboxyl group-containing diol such as 2,2-bis(hydroxymethyl)propionic acid, 2,2-bis(hydroxymethyl)butanoic acid or 2,2-bis(hydroxymethyl)valeric acid, ionic groups such as the carboxylic groups can be introduced onto the skeleton of the polyurethane elastomer, making it possible to further enhance the wettability to water.

[0036] From the standpoint of setting the storage moduli of the polyurethane at 23˚C and 50˚C within a range of from 90 to 900 MPa, the proportion of the soft component (polyol component) is set to preferably from 40 to 65 mass%, and more preferably from 45 to 60 mass%. At an amount of the soft component below 40 mass%, the temperature dependence of the storage moduli at 23˚C and 50˚C becomes higher, making it difficult to achieve a range of from 90 to 900 MPa. On the other hand, if the amount of the soft component exceeds 65 wt%, the storage moduli tend to fall below 90 MPa.

[0037] From the standpoint of more easily increasing the storage moduli of the polyurethane, it is especially preferable for the soft component to be a polycarbonate-type polyol, such as a branched polycarbonate polyol; poly(3-methyl-1,5-pentylene carbonate) diol or poly(methyl-1,8-octamethylene carbonate) diol; or a polycarbonate polyol obtained by copolymerizing such polycarbonate polyols as poly(3-methyl-1,5-pentylene carbonate) diol, poly(methyl-1,8-octamethylene carbonate) diol, polyhexamethylene carbonate diol, polypentamethylene carbonate diol, polytetramethylene carbonate diol, polynonanemethylene carbonate diol and polycyclohexane carbonate.

[0038] Moreover, it is preferable for the polymeric elastomer in the present embodiment to have a ratio of the storage modulus at 23˚C to the storage modulus at 50˚C (storage modulus at 23˚C/storage modulus at 50˚C) of 4 or less. By setting the ratio of the storage modulus at 23˚C to the storage modulus at 50˚C (storage modulus at 23˚C/storage modulus at 50˚C) to 4 or less, the storage moduli are less subject to change even when temperature changes arise during polishing, thereby enhancing the stability over time during polishing. It is especially preferable to set the ratio of the storage modulus at 23˚C to the storage modulus at 50˚C (storage modulus at 23˚C/storage modulus at 50˚C) to 3 or less. The lower limit value is not subject to any particular limitation; however, in order for the storage modulus to be less subject to change due to the temperature during polishing, a value of 1/3 or more is preferred.

[0039] The foregoing range can be achieved by suitably adjusting the soft component and the hard component so as to set the storage moduli in the above-described range.

[0040] For example, in cases where a polyurethane resin is employed as the polymeric elastomer, it is desirable to use a soft component (polyol component) having a glass transition temperature of -10˚C or below so as to set the glass transition temperature of the polyurethane to -10˚C, to select as the hard components (isocyanate component and chain extender component) an alicyclic diisocyanate or an aromatic diisocyanate, and a chain extender component having a high cohesiveness and a high elastic modulus which is obtained from a combination of a short-chain polyol (examples of which include diols, triols and pentaols) with a short-chain polyamine (examples of which include diamines, triamines and tetramines), and to set the ratio of the soft component at preferably from 40 to 65 mass%, and more preferably from 45 to 60 mass%. Also, a polycarbonate polyol is preferred as the soft component of the polyurethane because it makes the elastic modulus of the polyurethane easy to increase.

[0041] In order to adjust, for example, the performance or manufacturability of the polishing pad, two or more polymeric elastomers may be included. The storage moduli at 23˚C to 50˚C of the polymeric elastomer in such a case can be theoretically calculated as the sum of the values obtained by multiplying the storage modulus of each polymeric elastomer by the mass fraction thereof.

[0042] Moreover, the polymeric elastomer of the present embodiment has a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%. At a water absorption ratio below 0.2 mass%, retaining the abrasive slurry becomes difficult, as a result of which the polishing efficiency and the polishing uniformity tend to decline. At above 5 mass%, the polymeric elastomer which restrains the fiber bundles absorbs water and softens, as a result of which the change over time during polishing tends to increase. Moreover, it is preferable for the water absorption ratio when saturated with water at 50˚C to be in a range of from 0.5 to 3 mass%. When the water absorption ratio of the polymeric elastomer is in such a range, a high wettability of the polishing pad by the abrasive slurry is maintained, in addition to which a decline over time in the stiffness can be better suppressed. This enables a high polishing rate, polishing uniformity and polishing stability to be maintained.

[0043] The water absorption ratio of polymeric elastomer, which will be subsequently described in greater detail, refers herein to the water absorption ratio when a polymeric elastomer film that has been subjected to drying treatment is immersed in room-temperature water and allowed to swell to saturation. The water absorption ratio in cases where two or more types of polymeric elastomer are included can be theoretically calculated as the sum of the values obtained by multiplying the water absorption ratio of each polymeric elastomer by the mass fraction thereof.

[0044] The polymeric elastomer having such a water absorption ratio can be obtained, for example, by adjusting the composition and crosslink density of the polymers making up the polymeric elastomer, introducing hydrophilic functional groups, and selecting the amounts thereof.

[0045] For example, the water absorption ratio and hydrophilicity can be adjusted by introducing to the polymeric elastomer at least one type of hydrophilic group selected from the group consisting of carboxylic groups, sulfonic acid groups, and polyalkylene glycol groups having 3 or fewer carbons. In this way, the wettability of the polishing pad by the abrasive slurry can be increased. Such hydrophilic groups may be introduced onto the polymeric elastomer by the copolymerization of a monomer having hydrophilic groups as a monomer component during production of the polymeric elastomer. Setting the copolymerization ratio of such a monomer component having hydrophilic groups at from 0.1 to 10 mass%, and especially from 0.5 to 5 wt%, is preferable from the standpoint of minimizing swelling and softening due to water absorption and increasing the water absorption ratio and wettability.

[0046] The polymeric elastomers may be used singly or as combinations of two or more thereof. Of such polymeric elastomers, a polyurethane resin is preferred in that it has excellent adhesive properties for packing ultrafine fibers into bundles or for restraining and binding together the fiber bundles, in addition to which it increases the hardness of the polishing pad and has an excellent stability over time during polishing. Also, the polyurethane resin having at least one type of hydrophilic group selected from the group consisting of carboxylic groups, sulfonic acid groups and polyalkylene glycol groups of 3 or fewer carbons is desirable from the standpoint of the polishing pad stiffness, wettability and stability over time during polishing.

[0047] In cases where the polymeric elastomer is the polyurethane resin, specific examples of carboxylic groups include the carboxylic groups of 2,2-bis(hydroxymethyl)propionic acid, 2,2-bis(hydroxymethyl)butanoic acid and 2,2-bis (hydroxymethyl)valeric acid. By concomitantly using, for example, these diols having the carboxylic groups, it is possible to introduce carboxylic groups onto the skeleton of the polyurethane elastomer. Illustrative examples of polyalkylene glycol groups having 3 or fewer carbons include polyethylene glycol, polypropylene glycol and copolymers thereof. Although polyurethane resins having at least one type of hydrophilic group selected from among carboxylic groups, sulfonic acid groups and polyalkylene glycol groups of 3 or fewer carbons do have the advantage of an enhanced wettability, the water absorption ratio tends to rise and is generally from 5 to 15 mass%. Therefore, in order to set the water absorption ratio in the range of 0.2 to 5 mass% in the present embodiment, it is desirable to set the amount of at least one hydrophilic group selected from the group consisting of carboxylic groups, sulfonic acid groups and polyalkylene glycol groups of 3 or fewer carbons to preferably from 0.1 to 10 mass%, and more preferably from 0.5 to 5 mass%. In addition, it is preferable to use as the polyol a component having low water absorption, such as the above-described polyester polyol or polycarbonate polyol.

[0048] For example, in cases where the polymeric elastomer is a polyurethane resin obtained by using as the polyol component a noncrystalline polycarbonate diol together with a carboxylic group-containing diol, and using an alicyclic diisocyanate as the diisocyanate component, the use of such a polymeric elastomer is preferred because of the ease of setting the glass transition temperature of the polymeric elastomer to -10˚C or below, setting the storage moduli at 23˚C and 50˚C to from 90 to 900 MPa, and setting the water absorption ratio when saturated with water at 50˚C to from 0.2 to 5 mass%.

[0049] The hard components (isocyanate component and chain extender component) of the polyurethane resin used in the embodiment may be, for example, the above-described isocyanate component and the above-described chain extender component having a high cohesiveness. Also, the ratio of the soft component (polyol component) is preferably set to 65 mass% or less, and more preferably 60 mass% or less. At an amount of the soft component in excess of 65 wt%, the water absorption ratio tends to become high. In cases where the polymeric elastomer is an aqueous polyurethane, to achieve a water absorption ratio of from 0.2 to 5 mass%, it is preferable for the aqueous polyurethane to have an average particle size of from 0.01 to 0.2 μm. At an average particle size of less than 0.01 μm or more than 0.2 μm, the water absorption ratio will tend to exceed 5 mass%.

[0050] In cases where the polymeric elastomer is a polyurethane resin, to control the water absorption ratio and the storage moduli, it is preferable also to form a crosslinked structure by adding a crosslinking agent having in the molecule two or more functional groups capable of reacting with the functional groups in the above-mentioned monomer units which form the polyurethane, or by adding a self-crosslinking compound such as a polyisocyanate compound or a polyfunctional block isocyanate-type compound.

[0051] Examples of combinations of the functional group in the above-mentioned monomer unit with the functional group in the crosslinking agent include a carboxylic group with an oxazoline group, a carboxylic group with a carbodiimide group, a carboxylic group with an epoxy group, a carboxylic group with a cyclocarbonate group, a carboxylic group with an aziridine group, and a carbonyl group with a hydrazine derivative or a hydrazide derivative. Of these, combinations of the monomer unit having the carboxylic group with the crosslinking agent having the oxazoline group, the carbodiimide group or the epoxy group, combinations of the monomer unit having the hydroxyl group or the amino group with the crosslinking agent having the block isocyanate group, and combinations of the monomer unit having the carbonyl group with the hydrazine derivative or the hydrazide derivative are especially preferred on account of the ease of crosslinkage formation and the excellent stiffness and wear resistance of the polishing pad thereby obtained. Formation of the crosslinked structure in a heat treatment step following impregnation of the fiber-entangled body with an aqueous liquid of the polyurethane resin is preferred from the standpoint of maintaining the stability of the aqueous liquid of the polymeric elastomer. Of the above, the carbodiimide group and/or the oxazoline group are especially preferred on account of their excellent crosslinking ability and the pot life of the aqueous liquid, and also because these pose no problems in terms of safety. Illustrative examples of crosslinking agents having the carbodiimide group include water-dispersible carbodiimide compounds such as Carbodilite E-01, Carbodilite E-02 and Carbodilite V-02, all available from Nisshinbo Industries, Inc. Illustrative examples of crosslinking agents having the oxazoline group include water-dispersible oxazoline compounds such as Epocros K-2010E, Epocros K-2020E and Epocros WS-500, all available from Nippon Syokubai Co., Ltd. The amount of the crosslinking agent included in the polyurethane resin, expressed in terms of the active ingredient of the crosslinking agent with respect to the polyurethane resin, is preferably from 1 to 20 mass%, and more preferably from 1.5 to 10 mass%.

