Description

Title of Invention: POLISHING PAD

Technical Field

[0001]

The present invention relates to a polishing pad. The polishing pad of the present invention is used for polishing optical materials, semiconductor devices, glass substrates for hard disk drives and the like. It is particularly suitable for polishing devices in which an oxide layer, a metal layer, or the like is formed on a semiconductor wafer.

Background Art

[0002]

Generally, a CMP (chemical mechanical polishing) technique is used as a polishing method to flatten the surface of optical materials, semiconductor wafers, semiconductor devices, substrates for hard disk drives.

The CMP method is described with reference to Fig.1. As shown in Fig.1, polishing apparatus 1 for performing CMP method is equipped with a polishing pad 3. The polishing pad 3 includes a polishing layer 4, which is the layer that contacts a workpiece 8 held by a platen 16 and a retainer ring (not shown in Fig. 1) that prevents displacement of the workpiece 8 and performs polishing, and a cushion layer 6 that supports the polishing layer 4. The polishing pad 3 is rotated while the workpiece 8 is pressed thereagainst, thereby polishing the workpiece 8. During polishing, a slurry 9 is supplied between the polishing pad 3 and the workpiece 8. The slurry 9 is a mixture (dispersion) of water with various chemical components and fine hard abrasive grains, and the chemical components and abrasive grains flow while enhancing the polishing effect through relative movement with the workpiece 8. The slurry 9 is

supplied to the polishing surface and discharged through grooves or holes.

[0003]

Generally, the polishing pad including rigid polyurethane materials as the polishing layer is used for polishing semiconductor devices. The rigid polyurethane materials are obtained by reacting a prepolymer containing an isocyanate component (such as toluenediisocyanate (TDI)) and a high molecular weight polyol (such as polyoxytetramethylene glycol (PTMG)) with a diamine-based curing agent (such as 4,4'-methylenebis(2-chroloaniline) (MOCA)). The high molecular weight polyol contained in the prepolymer forms a soft segment of the polyurethane. PTMG which is easy to handle and exhibits moderate rubber elasticity has been commonly used as the high molecular weight polyol. But recently with the micro-miniaturization of the wiring of the semiconductor devices when polishing the workpiece in which there are level differences of various height with the conventional polishing pad, there are cases where level difference elimination performance and flattening performance are insufficient. Use of the high molecular weight polyol except PTMG has been considered.

Patent Document 1 discloses the polishing pad which provides decreased defectivity by using a mixture of a PPG and a PTMG as a high molecular weight polyol contained in a prepolymer.

Citation List

Patent Documents

[0004]

Patent Document 1: JP 2011-040737 A

Summary of Invention

Technical Problem

[0005]

However, the polishing pad of Patent Document 1 does not provide sufficient level difference elimination performance and flattening performance, because the mixture of PPG and PTMG is used for it.

The present invention has been made in view of the above problems. One of the objects of the invention is to provide a polishing pad that excels in level difference elimination performance and flattening performance.

Solution to Problem

[0006]

The present inventors made intensive studies in order to solve the above problems and as a result, and found a polishing pad provided with a polishing layer having excellent level difference elimination performance and flattening performance when polishing a workpiece in which there are level differences of various height by adjusting the ratio of the content proportion of a crystalline phase to the content proportion of an amorphous phase and the ratio of the content proportion of an intermediate phase to the content proportion of the anamorphous phase in the polishing layer, as measured by a pulse NMR method in a wet state.

Furthermore, the present inventors found that when the polishing layer transitions from a dry state to a wet state, the change of the content proportion of the intermediate phase is small and the content proportion of the amorphous phase in the polishing layer increases and that a polishing pad capable of solving the above problem can be obtained when the specific change occurs in each of the intermediate phase and the amorphous phase.

That is, the present invention encompasses the following:

[1] A polishing pad having a polishing layer comprising a polyurethane resin foam prepared from an isocyanate-terminated prepolymer and a curing agent as raw materials, characterized in that:

a ratio of a content proportion (%) of a crystalline phase to a content proportion (%) of an amorphous phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a wet state, is not less than 0.5 and not more than 1.0; and

a ratio of a content proportion (%) of an intermediate phase to the content proportion (%) of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state, is not less than 0.4 and not more than 0.9.

[2] The polishing pad according to item [1], wherein the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 30.0 % and not more than 55.0 %.

[3] The polishing pad according to item [1], wherein the content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 15.0 % and not more than 35.0 %.

[4] The polishing pad according to item [1], wherein the isocyanate-terminated prepolymer contains a constituent unit derived from a polyisocyanate compound and a constituent unit derived from a high molecular weight polyol,

wherein the constituent unit derived from the high molecular weight polyol contains at least a constituent unit derived from a polyester diol and a constituent unit derived from a PTMG.

[5] The polishing pad according to item [4], wherein the number average molecular weight of polyester diol forming the constituent unit derived from the polyester diol is not less than 600 and not more than 2500.

[6] The polishing pad according to item [4], wherein the constituent unit derived from the PTMG is not less than 30 % by weight and not more than 80 % by weight relative to the total weight of the constituent unit derived from the high molecular weight polyol.

[7] The polishing pad according to item [4], wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the PTMG, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the PTMG is not less than 400 and not more than 500.

[8] The polishing pad according to item [4], wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the polyester diol, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the polyester diol is not less than 550 and not more than 700.

[9] A polishing pad having a polishing layer comprising a polyurethane resin foam prepared from an isocyanate-terminated prepolymer and a curing agent as raw materials, and characterized in that:

a value obtained by subtracting a content proportion (%) of an intermediate phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a dry state from a content proportion (%) of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in a wet state is not less than -2.0 % and not more than 2.0 %, and

a value obtained by subtracting a content proportion (%) of an amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state from a content proportion (%) of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 2.0 % and not more than 5.7 %.

[10] The polishing pad according to item [9], wherein a content proportion of a crystalline phase is smaller than the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state.

[11] The polishing pad according to item [9], wherein the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 30.0 % and not more than 55.0 %.

[12] The polishing pad according to item [9], wherein the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state is not less than 30.0 % and not more than 50.0 %.

[13] The polishing pad according to item [9], wherein the isocyanate-terminated prepolymer contains a constituent unit derived from a polyisocyanate compound and a constituent unit derived from a high molecular weight polyol,

wherein the constituent unit derived from the high molecular weight polyol contains a constituent unit derived from a polyester diol and a constituent unit derived from a PTMG.

[14] The polishing pad according to item [13], wherein the number average molecular weight of polyester diol forming the constituent unit derived from the polyester diol is not less than 600 and not more than 2500.

[15] The polishing pad according to item [13], wherein the constituent unit derived from the PTMG is not less than 30 % by weight and not more than 80 % by weight relative to the total weight of the constituent unit derived from the high molecular weight polyol.

[16] The polishing pad according to item [13], wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the PTMG, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the PTMG is not less than 400 and not more than 500.

[17] The polishing pad according to item [13], wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from polyester diol, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the polyester diol is not less than 550 and not more than 700.

Advantageous Effects of Invention

[0007]

When the ratio of the content proportion of a crystalline phase to the content proportion of an amorphous phase in the polishing layer, as measured by a pulse NMR method in a wet state is adjusted to fall within the specific range, the proportion of the amorphous phase with high mobility is higher than those of the crystalline phase and the intermediate phase. Thus, it is considered that, because the polishing layer is moderately softened during polishing, the polishing pad exhibits excellent level difference elimination performance and flattening performance even on a workpiece in which level differences of various heights coexist.

