

(54)[Title] LAYERED SHEETS AND PROCESSES FOR PRODUCING THE SAME

[Detailed Description of the Invention]

[Technical Field]

[0001]

The present invention relates to a layered sheet (a holding sheet and a backing sheet) used for holding and fixing optical materials such as lenses and reflecting mirrors, semiconductor wafers such as silicon wafers, glass substrates, metal substrates, disks, etc., to a polishing head when polishing the surfaces thereof, a layered sheet (pressure-sensitive adhesive sheet) used for holding or protecting semiconductor products such as semiconductor wafers, optical products, etc., in the step of precise processing the products, and a process for producing the same.

[Background Art]

[0002]

Typical examples of materials requiring high surface flatness include a single crystal silicon disk referred to as a silicon wafer for manufacturing semiconductor integrated circuits (IC, LSI). The silicon wafer is required to have a finished flat surface with high accuracy in each of steps of laminating and forming an oxide layer and a metal layer in order to form the reliable semiconductor junction of various thin films used for forming circuits in the steps of producing an IC, LSI, etc. In the polishing and finishing steps, a polishing pad is generally stuck to a rotatable support disk referred to as a platen, and a material to be polished such as a silicon wafer is stuck to a polishing head.

[0003]

As a method for fixing a material to be polished such

as a silicon wafer and glass to a polishing head, there have been conventionally adopted (1) a wax mounting method for fixing a polishing head and a material to be polished via wax, (2) a vacuum chuck method for fixing a material to be polished to a polishing head by suction, and (3) a no-wax mounting method for fixing a material to be polished by an artificial leather or polymer foaming sheet stuck to a polishing head.

[0004]

In the wax mounting method, there is a problem that the material to be polished is unlikely to be attached and detached, the wax should be removed by cleaning the material to be polished after polishing, and thus the operating steps are complicated since the wax is used.

[0005]

The vacuum chuck method has a problem that the material to be polished transforms in a suction port part and thereby the surface accuracy of the material to be polished after polishing is deteriorated.

[0006]

The no-wax mounting method has advantages of easy attachment and detachment of the material to be polished and excellent production efficiency. However, the method has a problem that the surface smoothness of the material to be polished after polishing is also deteriorated when the surface accuracy of the holding surfaces of the artificial leather and polymer foaming sheet is poor.

[0007]

The use of a backing material which is provided with an adhesive resin layer made of a resin on the surface of

a foamed layer is proposed as a method for solving the problem of the no-wax mounting method (Patent Literature 1). A sheet-shaped elastic foam, in which independent cells having an elongated shape and a larger diameter toward the surface of a foamed layer are provided for a foamed layer, is proposed (Patent Literature 2).

[0008]

However, in a process for producing the backing material in Patent Literature 1, the operating steps are complicated since the adhesive resin layer are separately provided and an elastic layer is produced by wet coagulation. Also, the process has problems of high environmental burden since a solvent has to be used and necessity of a large amount of water for the extraction of the solvent in the production. It is difficult to form the above cells in Patent Literature 2, and furthermore, it is considered that the modification of the foamed layer is increased since the void rate of the surface of the foamed layer is increased, thereby deteriorating the surface smoothness of the material to be polished after polishing.

[0009]

Patent Literature 1: JP-A 2002-355754

Patent Literature 2: JP-A 6-23664

[Disclosure of Invention]

[Problems to be solved by the Invention]

[0010]

An object of the present invention is to provide a process for extremely easily producing a layered sheet which has a holding surface having high surface accuracy. In addition, another object of the invention is to provide a layered sheet

obtained by the above method.

[Means for solving the Problems]

[0011]

The present inventors made extensive study to solve the problem described above, and as a result, they found that the object can be achieved by the following process for producing the same, and the present invention was thereby completed.

[0012]

The present invention relates to a process for producing a layered sheet including the steps of: preparing a cell dispersed urethane composition by a mechanical foaming method; applying the cell dispersed urethane composition onto a base material sheet; forming a polyurethane foamed layer by curing the cell dispersed urethane composition; and regulating a thickness of the polyurethane foamed layer uniformly.

[0013]

Another present invention relates to a process for producing a layered sheet including the steps of: preparing a cell dispersed urethane composition by a mechanical foaming method; applying the cell dispersed urethane composition onto a base material sheet; laminating a release sheet on the cell dispersed urethane composition; forming a polyurethane foamed layer by curing the cell dispersed urethane composition while making the thickness thereof uniform with a pressing means; and releasing the release sheet on the polyurethane foamed layer.