[0052] In order to increase adhesion with the ultrafine fibers and increase the rigidity of the fiber bundles, and in order to facilitate adjustments, such as setting the glass transition temperature to -10˚C or below, setting the storage moduli at 23˚C and 50˚C in a range of 90 to 900 MPa, and setting the water absorption ratio when saturated with water at 50˚C to 0.2 to 5 mass%, the content of the polyol component in the polyurethane resin is preferably 65 mass% or less, and more preferably 60 mass% or less. Also, the content of at least 40 mass%, and especially at least 45 mass%, is preferred in that a suitable elasticity is imparted, making it possible to minimize the occurrence of scratches.

[0053] The polyurethane resin may additionally include, within ranges that do not compromise the advantageous effects of the invention: penetrating agents, foam inhibitors, lubricants, water repellents, oil repellents, thickeners, bulking agents, curing accelerators, antioxidants, ultraviolet absorbers, mold inhibitors, blowing agents, water-soluble polymeric compounds such as polyvinyl alcohol and carboxymethyl cellulose, dyes, pigments, and inorganic fine particles.

[0054] Preferably, the polymeric elastomer is present inside ultrafine fiber bundles of from 5 to 70 ultrafine fibers having an average fineness of 0.01 to 0.8 dtex which make up the ultrafine fiber-entangled body. The ultrafine fibers converge as bundles under the effect of the polymeric elastomer present inside the ultrafine fiber bundles. Owing to the convergence of the ultrafine fibers, a part or all of the interior of the fiber bundle converges as a bundle, in addition to which the bundle of ultrafine fibers is restrained. The convergence of the ultrafine fibers as a bundle, together with the restraint of the fiber bundle, increases the stiffness of the polishing pad, which is advantageous from the standpoint of enhancing the planarizing performance, the polishing uniformity and the stability over time.

[0055] A volumetric ratio of a portion excluding voids in the polishing pad (also referred to below as the filling ratio of the polishing pad) is preferably in a range of from 40 to 95 wt%. That is, the presence of the voids such that the void volume is in a range of from 5 to 60% is preferable both for a suitable stiffness of the polishing pad and for slurry retention by the polishing pad.

[0056] In this case, the void volume in the polymeric elastomer-impregnated polishing pad of 50% or more is desirable because slurry retention, suitable stiffness and moreover cushionability are concurrently achieved, which is excellent for polishing bare silicon wafers. An upper limit in this case of 70% or less is desirable because this results in a good polishing rate and flatness in rough polishing such as bare silicon wafer polishing.

[0057] From the standpoint of enhancing slurry retention, it is more desirable for some of the voids to form continuous pores which afford communication with the interior of the polishing pad.

[0058] Moreover, the polymeric elastomer is preferably an aqueous polyurethane because of the good wettability to abrasive slurry, and the aqueous polyurethane preferably has an average particle size of 0.01 to 0.2 μm. At an average particle size of at least 0.01 μm, the water resistance is good, resulting in an excellent stability over time during polishing. An average particle size of 0.2 μm or less enhances the fiber bundle restraining strength, confers good planarizing properties, and increases the pad life during polishing, providing good stability over time. To adjust the above particle size, it is preferable, for example, that the polymeric elastomer includes at least one type of hydrophilic group selected from the group consisting of carboxylic groups, sulfonic acid groups and polyalkylene glycol groups having 3 or fewer carbons.

[0059] The mass ratio of the ultrafine fiber-entangled body to the polymeric elastomer (ultrafine fiber-entangled body/ polymeric elastomer) is preferably from 55/45 to 95/5. A mass ratio for the ultrafine fiber-entangled body of 55% or more has a good effect for the stability over time during polishing, and tends to enhance the polishing efficiency. At a mass ratio for the ultrafine fiber-entangled body of 95% or less, the restraining strength of the polymeric elastomer at the interior of the fiber bundles is maintained, resulting in excellent planarizing properties and little pad wear during polishing. The mass ratio of the ultrafine fiber-entangled body to the polymeric elastomer is most preferably in a range of from 60/40 to 90/10.

[0060] To maintain a good slurry retention and maintain a high stiffness, the apparent density of the polishing pad of the embodiment is preferably in a range of 0.4 to 1.2 g/cm^3, and more preferably from 0.5 to 1.0 g/cm^3. In a use for bare silicon wafer polishing, to achieve both an enhanced polishing rate and planarity, the apparent density is preferably from 0.3 to 0.75 g/cm^3, and more preferably from 0.4 to 0.65 g/cm^3.

[0061] In the present embodiment, the average length of the ultrafine fiber bundles is not subject to any particular limitation. However, having the average length be at least 100 mm, and preferably at least 200 mm, is desirable in that the fiber density can be easily increased, the stiffness of the polishing pad can be easily increased, and the loss of fibers can be suppressed. If the length of the fiber bundles is too short, a higher fiber density will be difficult to achieve, in addition to which a sufficiently high stiffness is not attained, and ultrafine fibers will have a greater tendency to shed during polishing. The upper limit is not subject to any particular limitation. For example, when an ultrafine fiber-entangled body from a nonwoven fabric manufactured by the below-described spunbonding process is included, fibers having lengths of several meters, several hundreds of meters, several kilometers or more may be included as far as they are not physically cut.

[0062] The polishing pad of the embodiment preferably has a composite construction obtained by filling the polymeric elastomer into the ultrafine fiber-entangled body.

[0063] In the polishing pad of the embodiment, having the polymeric elastomer present at the interior of the ultrafine fiber bundles is preferable for increasing the stiffness of the polishing pad, and it is more preferable for the ultrafine fibers which make up the ultrafine fiber bundles to be bundled under the effect of the polymeric elastomer. By having the ultrafine fibers bundled in this way, the stiffness of the polishing pad is further increased. Bundling the ultrafine fibers makes it difficult for the individual fibers to move, thereby increasing the stiffness of the polishing pad and enabling a high planarizing performance to be readily achieved. Also, the loss of fibers decreases and the aggregation of abrasive particles at fibers that have been shed can be prevented, thereby minimizing the occurrence of scratches. As used herein, the feature that the ultrafine fibers are bundled refers to a state where a large portion of the ultrafine fibers present at the interior of the ultrafine fiber bundles (preferably at least 10%, more preferably at least 20%, even more preferably at least 50%, and most preferably at least 60%, of the number of fibers) are bonded and restrained by the polymeric elastomer present at the interior of the ultrafine fiber bundles.

[0064] Moreover, it is also preferable for a plurality of ultrafine fiber bundles to be mutually bonded by the polymeric elastomer present outside of the ultrafine fiber bundles, and to exist in a bulk state. By binding together the ultrafine fiber bundles in this way, the shape stability of the polishing pad is enhanced, thus increasing the polishing stability.

[0065] The bundled and restrained state of the ultrafine fibers and the bound state between the ultrafine fiber bundles can be confirmed from electron micrographs of cross-sections of the polishing pad.

[0066] The polymeric elastomer which bundles the ultrafine fibers and the polymeric elastomer which binds together the ultrafine fiber bundles is preferably a nonporous elastomer. Here, "nonporous" signifies a state in which there are substantially no voids (closed pores) as would exist in porous or sponge-like (referred to below simply as "porous") polymeric elastomers. Concretely, this means, for example, that it is not a polymeric elastomer having many tiny pores as would be obtained by coagulating a solvent-based polyurethane. In cases where the polymeric elastomer for bundling or binding is nonporous, because the polishing stability increases and slurry debris and pad debris do not readily accumulate in the voids during polishing, the polishing pad is less subject to wear, enabling a high polishing rate to be maintained for an extended period of time. In addition, because the adhesive strength with respect to the ultrafine fibers is high, the occurrence of scratches that arise from the shedding of fibers can be suppressed. Moreover, because a higher stiffness can be achieved, a polishing pad having an excellent planarization performance is obtained.

[0067] The polishing pad in the present embodiment preferably has a water absorption ratio when swollen to saturation with 50˚C water, of preferably 10 to 80 mass%, and more preferably 15 to 70 mass%. At such a water absorption ratio of at least 10 mass%, the abrasive slurry is easily retained, as a result of which the polishing rate increases and the polishing uniformity tends to improve. At such a water absorption ratio of 80 mass% or less, a high polishing rate is achieved. Moreover, because properties such as hardness do not readily change during polishing, the stability over time in the planarization performance tends to be outstanding.

[0068] By subjecting the polishing pad of the present embodiment to a pad-flattening treatment by buffing or the like, a seasoning treatment (conditioning treatment) using a pad dressing such as a diamond prior to polishing, or a dressing treatment at the time of polishing, the ultrafine fiber bundles present near the surface can be separated or fibrillated, enabling the ultrafine fibers to be formed at the surface of the polishing pad. The fiber density of the ultrafine fibers at the polishing pad surface is preferably at least 600 fibers/mm^2, more preferably at least 1,000 fibers/mm^2, and most preferably at least 2,000 fibers/mm^2. If the fiber density is too low, the retention of the abrasive slurry will tend to be insufficient. From the standpoint of manufacturability, the upper limit in the fiber density, although not subject to any particular limitation, is about 1,000,000 fibers/mm^2. The ultrafine fibers at the surface of the polishing pad may or may not stand upright. In cases where the ultrafine fibers stand upright, the surface of the polishing pad becomes softer, further increasing the scratch-reducing effect. On the other hand, in cases where the degree of uprightness of the ultrafine fibers is low, this is advantageous for applications in which importance is placed on the micro-flatness. It is preferable in this way to suitably select the surface state according to the intended application.

Method for Manufacturing the Polishing Pad

[0069] Next, an example of a method for manufacturing the polishing pad of the present embodiment is described in detail.

[0070] The polishing pad of the embodiment can be obtained by a manufacturing method which includes, for example, a web fabricating step which fabricates a filament web composed of islands-in-the-sea type composite fibers obtained by melt spinning a water-soluble thermoplastic resin and a water-insoluble thermoplastic resin; a web entangling step which forms an entangled web sheet by stacking together a plurality of the filament webs and entangling the webs; a wet heat shrinkage treatment step which shrinks the entangled web sheet to a surface area shrinkage ratio of at least 30% by subjecting the sheet to wet heat shrinkage; an ultrafine fiber-entangled body-forming step which forms an ultrafine fiber-entangled body composed of ultrafine fibers by dissolving the water-soluble thermoplastic resin within the entangled web sheet in hot water; and a polymeric elastomer filling step which impregnates the ultrafine fiber-entangled body with an aqueous liquid of a polymeric elastomer and dry-coagulates the elastomer.

[0071] In the above manufacturing method, by passing through the step wherein the entangled web sheet containing filaments is subjected to wet heat shrinkage, the entangled web sheet can be shrunk to a considerable degree compared with a case in which an entangled web sheet containing staple fibers is subjected to wet heat shrinkage, thereby increasing the fiber density of the ultrafine fibers. Moreover, by dissolving and extracting the water-soluble thermoplastic resin in the entangled web sheet, an ultrafine fiber-entangled body composed of ultrafine fiber bundles is formed. At this time, voids are formed in the areas where the water-soluble thermoplastic resin has been dissolved and extracted. Next, by thoroughly impregnating a high-concentration aqueous liquid of the polymeric elastomer into these voids and by dry-coagulating the elastomer, the ultrafine fibers making up the ultrafine fiber bundles converge together, and the ultrafine fiber bundles also mutually converge. In this way, there can be obtained the polishing pad which has a high fiber density, a low void volume and, because the ultrafine fibers have been made to converge as bundles, a high stiffness.