Furthermore, it is considered that when the polishing layer transitions from a dry state to a wet state, the change of the content proportion of the intermediate phase is small and the content proportion of the amorphous phase is higher than those of the crystalline phase and the intermediate phase and thus, the polishing layer is moderately softened during polishing. The polishing pad with such polishing layer is the polishing pad which exhibits excellent level difference

elimination performance and flattening performance on a workpiece in which level differences of various heights coexist.

Brief Description of Drawings

[0008]

[Fig.1] Fig.1 is a schematic diagram showing a polishing state.

[Fig.2] Fig.2 is a cross-sectional view of a polishing pad.

[Fig.3] Fig.3 is a schematic diagram illustrating level difference elimination performance and flattening performance.

Form to Carry Out Invention

[0009]

Embodiments of the present invention are described below. The present invention is not limited to the embodiments.

[0010]

<<Polishing Pad>>

The structure of a polishing pad 3 is described with reference to Fig.2. As shown in Fig.2, the polishing pad 3 includes a polishing layer 4 and a cushion layer 6. The polishing pad 3 preferably has a disk like shape, but is not particularly limited thereto. The size (diameter) may be appropriately determined according to the size of the polishing apparatus 1 equipped with the polishing pad 3. For example, the diameter may be about 10 cm to 2 m.

In the polishing pad 3 of the present invention, the polishing layer 4 is preferably bonded to the cushion layer 6 via an adhesive layer 7, as shown in Fig.2.

The polishing pad 3 is attached to the polishing platen 10 of the polishing apparatus 1 with a double sided tape or the like provided on the cushion layer 6. The polishing pad 3 is rotated by the polishing apparatus 1, while a workpiece 8 is pressed thereagainst, thereby polishing the workpiece 8.

[0011]

<Polishing Layer>

(Composition)

The polishing pad 3 includes a polishing layer 4, which is a layer for polishing the workpiece 8. The material constituting the polishing layer 4 is a polyurethane resin foam. The materials, the manufacturing method, and the like of the polyurethane resin foam are described later.

The size (diameter) of the polishing layer 4 is the same as that of the polishing pad 3, and may be about 10 cm to 2 m in diameter. The thickness of the polishing layer 4 is usually about 0.8 to 5 mm.

The polishing layer 4 is rotated together with the polishing platen 10 of the polishing apparatus 1, and the workpiece 8 is polished by causing the chemical components and abrasive grains contained in the slurry 9, which is supplied onto the polishing layer 4, to move relative to the workpiece 8.

The hollow microspheres 4A (foaming) may be dispersed in the polishing layer 4 or may not. The hollow microspheres 4A are preferably dispersed in the polishing layer 4.

[0012]

(Grooving)

It is preferable that the surface of the polishing layer 4 on the side facing the workpiece 8 is provided with grooves as required. The grooves are not particularly limited, but may be either slurry discharge grooves that communicate with the periphery of the polishing layer 4, slurry retention grooves that do not communicate with the periphery of the polishing layer 4, or both. Examples of slurry discharge grooves include lattice shaped grooves and radial grooves, and examples of slurry retention grooves include concentric grooves and perforations (through holes). These may be used in combination.

[0013]

(Shore D Hardness)

The Shore D hardness of the polishing layer 4 of the present invention is not particularly limited, but is for example, not less than 20 and not more than 100, preferably not less than 30 and not more than 80, and more preferably not less

than 40 and not more than 70. When the Shore D hardness is low, it may become difficult to planarize fine unevenness in low pressure polishing. When it excessively high, the abrasive grains and the like may be pressed strongly against the workpiece 8, and scratches may occur on the processed surface of the workpiece 8.

[0014]

(Density)

The density of the polishing layer 4 of the present invention is not particularly limited, but is for example, not less than 0.60 g/cm^3 and not more than 1.25 g/cm^3, and preferably not less than 0.65 g/cm^3 and not more than 1.15 g/cm^3. When the density of the polishing layer 4 is within the above range, the hardness of the polishing layer 4 can be maintained, which tends to allow favorable level difference elimination performance to be obtained.

[0015]

In the polishing pad 3 of the present invention, when the hollow microspheres 4A are used, the air bubbles are incorporated into the polyurethane resin molded body by means of the hollow microspheres 4A. The term “hollow microspheres” refers to microspheres having an internal void. The shapes of the hollow microspheres 4A include spherical, elliptical, and shapes similar thereto. Examples include pre-expanded types and unexpanded heat expandable microspheres which are allowed to expand upon heating.

[0016]

(Level Difference Elimination Performance and Flattening Performance)

The polishing pad of the present invention is characterized in that it exhibits excellent level difference elimination performance and flattening performance by having the specific polishing layer.

The polishing pad 3 of the present invention has excellent level difference elimination performance.

Here, the term “level difference elimination performance” refers to the performance of reducing the level differences of a patterned wafer having level differences (unevenness) during polishing. The schematic diagram of the experiment for measuring level difference elimination performance is shown in Fig.3. At the point of time of Fig.3 (a) level differences of various heights coexist on the workpiece 8. With the progress of polishing by the polishing pad with high level difference elimination performance, level differences on the patterned wafer are preferentially polished to the same height as regions having no wirings, whereby the level differences are eliminated in a short time (Fig.3 (b)). In contrast a polishing pad requiring a long time to eliminate level differences on patterned wafer constitutes a polishing pad with low level difference elimination performance.

[0017]

One of the objects of the present invention is to improve level difference elimination performance and flattening performance when polishing the workpiece in which level difference of various heights coexist.

Level difference elimination performance and flattening performance are more concretely described using Fig.3. For example, the workpiece is composed of a base and a metal film on the base and the metal film is polished with the polishing pad of the present invention. As an example, as shown in Fig.3 the workpiece 8 is composed of the base 81 and the metal film 82 formed on the base (note that Fig.3 is the cross-sectional view of the work piece 8). Before polishing as shown in Fig.3(a), the formed metal film 82 is characterized in that a thickness of a portion of the metal film 82 formed directly on a non-wiring region 811 of the base 81 from a surface (the highest level) 813 thereof is small, while a thickness of a portion of the metal film 82 formed directly on wiring regions 812, 813 of the base 81 from the surface thereof is large to generate level differences (82A, 82B). And the thickness of the metal film 82

increases as a width of the wirings becomes narrower. Namely, the height of the level difference 82B directly on the wirings 813 with a small wiring width is X, the height of the level difference 82A directly on the wirings 812 with a large wiring width is Y, and X is larger than Y.

When such a workpiece 8 is polished by the polishing pad having excellent level difference elimination performance and flattening performance, as shown in Fig. 3(b), the wiring regions 812 are preferentially polished to eliminate the level differences, whereby the surface of the metal film 82 of the workpiece 8 is flattened regardless of the location such as the non-wiring region 811 and the wiring regions 812 and 813. Thereafter, the metal film 82 of the workpiece 8 is polished in a flattened state.

In contrast, polishing by the polishing pad with low level difference elimination performance takes a long time for the thickness of the metal film directly on the wiring regions 812, 813 to become equal to that on the non-wiring region 811. By the polishing pad with low flattening performance not only the metal film directly on the wiring regions but also the other regions are polished, whereby the metal film is not flattened.

Note that level difference elimination performance is a performance indicating the degree of flattening of the level differences (unevenness) on a patterned wafer during polishing. Specifically, a patterned wafer having unevenness is polished, and the remaining level differences (the degree of flattening of the level difference portions) of the wafer after polishing are measured to evaluate. Flattening performance is evaluated by checking whether the metal film is flattened without level differences between the non-wiring region and the wiring regions after polishing.