[0014]

As described above, a gas such as air is dispersed as

fine cells in a starting material by the mechanical foaming method to prepare the cell dispersed urethane composition. Then, the cell dispersed urethane composition is cured, and thereby the polyurethane foamed layer having an extremely small cell diameter and having spherical cells (including roughly spherical cells) can be extremely easily formed. In the mechanical foaming method of the present invention, a gas such as air is dispersed, without being dissolved, in the starting material, and thus there is an advantage that generation of new cells (post-expansion phenomenon) after a step of uniformly regulating a thickness of the polyurethane foamed layer can be suppressed and the accuracy of a thickness and specific gravity can be easily controlled. In addition, the mechanical foaming method does not necessitate use of a solvent, and is not only excellent in costs but is also preferable from an environmental viewpoint. In the polyurethane foamed layer, a holding surface holding a material to be polished has extremely high surface accuracy, and the surface smoothness of a material to be polished after polishing is extremely excellent when the material to be polished is held using the layered sheet having the foamed layer. The polyurethane foamed layer has spherical cells, and thus has excellent durability. Accordingly, when the material to be polished is polished with the layered sheet having the foamed layer, polishing rate stability is improved.

[0015]

A layered sheet of the present invention is obtained by the production process.

[0016]

The polyurethane foamed layer preferably has spherical

fine cells having an average cell diameter of 20 to 300 μm .

[0017]

The polyurethane foamed layer preferably has an average cell diameter difference (a maximum value of the average cell diameter-a minimum value of the average cell diameter) of 50 μm or less in a thickness direction. When variance in the cell diameter is large in the thickness direction of the polyurethane foamed layer, an area having a low resin density has durability inferior to that of the other area, and the area easily causes the thickness change (settling phenomenon). As a result, the surface accuracy of the holding surface holding the material to be polished tends to be reduced, and the surface smoothness of the material to be polished after polishing tends to be also reduced. In addition, the polishing rate stability tends to be deteriorated. When the average cell diameter difference in the thickness direction is 50 μm or less, the thickness change of the polyurethane foamed layer can be effectively suppressed.

[0018]

The polyurethane foamed layer preferably has a specific gravity of 0.2 to 0.5. In addition, the polyurethane foamed layer preferably has an Asker C hardness of 10 to 50 degrees. Furthermore, the polyurethane foamed layer preferably has a compression rate of 2 to 10%.

[Best mode for carrying out the invention]

[0019]

The process for producing a layered sheet of the present invention comprises the steps of: preparing a cell dispersed urethane composition by a mechanical foaming method; applying the cell dispersed urethane composition onto a base material

sheet; forming a polyurethane foamed layer by curing the cell dispersed urethane composition; and regulating a thickness of the polyurethane foamed layer uniformly.

[0020]

Another process for producing a layered sheet of the present invention comprises the steps of: preparing a cell dispersed urethane composition by a mechanical foaming method; applying the cell dispersed urethane composition onto a base material sheet; laminating a release sheet on the cell dispersed urethane composition; forming a polyurethane foamed layer by curing the cell dispersed urethane composition while making the thickness thereof uniform with a pressing means; and releasing the release sheet on the polyurethane foamed layer.

[0021]

The cell dispersed urethane composition may be prepared by a mechanical foaming method (including a mechanical frothing method), and is not particularly limited with respect to other aspects. For example, the cell dispersed urethane composition is prepared by the following methods.

[0022]

(1) The first component wherein a silicon-based surfactant is added to an isocyanate-terminated prepolymer produced by an isocyanate component with a high-molecular-weight polyol or the like is mechanically stirred in the presence of an unreactive gas, to disperse the unreactive gas as fine cells thereby forming a cell dispersion. Then, the second component containing active hydrogen-containing compounds such as high-molecular-weight and low-molecular-weight polyols are added to, and mixed with,

the cell dispersion to prepare a cell dispersed urethane composition. If necessary, a catalyst and a filler such as carbon black may be added to the second component.

[0023]

(2) A silicon-based surfactant is added to the first component containing an isocyanate component (or an isocyanate-terminated prepolymer) and/or the second component containing active hydrogen-containing compounds, and the component(s) to which the silicon-based surfactant is added is mechanically stirred in the presence of an unreactive gas, to disperse the unreactive gas as fine cells thereby forming a cell dispersion. Then, the remaining component is added to, and mixed with, the cell dispersion to prepare a cell dispersed urethane composition.

[0024]

(3) A silicon-based surfactant is added to at least either of the first component containing an isocyanate component (or an isocyanate-terminated prepolymer) or the second component containing active hydrogen-containing compounds, and the first and second components are mechanically stirred in the presence of an unreactive gas, to disperse the unreactive gas as fine cells thereby preparing a cell dispersed urethane composition.

[0025]

Polyurethane is preferable as a forming material for the foamed layer of the layered sheet since spherical fine cells and interconnected cells can be easily formed by the mechanical foaming method.

[0026]

As the isocyanate component, a compound known in the

field of polyurethane can be used without particular limitation. The isocyanate component includes, for example, aromatic diisocyanates such as 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 2,2'-diphenyl methane diisocyanate, 2,4'-diphenyl methane diisocyanate, 4,4'-diphenyl methane diisocyanate, polymeric MDI, carbodiimide modified MDI(for example, Millionate MTL made by Nippon Polyurethane Industry Co., Ltd.), 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, p-xylylene diisocyanate and m-xylylene diisocyanate, aliphatic diisocyanates such as ethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate and 1,6-hexamethylene diisocyanate, and cycloaliphatic diisocyanates such as 1,4-cyclohexane diisocyanate, 4,4'-dicyclohexyl methane diisocyanate, isophorone diisocyanate and norbornane diisocyanate. These may be used alone or as a mixture of two or more thereof.