[0072] By controlling the shrinkage treatment and adjusting the amount of polymeric elastomer impregnated into the voids so as to set the void volume of the polishing pad to 50% or more, the polishing pad suitable for use on bare silicon wafers can be obtained, in which the polishing pad has an appropriate stiffness and both an improved abrasive-slurry retention and an improved cushionability.

[0073] Each of the manufacturing steps is described below in greater detail.

(1) Web Fabricating Step

[0074] In this step, first a filament web composed of islands-in-the-sea type composite fibers obtained by melt spinning a water-soluble thermoplastic resin and a water-insoluble thermoplastic resin is produced.

[0075] The islands-in-the-sea type composite fibers are obtained by respectively melt spinning a water-soluble thermoplastic resin and a water-insoluble thermoplastic resin having a low compatibility with the water-soluble thermoplastic resin, then by combining the two. Ultrafine fibers are then formed by dissolving and removing, or decomposing and removing, the water-soluble thermoplastic resin from the islands-in-the-sea type composite fibers. From an industrial standpoint, it is preferable for the size of the islands-in-the-sea type composite fibers to be from 0.5 to 3 dtex.

[0076] In the embodiment, islands-in-the-sea type composite fibers are described in detail as the composite fibers employed to form ultrafine fibers. However, in place of islands-in-the-sea type fibers, other known ultrafine fiber-generating fibers such as fibers having a multilayer laminated cross-section can be also used.

[0077] As the water-soluble thermoplastic resin, a thermoplastic resin which can be dissolved and removed or decomposed and removed using, for example, water, an alkaline aqueous solution or an acidic aqueous solution, and which is melt-spinnable may be advantageously used. Examples of such water-soluble thermoplastic resins include polyvinyl alcohol resins (PVA resins) such as polyvinyl alcohol and polyvinyl alcohol copolymers; modified polyesters containing polyethylene glycol and/or an alkali metal salt of sulfonic acid as the copolymerizing ingredients; and polyethylene oxide. Of these, the use of a PVA resin is especially preferred for the following reasons.

[0078] When islands-in-the-sea type composite fibers using a PVA resin as the water-soluble thermoplastic resin component are employed, the ultrafine fibers formed by dissolving the PVA resin undergo a considerable degree of crimping. As a result, an ultrafine fiber-entangled body having a higher fiber density is obtained. Alternatively, in cases where islands-in-the-sea type composite fibers in which a PVA resin serves as the water-soluble thermoplastic resin component are used, when the PVA resin is dissolved, because the formed ultrafine fibers and the polymeric elastomer substantially do not decompose or dissolve, the physical properties of the ultrafine fibers and the polymeric elastomer do not readily decline. Moreover, the burden on the environment is also low.

[0079] The PVA resin can be obtained by saponifying a copolymer in which vinyl ester units serve as a primary component. Illustrative examples of vinyl monomers for forming the vinyl ester units include vinyl acetate, vinyl formate, vinyl propionate, vinyl valerate, vinyl caprate, vinyl laurate, vinyl stearate, vinyl benzoate, vinyl pivalate and vinyl versatate. These may be used singly or as combinations of two or more thereof. Of these, vinyl acetate is preferred from an industrial standpoint.

[0080] The PVA resin may be a homo-PVA composed only of vinyl ester units, or may be a modified PVA containing as constituent units copolymerizable monomer units other than vinyl ester units. In terms of the ability to control the melt spinnability, the water solubility and the physical properties of the fibers, the modified PVA is more preferred. Illustrative examples of copolymerizable monomer units other than the vinyl ester units include α-olefins having 4 or fewer carbons, such as ethylene, propylene, 1-butene and isobutene; and vinyl ethers such as methyl vinyl ether, ethylene vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether and n-butyl vinyl ether. The content of copolymerizable monomer units other than vinyl ester units is in a range of preferably from 1 to 20 mol%, more preferably from 4 to 15 mol%, and even more preferably from 6 to 13 mol%. Of these, an ethylene-modified PVA containing from 4 to 15 mol%, and especially from 6 to 13 mol%, of the ethylene units is preferred because the resulting islands-in-the-sea type composite fibers have higher physical properties.

[0081] From the standpoint of forming a stable islands-in-the-sea structure, exhibiting a melt viscosity with excellent melt spinning properties, and having a rapid dissolution rate during dissolution, it is desirable for the PVA resin to have a viscosity-average degree of polymerization in a range of from 200 to 500, preferably from 230 to 470, and most preferably from 250 to 450. The above degree of polymerization is measured in general accordance with JIS-K6726. That is, the viscosity-average degree of polymerization is calculated according to the following formula from the intrinsic viscosity $[\eta]$ measured in 30°C water after the PVA resin is re-saponified and purified.

[0082]

$$\text{Viscosity-average degree of polymerization } P = ([\eta] \times 103/8.29)\ (1/0.62)$$

The degree of saponification of the PVA resin is preferably from 90 to 99.99 mol%, more preferably from 93 to 99.98 mol%, even more preferably from 94 to 99.97 mol%, and most preferably from 96 to 99.96 mol%. When the degree of saponification is in such a range, a PVA resin having an excellent water solubility, good thermal stability, excellent melt spinnability and excellent biodegradability can be obtained.

[0083] From the standpoint of having excellent mechanical properties and thermal stability, and also from the standpoint of having an excellent melt spinnability, it is desirable for the melting point of the above PVA resin to be in a range of from 160 to 250˚C, preferably 170 to 227˚C, more preferably from 175 to 224˚C, and most preferably from 180 to 220˚C. When the melting point of the PVA resin is too high, the melting point and the degradation temperature become similar, as a result of which the melt spinnability tends to decrease due to the occurrence of decomposition during melt spinning.

[0084] Also, when the melting point of the PVA resin is too much lower than the melting point of the above-mentioned water-insoluble thermoplastic resin, this is undesirable because the melt spinnability decreases. From this standpoint, the melting point of the PVA resin is preferably not more than 60˚C lower, and more preferably not more than 30˚C lower, than the melting point of the water-insoluble thermoplastic resin.

[0085] The water-insoluble thermoplastic resin is preferably a thermoplastic resin which is not dissolved and removed, or decomposed and removed, by water, an alkaline aqueous solution, an acid aqueous solution or the like, and which is capable of being melt spun.

[0086] Illustrative examples of the water-insoluble thermoplastic resin include various types of the above-described thermoplastic resins that can be used to form the ultrafine fibers making up the polishing pad.

[0087] The water-insoluble thermoplastic resin may contain various additives. Examples of such additives include catalysts, discoloration inhibitors, heat stabilizers, flame inhibitors, lubricants, stain blockers, fluorescent whiteners, delusterants, colorants, gloss enhancers, antistatic agents, fragrances, deodorants, antimicrobial agents, miticides and inorganic fine particles.

[0088] Next, the method for melt spinning the above water-soluble thermoplastic resin and the above water-insoluble thermoplastic resin to form an islands-in-the-sea type composite fiber, and for forming a filament web from the resulting islands-in-the-sea type composite fibers, is described in detail.

[0089] The filament web can be obtained by, for example, melt-spinning and thereby combining the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin, then by drawing and subsequently depositing the fibers using a spunbonding process. By forming a web using a spunbonding process in this way, there can be obtained a filament web composed of islands-in-the-sea type composite fibers which does not shed many fibers and has a high fiber density and good shape stability. As used herein, "filament" refers to a fiber which has been manufactured without passing through such a cutting step as a case in the manufacture of a staple fiber.

[0090] In the manufacture of the islands-in-the-sea type composite fibers, the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are separately melt-spun, and are combined. The mass ratio of the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin is in a range of preferably from 5/95 to 50/50, and more preferably from 10/90 to 40/60. When the mass ratio of the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin is in this range, an ultrafine fiber-entangled body having a high density can be obtained, and the ultrafine fiber formability is also excellent.

[0091] After the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin have been combined by melt spinning, a filament web is formed by spunbonding as described below.

[0092] First, the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are each melt-mixed in separate extruders, and strands of the molten resins are simultaneously discharged from the respective differing spinnerets. Next, the discharged strands are combined in a combining nozzle, then discharged from the nozzle orifices in the spinning head to form an islands-in-the-sea type composite fiber. To obtain fiber bundles having low individual fiber fineness and a high fiber density, it is desirable for the number of islands in the islands-in-the-sea type composite fiber during molten composite spinning to be preferably from 4 to 4,000 islands/fiber, and more preferably from 10 to 1,000 islands/fiber.

[0093] The above islands-in-the-sea type composite fiber is cooled in a cooling device, following which a suction apparatus such as an air jet nozzle is used to draw the fiber with a high-speed stream of air at a velocity equivalent to the take-up speed of 1,000 to 6,000 m/min in such a way as to achieve the target fineness. Next, the drawn composite fibers are deposited onto a movable collecting surface, thereby forming a filament web. At this time, if necessary, the deposited filament web may be subjected to localized pressure bonding. A basis weight for the fiber web in a range of from 20 to 500 g/m^2 enables a uniform ultrafine fiber-entangled body to be obtained, and is also desirable from an industrial standpoint.

(2) Web Entangling Step

[0094] Next, the web entangling step in which a sheet of entangled webs is formed by stacking and entangling a plurality of the above filament webs is described.

[0095] An entangled web sheet is formed by using a known nonwoven fabric manufacturing process such as needlepunching or hydroentanglement to carry out an entangling treatment on the filament webs. By way of illustration, a description is given below of the entangling treatment by needlepunching.

[0096] First, a silicone finish or a mineral oil finish, such as a needle break preventing finish, an antistatic finish or an entanglement enhancing finish, is applied to the filament web. To reduce variations in the basis weight, the finish may be applied after superimposing two or more fiber webs in a crosslapped manner.

[0097] Next, the entangling treatment is carried out in which the fibers are three-dimensionally entangled by needlepunching. By carrying out the needlepunching treatment, an entangled web sheet which has a high fiber density and does not readily shed fibers can be obtained. The basis weight of the entangled web sheet is suitably selected in accordance with the thickness and other properties of the target polishing pad. For example, a basis weight in a range of 100 to 1500 g/m^2 is desirable from the standpoint of excellent handleability.

[0098] The type and amount of the finish, and the needle conditions (e.g., needle shape, needle depth, punch density) in needlepunching are suitably selected in such a way as to give the entangled web sheet a high delamination strength between the layers of the sheet. The higher number of barbs is preferable within a range where needle breakage does not arise. By way of illustration, the number of barbs may be selected from among 1 to 9 barbs. The needle depth is preferably set in such a way that the barbs penetrate to the surface of the stacked webs and within a range where the pattern after needlepunching does not emerge strongly on the web surface. Also, the needle punch density is adjusted according to such factors as the shape of the needles and the type and amount of the finish used, although a density of from 500 to 5,000 punches/cm^2 is preferred. Carrying out the entangling treatment in such a way that the ratio of the basis weight following the entangling treatment to the basis weight before the entangling treatment is 1.2 or more, and especially 1.5 or more, is preferable from the standpoint of obtaining an ultrafine fiber-entangled body having a high fiber density and reducing the shedding of fibers. The upper limit is not subject to any particular limitation, although the ratio of 4 or less is preferable to avoid increased production costs due to a decrease in throughput.

[0099] If the polishing pad is to be used for polishing bare silicon wafers, it is preferable to set the void volume of the polishing pad to at least 50%. For this reason, the amount of polymeric elastomer filled into the polishing pad may be adjusted depending on whether the fiber density is to be increased or decreased.