[0018]

(Crystalline Phase, Intermediate Phase, Amorphous Phase)

The proportions of the crystalline phase, the intermediate phase and the amorphous phase in the polishing layer are

measured by a pulse NMR method. In the pulse NMR measurement, a free induction decay (FID) signal can be classified into three components by waveform separation through sequentially subtracting components starting from a component having a longer spin-spin relaxation time by at least squares method. More specifically, the initial value of the obtained FID signal is proportional to the number of protons in the measurement sample. When the measurement sample contains three components, the FID signal appears as the sum of the response signals of these three components. On the other hand, since the respective components contained in the measurement sample differ in mobility, the decay rates of the response signals vary among the components, resulting in different spin-spin relaxation times. Therefore, the FID signal can be classified into three components by a least squares method and the polyurethane resin foam is divided into a short phase (S phase), a middle phase (M phase) and a long phase (L phase), respectively in an ascending order of the spin-spin relaxation time, and the content proportion of each phase is obtained. Note that regarding the content proportions of the S phase, the M phase and the L phase, for example, in the pulse NMR measurement, mainly the crystalline phase is observed as the S phase, mainly the amorphous phase is observed as the L phase, and mainly the intermediate phase is observed as the M phase. In addition, in the pulse NMR measurement, mainly the hard segment portion is observed as the S phase, and mainly the soft segment portion is observed as the L phase.

Note that the spin-spin relaxation time can be obtained by performing measurement by the solid echo method using, for example, “JNM-MU25” manufactured by JEOL, Ltd.

[0019]

During polishing the temperature of the polishing pad reaches 40°C. When the hardness of the polishing pad becomes excessively high due to an increase in the proportion of the hard segment during polishing, scratches tend to occur and defect performance may deteriorate. In contrast, when the

polishing pad softens due to an increase in the proportion of the soft segment, level difference elimination performance and flattening performance deteriorate, which is undesirable. Here, the crystalline phase, which is a component with low mobility, corresponds to the hard segment component and the amorphous phase, which is a component with high mobility, corresponds to the soft segment component. The proportions of the hard segment component and the soft segment component affect physical properties such as the hardness of the polishing pad.

The pulse NMR measurement is conventionally conducted in a dry state. However, as described above, polishing is actually conducted while supplying the slurry which is a mixture of water with various chemical components and fine hard abrasive grains. Although the actual experimental results are described in Examples, it has been found that the results of the pulse NMR measurement in a dry state differ from those in a wet state.

[0020]

Note that in the present specification, the pulse NMR measurement in a wet state includes immersing a polishing layer material in pure water for 24 hours, subsequently wiping off the pure water on a surface of the polishing layer material with a Kimtowel (registered trademark), and then performing the pulse NMR measurement at a predetermined temperature (40 °C in the present invention).

[0021]

In the polishing layer of the polishing pad of the first embodiment a ratio of a content proportion of a crystalline phase to a content proportion of an amorphous phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a wet state, is not less than 0.5 and not more than 1.0. The ratio of a content proportion of a crystalline phase to a content proportion of an amorphous phase is preferably not less than 0.55 and not more than 0.95, more preferably not less than 0.60 and not more than 0.90, and further preferably not less than 0.55 and not more than 0.85. A ratio of a content

proportion of an intermediate phase to the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state, is not less than 0.4 and not more than 0.9. The ratio of a content proportion of an intermediate phase to the content proportion of the amorphous phase is preferably not less than 0.45 and not more than 0.85, more preferably not less than 0.50 and not more than 0.80.

The ratio of the content proportion of a crystalline phase to the content proportion of an amorphous phase and the ratio of the content proportion of an intermediate phase to the content proportion of an amorphous phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a wet state satisfy the above range and thereby the proportion of the amorphous phase with high mobility is higher than those of the crystalline phase and the intermediate phase during polishing. Due to moderate softening of the polishing layer during polishing the polishing pad having excellent level difference elimination performance and flattening performance can be obtained.

[0022]

In the polishing layer of the polishing pad of the first embodiment the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is preferably not less than 30.0 % and not more than 55.0 %, more preferably not less than 32.0 % and not more than 50.0 %, and further preferably not less than 35.0 % and not more than 50.0 %. The content proportion of the amorphous phase satisfies the above range and thereby in an appropriate proportion the amorphous phase with high mobility is present. Due to moderate softening of the polishing layer during polishing level difference elimination performance and flattening performance tend to be excellent.

[0023]

In the polishing layer of the polishing pad of the first embodiment the content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at

40 °C in the wet state is not less than 15.0 % and not more than 35.0 %, more preferably not less than 17.0 % and not more than 33.0 %, and further preferably not less than 20.0 % and not more than 30.0 %.

[0024]

In the polishing layer of the polishing pad of the first embodiment the content proportion of the crystalline phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 25.0 % and not more than 45.0 %, preferably not less than 28.0 % and not more than 42.0 %, and more preferably not less than 28.0 % and not more than 35.0 %. The content proportion of the crystalline phase satisfies the above range and thereby in an appropriate proportion the crystalline phase with low mobility is present. By the polishing layer having a moderate hardness during polishing, level difference elimination performance and flattening performance tend to be excellent.

[0025]

As another embodiment, in the polishing layer of the polishing pad of the present invention a value obtained by subtracting a content proportion of an intermediate phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a dry state from a content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in a wet state is not less than -2.0 % and not more than 2.0 %, preferably not less than -1.5 % and not more than 1.8 %, and more preferably not less than -0.9 % and not more than 1.5 %.

A value obtained by subtracting a content proportion of an amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state from a content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 2.0 % and not more than 5.7 %, preferably not less than 2.5 % and not more than 5.6 %, more preferably not less than 3.0 % and

not more than 5.6 %, and further preferably not less than 4.0 % and not more than 5.5 %.

The value obtained by subtracting a content proportion of an intermediate phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a dry state from a content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in a wet state and the value obtained by subtracting a content proportion of an amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state from a content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state satisfy the above range and thereby when the polishing layer transitions from a dry state to a wet state, the change of the content proportion of the intermediate phase is small and the proportion of the amorphous phase with high mobility moderately increase. Due to moderate softening of the polishing layer during polishing, level difference elimination performance and flattening performance are excellent.

[0026]

In the polishing layer of the polishing pad of the second embodiment the content proportion of the crystalline phase in the polishing layer measured by a pulse NMR method at 40 °C in the wet state is preferably smaller than that of the amorphous phase. It satisfies the above range and thereby the proportion of the amorphous phase with high mobility is larger than that of the crystalline phase with low mobility. Due to moderate softening of the polishing layer during polishing, level difference elimination performance and flattening performance tend to be excellent.

[0027]

In the polishing layer of the polishing pad of the second embodiment the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is preferably not less than 30.0 % and not more

than 55.0 %, more preferably not less than 32.0 % and not more than 50.0 %, and further preferably not less than 35.0 % and not more than 50.0 %. The content proportion of the amorphous phase satisfies the above range and thereby in an appropriate proportion the amorphous phase with high mobility is present. Due to moderate softening of the polishing during polishing, level difference elimination performance and flattening performance tend to be excellent.

[0028]

Furthermore, In the polishing layer of the polishing pad of the second embodiment the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state is preferably not less than 30.0 % and not more than 50.0 %, more preferably not less than 32.0 % and not more than 48.0 %, and further preferably not less than 34.0 % and not more than 45.0 %. The content proportion of the amorphous phase satisfies the above range and thereby the proportion of the amorphous phase in the wet state can be easily adjusted.

[0029]

In the polishing layer of the polishing pad of the second embodiment the content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 15.0 % and not more than 35.0 %, more preferably not less than 17.0 % and not more than 33.0 %, and further preferably not less than 20.0 % and not more than 30.0 %.

[0030]

In the polishing layer of the polishing pad of the second embodiment the content proportion of the crystalline phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 25.0 % and not more than 45.0 %, preferably not less than 28.0 % and not more than 42.0 %, and more preferably not less than 28.0 % and not more than 35.0 %. The content proportion of the crystalline phase

satisfies the above range and thereby in an appropriate proportion the crystalline phase with low mobility is present. By the polishing layer having moderate hardness during polishing, level difference elimination performance and flattening performance tend to be excellent.