[0027]

As the isocyanate component, it is possible to use not only the above-described diisocyanate compounds but also multifunctional(trifunctional or more) polyisocyanates. As the multifunctional isocyanate compounds, a series of diisocyanate adduct compounds are commercially available as Desmodul-N (Bayer) and Duranate™ (Asahi Chemical Industry Co., Ltd.).

[0028]

Among the isocyanate components described above, 4,4'-diphenylmethane diisocyanate or carbodiimide modified MDI is preferably used.

[0029]

As the high-molecular-weight polyol, a compound known in the field of polyurethane can be used without particular limitation. The high-molecular-weight polyol includes, for example, polyether polyols represented by polytetramethylene ether glycol and polyethylene glycol, polyester polyols represented by polybutylene adipate, polyester polycarbonate polyols exemplified by reaction products of polyester glycols such as polycaprolactone polyol and polycaprolactone with alkylene carbonate, polyester polycarbonate polyols obtained by reacting ethylene carbonate with a multivalent alcohol and reacting the resulting reaction mixture with an organic dicarboxylic acid, polycarbonate polyols obtained by ester exchange reaction of a polyhydroxyl compound with aryl carbonate, and polymer polyols such as polyether polyol in which polymer particles are dispersed. These may be used singly or as a mixture of two or more thereof. To produce the polyurethane foamed layer having an independent cell structure, a polyether polyol is preferably only used.

[0030]

To produce the polyurethane foamed layer having an interconnected cell structure, a polymer polyol is preferably used, and a polymer polyol in which polymer particles made of acrylonitrile and/or styrene-acrylonitrile copolymers are dispersed is particularly preferably used. This polymer polyol is contained in an amount of preferably 20 to 100 wt%, more preferably 30 to 60 wt%, in the whole polymer polyol used. The polymer polyol described above of 60 to 85 wt% are preferably contained in the active hydrogen-containing compound, and more preferably 70 to 80 wt%. A cell film is easily broken by using a specific amount of the polymer polyol

described above, and an interconnected cell structure is easily formed.

[0031]

A number-average molecular weight of the high-molecular-weight polyol is not particularly limited, but is preferably 1500 to 6000, from the viewpoint of the elastic characteristics of the resulting polyurethane. When the number-average molecular weight is less than 1500, the polyurethane obtained therefrom does not have sufficient elastic characteristics, thus easily becoming a brittle polymer. Accordingly, a foamed layer made of this polyurethane is rigid to reduce the holding property of the material to be polished. On the other hand, when the number-average molecular weight is higher than 6000, polyurethane obtained therefrom becomes too soft. Therefore, a foamed layer made of this polyurethane tends to be inferior in durability.

[0032]

Examples of the low-molecular-weight polyol that can be used together with a high-molecular-weight polyol described above include: ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentanediol, diethylene glycol, triethyleneglycol, 1,4-bis(2-hydroxyethoxy)benzene and the like. Other examples that can be used together with the high-molecular-weight polyol also include: low-molecular-weight polyamine such as ethylenediamine, tolylenediamine, diphenylmethanediamine,

diethylenetriamine and the like. These low-molecular-weight polyols, low-molecular-weight polyamines may be used alone or as a mixture of two or more thereof.

[0033]

The ratio of the high-molecular-weight polyol and low-molecular-weight polyol or the like is determined according to characteristics necessitated for the polyurethane foamed layer manufactured therefrom.

[0034]

To form the polyurethane foamed layer having an interconnected cell structure, the low-molecular-weight polyol and/or the low-molecular-weight polyamine are contained in the total amount of preferably 2 to 15 wt%, more preferably 5 to 10 wt%, in the active hydrogen-containing compound. By using the low-molecular-weight polyol etc. in specified amounts, cell films are easily broken to easily form an interconnected cell structure and further the mechanical characteristics of the polyurethane foamed layer are improved.

[0035]

In the case where a polyurethane is produced by means of a prepolymer method, a chain extender is used in curing of a prepolymer. A chain extender is an organic compound having at least two active hydrogen groups and examples of the active hydrogen group include: a hydroxyl group, a primary or secondary amino group, a thiol group (SH) and the like. Concrete examples of the chain extender include: polyamines such as 4,4'-methylenebis(o-chloroaniline)(MOCA), 2,6-dichloro-p-phenylenediamine, 4,4'-methylenebis(2,3-dichloroaniline),

3,5-bis(methylthio)-2,4-toluenediamine,
 3,5-bis(methylthio)-2,6-toluenediamine,
 3,5-diethyltoluene-2,4-diamine,
 3,5-diethyltoluene-2,6-diamine, trimethylene
 glycol-di-p-aminobenzoate, polytetramethylene
 oxide-di-p-aminobenzoate,
 4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane,
 4,4'-diamino-3,3'-diisopropyl-5,5'-dimethyldiphenylmethane,
 4,4'-diamino-3,3',5,5'-tetraisopropyldiphenylmethane,
 1,2-bis(2-aminophenylthio)ethane,
 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane,
 N,N'-di-sec-butyl-4,4'-diaminodiphenylmethane,
 3,3'-diethyl-4,4'-diaminodiphenylmethane,
 m-xylylenediamine, N,N'-di-sec-butyl-p-phenylenediamine,
 m-phenylenediamine and p-xylylenediamine;
 low-molecular-weight polyol component; and a
 low-molecular-weight polyamine component. The chain
 extenders described above may be used either alone or in mixture
 of two kinds or more.