[0100] A delamination strength for the entangled web sheet of at least 2 kg/2.5 cm, and especially at least 4 kg/2.5 cm, is desirable for obtaining an ultrafine fiber-entangled body which has a good shape retention, sheds few fibers, and has a high fiber density. The delamination strength serves as an indicator of the degree of three-dimensional entangling. In cases where the delamination strength is too low, the ultrafine fiber-entangled body will not have a sufficiently high fiber density. The upper limit in the delamination strength of the entangled nonwoven fabric is not subject to any particular limitation; however, from the standpoint of the entangling treatment efficiency, it is preferably not more than 30 kg/2.5 cm.

[0101] For the purpose of adjusting the hardness of the polishing pad, it is possible, insofar as the advantageous effects of the invention are attainable, to use as the sheet of entangled webs a laminated structure such as an entangled nonwoven fabric that has been entangled and thereby united with a knit or woven fabric (e.g., knit or woven fabric/entangled nonwoven fabric, entangled nonwoven fabric/knit or woven fabric/entangled nonwoven fabric). Such a laminated structure is obtained by carrying out an entangling treatment wherein a knit or woven fabric composed of ultrafine fibers is additionally superimposed on the sheet of entangled webs (a nonwoven fabric) obtained as described above and subjected to needlepunching and/or hydroentanglement.

[0102] The ultrafine fibers making up such a knit or woven fabric are not subject to any particular limitation. Specifically, examples preferably used include polyester fibers formed from polyethylene terephthalate (PET), polytrimethylene terephthalate, polybutylene terephthalate (PBT) or a polyester elastomer; polyamide fibers formed from polyamide 6, polyamide 66, aromatic polyamides or polyamide elastomers; and urethane polymers, olefin polymers and acrylonitrile polymers. Of these, fibers formed of PET, PBT, polyamide 6, polyamide 66 or the like are preferred from an industrial standpoint.

[0103] Specific examples of the component removed from the islands-in-the-sea type composite fibers which form the above knit or woven fabric include polystyrene and copolymers thereof, polyethylene, PVA resins, copolymeric polyester and copolymeric polyamide. Of these, the use of a PVA resin is preferred on account of the large shrinkage that arises at the time of removal by dissolution.

(3) Wet Heat Shrinkage Treatment Step

[0104] Next, the wet heat shrinkage treatment step for increasing the fiber density and degree of entanglement in the sheet of entangled webs by subjecting the sheet to wet heat shrinkage is described. In this step, subjecting the entangled web sheet containing filaments to wet heat shrinkage enables a considerable shrinkage compared with when an entangled web sheet containing staple fibers is subjected to wet heat shrinkage, thereby resulting in a particularly high fiber density for the ultrafine fibers.

[0105] The wet heat shrinkage treatment is preferably carried out by steam heating. The steam heating conditions preferably entail a heat treatment at an ambient temperature in a range of 60 to 130°C and a relative humidity of at least 75%, more preferably at least 90%, for a period of 60 to 600 seconds. Such heating conditions are preferable because the entangled web sheet can be shrunk at a high shrinkage ratio. If the relative humidity is too low, water in contact with the fibers will rapidly dry, as a result of which shrinkage may be inadequate.

[0106] It is desirable for the wet heat shrinkage treatment to shrink the entangled web sheet by a surface area shrinkage ratio of at least 30%, preferably at least 35%, and more preferably at least 40%. By inducing the shrinkage at such a high shrinkage ratio, a high fiber density can be achieved. The upper limit in the surface area shrinkage ratio is not subject to any particular limitation. However, from the standpoint of the shrinkage limit and the treatment efficiency, a shrinkage ratio of up to about 80% is preferred.

[0107] The surface area shrinkage ratio (%) is calculated from the following formula (1):

$$[(\text{surface area of sheet side before shrinkage treatment} - \text{surface area of sheet side after shrinkage treatment})/\text{surface area of sheet side before shrinkage treatment}] \times 100 \quad (1)$$

This surface area refers to the average surface area obtained from the surface area of the front side of the sheet and the surface area of the back side of the sheet.

[0108] The ratio of the void volume of the entangled web sheet that has been subjected to the wet heat shrinkage treatment in this way can be adjusted by hot rolling or hot pressing the sheet at or above the heat distortion temperature of the islands-in-the-sea type composite fiber. By making the hot pressing conditions stronger, it is possible to increase the fiber density and achieve greater compactness.

[0109] It is desirable for the change in the basis weight of the entangled web sheet before and after the wet heat shrinkage treatment to be such that the basis weight following shrinkage treatment, as compared with the basis weight before shrinkage treatment, is at least 1.2 times (mass ratio), and more preferably at least 1.5 times, but not more than 4 times, and more preferably not more than 3 times.

(4) Fiber Bundle-Binding Step

[0110] Prior to carrying out an ultrafine fiber-forming treatment on the entangled web sheet, for the purpose of increasing the shape stability of the entangled web sheet, or for the purpose of adjusting or reducing the void volume of the resulting polishing pad, if necessary, the fiber bundles may be bonded beforehand by impregnating the shrinkage-treated entangled web sheet with an aqueous liquid of the polymeric elastomer and dry coagulating the elastomer.

[0111] In this step, the polymeric elastomer is filled into the entangled web sheet by impregnating the shrinkage-treated entangled web sheet with an aqueous liquid of the polymeric elastomer and dry coagulating the elastomer. Because the aqueous liquid of the polymeric elastomer has a low viscosity even at high concentrations, and also has an excellent penetrability during impregnation, a high degree of filling at the interior of the entangled web sheet is easily achieved. It also has an excellent adherence to the fibers. Therefore, by carrying out this step, it is possible to tightly restrain the islands-in-the-sea type composite fibers.

[0112] As used herein, "aqueous liquid of elastomeric polymer" refers to an aqueous solution obtained by dissolving the polymeric elastomer-forming ingredients in an aqueous solvent, or an aqueous dispersion obtained by dispersing the polymeric elastomer-forming ingredients in an aqueous medium. Here, "aqueous dispersion" includes suspension type dispersions and emulsion type dispersions. The use of the aqueous dispersion is especially preferred on account of the excellent water resistance.

[0113] The method of preparing the polyurethane resin as the aqueous solution or the aqueous dispersion is not subject to any particular limitation. Use may be made of a known method, such as a method wherein the polyurethane resin is imparted with dispersibility in an aqueous medium by including therein a monomer unit having a hydrophilic group such as a carboxylic group, a sulfonic acid group or a hydroxyl group, or a method wherein a surfactant is added to the polyurethane resin so as to emulsify or suspend the resin. Because such aqueous polymeric elastomers have an excellent water-wettability, they have an excellent ability to retain the abrasive, both uniformly and in a large amount.

[0114] Illustrative examples of surfactants that may be used in such emulsification or suspension include anionic surfactants such as sodium lauryl sulfate, ammonium lauryl sulfate, sodium polyoxyethylene tridecyl ether acetate, sodium dodecylbenzene sulfonate, sodium alkyldiphenyl ether disulfonate and sodium dioctylsulfosuccinate; and non-ionic surfactants such as polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether and polyoxyethylene-polyoxypropylene block copolymer. Moreover, a so-called reactive surfactant which has reactivity may also be used. It is also possible, by suitably selecting the cloud point of the surfactant, to impart thermosensitive gelling properties to the polyurethane resin. However, when a large amount of surfactants is used, this sometimes has adverse effects on the polishing performance and the polishing stability over time. Hence, it is preferable to keep the amount of surfactants used to the minimum required.

[0115] By setting the solids concentration of the aqueous liquid of the polymeric elastomer to at least 10 mass%, and preferably at least 15 mass%, the void volume ratio can be reduced.

[0116] Examples of methods for impregnating the aqueous liquid of the polymeric elastomer into the entangled web sheet include methods involving the use of a knife coater, bar coater or roll coater, and dipping methods.

[0117] The polymeric elastomer may then be coagulated by drying the entangled web sheet into which the aqueous liquid of the polymeric elastomer has been impregnated. Examples of drying methods include methods which involve a heat treatment in a drying device at 50 to 200˚C, and methods wherein infrared heating is followed by a heat treatment in a drying device.

[0118] In cases where the entangled web sheet is dried after the aqueous liquid of the polymeric elastomer has been impregnated into the entangled web sheet, a uniform filled state sometimes cannot be achieved on account of migration of the aqueous liquid to the surface layer of the entangled web sheet. In such cases, the migration can be suppressed by, for example, adjusting the particle size of the polymeric elastomer in the aqueous liquid; adjusting the type and amount of ionic groups on the polymeric elastomer, or adjusting the stability thereof by means of the pH or the like; or lowering the water dispersion stability at about 40 to 100˚C through the concomitant use of a monovalent or divalent alkali metal salt or alkaline earth metal salt, a nonionic emulsifying agent, an associative water-soluble thickening agent, an associative thermosensitive gelling agent such as a water-soluble silicone compound, a water-soluble polyurethane compound, or an organic or inorganic substance which changes the pH under the effect of heating. If necessary, the migration may be induced so that the polymeric elastomer is preferentially distributed in the surface.

(5) Ultrafine Fiber-Forming Step

[0119] Next, the ultrafine fiber-forming step, which is a step in which ultrafine fibers are formed by dissolving the water-soluble thermoplastic resin in hot water, is described.

[0120] This is a step in which ultrafine fibers are formed by removing the water-soluble thermoplastic resin. At this time, voids are formed in areas where the water-soluble thermoplastic resin in the entangled web sheet has been dissolved and extracted. The polymeric elastomer is filled into these voids in the subsequent polymeric elastomer filling step, as a result of which the ultrafine fibers converge as bundles, and the bundles of ultrafine fibers are restrained.

[0121] The ultrafine fiber-forming treatment is a treatment in which the entangled web sheet, or a composite of the entangled web sheet with the polymeric elastomer, is subjected to hot-water heat treatment with water, an alkaline aqueous solution, an acidic aqueous solution or the like so as to dissolve and remove, or decompose and remove, the water-soluble thermoplastic resin.

[0122] In a preferred example of the hot-water heat treatment conditions, a first stage consisting of 5 to 300 seconds of immersion in 65 to 90˚C hot water is followed by a second stage consisting of 100 to 600 seconds of treatment in 85 to 100˚C hot water. Also, to increase the dissolution efficiency, if necessary, nipping treatment with rollers, high-pressure water jet treatment, ultrasonic treatment, shower treatment, agitation treatment, rubbing treatment or the like may be carried out.

[0123] In this step, when the water-soluble thermoplastic resin dissolves from the islands-in-the-sea type composite fibers to form the ultrafine fibers, the ultrafine fibers undergo considerable shrinkage. Because the fiber density rises through such shrinkage, the ultrafine fiber-entangled body having a high-density is obtained.

(6) Polymeric Elastomer Filling Step

[0124] Next, a step is described wherein, by filling the polymeric elastomer into the interior of the ultrafine fiber bundles formed of the ultrafine fibers, the ultrafine fibers are made to converge as bundles, in addition to which the individual ultrafine fiber bundles are restrained and, moreover, the ultrafine fiber bundles are bound to each other.