[0031]

<Cushion Layer>

(Composition)

The polishing pad 3 of the present invention has the cushion layer 6. The cushion layer 6 preferably makes the polishing layer 4 abut the workpiece 8 more uniformly. Examples of the material of the cushion layer 6 include resin; impregnated material obtained by impregnating the base with a resin; materials having flexibility such as synthetic resin and rubber; and a sponge material made of the resin. Examples of resin include resins such as polyurethane, polyethylene, polybutadiene and silicone, rubber such as natural rubber, nitrile rubber and polyurethane rubber.

[0032]

The cushion layer 6 may be a foam having a bubble structure and the like. As a foam having the bubble structure, a suede-like material having teardrop-shaped bubbles obtained by a wet film forming method and a sponge-like material in which refine bubbles are formed can be preferably used as well as materials having the voids inside such as non-woven fabric.

Among these when the impregnated material obtained by impregnating the non-woven fabric with polyurethane resin and the sponge-like material are used as the cushion layer, due to the good compatibility with the polishing layer, excellent level difference elimination performance can be maintained.

[0033]

<Adhesive Layer>

The adhesive layer 7 is a layer for bonding the cushion layer 6 and the polishing layer 4, and is generally composed of a double sided tape or an adhesive. Any double sided tape or

adhesive (e.g., adhesive sheet) known in the technical field may be used.

The polishing layer 4 and the cushion layer 6 are bonded together with the adhesive layer 7. The adhesive layer 7 may be formed of for example, at least one adhesive selected from acrylic, epoxy, and urethane adhesives. For example, an acrylic adhesive may be used, and the thickness may be set to 0.1 mm.

[0034]

<<Method for Producing Polishing Pad>>

A method for producing the polishing pad 3 of the present invention is now described.

[0035]

<Materials for Polishing Layer>

As the material for the polishing layer 4, a polyurethane resin foam is used. Examples of specific main components include a material obtained by reacting an isocyanate-terminated prepolymer with a curing agent. For foaming, a foaming agent is added to the material.

[0036]

Hereinafter, a method for producing the material for the polishing layer 4 is described by way of example using an isocyanate-terminated prepolymer and a curing agent.

[0037]

An example of a method for producing the polishing layer 4 using an isocyanate-terminated prepolymer and a curing agent includes: a material preparing step of preparing at least an isocyanate-terminated prepolymer and a curing agent; a mixing step of mixing at least the isocyanate-terminated prepolymer and the curing agent to obtain a mixed liquid for molding a molded body; and a molding step of forming the polishing layer 4 from the mixed liquid for molding the molded body.

[0038]

Hereinafter, the material preparing step, the mixing step, and the molding step are described separately.

[0039]

<Material Preparing Step>

For producing the polishing layer 4 of the present invention, as raw materials for a polyurethane resin foam, an isocyanate-terminated prepolymer, a curing agent and hollow microspheres are prepared. Here, the isocyanate-terminated prepolymer is a urethane prepolymer (also simply referred to as prepolymer) used to form the polyurethane resin foam.

[0040]

The respective components are now described.

[0041]

(Isocyanate-terminated Prepolymer)

The isocyanate-terminated prepolymer can contain a constituent unit derived from a polyisocyanate compound and a constituent unit derived from a polyol, is a compound obtained by reacting the following polyisocyanate compound with the polyol under the condition commonly used, and contains urethane bond and isocyanate group within the molecule. Another component may also be contained in the isocyanate-terminated prepolymer insofar as the effects of the present invention are not impaired. Two or more of the isocyanate-terminated prepolymer can be used in the view of the adjustment of the physical property and the handling.

[0042]

As the isocyanate-terminated prepolymer commercial product may be used or the compound synthesized by reacting polyisocyanate compound with polyol may be used. The reaction is not particularly limited and the addition polymerization reaction may be carried out using known methods and conditions in the production of polyurethane resin. The isocyanate-terminated prepolymer can be produced for example, by the method wherein the polyisocyanate compound heated at 50 °C is added to the polyol heated at 40 °C while stirring under a nitrogen atmosphere; and after 30 minutes the mixture is heated to 80 °C and reacted at 80 °C for 60 minutes.

[0043]

(Polyisocyanate Compound)

In the present specification, the term “polyisocyanate compound” refers to a compound having two or more isocyanate groups within the molecule.

The polyisocyanate compound is not particularly limited as long as it has two or more isocyanate groups in the molecule. The Examples of diisocyanate compounds having two isocyanate groups within the molecule include: m- phenylenediisocyanate, p-phenylenediisocyanate, 2,6-tolylene diisocyanate (2,6-TDI), 2,4-tolylene diisocyanate (2,4-TDI), naphthalene-1,4-diisocyanate, diphenylmethane-4,4′ -diisocyanate (MDI), 4,4′ -methylene-bis(cyclohexyl isocyanate) (hydrogenated MDI), 3,3′ -dimethoxy-4,4′ -biphenylenediisocyanate, 3,3′ -dimethyldiphenylmethane-4,4′ -diisocyanate, xylylene-1,4-diisocyanate, 4,4′ -diphenylpropane diisocyanate, trimethylenediisocyanate, hexamethylenediisocyanate, propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate, p-phenylenediisothiocyanate, xylylene-1,4-diisothiocyanate, ethylidynediisothiocyanate. These polyisocyanate compounds may be used alone or in combination of two or more.

[0044]

Among these polyisocyanate compounds, it is preferred that the compound contains 2,4-TDI and/or 2,6-TDI. 2,4-TDI is further preferable.

[0045]

(Polyol Compound as Raw Material for Prepolymer)

In the present specification, the term “high molecular weight polyol compound” refers to a compound having two or more hydroxy(OH) groups within the molecule. The term “high molecular weight” refers to the molecular weight of not less than 500.

Examples of polyol compound as a raw material for the prepolymer is not particularly limited as long as the object of

the present invention can be achieved and include: diol compounds such as ethylene glycol, diethylene glycol (DEG), and butylene glycol; triol compounds; polyether polyol compounds such as poly(oxytetramethylene) glycol (also referred to as polytetramethylene ether glycol, PTMG), polypropylene glycol (PPG), polyether polycarbonate diol (PEPCD) and polyester polyol.

[0046]

In the first embodiment to obtain the polishing layer satisfying the condition that a ratio of a content proportion of a crystalline phase to a content proportion of an amorphous phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a wet state, is not less than 0.5 and not more than 1.0; and that a ratio of a content proportion of an intermediate phase to the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state, is not less than 0.4 and not more than 0.9, among the above components a constituent unit derived from a high molecular weight polyol preferably contains a constituent unit derived from a polyoxytetramethylene glycol (PTMG) and a constituent unit derived from a polyester diol. As a preferable embodiment, another polyol component may be used as well as PTMG and polyesterdiol.

In the second embodiment to obtain the polishing layer satisfying the condition that a value obtained by subtracting a content proportion of an intermediate phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a dry state from a content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in a wet state is not less than -2.0 % and not more than 2.0 %, and that a value obtained by subtracting a content proportion of an amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state from a content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than

2.0 % and not more than 5.7 %, among the above components a constituent unit derived from a high molecular weight polyol preferably contains a constituent unit derived from a polyoxytetramethylene glycol (PTMG) and a constituent unit derived from a polyester diol. As a preferable embodiment, another polyol component may be used as well as PTMG and polyester diol.