[0036]

A ratio between an isocyanate component, a polyol
 component and a chain extender in the invention can be altered
 in various ways according to molecular weights thereof,
 desired physical properties of polyurethane foamed layer and
 the like. In order to obtain a foamed layer with desired
 polishing
 characteristics, a ratio of the number of isocyanate groups
 in an isocyanate component relative to a total number of active
 hydrogen groups (hydroxyl groups + amino groups) in a polyol
 component and a chain extender is preferably in the range

of from 0.80 to 1.20 and more preferably in the range of from 0.99 to 1.15. When the number of isocyanate groups is outside the aforementioned range, there is a tendency that curing deficiency is caused, required cell, specific gravity, hardness and compressibility are not obtained.

[0037]

The isocyanate-terminated prepolymer is preferably a prepolymer having a molecular weight of about 800 to 50000 because of its excellent workability, physical properties etc. When the prepolymer is solid at an ordinary temperature, the prepolymer is melted by preheating at a suitable temperature prior to use.

[0038]

The silicon-based surfactant includes, for example, a surfactant containing polyalkylsiloxane/polyether copolymer. Such silicon-based surfactant can be exemplified by SH-192 and L-5340 (made by Toray Dow Corning Silicone Co., Ltd.) as preferable compounds.

[0039]

Various additives may be mixed; such as a stabilizer including an antioxidant, a lubricant, a pigment, a filler, an antistatic agent and others.

[0040]

The unreactive gas used for forming fine bubbles is preferably not combustible, and is specifically nitrogen, oxygen, a carbon dioxide gas, a rare gas such as helium and argon, and a mixed gas thereof, and the air dried to remove water is most preferable in respect of cost.

[0041]

As a stirring device for dispersing an unreactive gas

in a fine-cell state, any known stirring devices can be used without particular limitation, and specific examples include a homogenizer, a dissolver, a twin-screw planetary mixer, a mechanical froth foaming machine etc. The shape of a stirring blade of the stirring device is not particularly limited, and a whipper-type stirring blade is preferably used to form fine cells. For obtaining the intended polyurethane foamed layer, the number of revolutions of the stirring blade is preferably 500 to 2000 rpm, more preferably 800 to 1500 rpm. The stirring time is suitably regulated depending on the intended density.

[0042]

In a preferable mode, different stirring devices are used for preparing a cell dispersion in the foaming process and for stirring the first and the second components to mix them, respectively. Stirring in the mixing step may not be stirring for forming cells, and a stirring device not generating large cells is preferably used in the mixing step. Such a stirring device is preferably a planetary mixer. The same stirring device may be used in the foaming step of preparing a cell dispersion and in the mixing step of mixing the respective components, and stirring conditions such as a revolution rate of the stirring blade are preferably regulated according to necessary.

[0043]

Then, the cell dispersed urethane composition prepared by the method described above is applied onto a base material sheet, and then the cell dispersed urethane composition is cured to form a polyurethane foamed layer.

[0044]

The forming material for the base material sheet is not particularly limited. Examples thereof include polyethylene terephthalate, polyester, polyethylene, polypropylene, polystyrene, polyimide, polyvinyl alcohol, polyvinyl chloride, a fluorine-containing resin such as polyfluoroethylene, nylon and cellulose.

[0045]

The thickness of the base material sheet is not limited. However, the thickness is preferably about 0.05 to about 0.3 mm in terms of the strength and flexibility or the like thereof.

[0046]

A method of applying the cell dispersed urethane composition onto the base material sheet can make use of coating methods using, for example, roll coaters such as a gravure coater, kiss-roll coater and comma coater, die coaters such as a slot coater and fountain coater, and a squeeze coater, a curtain coater etc., and any methods can be used insofar as a uniform coating film can be formed on the base material sheet.

[0047]

Post cure by heating the polyurethane foam, formed by applying the cell dispersed urethane composition onto the base material sheet and then reacting the composition until it does not flow, has an effect of improving physical properties of the polyurethane foam and is thus extremely preferable. Post cure is carried out preferably at 40 to 70°C for 10 to 60 minutes and conducted preferably at a normal pressure in order to stabilize the shape of cells.

[0048]

In the production of the polyurethane foamed layer,

known catalysts promoting a polyurethane reaction, such as tertiary amine-based catalysts, may be used. The type and amount of the catalyst added are determined in consideration of flow time for application onto a base material sheet after the step of mixing the respective components.