[0125] In the ultrafine fiber-forming step (5), by subjecting the islands-in-the-sea type composite fibers to ultrafine fiber-forming treatment, the water-soluble thermoplastic resin was removed, resulting in the formation of voids at the interior of the ultrafine fiber bundles. In the present step, by suitably filling such voids with the polymeric elastomer, the ultrafine fibers are made to converge as bundles, in addition to which the individual ultrafine fiber bundles are restrained and the ultrafine fiber bundles are bound to each other, which makes it possible to set the void volume ratio in the polishing pad to, for example, 50% or less. Also, by filling with the polymeric elastomer to a sufficient degree, the void volume ratio is lowered, making it possible to give the polishing pad a dense structure. Moreover, when the ultrafine fibers are formed into ultrafine fiber bundles, the aqueous fluid of the polymeric elastomer readily impregnates therein by way of a capillary effect, further facilitating the convergence of the ultrafine fibers into bundles and the restraint of the ultrafine fiber bundles.

[0126] The aqueous liquids of the polymeric elastomer that may be used in this step are the same as the aqueous liquids of polymeric elastomers that were mentioned above in the fiber bundle-binding step (4).

[0127] A method similar to that used in the fiber bundle-binding step (4) may be suitably used in the present step as the method of filling the polymeric elastomer into the interior of the ultrafine fiber bundles formed of ultrafine fibers. In addition, the void volume ratio may be adjusted to the desired value by suitably combining the fiber bundle-binding step (4) and the polymeric elastomer filling step (6). In this way, the polishing pad is formed.

Post-Treatment of Polishing Pad

[0128] If necessary, the polishing pad obtained may be subjected to a post-treatment, such as molding, flattening, napping, lamination, surface treatment and washing.

[0129] The molding and flattening are treatments wherein the polishing pad obtained is hot-press molded to a given thickness, or is cut to a given outside shape by grinding. The polishing pad is preferably ground to a thickness of about 0.5 to 3 mm.

[0130] The napping refers to a treatment in which a mechanical frictional force or abrasive force is applied to the surface of the polishing pad by means of sandpaper, card clothing, a diamond dresser or the like so as to separate the ultrafine fibers that have been made to converge into bundles. By the napping, the fiber bundles existing in the polishing pad surface are fibrillated to form a large number of ultrafine fibers on the surface.

[0131] The lamination refers to a treatment in which the stiffness is adjusted by superimposing and laminating the resulting polishing pad on a backing material. For example, by laminating the polishing pad together with an elastomer sheet having a low hardness, the global planarity of the surface being polished (the planarity of the overall substrate being polished) can be further increased. Adhesion during such lamination may be melt adhesion or adhesion using a non-pressure-sensitive adhesive or a pressure-sensitive adhesive. Illustrative examples of such backing materials include sheet-like backing materials, such as elastic sponge bodies obtained from polyurethane or the like; nonwoven fabrics impregnated with polyurethane (such as the product available from Nitta Haas Inc. under the trade name Suba 400); elastomeric resin films composed of a rubber such as natural rubber, nitrile rubber, polybutadiene rubber or silicone rubber, or a thermoplastic elastomer such as polyester thermoplastic elastomer, polyamide thermoplastic elastomer or fluorinated thermoplastic elastomer; foamed plastics; and knit fabrics or woven fabrics.

[0132] The surface treatment refers to a treatment in which grooves or holes in the form of a grid, concentric circles or spirals are formed on the surface of the polishing pad in order to adjust the ability to retain and the ability to discharge the abrasive slurry.

[0133] The cleaning refers to a treatment of cleaning away impurities such as particles and metal ions which adhere to the resulting polishing pad by using cold water or warm water, or to a cleaning treatment with an aqueous solution or solvent containing an additive which has a cleansing action, such as a surfactant.

[0134] The polishing pad of the present embodiment is preferably used for polishing silicon wafers, compound semiconductor wafers, semiconductor wafers, semiconductor devices, liquid crystal members, optical components, quartz, optical substrates, electronic circuit substrates, electronic circuit mask substrates, multilayer wiring substrates, hard disks, and microelectromechanical system (MEMS) substrates. Because the polishing pad of the embodiment has the void volume ratio that has been set to at least 50%, it is particularly effective for polishing bare silicon wafers.

[0135] Specific examples of semiconductor wafers and semiconductor devices include dielectric films made of silicon, silicon oxide, silicon oxyfluoride and organic polymers; wiring metal films made of copper, aluminum or tungsten; and barrier metal films made of tantalum, titanium, tantalum nitride or titanium nitride.

[0136] In polishing, the polishing pad may be used in any polishing step, such as primary polishing, secondary polishing (adjustment polishing), finish polishing and mirror polishing. Portions to be polished may be the front, rear or end surface of a substrate.

Examples

[0137] The invention is illustrated more concretely below with examples, although the invention is not limited in any way by the examples.

Example 1

[0138] Islands-in-the-sea type composite fibers were formed by discharging a water-soluble thermoplastic polyvinyl alcohol resin (abbreviated below as "PVA resin") and an isophthalic acid-modified polyethylene terephthalate having a degree of modification of 6 mol% (having a water absorption ratio when saturated with water at 50˚C of 1 mass% and a glass transition temperature of 77˚C; abbreviated below as "modified PET") in a mass ratio of 20:80 from a spinneret for melt spinning composite fibers. The spinneret produced composite fibers having 50 islands/fiber, and the spinneret temperature was 260˚C. The ejector pressure was adjusted so as to give a spinning speed of 4,000 m/min, and filaments having an average fineness of 2.0 dtex was collected on a net, thereby giving a spunbonded sheet (filament web) with a basis weight of 40 g/m^2.

[0139] Twelve of the resulting spunbonded sheets were superimposed in a crosslapped arrangement to produce a stack of webs having a total basis weight of 480 g/m^2. A needle break-preventing oil agent was then sprayed onto the resulting stacked webs. Next, using 1-barb 42-gauge needles and 6-barb 42-gauge needles, the stacked webs were entangled by needlepunching at 1800 punches/cm^2, thereby giving a sheet of entangled webs. The entangled web sheet thus obtained had a basis weight of 750 g/m^2. The surface area shrinkage due to the needlepunching treatment was 35%.

[0140] Next, the resulting entangled web sheet was steam-treated for 90 seconds at 70˚C and 90% RH. The surface area shrinkage at this time was 40%. The sheet was then dried in a 140˚C oven and subsequently hot pressed at 140˚C to give an entangled web sheet having a basis weight of 1,250 g/m^2, an apparent density of 0.65 g/cm^3 and a thickness of 1.9 mm. The entangled web sheet had a thickness after hot pressing which was 0.80 times as thick as the sheet prior to hot pressing.

[0141] Next, the hot-pressed entangled web sheet was impregnated with an aqueous dispersion of polyurethane elastomer A (solids concentration, 20 mass%) as the first polyurethane elastomer. Polyurethane elastomer A was a noncrystalline polycarbonate-based non-yellowing-type polyurethane resin which was prepared by polymerizing 55 mass% of, as the soft component, a polyol component obtained by mixing a noncrystalline polycarbonate polyol (a copolymeric polyol composed of 3-methyl-1,5-pentylene carbonate and hexamethylene carbonate) and a polyalkylene glycol having 2 to 3 carbons in a molar ratio of 99.7 : 0.3 and adding to the mixture 1.5 mass% of a carboxylic group-containing monomer (2,2-bis(hydroxymethyl)propionic acid), with 4,4'-dicyclohexylmethane diisocyanate, a short-chain polyamine and a short-chain polyol as the hard components. The water absorption ratio of polyurethane elastomer A was 3 mass%, the storage modulus at 23˚C was 300 MPa, the storage modulus at 50˚C was 150 MPa, the glass transition temperature was -20˚C, and the average particle size of the aqueous dispersion was 0.03 μm. The amount of adherent solids of the aqueous dispersion at this time was 10 mass% with respect to the mass of the entangled web sheet. The entangled web sheet impregnated with the aqueous dispersion was subjected to dry coagulation treatment at 90˚C and 50% RH, then dried at 140˚C. The dried sheet was then hot-pressed at 140˚C, giving a sheet having a basis weight of 1,370 g/m^2, an apparent density of 0.76 g/cm^3 and a thickness of 1.8 mm.

[0142] Next, the entangled web sheet filled with polyurethane elastomer A was treated with nip rollers, then immersed for 10 minutes in 95˚C hot water while being subjected to high-pressure water jet treatment so as to dissolve and remove the PVA resin. This was followed by drying, thereby giving a composite of polyurethane elastomer A with an ultrafine fiber-entangled body, in which the composite was composed of ultrafine fibers having an average fineness of 0.05 dtex, and had a basis weight of 1,220 g/m^2, an apparent density of 0.66 g/cm^3 and a thickness of 1.85 mm.

[0143] This composite was then impregnated with an aqueous dispersion of polyurethane elastomer B (solid concentration, 30 mass%) as the second polyurethane elastomer. Polyurethane elastomer B was a polyurethane resin prepared by using 100 parts by mass of a polycarbonate-based non-yellowing-type polyurethane resin, adding 5 parts by mass of a carbodiimide crosslinking agent, and heat treating so as to form a crosslinked structure, in which the polycarbonate-based non-yellowing-type polyurethane resin was obtained by polymerizing 50 mass% of the soft component obtained by mixing a noncrystalline polycarbonate polyol (a copolymeric polyol composed of hexamethylene carbonate and pentamethylene carbonate) and a polyalkylene glycol having 2 to 3 carbons in a molar ratio of 99.9 : 0.1, and adding to the mixture 1.5 mass% of a carboxylic group-containing monomer (2,2-bis(hydroxymethyl)propionic acid), with 4,4'-dicyclohexylmethane diisocyanate, a short-chain amine and a short-chain diol as the hard components. The water absorption ratio for polyurethane elastomer B was 2 mass%, the storage modulus at 23˚C was 450 MPa, the storage modulus at 50˚C was 300 MPa, the glass transition temperature was -25˚C, and the average particle size of the aqueous dispersion was 0.05 μm. The amount of adherent solids of the aqueous dispersion at this time was 15 mass% with respect to the mass of the composite. Next, the composite impregnated with the aqueous dispersion was subjected to coagulation treatment at 90˚C and 50% RH, then to drying treatment at 140˚C. The dried composite was then hot-pressed at 140˚C, giving a polishing pad precursor. The resulting polishing pad precursor had a basis weight of 1,390 g/m^2, an apparent density of 0.80 g/cm^3 and a thickness of 1.75 mm.

[0144] In the polishing pad precursor thus obtained, all 50 fibers of the ultrafine fibers making up each fiber bundle converged as a bundle. Moreover, the polymeric elastomer was present at the interior of the ultrafine fiber bundles, and restrained the bundles.

[0145] The resulting polishing pad precursor was subjected to grinding treatment to flatten the surface, thereby giving a flattened pad having a basis weight of 1,120 g/m^2, an apparent density of 0.80 g/cm^3 and a thickness of 1.4 mm. In addition, the pad was cut into circular shapes having a diameter of 51 cm, following which grooves having a width of 2.0 mm and a depth of 1.0 mm were formed in a grid at 15.0 mm intervals on the surface, thereby giving circular polishing pads. The mass ratio of the ultrafine fiber-entangled body to the polyurethane elastomer was 76/24, and the ratio of polymeric elastomer A to polymeric elastomer B was 40/60. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 1.