[0047]

When the combination of polyoxytetramethylene glycol (PTMG) and polyester diol, the weight proportion of PTMG is preferably not less than 30 % by weight and not more than 80 % by weight relative to the total weight of the high molecular weight polyol compound which is a raw material for prepolyer.

[0048]

The above polyester diol is particularly limited as long as it is a reaction product of acid and diol component. Examples of acid includes oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid. Examples of diol component used for synthesizing polyester diols include ethylene glycol, diethylene glycol (DEG), butylene glycol (1,4-butanediol), neopentyl glycol, 1,3-butanediol, 1,5-pentanediol, and 1,6-hexanediol. Since the content proportions of the crystalline phase and the amorphous phase are easily adjusted, among the above compound the polyester diol obtained by reacting adipic acid with 1,4-butanediol is preferable.

[0049]

The number average molecular weight (Mn) of polyester diol for forming the constituent unit derived from the polyester diol is preferably not less than 600 and not more than 2500, more preferably not less than 800 and not more than 2000. The number average molecular weight can be measured by gel permeation chromatography (GPC). When the number average molecular weight of the polyol compound is measured from a polyurethane resin,

each component may be decomposed by a conventional method such as amine decomposition, and then the number average molecular weight of the polyol compound is estimated by GPC. Due to the number average molecular weight (Mn) being in the range of 600 to 2500 the necessary rubber elasticity can be imparted to the polishing pad and the effect of the present invention tend to be obtained.

[0050]

(NCO Equivalent of Isocyanate-terminated Prepolymer)

When using two or more isocyanate-terminated prepolymer are used, an NCO equivalent of the isocyanate-terminated prepolymer containing a constituent unit derived from a PTMG is preferably not less than 400 and not more than 500, more preferably not less than 420 and not more than 490. An NCO equivalent of the isocyanate-terminated prepolymer containing a constituent unit derived from a polyester diol is preferably not less than 550 and not more than 700, more preferably not less than 570 and not more than 660. When using two or more isocyanate-terminated prepolymer are used, an NCO equivalent of the isocyanate-terminated prepolymer after mixing is preferably not less than 400 and not more than 650, more preferably not less than 410 and not more than 570. The NCO equivalent of the isocyanate-terminated prepolymer satisfies the above range and thereby excellent level difference elimination performance and flattening performance tend to be obtained.

Accordingly, when a commercially available isocyanate-terminated prepolymer is used, a product having an NCO equivalent within the above range is preferred, and when the compound is synthesized, it is preferred that the NCO equivalent fall within the above range by appropriately selecting the proportions of the raw materials described below.

[0051]

(Additives)

As described above, additives such as oxidizing agents may be added as needed to the material for the polishing layer 4.

[0052]

(Curing Agent)

In the method for producing the polishing layer 4 of the present invention, a curing agent (also referred to as a chain extender) is mixed with the isocyanate-terminated prepolymer and the like in the mixing step. By adding the curing agent, in the subsequent molding step, the ends of the main chain of the isocyanate-terminated prepolymer react with the curing agent to form polymer chains and cure.

Examples of curing agents include: polyamine compounds such as ethylenediamine, propylenediamine, hexamethylenediamine, isophoronediamine, dicyclohexylmethane-4,4'-diamine, 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA), 4-methyl-2,6-bis(methylthio)-1,3-benzenediamine, 2-methyl-4,6-bis(methylthio)-1,3-benzenediamine, 2,2-bis(3-amino-4-hydroxyphenyl)propane, 2,2-bis[3-(isopropylamino)-4-hydroxyphenyl]propane, 2,2-bis[3-(1-methylpropylamino)-4-hydroxyphenyl]propane, 2,2-bis[3-(1-methylpentylamino)-4-hydroxyphenyl]propane, 2,2-bis(3,5-diamino-4-hydroxyphenyl)propane, 2,6-diamino-4-methylphenol, trimethylethylene-bis-4-aminobenzoate, and polytetramethylene oxide-di-p-aminobenzoate; polyhydric alcohol compounds such as ethylene glycol, propylene glycol, diethylene glycol, trimethylene glycol, tetraethylene glycol, triethylene glycol, dipropylene glycol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-butanediol, 3-methyl-1,2-butanediol, 1,2-pentanediol, 1,4-pentanediol, 2,4-pentanediol, 2,3-dimethyltrimethylene glycol, tetramethylene glycol, 3-methyl-4,3-pentanediol, 3-methyl-4,5-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 1,4-hexanediol, 2,5-hexanediol, 1,4-cyclohexanedimethanol, neopentyl glycol, glycerin, trimethylolpropane, trimethylolethane, trimethylolmethane, poly(oxytetramethylene) glycol, polyethylene glycol, and polypropylene glycol. The polyamine compound may have a hydroxy group. Examples of such amine compounds include

2-hydroxyethylethylenediamine, 2-hydroxyethylpropylenediamine, di-2-hydroxyethylethylenediamine, di-2-hydroxyethylpropylenediamine, 2-hydroxypropylethylenediamine, and di-2-hydroxypropylethylenediamine. Among the polyamine compounds, diamine compounds are preferred, and for example, 3,3'-dichloro-4,4'-diaminodiphenylmethane (methylene-bis-o-chloroaniline) (hereinafter sometimes abbreviated as "MOCA") is more preferred.

[0053]

Note that when two or more high molecular weight polyol are used as the raw material of the isocyanate-terminated prepolymer, two or more high molecular weight polyol are mixed and the compound obtained by reacting the mixture with polyisocyanate compound may be used. Alternatively, after each of two or more high molecular weight polyol is reacted with polyisocyanate compound, these reactants are mixed and the mixture may be cured.

[0054]

(Hollow Microspheres)

The polishing layer 4 can be molded by using hollow microspheres 4A with an outer shell and a hollow interior as the material. Commercially available hollow microspheres can be used as the material of hollow microspheres 4A. Alternatively, microspheres synthesized by conventional methods can be used. The material for the outer shell of the hollow microspheres 4A is not particularly limited, but examples include polyvinyl alcohol, polyvinylpyrrolidone, poly(meth)acrylic acid, polyacrylamide, polyethylene glycol, polyhydroxyether acrylate, maleic acid copolymer, polyethylene oxide, polyurethane, poly(meth)acrylonitrile, polyvinylidene chloride, polyvinyl chloride, and organic silicone resins, as well as copolymers obtained by combining two or more of the monomers constituting these resins (such as acrylonitrile-vinylidene chloride copolymer). Commercially available hollow microspheres include, but are not limited to, the Expancel series (trade

names, manufactured by Japan Fillite co., ltd.) and Matsumoto Microsphere (trade name, manufactured by Matsumoto Yushi Co., Ltd.).

The gas contained in the hollow microspheres 4A is not particularly limited, but the examples thereof include hydrocarbons, specifically isobutane, pentane and isopentane.

[0055]

The shape of the hollow microsphere 4A is not particularly limited, and may be, for example, a spherical shape or a substantially spherical shape. The average particle size of the hollow microsphere 4A is not particularly limited, and is preferably 5 to 200 μm, more preferably 5 to 80 μm, further preferably 5 to 50 μm, particularly preferably 5 to 35 μm. The average particle size can be measured with, for example, laser diffraction particle size distribution measurement apparatus (for example, Mastersizer-2000 manufactured by Spectris Co., Ltd.).

[0056]

The hollow microsphere 4A is preferably added in an amount of 0.1 to 10 parts by mass, more preferably 1 to 5 parts by mass, still more preferably 1 to 4 parts by mass based on 100 parts by mass of the isocyanate-terminated prepolymer.