[0049]

Production of the polyurethane foamed layer may be carried out in a batch system wherein the respective components are weighed, introduced into a container, and mechanically stirred, or in a continuous production system wherein the respective components and an unreactive gas are continuously fed to a stirring device and mechanically stirred, and the resulting cell dispersed urethane composition is sent onto a base material sheet to form a product.

[0050]

In the process for producing the layered sheet of the present invention, it is necessary that after the polyurethane foamed layer is formed on the base material sheet or while the polyurethane foamed layer is formed, the thickness of the polyurethane foamed layer is uniformly regulated. A method of uniformly regulating the thickness of the polyurethane foamed layer includes, but is not limited to, a method of buffing the polyurethane foam with an abrasive, a method of pressing it with a pressing plate, etc. When buffing the polyurethane foamed layer, a layered sheet having no skin layer formed on the surface of the polyurethane foamed layer is obtained. When pressing the polyurethane foamed layer, a layered sheet having a skin layer formed on the surface of the polyurethane foamed layer is obtained. The conditions when pressing are not particularly limited. However, the

temperature is preferably regulated to be a glass transition point or more.

[0051]

On the other hand, the cell dispersed urethane composition prepared by the method described above is applied onto the base material sheet, and a release sheet is laminated on the cell dispersed urethane composition. Thereafter, the cell dispersed urethane composition may be cured to form a polyurethane foamed layer while the thickness thereof is made uniform with a pressing means. The process is particularly preferable since the process can control the thickness of the layered sheet extremely uniformly.

[0052]

A material for forming the release sheet includes, but is not limited to, resin of the same kind of the base material sheet and paper. The release sheet is preferably a sheet with less dimensional change upon heating. The surface of the release sheet may be subjected to a release treatment.

[0053]

A pressing means for pressing a sandwich sheet made of the base material sheet, the cell dispersed urethane composition (cell dispersed urethane layer) and the release sheet to make the thickness of the sandwich sheet uniform is not particularly limited, and for example, a method of pressing it to a predetermined thickness with a coater roll, a nip roll or the like. In considering the fact that, after compression, the size of cells in the foamed layer is increased about 1.2 to 2 times, it is preferable in compression to satisfy the following equation: (Clearance of a coater or nip) - (thickness of the base material sheet and release sheet) =

(50 to 85% of the thickness of the polyurethane foamed layer after curing). The specific gravity of the cell dispersed urethane composition before passing a roll is preferably 0.24 to 1 in order to obtain a polyurethane foamed layer having a specific gravity of 0.2 to 0.5.

[0054]

After the thickness of the sandwich sheet is made uniform, the polyurethane foam is reacted until it does not flow, followed by post cure to form a polyurethane foamed layer. The conditions for post cure are the same as described above.

[0055]

The release sheet on the polyurethane foamed layer is then released to obtain a layered sheet. In this case, a skin layer is formed on the polyurethane foamed layer. After the release sheet is released, the skin layer may be removed by buffing the polyurethane foamed layer.

[0056]

The thickness of the polyurethane foamed layer is particularly not limited. However, the thickness is preferably 0.2 to 1.2 mm, and more preferably 0.6 to 1 mm.

[0057]

Cells in the polyurethane foamed layer may be independent cells, and may be interconnected cells.

[0058]

The average cell diameter of the cells in the polyurethane foamed layer is preferably 20 to 300 μm , and more preferably 50 to 150 μm . When the average cell diameter deviates from this range, the surface smoothness of the material to be polished after polishing tends to be deteriorated.

[0059]

The average cell diameter difference (maximum value of average cell diameter - minimum value of average cell diameter) of the polyurethane foamed layer in the thickness direction is preferably 50 μm or less, and more preferably 30 μm or less. A method for calculating the average cell diameter difference is based on the description of Example in detail.

[0060]

A specific gravity of the polyurethane foamed layer is preferably 0.2 to 0.5, and more preferably 0.25 to 0.4. When the specific gravity is less than 0.2, the cell rate tends to be excessively increased to deteriorate the durability. On the other hand, when the specific gravity is more than 0.5, the crosslinking density of the material should be lowered to attain a certain fixed modulus of elasticity. In this case, permanent distortion tends to be increased and durability tends to be deteriorated.

[0061]

A hardness of the polyurethane foamed layer, as determined by an Asker C hardness meter, is preferably 10 to 50 degrees, and more preferably 15 to 35 degrees. When the Asker C hardness is less than 10 degrees, the durability of the layered sheet tends to be reduced or the surface smoothness of the material to be polished after polishing tends to be deteriorated. On the other hand, when the Asker C hardness is more than 50 degrees, the holdability of the material to be polished tends to be deteriorated.

[0062]

The compression rate of the polyurethane foamed layer

is preferably 2 to 10%, and more preferably 4 to 8%. When the compression rate is less than 2%, the holdability of the material to be polished tends to be deteriorated. When the compression rate is more than 10%, the durability and the surface smoothness of the material to be polished after polishing tends to be deteriorated.

[0063]

The thickness fluctuation of the polyurethane foamed layer is preferably 100 μm or less, and more preferably 60 μm or less. When the thickness fluctuation is more than 100 μm , the layered sheet has large waviness. As a result, the surface smoothness of the material to be polished after polishing tends to be deteriorated.