Example 2

[0146] The same procedure as in Example 1 was carried out up to the production of the entangled web sheet. After being hot-pressed without being impregnated with polyurethane elastomer A, the entangled web sheet was then immersed for 10 minutes in 95˚C hot water and the PVA resin was dissolved and removed, thereby giving an ultrafine fiber-entangled body composed of bundles of ultrafine fibers. The resulting ultrafine fiber-entangled body was then impregnated with an aqueous dispersion of polyurethane elastomer B (solids concentration, 40 mass%). At this time, the amount of adherent solids of the aqueous dispersion was 20 mass% with respect to the mass of the ultrafine fiber-entangled body. Next, the ultrafine fiber-entangled body impregnated with the aqueous dispersion was coagulated at 90˚C and 50% RH. This was followed by drying treatment at 140˚C, then hot pressing at 140˚C, thereby giving a polishing pad precursor. The resulting polishing pad precursor was post-treated in the same way as in Example 1, giving a flattened pad having a basis weight of 1,080 g/m^2, an apparent density of 0.77 g/cm^3 and a thickness of 1.4 mm. Following a treatment to form grooves, circular polishing pads were obtained. In the resulting polishing pads, all 50 fibers of the ultrafine fibers making up each fiber bundle converged as a bundle. Moreover, the polymeric elastomer was present at the interior of the ultrafine fiber bundles, and restrained the bundles. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 1.

Example 3

[0147] Aside from not carrying out the hot pressing treatment before the impregnation of polyurethane elastomer A and also not carrying the hot pressing treatment after impregnation and drying, polishing pads were obtained in the same way as in Example 1.

[0148] The polishing pad precursor thus obtained had a basis weight of 1,360 g/m^2, an apparent density of 0.62 g/cm^3 and a thickness of 2.2 mm, in addition to which the mass ratio of the ultrafine fiber-entangled body to the polyurethane elastomer was 70/30. In the resulting polishing pad precursor, all 50 fibers of the ultrafine fibers making up each fiber bundle converged as a bundle. Moreover, the polymeric elastomer was present at the interior of the ultrafine fiber bundles, and restrained the bundles. Polishing pads obtained by carrying out flattening and groove-forming treatment in the same way as in Example 1 were evaluated by the below-described methods. The results are shown in Table 1.

Example 4

[0149] Aside from the use as the first polyurethane elastomer of, instead of polyurethane elastomer A, a polycarbonate-based non-yellowing-type polyurethane elastomer C (water absorption ratio, 4%; storage modulus at 23˚C, 250 MPa; storage modulus at 50˚C, 100 MPa; glass transition temperature, -30˚C; average particle size of aqueous dispersion, 0.03 μm) obtained by polymerizing 58 mass% of, as the soft component, a polyol component composed of a polyether-based polyalkylene glycol mixed with a polycarbonate polyol in a molar ratio of 88:12 and additionally containing 1.2 mass% of a carboxylic group-containing monomer (2,2-bis(hydroxymethyl)propionic acid), with isophorone diisocyanate, a short-chain polyamine and a short-chain polyol as the hard components; and aside from the use as the second polyurethane elastomer of, instead of polyurethane elastomer B, a polyurethane elastomer D (water absorption ratio, 4%; storage modulus at 23˚C, 300 MPa, storage modulus at 50˚C, 125 MPa; glass transition temperature, -30˚C; average particle size of aqueous dispersion, 0.05 μm) obtained by increasing the polyol component of polyurethane elastomer B by 10 mass% to set the amount of the polyol component relative to the polyurethane elastomer at 60 mass%, polishing pads were produced in the same way as in Example 1. In the resulting polishing pads, all 50 fibers of the ultrafine fibers making up each fiber bundle converged as a bundle. Moreover, the polymeric elastomer was present at the interior of the ultrafine fiber bundles, and restrained the bundles. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 1.

Example 5

[0150] Aside from carrying out melt spinning by discharging a PVA resin and a modified PET in a mass ratio of 20:80

from a spinneret having 9 islands/fiber, polishing pads were obtained in the same way as in Example 1. The average fineness of the ultrafine fibers was 0.28 dtex. In the resulting polishing pads, all 9 fibers of the ultrafine fibers making up each bundle converged as a bundle. Moreover, the polymeric elastomer was present at the interior of the ultrafine fiber bundles, and restrained the bundles. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 1.

Example 6

[0151] Aside from changing as follows the polishing conditions in the below-described polishing pad evaluations, the polishing performance was evaluated in the same way using the polishing pads obtained in Example 1. The polishing conditions were as follows.

[0152] (1) Aside from changing the silicon wafer having an oxide film to a bare silicon wafer and changing the slurry used in polishing to Glanzox 1103, available from Fujimi Incorporated, evaluation was carried out in the same way.

[0153] (2) Aside from changing the slurry used in polishing to the polishing slurry GPL-C1010, available from Showa Denko KK, and changing the slurry flow rate to 200 mL, evaluation was carried out in the same way.

[0154] (3) Aside from changing the wafer to a tungsten wafer and changing the slurry used in polishing to W-2000, available from Cabot Corporation (34 g of hydrogen peroxide added per 1,030 g of slurry), evaluation was carried out in the same way.

[0155] (4) Aside from changing the wafer to a GaAs wafer, changing the slurry used in polishing to INSEC-FP, available from Fujimi Incorporated, and changing the polishing pressure to 20 kPa, evaluation was carried out in the same way.

[0156] The results are shown in Table 3.

Example 7

[0157] The same procedure as in Example 1 was carried out up to the impregnation of polyurethane elastomer A to the interior of a hot-pressed entangled web sheet (basis weight, 1,280 g/m^2; apparent density, 0.56 g/cm^3; thickness, 2.3 mm) and the subsequent dry-coagulation. A sheet having a basis weight of 1,340 g/m^2, an apparent density of 0.69 g/cm^3 and a thickness of 1.95 mm was obtained without carrying out hot pressing.

[0158] Next, the entangled web sheet filled with polyurethane elastomer A was treated with nip rollers, then immersed in 95˚C hot water for 10 minutes while being high-pressure-water jet treated so as to dissolve and remove the PVA resin, and subsequently dried, thereby giving a composite of polyurethane elastomer A and an ultrafine fiber-entangled body in which the composite had the average fineness of the ultrafine fibers of 0.05 dtex, a basis weight of 1,050 g/m^2, an apparent density of 0.57 g/cm^3 and a thickness of 1.85 mm.

[0159] This composite was then impregnated with polyurethane elastomer B as the second polyurethane elastomer, following which the elastomer was dry-coagulated, and hot pressing was not carried out, thereby giving a polishing pad precursor. The polishing pad precursor had a basis weight of 1,170 g/m^2, an apparent density of 0.60 g/cm^3 and a thickness of 1.95 mm.

[0160] The polishing pad precursor was then subjected to grinding treatment for surface flattening, thereby giving a flattened pad having a basis weight of 1,000 g/m^2, an apparent density of 0.57 g/cm^3 and a thickness of 1.75 mm. This pad was cut into circular shapes having a diameter of 51 cm, and grooves with a width of 2.0 mm and a depth of 1.0 mm were formed in a grid on the surface at intervals of 15.0 mm, thereby giving circular polishing pads. The mass ratio of the ultrafine fiber-entangled body to the polyurethane elastomer was 76/24, and the ratio of polymeric elastomer A to polymeric elastomer B was 40/60. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 1.

Example 8

[0161] Aside from changing in the same way in (1) to (3) of Example 6 the polishing conditions in the below-described polishing pad evaluations, the polishing performance was evaluated in the same way using the polishing pads obtained in Example 7.

[0162] The results are shown in Table 4.

Comparative Example 1

[0163] Ny filaments having an average fineness of 2 dtex were melt-spun by melt-spinning Ny 6. The resulting filaments were collected on a net, thereby giving a spunbonded sheet (filament web) having a basis weight of 30 g/m^2.

[0164] Stacked webs were formed in the same way as in Example 2 from the resulting spunbonded sheet. Next, the resulting stacked webs were entangled by needlepunching in the same way as in Example 1, thereby giving an entangled web sheet. The resulting entangled web sheet had a basis weight of 800 g/m^2. Hot pressing at 140˚C was then carried out, thereby giving an entangled web sheet having an apparent density of 0.42 g/cm^3 and a thickness of 1.9 mm.

[0165] Next, an aqueous dispersion of polyurethane elastomer B (solids concentration, 30 mass%) was impregnated into the hot-pressed entangled web sheet. The amount of adherent solids of the aqueous dispersion at this time was 20 mass% with respect to the mass of the entangled web sheet. The entangled web sheet impregnated with the aqueous dispersion was then subjected to coagulation treatment at 90˚C and 90% RH, and also subjected to drying treatment at 140˚C, after which hot pressing treatment was carried out at 140˚C, thereby giving a polishing pad precursor having a basis weight of 920 g/m^2, an apparent density of 0.54 g/m^2 and a thickness of 1.7 mm. Buffing treatment was then carried out to flatten the front and back faces, thereby giving a polishing pad. The resulting polishing pad was evaluated by the below-described methods. The results are shown in Table 2.

Comparative Example 2

[0166] Instead of using an aqueous dispersion of polyurethane elastomer A to form a polyurethane elastomer, an aqueous dispersion of polyurethane elastomer E (solids concentration, 20 mass%) was impregnated as the polymeric elastomer. Polyurethane elastomer E was a non-yellowing-type polyurethane resin obtained by polymerizing a polyol (60 mass% relative to the polyurethane elastomer) composed of polyethylene glycol and polytetramethylene glycol in a 15/85 mixture with isophorone diisocyanate, a short-chain polyamine and a short-chain polyol as the hard components. Polyurethane elastomer E had a water absorption ratio of 12 mass%, a storage modulus at 23˚C of 200 MPa, a storage modulus at 50˚C of 80 MPa, a glass transition temperature of -48˚C, and an average particle size in the aqueous dispersion of 0.4 μm. Aside from this, polishing pads were produced in the same way as in Example 2. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 2.

Comparative Example 3

[0167] Aside from using polyurethane elastomer F (water absorption ratio, 8%; storage modulus at 23˚C, 80 MPa, storage modulus at 50˚C, 30 MPa; glass transition temperature, -32˚C; average particle size of aqueous dispersion, 0.02 μm) obtained by increasing the polyol component of polyurethane elastomer B to 65 mass%, polishing pads were produced in the same way as in Example 2. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 2.

Comparative Example 4

[0168] Aside from the use of polyurethane elastomer G (water absorption ratio, 1%; storage modulus at 23˚C, 1,000 MPa, storage modulus at 50˚C, 200 MPa; glass transition temperature, 0˚C; average particle size of aqueous dispersion, 0.08 μm) obtained by changing the polyol component of polyurethane elastomer B to hexamethylene carbonate diol, using 30 mass% of the soft (polyol) component and polymerizing this with 4,4'-dicyclohexylmethane diisocyanate, a short-chain amine and a short-chain diol as the hard components, polishing pads were produced in the same way as in Example 2. The resulting polishing pads were evaluated by the below-described methods. The results are shown in Table 2.

[0169] The polishing pads obtained were evaluated by the following methods.