[0057]

The foaming agent conventionally used may be used together with the hollow microsphere 4A, or any gas nonreactive with the above each component may be blown in the following mixing step, in addition to the above components, as long as the effects of the present invention are not impaired. Examples of the foaming agent include water and the foaming agent mainly containing a hydrocarbon having 5 or 6 carbon atoms. Examples of the hydrocarbon include chain hydrocarbons such as n-pentane and n-hexane, and alicyclic hydrocarbons such as cyclopentane and cyclohexane.

[0058]

<Mixing Step>

In the mixing step, isocyanate-terminated prepolymer, additives, and curing agent obtained in the above preparing step are fed into a mixer and stirred and mixed. The mixing step is carried out in a state where the above components are heated to a temperature at which fluidity can be ensured.

[0059]

<Molding Step>

In the molded body molding step, the mixed liquid for molding obtained in the above mixing step is poured into a mold preheated to 60 to 120 °C, and is primarily cured at 100 to 150 °C for 30 minutes to 1 hour. Thereafter, the cured molded body is removed from the mold and heated at about 100 to 150 °C for about 2 to 6 hours to secondarily cure the molded body, thereby forming a cured polyurethane resin (polyurethane resin foam). At this time, the urethane prepolymer and the curing agent react with each other to form a polyurethane resin, whereby the mixed liquid is cured.

When the viscosity of urethane prepolymer (isocyanate-terminated prepolymer) is too high, the fluidity is lowered and the urethan prepolymer is difficult to be mixed almost uniformly during mixing. When the temperature is raised and the viscosity is lowered, the pot life is shortened. As a result, "mix spots" are generated and the variation in the size of the hollow microsphere 4A formed in the foam occur. On the contrary when the viscosity is too low, the bubbles move in the mixture and a foam in which the hollow microspheres 4A are dispersed almost uniformly is difficult to obtain. Thus, the viscosity of the prepolymer at 50 to 80 °C is preferably set within a range of 500 to 10000 mPa·s. For example, the viscosity can be set by changing the molecular weight of the prepolymer (the degree of the polymerization). The prepolymer is heated to about 50 to 80 °C to be flowable.

[0060]

In the molding step, if necessary, the cast mixed liquid is allowed to react in the mold to form a foamed body. At this

time, the prepolymer is crosslinked and cured by the reaction between the prepolymer and the curing agent.

[0061]

After obtaining the polyurethane resin foam, the polyurethane resin foam is sliced into a sheet to form a plurality of polishing layers 4. A general slicing machine can be used for slicing. During slicing, the lower portion of the polishing layer 4 is held, and the upper portion is sliced successively from the top to a predetermined thickness. The thickness to be sliced is set, for example, in the range of 0.8 to 2.5 mm. When the polyurethane resin foam is molded in the molding box having a thickness of 50 mm, for example, the upper part having a thickness of 10 mm and the lower part having a thickness of 10 mm are not used because of flaws and the like and the central part having a thickness of 30 mm is sliced into 10 to 25 polishing layers 4. Thereby the polyurethane resin foam in which the hollow microspheres 4A are formed almost uniformly is obtained.

[0062]

The grooving is performed on the polishing surface of the polishing layer 4 as necessary. By performing the cutting and the like on the polishing surface with the required cutter, a groove having a predetermined pitch, a predetermined width and a predetermined depth can be formed. Examples of the slurry holding groove includes the circular groove formed concentrically and the slurry discharging groove includes the straight-line groove formed into a lattice-like state and the straight-line groove formed radically from the center of the polishing layer.

[0063]

The polishing layer 4 obtained in this manner is then provided, on the surface opposite to the polishing surface, with a double sided tape. The double sided tape is not particularly limited, and any double sided tape known in the technical field may be arbitrarily selected and used.

[0064]

<Manufacturing Method of Cushion Layer 6>

As described above, examples of the material for the cushion layer 6 includes the impregnated material obtained by impregnating the resin fiber such as the non-woven fabric and the woven fabric made of the polyethylene fiber, the polyester fiber and the like with the resin solution such as urethane; the suede material made of the resin material such as urethane; and the sponge material made of the material such as urethane. In the present invention as the cushion layer 6 the known materials can be used and as the manufacturing method the known method can be used.

[0065]

<Bonding Step>

In the bonding step, the formed polishing layer 4 and cushion layer 6 are bonded together by means of the adhesive layer 7. As the adhesive layer 7, for example, an acrylic adhesive is used, and the adhesive layer 7 is formed so as to have a thickness of 0.1 mm. That is, the acrylic adhesive is applied in a substantially uniform thickness to the surface on the side opposite to the polishing surface of the polishing layer 4. The surface on the side opposite to the polishing surface P of the polishing layer 4 and the surface of the cushion layer 6 (the surface on which the skin layer is formed) are then pressed together via the applied adhesive, thereby bonding the polishing layer 4 and the cushion layer 6 with the adhesive layer 7. Thereafter, the bonded body is cut into a desired shape such as a circular shape, and inspection is carried out, such as confirming that no dirt or foreign matter is attached, thereby completing the polishing pad 3.

Examples

[0066]

The present invention is described in further detail below with reference to Examples; however, the present invention is not limited to these Examples.

[0067]

In the Examples and the Comparative Examples, unless otherwise specified, the term “parts” refers to “parts by mass”.

[0068]

The NCO equivalent refers to the numerical value representing the molecular weight per one NCO group of the prepolymer (PP), which is obtained by the formula: (NCO equivalent) = (mass(parts) of polyisocyanate compound + mass(parts) of polyol compound)/[(number of functional groups per molecule of polyisocyanate compound × mass(parts) of polyisocyanate compound / molecular weight of polyisocyanate compound) − (number of functional groups per molecule of polyol compound × mass(parts) of polyol compound/molecular weight of polyol compound)].

[0069]

(Polishing Layer)

Two types of urethane prepolymers (PP1, PP2) were prepared by reacting 2,4-tolylene diizocyanate (TDI) as isocyanate compound; PTMG or polyester polyol (the compound obtained by reacting adipic acid with 1,4-butanediol (adipic acid BG based ester)); and diethylene glycol (DEG), respectively (See Table 1 showing the content used for the preparation of the urethane prepolymer). 1.8 parts of hollow microspheres having an average particle size of 6.0 μm (balloon: Expancel 920DU20 (manufactured by Japan Fillite co., ltd.)) were added to 100 parts of the urethane prepolymer mixtures obtained by mixing the prepolymers in the proportions shown in Table 2 and mixed to obtain the mixed liquid. The obtained mixed liquid was charged into a first liquid tank and kept warm at 60 °C. Next, separately 26.2 parts of MOCA were charged into a second liquid tank, heated to melt and kept warm at 120 °C as a curing agent. The liquids in the first and second tanks were fed into a mixing machine

equipped with two inlets at an R-value of 0.9, where the R-value represents the equivalent ratio of amino and hydroxy groups in the curing agent to the terminal isocyanate groups of the prepolymer. The two fed liquids were mixed and stirred, then injected into a mold preheated at 80 °C in the molding machine, followed by mold clamping and heating at 80 °C for 30 minutes for primary curing. After the primary curing molded body is demolded, the molded body was subjected to secondary curing in an oven at 120 °C for 4 hours to obtain a urethane molded body. The obtained urethane molded body was allowed to cool to 25 °C, and then heated again in an oven at 120 °C for 5 hours, and sliced to a thickness of 1.3 mm to obtain polishing layer B used for Example 1 shown in Table 2. Polishing layer A, C, D and E were produced in the similar steps according to Table 1 and Table 2. The density and Shore D hardness of each polishing layer were shown in Table 2. The content proportions of the crystalline phase, the intermediate phase, and the amorphous phase (measured at 40 °C in a wet state and in a dry state, respectively) were shown in Table 3. Note that T (1), T (2), and T (3) in Table 3 are the spin-spin relaxation times of the crystalline phase, the intermediate phase, and the amorphous phase, respectively and the unit is msec (millisecond). The predetermined values obtained from these data were shown in Table 4.