[0064]

Since the layered sheet having the skin layer formed on each of the polyurethane foamed layers of the present invention has a holding surface having high surface accuracy, and the skin layer itself has adhesiveness, the layered sheet can sufficiently hold the material to be polished. However, an adhesive layer may be separately provided.

[0065]

Although the layered sheet having no skin layer formed on the polyurethane foamed layer of the present invention has a holding surface having high surface accuracy, and can moisten the holding surface with water or the like to sufficiently hold the material to be polished. However, an adhesive layer may be separately provided.

[0066]

A double-side tape for sticking the layered sheet to a polishing head may be provided on the surface of the base

material sheet of the layered sheet. The double-side tape has a general constitution in which an adhesive layers are provided on both the surfaces of a base material such as a nonwoven fabric and a film. Examples of compositions of the adhesive layers include a rubber adhesive and acrylic adhesive.

[Examples]

[0067]

Description will be given of the invention with examples, while the invention is not limited to description in the examples.

[0068]

[Measurement and Evaluation Method]

(Measurement of Average Cell Diameter)

The prepared polyurethane foamed layer was sliced with a microtome cutter into measurement samples each with the thinnest possible thickness of 1 mm or less. A surface of a sample was photographed with a scanning electron microscope (manufactured by Hitachi Science System Co. with a model number of S-3500N) at a magnification of $\times 100$. An effective circular diameter of each of all cells in an arbitrary area was measured with an image analyzing soft (manufactured by MITANI Corp. with a trade name WIN-ROOF) and an average cell diameter was calculated from the measured values.

[0069]

(Measurement of average cell diameter difference)

A section of the produced polyurethane foamed layer was observed at a magnification of $\times 65$ times with SEM. Three straight lines which equally divide the polyurethane foamed layer into four in the thickness direction were drawn on the

obtained image. The average value of the line segment lengths of straight lines crossing cells in arbitrary distance of 2 mm of the straight lines was calculated, and this was defined as an average cell diameter. For three straight lines, the average cell diameters were respectively calculated, and the average cell diameter difference (maximum value - minimum value) in the thickness direction was calculated from the maximum value and minimum value of the obtained average cell diameter.

[0070]

(Measurement of specific gravity)

Determined according to JIS Z8807-1976. The prepared polyurethane foamed layer cut out in the form of a strip of 4 cm×8.5 cm (thickness: arbitrary) was used as a sample for measurement of specific gravity and left for 16 hours in an environment of a temperature of $23\pm 2^{\circ}\text{C}$ and a humidity of $50\%\pm 5\%$. Measurement was conducted by using a specific gravity hydrometer (manufactured by Sartorius Co., Ltd).

[0071]

(Measurement of hardness)

A hardness was measured in accordance with JIS K-7312. The prepared polyurethane foamed layer was cut into samples with a size of 5 cm×5 cm (with arbitrary thickness), and the samples were left for 16 hours in an environment at a temperature of $23^{\circ}\text{C}\pm 2^{\circ}\text{C}$ and humidity of $50\%\pm 5\%$. When measured, the samples were piled up to a thickness of 10 mm or more. A hardness meter (Asker C hardness meter, pressurized surface height 3 mm, manufactured by Kobunshi Keiki Co., Ltd.) was contacted with a pressurized surface, and 30 seconds later, the hardness was measured.

[0072]

(Measurement of compression rate)

A polyurethane foamed layer was cut out in a circle (with arbitrary thickness) having a diameter of 7 mm into samples, and the samples were left for 40 hours in an environment at a temperature of $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and humidity of $50\% \pm 5\%$. When measured, a compression rate was measured with a thermometric analysis measuring device TMA (manufactured by Seiko Instruments Inc. with a model number of SS6000). The calculating equation of the compression rate is as follows.
Compression rate (%) = $\{(T1 - T2) / T1\} \times 100$

T1: the thickness of a polyurethane foamed layer when applying a stress of 4.9 KPa (50 g/cm^2) to the polyurethane foamed layer from an unloaded condition for 60 seconds

T2: the thickness of a polyurethane foamed layer when applying a stress of 29.4 KPa (300 g/cm^2) from a state of T1 for 60 seconds

[0073]

(Evaluation of polishing rate stability)

As a polishing device, SPP600S (manufactured by Okamoto Machine Tool Works, Ltd.) was used. A glass plate was stuck to the produced layered sheet to evaluate the polishing rate stability. The polishing conditions are as follows:

Glass plate: 6 inches ϕ , thickness: 1.1 mm (optical glass, BK7)

Slurry: Ceria slurry (CeO_2 , 5 wt%)

Slurry amount: 250 ml/min

Polishing pad: MH C 14B (manufactured by Nitta Haas Incorporated)

Polishing pressure: 20 kPa

Number of revolutions of polishing platen: 45 rpm

Number of revolutions of glass plate: 40 rpm

Polishing time: 10 min/plate

Number of glass plates polished: 500

First, the average polishing rate (Å/min) for each of polished glass plates is calculated. The calculation method is as follows:

Average polishing rate = [amount of weight change [g] of glass plate before and after polishing / (glass plate density [g/cm³] x polishing area [cm²] of glass plate x polishing time [min])] x 10⁸

A polishing rate stability (%) is calculated by determining the maximum average polishing rate, minimum average polishing rate and average polishing rate of from a first glass plate to a final treated glass plate (100 plates, 300 plates or 500 plates) and then substituting the above values in the following equation. A lower value of the polishing rate stability (%) is indicative of less change in polishing rate even when a large number of glass plates are polished. In the present invention, it is preferable that the polishing rate stability after treatment of 500 plates is within 10%.