Evaluation Methods

(1) Average Fineness of Ultrafine Fibers, and Verification of Converging State of Ultrafine Fibers of Fiber Bundles

[0170] The polishing pad obtained was cut in the thickness direction with a cutter blade, thereby forming a cut face in the thickness direction. The cut face was dyed with osmium oxide, then examined at a magnification of 500 to 1,000x with a scanning electron microscope (SEM), and the image was photographed. The cross-sectional area of the ultrafine fibers present in the cut face was then determined from the resulting image. This was calculated from the average cross-sectional surface area obtained by averaging the cross-sectional areas at 100 randomly selected places and from the density of the resin making up the fibers. In addition, the image obtained was observed. When not only ultrafine fibers making up the outside edge of the fiber bundle but also ultrafine fibers at the interior were bonded and integrally united to each other by the polymeric elastomer, the ultrafine fibers were judged to be "converging". When little or no polymeric elastomer was present at the interior of the fiber bundles and the ultrafine fibers were in a substantially unbonded and un-united state, the ultrafine fibers were judged to be "non-converging".

(2) Storage Moduli of Polymeric Elastomer at 23°C and 50°C

[0171] The polymeric elastomer used in the polishing pad was prepared as film samples having a length of 4 cm, a width of 0.5 cm and a thickness of 400 μm ± 100 μm. Next, the sample thickness was measured with a micrometer, following which a dynamic viscoelastic analyzer (DVE Rheospectra, manufactured by Rheology Co., Ltd.) was used to measure the dynamic viscoelastic moduli at 23°C and 50°C under the following conditions: frequency, 11 Hz; temperature ramp-up rate, 3°C/min. The storage moduli were computed from the measured results. In cases where two types of polymeric elastomer were used, samples of each were prepared and measured, and the sum of the values obtained by multiplying by the respective mass ratio was used as the storage modulus for the polymeric elastomers.

(3) Glass Transition Temperature of Polymeric Elastomer

[0172] The polymeric elastomer used in the polishing pad was prepared as a film having a length of 4 cm, a width of 0.5 cm and a thickness of 400 μm ± 100 μm. The sample thickness was measured with a micrometer, following which the dynamic viscoelasticity was measured at a frequency of 11 Hz and a temperature ramp-up rate of 3°C/min using a dynamic viscoelastic analyzer (DVE Rheospectra, manufactured by Rheology Co., Ltd.), and the main dispersion peak temperature of the loss modulus was treated as the glass transition temperature. In cases where two types of polymeric elastomer were used, samples of each were prepared and measured, and the sum of the values obtained by multiplying by the respective weight ratio was used as the storage modulus for the polymeric elastomers.

(4) Water Absorption Ratio of Polymeric Elastomer upon Saturation with Water at 50°C

[0173] A 200 μm thick film obtained by drying the polymeric elastomer at 50°C was heat-treated at 130°C for 30 minutes, then held for 3 days at 20°C and 65% RH to form a dry sample which was immersed in 50°C water for two days. The sample was then removed from the 50°C water, immediately after which excess water droplets, etc. on the topmost surface of the film were wiped off with a JK Wiper 150-S (Nippon Paper Crecia Co., Ltd.), thereby giving a water-swollen sample. The weights of the dry sample and the water-swollen sample were measured, and the water absorption ratio was determined according to the following formula.

[0174]

Water absorption ratio (mass%) = [(mass of water-swollen sample – mass of dry sample)/(mass of dry sample)] × 100

In cases where two types of polymeric elastomer were used, samples of each were prepared and measured, and the sum of the values obtained by multiplying by the respective weight ratio was used as the storage modulus for the polymeric elastomers.

[0175] (5) Water Absorption Ratio of Ultrafine Fibers upon Saturation with Water at 50°C (water absorption ratio of thermoplastic resin making up ultrafine fibers upon saturation with water at 50°C)

A 200 μm thick film obtained by hot-pressing the thermoplastic resin making up the ultrafine fibers at a temperature of the melting point + 20 to 100°C was heat-treated at 130°C for 30 minutes, then held for 3 days at 20°C and 65% RH to form a dry sample, which was subsequently immersed in 50°C water for two days. The sample was then removed from the water, immediately after which excess water droplets, etc. on the topmost surface of the film were wiped off with a JK Wiper 150-S (Nippon Paper Crecia Co., Ltd.), thereby giving a water-swollen sample. The weights of the dry sample and the water-swollen sample were measured, and the water absorption ratio was determined according to the following formula.

[0176]

Water absorption ratio (mass%) = [(mass of water-swollen sample – mass of dry sample)/(mass of dry sample)] × 100

(6) Average Particle Size of Aqueous Polyurethane

[0177] The average particle size of the water-dispersed polymeric elastomer was determined through measurement by dynamic light scattering using a ELS-800 system (Otsuka Chemical Co., Ltd.) and analysis by the cumulant method (described in *Koroido kagaku* [Colloidal chemistry] Vol. IV: *Koroido kagaku jikken-hō* [Experimental methods in colloidal chemistry], published by Tokyo Kagaku Dojin). In cases where two types of polymeric elastomer were used, samples of each were measured, and the sum of the values obtained by multiplying by the respective weight ratio was used as the storage modulus for the polymeric elastomers.

(7) Apparent Density of Polishing Pad and Void Volume Ratio of Polishing Pad (volumetric ratio of void areas in polishing pad)

[0178] The apparent density of the polishing pad was measured in general accordance with JIS L1096. At the same time, the theoretical density of the composite of the ultrafine fiber-entangled body with the polymeric elastomer in the absence of voids was calculated from the compositional ratios of the respective components in the polishing pad and the densities of each of these components. In addition, the ratio of the apparent density to the theoretical density was treated as the volumetric ratio of the filled areas in the polishing pad, and [1 - (ratio of apparent density to theoretical density)] × 100 (%) was treated as the void volume ratio of the polishing pad (volumetric ratio of void areas in the polishing pad). The densities of the components used in Example 1 were as follows: modified PET, 1.38 g/cm^3; polyurethane elastomer, 1.05 g/cm^3; PVA resin, 1.25 g/cm^3.

(8) Evaluation of Polishing Performance by Polishing Pad

[0179] A pressure-sensitive adhesive tape was bonded to the back side of a circular polishing pad, following which the pad was mounted on a CMP polisher (PP0-60S, manufactured by Nomura Machine Tool Works, Ltd.). Next, using a 200-grit diamond dresser (MEC 200L, available from Mitsubishi Materials Corporation), conditioning (seasoning) was carried out by grinding the surface of the polishing pad for 18 minutes at a pressure of 177 kPa and a dresser rotational speed of 110 rpm under a flow of distilled water at a rate of 120 mL/min.

[0180] Next, a 6-inch diameter silicon wafer having an oxide film surface was polished for 100 seconds at a platen speed of 50 rpm, a head speed of 49 rpm and a polishing pressure of 35 kPa while supplying an abrasive slurry (SS12, available from Cabot Corporation) at a rate of 120 mL/min. The thickness after polishing at 49 randomly selected points in the plane of the silicon wafer having an oxide film surface was measured, and the polishing rate (nm/min) was determined by dividing the polished thickness at each point by the polishing time. In addition, the polishing rate (R) was calculated as the average value of the polishing rates at the 49 points, and the standard deviation (σ) was determined.

[0181] The planarity was then evaluated from the following formula. A smaller planarity value indicates a better planarization performance.

[0182]

$$\text{Planarity (\%)} = (\sigma/R) \times 100$$

[0183] Next, the polishing pad used in the above polishing operation was held in a wet state at 25°C for 24 hours, then the polishing pad was seasoned and used again to carry out polishing, following which the polishing rate (R) and planarity were determined.

[0184] Seasoning and polishing were alternately repeated in this way 300 times, and the polishing rate (R) and planarity after 300 polishing cycles were determined.

[0185] The number of scratches at least 0.16 μm in size present on the surface of the silicon wafer having an oxide film after each polishing operation was determined using a wafer surface inspection system (Surfscan SP1, available from KLA-Tencor), based on which the tendency for scratching to occur was evaluated.

(9) Evaluation of Polishing Performance by Polishing Pad in Bare Silicon Wafer Polishing

[0186] A pressure-sensitive adhesive tape was bonded to the back side of a circular polishing pad, following which the pad was mounted on a CMP polisher (PP0-60S, manufactured by Nomura Machine Tool Works, Ltd.). Next, using a 200-grit diamond dresser (MEC 200L, available from Mitsubishi Materials Corporation), conditioning (seasoning) was carried out by grinding the surface of the polishing pad for 18 minutes at a pressure of 177 kPa and a dresser rotational speed of 110 rpm under a flow of distilled water at a rate of 120 mL/min.

[0187] Next, a 6-inch diameter silicon wafer was polished for 100 seconds at a platen speed of 50 rpm, a head speed of 49 rpm and a polishing pressure of 35 kPa while supplying Glanzox 1103 (Fujimi Incorporated) at a rate of 120 mL/min. The thickness after polishing at 49 randomly selected points in the plane of the silicon wafer was measured, and the polishing rate (nm/min) was determined by dividing the polished thickness at each point by the polishing time. In addition, the polishing rate (R) was calculated as the average value of the polishing rates at the 49 points, and the standard deviation (σ) was determined.

[0188] The planarity was then evaluated from the following formula. A smaller planarity value indicates a better planarization performance.

[0189]

$$\text{Planarity}\ (\%) = (\sigma/R) \times 100$$

[0190] Next, the polishing pad used in the above polishing operation was held in a wet state at 25°C for 24 hours, then the polishing pad was seasoned and used again to carry out polishing, following which the polishing rate (R) and planarity were determined.

[0191] Seasoning and polishing were alternately repeated in this way 300 times, and the polishing rate (R) and planarity after 300 polishing cycles were determined.

[0192] The results for Examples 1 to 5 and 7 are shown in Table 1, the results for Example 6 are shown in Table 3, the results for Example 8 are shown in Table 4, and the results for Comparative Examples 1 to 4 are shown in Table 2.

[0193]

[Table 1]

Example No.		1	2	3	4	5	7
Average fineness of ultrafine fibers	dtex	0.05	0.05	0.05	0.05	0.05	0.05
Number of ultrafine fibers of fiber bundles	number	50	50	50	50	9	50
Converging state of ultrafine fibers of fiber bundles	--	converging	converging	converging	converging	converging	converging
Type of thermoplastic resin in ultrafine fibers		isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate
Glass transition temperature of polymeric elastomer	˚C	-23	-25	-23	-30	-23	-23
Water absorption ratio of polymeric elastomer upon saturation (50˚C)	mass%	2.4	2	2.4	4	2.4	2.4
Storage modulus of polymeric elastomer at 23˚C	MPa	390	450	390	280	390	390
Storage modulus of polymeric elastomer at 50˚C	MPa	240	300	240	115	240	240
Ratio of storage moduli at 23˚C and 50˚C of polymeric elastomer	--	1.6	1.5	1.6	2.4	1.6	1.6

(continued)

Example No.		1	2	3	4	5	7
Polycarbonate ratio in polyol component of polymeric elastomer	%	>99	>99	>99	95	>99	>99
Average particle size of aqueous polyurethane	μm	0.04	0.05	0.04	0.04	0.04	0.04
Ultrafine fiber-entangled body/ polymeric elastomer (mass ratio)		76/24	83/17	70/30	76/24	76/24	76/24
Apparent density of polishing pad	g/cm^3	0.8	0.77	0.62	0.8	0.8	0.57
Void volume ratio of polishing pad	vol%	38	42	52	38	38	56
Polishing rate (initial)	nm/min	190	200	210	200	210	210
(after 24 hours)		200	200	220	210	220	220
(after 300 polishing cycles)		200	200	210	200	220	210
Planarity (initial)	%	6	6	7	6	7	7
(after 24 hours)		5	5	6	6	7	6
(after 300 polishing cycles)		5	6	6	7	6	7
Scratches (initial)	number	12	10	8	10	15	10
(after 24 hours)	number	10	10	10	10	12	10