Note that the measurement methods and the conditions of the density, Shore D hardness, and the pulse NMR measurement (in a wet state and in a dry state) are as follows.

[0070]

(Density)

The density (g/cm^3) of the polishing layer was measured in accordance with Japanese Industrial Standards (JIS K 6505).

[0071]

(Shore D Hardness)

Shore D hardness of the polishing layer was measured in accordance with Japanese Industrial Standards (JIS K 6253) using

Shore D type durometer. Here, the measurement sample was obtained by stacking a plurality of polishing layer as necessary to a total thickness of at least 4.5 mm.

[0072]

(Pulse NMR Measurement)

Device Minispec mq20 (20 MHz) manufactured by Bruker

Nuclide ^{1}H

Measurement T_2

Measurement method Solid echo method

Acquisition Scale 0.4 msec

Scan 128 times

Recycle Delay 0.5 sec

Measurement temperature 40 °C

After the device temperature reached the measurement temperature, a sample was set therein and allowed to stand for 5 minutes, and then the measurement was started. Immediately after the start of the measurement, the first measurement was performed, and then measurements were carried out every 5 minutes thereafter for a total of six measurements. The average value calculated from the five measurements from the second to the sixth, out of the six measurements, was taken as the measurement result. Samples were prepared by punching each of the polishing layers A to E into a circular shape having a diameter of 8 mm. For the dry state, the samples were kept for 40 hours in a thermo-hygrostat bath maintained at a temperature of 23 °C (±2 °C) and a relative humidity of 50 % (±5 %). For the wet state, the samples were immersed in pure water for 24 hours, and then the measurement was performed immediately after wiping off the water on the surfaces of the samples. The samples obtained by punching were packed into a sample tube to a height of 1 to 1.5 cm and used for the measurement with the device and under the conditions described above.

[0073]

[Table 1]

prepolymer	NCO equivalent	composition	remark
PP1	420	TDI/PTMG650/PTMG850/DEG	high hardness PTMG based PP
PP2	600	TDI/(adipic acid BG based ester(MW2000)/DEG	low hardness polyester based PP

TDI: 2,4-tolylene diisocyanate
PTMG650: PTMG having a number average molecular weight of 650
PTMG850: PTMG having a number average molecular weight of 850
BG: 1,4-butanediol

[0074]

[Table 2]

	formulation				NCO equivalent *1	hollow microspheres *2	density (g/cm3)	Shore D hardness
	used prepolymer and proportion	curing agent	PTMG compound ratio	R value				
polishing layer A (Comparative Example 1)	PP1:PP2=100:0	MOCA (MT)	100	0.90	420	920DU20	0.78	59.0
polishing layer B (Example 1)	PP1:PP2=70:30		70	0.90	460	920DU20	0.95	60.0
polishing layer C (Comparative Example 2)	PP1:PP2=0:100		0	0.90	600	920DU20	0.80	38.0
polishing layer D (Example 2)	PP1:PP2=50:50		50	0.90	494	920DU20	0.95	53.0
polishing layer E (Example 3)	PP1:PP2=30:70		30	0.90	531	920DU20	0.95	48.0

*1: NCO equivalent of Example 1 is NCO equivalent of the prepolymer after mixing.
*2: The hollow microspheres have an average particle size of 6.0 μm and are manufactured by Japan Fillite co., ltd.

	prepolymer (parts)	curing agent (parts)	hollow microspheres (parts)
polishing layer A (Comparative Example 1)	100	28.1	3.0
polishing layer B (Example 1)	100	26.2	1.8
polishing layer C (Comparative Example 2)	100	19.8	3.0
polishing layer D (Example 2)	100	24.5	1.8
polishing layer E (Example 3)	100	22.7	1.8

[0075]

[Table 3]

	40 ° C wet state					
	crystalline phase (%)	intermediate phase (%)	amorphous phase (%)	T (1)	T (2)	T (3)
polishing layer A	38.8	30.0	31.2	0.014	0.048	0.275
polishing layer B	32.6	26.7	40.7	0.014	0.050	0.274
polishing layer C	28.4	14.2	57.4	0.014	0.050	0.365
polishing layer D	32.4	28.5	39.1	0.015	0.050	0.269
polishing layer E	27.2	24.5	48.3	0.015	0.051	0.291

	40 ° C dry state					
	crystalline phase (%)	intermediate phase (%)	amorphous phase (%)	T (1)	T (2)	T (3)
polishing layer A	44.9	27.9	27.2	0.014	0.044	0.224
polishing layer B	37.5	26.4	36.1	0.014	0.045	0.234
polishing layer C	33.2	15.2	51.6	0.014	0.044	0.296
polishing layer D	37.9	27.4	34.7	0.014	0.046	0.229
polishing layer E	32.6	24.5	42.9	0.015	0.047	0.250

[0076]

[Table 4]

	40 ° C wet state		
	crystalline phase /intermediate phase	crystalline phase /amorphous phase	intermediate phase /amorphous phase
polishing layer A	1.29	1.24	0.96
polishing layer B	1.22	0.80	0.66
polishing layer C	2.00	0.49	0.25
polishing layer D	1.14	0.83	0.73
polishing layer E	1.11	0.56	0.51

	40 ° C wet - dry (difference between wet state and dry state)		
	crystalline phase (%)	intermediate phase (%)	amorphous phase (%)
polishing layer A	-6.1	2.1	4.0
polishing layer B	-4.9	0.3	4.6
polishing layer C	-4.8	-1.0	5.8
polishing layer D	-5.5	1.1	4.4
polishing layer E	-5.4	0.0	5.5

[0077]

(Cushion layer)

The commercial sponge-like urethane foam (Shore A hardness 60, density 0.55 g/cm^3, 1.3 mm thick) was used. Shore A hardness

of the cushion layer was determined in accordance with Japanese Industrial Standard (JIS K 7311) from the indentation depth of an indentor pressed against a surface of a test piece via a spring. The density of the cushion layer was determined in the same manner as that of the polishing layer.

[0078]

(Examples and Comparative Examples)

The polishing layers A to E and the cushion layers were bonded using a double-sided tape (0.1 mm thick, PET base with acrylic adhesive on both sides), respectively. Another layer of double-sided tape was applied to the surface on the side opposite to the adhesive-applied side of the cushion layer to fabricate the polishing pads used in the Examples 1 to 3 and Comparative Examples 1 and 2.

[0079]

(Evaluation of Polishing performance)

Using the polishing pads obtained for the Examples 1 to 3 and the Comparative Examples 1 and 2, polishing was conducted under the conditions described below. The results were shown in Table 5.

[0080]

(Polishing Conditions)

Polisher: F-REX300X (Ebara Corp.)

Disk: 34R (KINIK Co.)

Retainer ring: Retainer ring GXKD (Ebara Corp.)

Rotation speed: (Platen) 90 rpm; (Polishing head) 81 rpm

Polishing pressure: 1.7 psi

Abrasive temperature: 20 °C

Abrasive flow rate: 200 mL/min

Abrasive: CSL-9044C (A mixture of CSL-9044C stock solution and pure water at a weight ratio of 1:9 was used.) (manufactured by FUJIFILM Planar Solutions, LLC)

Workpiece: 300 mm substrate with Cu film

Polishing time: 60 s

Pad break-in: 32 N, 20 min

Conditioning: Ex-situ, 32N4scans

[0081]

(Level Differences Elimination Performance Evaluation Test)

The polishing pad was placed at the predetermined position of the polishing apparatus via a double-sided tape with an acrylic adhesive and polishing was conducted under the conditions described above. Level difference elimination performance was evaluated as follows. Patterned wafers (workpieces), each having a non-wiring region, a wiring width (line/space pattern) of 0.18 μm/0.18 μm, and a wiring width (line/space pattern) of 0.50 μm/0.50 μm, were polished. The height of the level differences remaining on each patterned wafer after polishing was measured using an atomic force microscope (product name: "NX-wafer", manufactured by Park SYSTEMS Corp.) in an NC-AFM (non-contact) measurement mode. The polishing rate of the Cu film was evaluated by measuring the thickness of the Cu film after polishing using a four-point probe sheet resistance measuring apparatus (manufactured by KLA Corporation, trade name "RS-200", measurement: DBS mode).