Polishing rate stability (%) = {(maximum average polishing rate - minimum average polishing rate) / average polishing rate of all glass plates} x 100

[0074]

Example 1

90 parts by weight of EP330N (made by Mitsui Takeda Chemical Corporation), 10 parts by weight of diethylene glycol, 5 parts by weight of a silicon-based surfactant (SH-192, made

by Toray Dow Corning Silicone Co., Ltd.), 0.2 part by weight of a catalyst (No.25, made by Kao Corporation) were introduced into a container and mixed. Then, the mixture was stirred vigorously for about 4 minutes at a revolution number of 900 rpm by a stirring blade so as to incorporate bubbles into the reaction system. Thereafter, 38.5 parts by weight of Millionate MTL (made by Nippon Polyurethane Industry Co., Ltd.) were added thereto and stirred for about 1 minute to prepare a cell dispersed urethane composition.

[0075]

The prepared cell dispersed urethane composition was applied onto a base material sheet (polyethylene terephthalate, thickness 0.2 mm) to form a cell dispersed urethane layer. The cell dispersed urethane layer was covered with a release sheet (polyethylene terephthalate, thickness 0.2 mm) subjected to release treatment. The cell dispersed urethane layer was regulated to be 1.0 mm in thickness with a nip roll and then cured at 70°C for 40 minutes to form a polyurethane foamed layer. Thereafter, the release sheet formed on the polyurethane foamed layer was released. Then, the surface of the polyurethane foamed layer was buffed to a thickness of 0.8 mm by a buffing machine (manufactured by Amitec) to give a form having regulated thickness accuracy. Thereafter, a template was stuck to the buffing surface of the polyurethane foamed layer, and a double-side tape (double tack tape, manufactured by Sekisui Chemical Co., Ltd.) was further stuck by a laminator to the surface of the base material sheet to produce a layered sheet. Fig. 1 shows a photomicrograph of a cross section of the polyurethane foamed layer. It can be seen that spherical cells are formed in the

polyurethane foamed layer.

[0076]

Example 2

The cell dispersed urethane composition prepared in Example 1 was applied onto a base material sheet (polyethylene terephthalate, thickness 0.2 mm) to form a cell dispersed urethane layer. Thereafter, the cell dispersed urethane layer was cured at 70°C for 40 minutes to form a polyurethane foamed layer. Then, the surface of the polyurethane foamed layer was buffed to a thickness of 0.8 mm by a buffing machine (manufactured by Amitec) to give a foam having regulated thickness accuracy. Thereafter, a template was stuck to a buffing surface of the polyurethane foamed layer, and a double-side tape (double tack tape, manufactured by Sekisui Chemical Co., Ltd) was further stuck by a laminator to the surface of the base material sheet to produce a layered sheet. Fig. 2 shows a photomicrograph of a cross section of the polyurethane foamed layer. It can be seen that spherical cells are formed in the polyurethane foamed layer.

[0077]

Example 3

The cell dispersed urethane composition prepared in Example 1 was applied onto a base material sheet (polyethylene terephthalate, thickness 0.2 mm) to form a cell dispersed urethane layer. The cell dispersed urethane layer was covered with a release sheet (polyethylene terephthalate, thickness 0.2 mm) subjected to release treatment. The cell dispersed urethane layer was regulated to be 0.8 mm in thickness with a nip roll, and then cured at 70°C for 40 minutes to form a polyurethane foamed layer. Thereafter, the release sheet

formed on the polyurethane foamed layer was released. A skin layer was formed on the polyurethane foamed layer. Thereafter, a template was stuck to the skin layer, and a double-side tape (double tack tape, manufactured by Sekisui Chemical Co., Ltd.) was further stuck by a laminator to the surface of the base material sheet to produce a layered sheet. Fig. 3 shows a photomicrograph of a cross section of the polyurethane foamed layer. It can be seen that spherical cells are formed in the polyurethane foamed layer.