(continued)

Example No.		1	2	3	4	5	7
(after 300 cycles)	number	8	11	10	14	12	8

[0194]

[Table 2]

Comparative Examples 1 to 4		1	2	3	4
Average fineness of ultrafine fibers	dtex	2	0.05	0.05	0.05
Number of ultrafine fibers of fiber bundles	number	1	50	50	50
Converging state of ultrafine fibers of fiber bundles	--	--	converging	converging	converging
Type of thermoplastic resin in ultrafine fibers		Ny6	isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate	isophthalate-modified polyethylene terephthalate
Glass transition temperature of polymeric elastomer	°C	-25	-48	-32	0
Water absorption ratio of polymeric elastomer upon saturation (50°C)	mass%	2	12	8	1
Storage modulus of polymeric elastomer at 23°C	MPa	450	200	80	1000
Storage modulus of polymeric elastomer at 50°C	MPa	300	80	30	200
Ratio of storage moduli at 23°C and 50°C of polymeric elastomer	--	1.5	2.5	2.7	5
Polycarbonate ratio in polyol component of polymeric elastomer	%	>99	0	>99	>90
Average particle size of aqueous polyurethane	μm	0.05	0.4	0.02	0.08
Ultrafine fiber-entangled body/ polymeric elastomer (mass ratio)		83/17	83/17	76/24	76/24
Apparent density of polishing pad	g/cm^3	0.54	0.8	0.8	0.8
Void volume ratio of polishing pad	vol%	52	40	38	38
Polishing rate (initial)	nm/min	160	200	210	210
(after 24 hours)		160	180	220	230

(continued)

Comparative Examples 1 to 4		1	2	3	4
(after 300 polishing cycles)		170	150	220	230
Planarity (initial)	%	8	8	14	6
(after 24 hours)		9	10	16	6
(after 300 polishing cycles)		10	15	20	10
Scratches (initial)	number	15	8	10	50
(after 24 hours)	number	40	20	18	80
(after 300 cycles)	number	60	40	25	140

[0195]

[Table 3]

Type of polishing pad		Polishing pad of Example 1			
Polishing Conditions		(1)	(2)	(3)	(4)
Polishing rate (initial)	nm/min	580	540	150	780
(after 24 hours)		620	560	140	800
(after 300 polishing cycles)		630	560	140	780
Planarity (initial)	%	7	7	7	8
(after 24 hours)		7	8	7	9
(after 300 polishing cycles)		8	8	8	9
Scratches (initial)	number	--	15	--	--
(after 24 hours)	number	--	12	--	--
(after 300 polishing cycles)	number	--	12	--	--

[0196]

[Table 4]

Type of polishing pad		Polishing pad of Example 7		
Polishing Conditions		(1)	(2)	(3)
Polishing rate (initial)	nm/min	720	620	140
(after 24 hours)		756	630	150
(after 300 polishing cycles)		760	610	160
Planarity (initial)	%	6	7	7
(after 24 hours)		7	6	8
(after 300 polishing cycles)		6	7	9
Scratches (initial)	number	--	13	--
(after 24 hours)	number	--	11	--

(continued)

Type of polishing pad		Polishing pad of Example 7		
Polishing Conditions		(1)	(2)	(3)
(after 300 polishing cycles)	number	--	14	--

[0197] As explained above, one aspect of the invention relates to a polishing pad which comprises an ultrafine fiber-entangled body formed of ultrafine fibers having an average fineness of 0.01 to 0.8 dtex, and a polymeric elastomer, wherein the polymeric elastomer has a glass transition temperature of -10˚C or below, storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

[0198] According to this arrangement, there can be obtained a polishing pad which is capable of carrying out, with long-term stability, polishing that achieves a high planarity while suppressing the occurrence of scratches.

[0199] It is preferable for the ultrafine fiber-entangled body to be composed of bundles of 5 to 70 ultrafine fibers, and for the polymeric elastomer to be present inside the ultrafine fiber bundles.

[0200] According to this arrangement, the polymeric elastomer makes the ultrafine fibers converge as bundles and also restrains the ultrafine fiber bundles, thereby increasing the stiffness of the polishing pad and enabling the planarization performance, polishing uniformity and stability over time to be enhanced.

[0201] It is preferable for the ultrafine fibers be formed of polyester fibers because this enables the ultrafine fiber-entangled body that is compact and has a high density to be formed.

[0202] It is preferable for the ultrafine fibers to be formed of a thermoplastic resin having a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 2 mass%.

[0203] This arrangement enables the polishing pad to be obtained which suppresses the decrease over time in the planarization performance and undergoes little fluctuation in polishing rate and polishing uniformity.

[0204] It is preferable that the polymeric elastomer is a polyurethane resin obtained by using a polyol, a polyamine and a polyisocyanate, and that 60 to 100 mass% of the polyol is a noncrystalline polycarbonate diol.

[0205] According to this arrangement, the resistance to the slurry used in polishing is high, enabling a good stability over time to be maintained during polishing.

[0206] It is preferable for the polymeric elastomer to be a polyurethane resin obtained by using as the polyol a non-crystalline polycarbonate diol together with a carboxylic group-containing diol, and by using an alicyclic diisocyanate as the polyisocyanate.

[0207] According to this arrangement, the polymeric elastomer can easily be adjusted to the glass transition temperature of -10˚C or less, the storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and the water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

[0208] It is preferable that the polymeric elastomer has a ratio of the storage modulus at 23˚C to the storage modulus at 50˚C (storage modulus at 23˚C/storage modulus at 50˚C) being 4 or less.

[0209] According to this arrangement, even when a temperature change occurs during polishing, the storage moduli do not readily change, as a result of which the stability over time during polishing can be enhanced.

[0210] It is preferable for the polymeric elastomer to be an aqueous polyurethane having an average particle size of 0.01 to 0.2 μm because a good water resistance is achieved and the fiber bundle restraining force increases.

[0211] It is preferable for the mass ratio of the ultrafine fiber-entangled body and the polymeric elastomer (ultrafine fiber-entangled body/polymeric elastomer) to be from 55/45 to 95/5 because the polishing efficiency is enhanced and the pad wear during polishing decreases.

[0212] It is preferable for void areas in the polishing pad to have a volume ratio of at least 50%.

[0213] According to this arrangement, because the polishing pad has both good slurry retention and suitable stiffness and cushionability, it can be advantageously used for polishing bare silicon wafers.

[0214] Another aspect of the invention relates to a method for manufacturing a polishing pad, the method comprising a step of filling the interior of bundles of ultrafine fibers which have an average fineness of from 0.01 to 0.8 dtex with a polymeric elastomer having a glass transition temperature of -10˚C or below, storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

[0215] According to this arrangement, the polishing pad which has a high stiffness and high abrasive slurry retention and which do not readily form scratches on the substrate being polished can be obtained.

[0216] In the method for manufacturing the polishing pad, it is preferable for the polymeric elastomer to be filled into the interior of an ultrafine fiber-entangled body composed of the bundles of the ultrafine fibers in such a way that void areas in the polishing pad have a volume ratio of at least 50%.

[0217] According to this arrangement, by adjusting the amount of the polymeric elastomer filled into the ultrafine fiber-entangled body so as to make the void volume ratio in the polishing pad of at least 50%, the polishing pad for polishing bare silicon wafers which has a suitable stiffness and an improved abrasive slurry retention and cushionability can be obtained.

Industrial Applicability

[0218] The polishing pad according to the present invention can be used as a polishing pad for polishing various devices, substrates and other products on which planarization or mirror polishing are carried out, examples of which include semiconductor substrates, semiconductor devices, compound semiconductor devices, compound semiconductor substrates, compound semiconductor products, LED substrates, LED products, silicon wafers, hard disk substrates, glass substrates, glass products, metal substrates, metal products, plastic substrates, plastic products, ceramic substrates and ceramic products.

Claims

1. A polishing pad, comprising: an ultrafine fiber-entangled body formed of ultrafine fibers having an average fineness of 0.01 to 0.8 dtex; and a polymeric elastomer, wherein the polymeric elastomer has a glass transition temperature of -10˚C or below, storage moduli at 23˚C and 50˚C of 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 5 mass%.

2. The polishing pad according to claim 1, wherein the ultrafine fiber-entangled body is composed of bundles of 5 to 70 ultrafine fibers, and the polymeric elastomer is present inside the ultrafine fiber bundles.

3. The polishing pad according to claim 1 or 2, wherein the ultrafine fibers are formed of polyester fibers.

4. The polishing pad according to any one of claims 1 to 3, wherein the ultrafine fibers are formed of a thermoplastic resin having a water absorption ratio, when saturated with water at 50˚C, of 0.2 to 2 mass%.

5. The polishing pad according to any one of claims 1 to 4, wherein the polymeric elastomer is a polyurethane resin obtained by using a polyol, a polyamine and a polyisocyanate, and wherein 60 to 100 mass% of the polyol is a noncrystalline polycarbonate diol.

6. The polishing pad according to claim 5, wherein the polymeric elastomer is a polyurethane resin obtained by using as the polyol a noncrystalline polycarbonate diol together with a carboxylic group-containing diol, and by using an alicyclic diisocyanate as the polyisocyanate.

7. The polishing pad according to any one of claims 1 to 6, wherein the polymeric elastomer has a ratio of the storage modulus at 23˚C to the storage modulus at 50˚C (storage modulus at 23˚C/storage modulus at 50˚C) being 4 or less.

8. The polishing pad according to any one of claims 1 to 7, wherein the polymeric elastomer is an aqueous polyurethane having an average particle size of from 0.01 to 0.2 μm.

9. The polishing pad according to any one of claims 1 to 8, wherein the mass ratio of the ultrafine fiber-entangled body and the polymeric elastomer (ultrafine fiber-entangled body/polymeric elastomer) is from 55/45 to 95/5.

10. The polishing pad according to any one of claims 1 to 9, wherein void areas in the polishing pad have a volume ratio of at least 50%.

11. A method for manufacturing a polishing pad, comprising: filling the interior of bundles of ultrafine fibers which have an average fineness of from 0.01 to 0.8 dtex with a polymeric elastomer having a glass transition temperature of -10˚C or below, storage moduli at 23˚C and 50˚C of from 90 to 900 MPa, and a water absorption ratio, when saturated with water at 50˚C, of from 0.2 to 5 mass%.

12. The method for manufacturing a polishing pad according to claim 11, wherein the polymeric elastomer is filled into the interior of an ultrafine fiber-entangled body composed of the bundles of the ultrafine fibers such that void areas in the polishing pad have a volume ratio of at least 50%.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
B24B37/00(2006.01)i, D04H3/14(2006.01)i, H01L21/304(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B24B37/00, D04H3/14, H01L21/304

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2002-79472 A (Kuraray Co., Ltd.), 19 March 2002 (19.03.2002), claims; paragraphs [0034] to [0042] & US 2002/0013984 A1 & TW 0491757 B & CN 1366300 A	1-12
Y	JP 2006-28659 A (Kuraray Co., Ltd.), 02 February 2006 (02.02.2006), claims; paragraphs [0077] to [0078] (Family: none)	1-12
Y	WO 2008/093850 A1 (Kuraray Co., Ltd.), 07 August 2008 (07.08.2008), paragraphs [0029] to [0057] (Family: none)	1-12

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

* Special categories of cited documents:

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