[0078]

Comparative Example 1

10 parts by weight of thermoplastic urethane (Rezamin 7285, made by Dainichiseika Color & Chemicals Mfg. Co., Ltd.) were dissolved in 90 parts by weight of dimethylformamide to prepare an urethane solution. The urethane solution was applied onto a base material sheet (polyethylene terephthalate, thickness 0.2 mm) to form an urethane film. Thereafter, the urethane film-base material sheet was dipped in a DMF-water mixture (DMF/water = 30/70) for 30 minutes and dipped in water for 24 hours to replace dimethylformamide by water, whereby a polyurethane foamed layer was formed. Then, a template was stuck to the surface of the polyurethane foamed layer, and a double-side tape (double tack tape, manufactured by Sekisui Chemical Co., Ltd.) was further stuck by a laminator to the base material sheet surface to produce a layered sheet. Fig. 4 shows a photomicrograph of a cross section of the polyurethane foamed layer. It can be seen that thin and long drop-shaped cells are formed in the polyurethane foamed layer.

[Table 1]

	Average cell diameter (μm)	Average cell diameter difference (μm)	Specific gravity	C hardness (degree)	Compression rate (%)	Average polishing rate ($\text{\AA}/\text{min}$)	Polishing rate stability (%)		
							100 plates	300 plates	500 plates
Example 1	80	12.0	0.26	22	4.3	3700	6	7	9
Example 2	60	25.4	0.27	21	4.0	3550	7	7	8
Example 3	70	21.1	0.29	23	4.2	3650	8	8	9
Comparative Example 1	-	102.0	0.26	27	4.5	3600	8	16	22

[0079]

As can be seen from Table 1, the polishing rate is not easily changed even if a large number of wafers are polished by using the layered sheet produced by the production process of the present invention.

[Brief Description of the Drawings]

[0080]

[Fig. 1]Fig. 1 is a photomicrograph (SEM photograph) of a polyurethane foamed layer of a layered sheet in Example 1.

[Fig. 2]Fig. 2 is a photomicrograph (SEM photograph) of a polyurethane foamed layer of a layered sheet in Example 2.

[Fig. 3]Fig. 3 is a photomicrograph (SEM photograph) of a polyurethane foamed layer of a layered sheet in Example 3.

[Fig. 4]Fig. 4 is a photomicrograph (SEM photograph) of a polyurethane foamed layer of a layered sheet in Comparative Example 1.

[Claims]

[Claim 1]

A process for producing a layered sheet for holding a material to be polished comprising the steps of:

preparing a cell dispersed urethane composition by a mechanical foaming method;

applying the cell dispersed urethane composition onto a base material sheet;

forming a polyurethane foamed layer (including no thermoplastic resin) by curing the cell dispersed urethane composition; and

regulating a thickness of the polyurethane foamed layer uniformly.

[Claim 2]

A process for producing a layered sheet for holding a material to be polished comprising the steps of:

preparing a cell dispersed urethane composition by a mechanical foaming method;

applying the cell dispersed urethane composition onto a base material sheet;

laminating a release sheet on the cell dispersed urethane composition;

forming a polyurethane foamed layer (including no thermoplastic resin) by curing the cell dispersed urethane composition while making the thickness thereof uniform with

a pressing means; and

releasing the release sheet on the polyurethane foamed layer.

[Claim 3]

A layered sheet for holding a material to be polished produced by the process according to claim 1 or 2.

[Claim 4]

The layered sheet for holding a material to be polished according to claim 3, wherein the polyurethane foamed layer has spherical fine cells having an average cell diameter of 20 to 300 μm .

[Claim 5]

The layered sheet for holding a material to be polished according to claim 4, wherein the polyurethane foamed layer has an average cell diameter difference (a maximum value of the average cell diameter-a minimum value of the average cell diameter) of 50 μm or less in a thickness direction.

[Claim 6]

The layered sheet for holding a material to be polished according to any one of claims 3 to 5, wherein the polyurethane foamed layer has a specific gravity of 0.2 to 0.5.

[Claim 7]

The layered sheet for holding a material to be polished according to any one of claims 3 to 6, wherein the polyurethane foamed layer has an Asker C hardness of 10 to 50 degrees.

[Claim 8]

The layered sheet for holding a material to be polished according to any one of claims 3 to 7, wherein the polyurethane foamed layer has a compression rate of 2 to 10%.

[Claim 9]

A process for producing the layered sheet for holding a material to be polished according to claim 1 or 2, wherein the polyurethane foamed layer contains an isocyanate component and an active hydrogen-containing compound as a raw material component,

wherein the isocyanate component is 4,4'-diphenylmethane diisocyanate or carbodiimide modified MDI.

[Claim 10]

The process for producing the layered sheet for holding a material to be polished according to any one of claims 1, 2 and 9,

wherein the polyurethane foamed layer contains an isocyanate component and an active hydrogen-containing compound as a raw material component,

wherein the active hydrogen-containing compound contains a high-molecular-weight polyol,

wherein the high-molecular-weight polyol includes a polymerpolyol in which polymer particles made of acrylonitrile and/or styrene-acrylonitrile copolymers are

dispersed;

the polymerpolyol is contained in an amount of 20 to 100 wt% in the high-molecular-weight polyol, and is contained in an amount of 60 to 85 wt% in the active hydrogen-containing compound.

[Claim 11]

The process for producing the layered sheet for holding a material to be polished according to claim 10 wherein the active hydrogen-containing compound contains 2 to 15 wt% of a low-molecular-weight polyol and/or low-molecular-weight polyamine.