More concretely, before polishing the height of the level differences of the patterned wafer (workpiece) was measured using an atomic force microscope and a four-point probe sheet resistance measuring apparatus. There was prepared a patterned wafer (workpiece) having 10,000 Å(angstrom) -high Cu film remaining on a non-wiring region, a 21,000 Å(angstrom)-high Cu film remaining on a line/space pattern region with a wiring width of 0.18 μm/0.18 μm, and a 14,000 Å(angstrom)-high Cu film remaining on a line/space pattern region with a wiring width of 0.50 μm/0.50 μm. This patterned wafer was polished once, and then the height of the Cu film remaining on each region was measured using an atomic force microscope and a four-point probe sheet resistance measuring apparatus. In Table 5 "o" was entered when the difference between the height of level differences remaining on all line/space pattern regions and that on a non-wiring region after polishing was not more than 1,000

Å(angstrom), and “x” was entered when the difference was more than 1,000 Å(angstrom) at any of the wiring widths.

[0082]

(Flattening Performance Evaluation Test)

Flattening performance was evaluated by measuring the height remaining on each of a non-wiring region, a line/space pattern region with a wiring width of 0.18 μm/0.18 μm, and a line/space pattern region with a wiring width of 0.50 μm/0.50 μm of the above patterned wafer (workpiece) after polishing under the above polishing condition using an atomic force microscope (AFM) and a four-point probe sheet resistance measuring apparatus under the above measurement condition.

More concretely, flattening performance was evaluated by measuring the height remaining on each region of the patterned wafer (workpiece) after polishing using an atomic force microscope (AFM) under the above measurement condition. In Table 5 “o” was entered when the difference between the maximum and minimum value of the height remaining on each region after polishing was not more than 1,000 Å(angstrom), and “x” was entered when the difference was more than 1,000 Å(angstrom).

[0083]

[Table 5]

	polishing layer	0.18 μm/0.18 μm		0.50 μm/0.50 μm		non-wiring	
		height after polishing(Å)	polishing rate (Å/min)	height after polishing(Å)	polishing rate (Å/min)	height after polishing(Å)	polishing rate (Å/min)
Comparative Example 1	polishing layer A	11836	9164	11456	2544	9853	147
Example 1	polishing layer B	10395	10605	10201	3799	9839	161
Comparative Example 2	polishing layer C	11542	9458	10014	3986	9149	851
Example 2	polishing layer D	10583	10417	10186	3814	9741	259
Example 3	polishing layer E	10675	10325	10142	3858	9689	311

	polishing layer	level difference	flattening performance
Comparative Example 1	polishing layer A	x	x
Example 1	polishing layer B	o	o
Comparative Example 2	polishing layer C	x	x
Example 2	polishing layer D	o	o
Example 3	polishing layer E	o	o

[0084]

From the results of Table 5 because in the polishing pads of Examples 1 to 3 the ratio of the content proportion of a crystalline phase to the content proportion of an amorphous phase and the ratio of the content proportion of an intermediate phase to the content proportion of the anamorphous phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a wet state satisfied the appropriate range, level difference elimination performance and flattening performance were found to be excellent.

From the results of Table 5 because in the polishing pads of Examples 1 to 3 a value obtained by subtracting a content proportion of an intermediate phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a dry state from a content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in a wet state and a value obtained by subtracting a content proportion of an amorphous phase in the polishing layer, as measured by the

pulse NMR method at 40 °C in the dry state from a content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state satisfied the appropriate range, level difference elimination performance and flattening performance were found to be excellent.

In the comparison with modified compound ratios when the compound ratio of the constituent unit derived from the PTMG was about not less than 30 % and not more than 80 %, the trend toward improvement of level difference elimination performance and flattening performance was observed. It is considered that the balance of the hard segment and the soft segment is improved due to the addition of the strong cohesion of the ester based constituent unit to make the structure of the polishing layer during polishing suitable and that level difference elimination performance and flattening performance deteriorate when the polishing layer is excessively soft.

[0085]

Industrial Applicability

The present invention contributes to the manufacturing and sale of polishing pads and has industrial applicability.

[0086]

Description of Code

1 Polishing apparatus
3 Polishing pad
4 Polishing layer
4A Hollow microsphere
6 Cushion layer
7 Adhesive layer
8 Workpiece
81 Base
82 Metal film
9 Slurry
10 Polishing platen

Claims

[Claim 1]

A polishing pad having a polishing layer comprising a polyurethane resin foam prepared from an isocyanate-terminated prepolymer and a curing agent as raw materials, characterized in that:

a ratio of a content proportion (%) of a crystalline phase to a content proportion (%) of an amorphous phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a wet state, is not less than 0.5 and not more than 1.0; and

a ratio of a content proportion (%) of an intermediate phase to the content proportion (%) of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state, is not less than 0.4 and not more than 0.9.

[Claim 2]

The polishing pad according to Claim 1, wherein the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 30.0 % and not more than 55.0 %.

[Claim 3]

The polishing pad according to Claim 1, wherein the content proportion of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 15.0 % and not more than 35.0 %.

[Claim 4]

The polishing pad according to Claim 1, wherein the isocyanate-terminated prepolymer contains a constituent unit derived from a polyisocyanate compound and a constituent unit derived from a high molecular weight polyol,

wherein the constituent unit derived from the high molecular weight polyol contains at least a constituent unit derived from a polyester diol and a constituent unit derived from a PTMG.

[Claim 5]

The polishing pad according to Claim 4, wherein a number average molecular weight of the polyester diol forming the constituent unit derived from the polyester diol is not less than 600 and not more than 2500.

[Claim 6]

The polishing pad according to Claim 4, wherein the constituent unit derived from the PTMG is not less than 30 % by weight and not more than 80 % by weight relative to the total weight of the constituent unit derived from the high molecular weight polyol.

[Claim 7]

The polishing pad according to Claim 4, wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the PTMG, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the PTMG is not less than 400 and not more than 500.

[Claim 8]

The polishing pad according to Claim 4, wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the polyester diol, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the polyester diol is not less than 550 and not more than 700.

[Claim 9]

A polishing pad having a polishing layer comprising a polyurethane resin foam prepared from an isocyanate-terminated prepolymer and a curing agent as raw materials, characterized in that:

a value obtained by subtracting a content proportion (%) of an intermediate phase in the polishing layer, as measured by a pulse NMR method at 40 °C in a dry state from a content proportion (%) of the intermediate phase in the polishing layer, as measured by the pulse NMR method at 40 °C in a wet state is not less than -2.0 % and not more than 2.0 %, and

a value obtained by subtracting a content proportion (%) of an amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state from a content proportion (%) of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 2.0 % and not more than 5.7 %.

[Claim 10]

The polishing pad according to Claim 9, wherein a content proportion of a crystalline phase is smaller than the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state.

[Claim 11]

The polishing pad according to Claim 9, wherein the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the wet state is not less than 30.0 % and not more than 55.0 %.

[Claim 12]

The polishing pad according to Claim 9, wherein the content proportion of the amorphous phase in the polishing layer, as measured by the pulse NMR method at 40 °C in the dry state is not less than 30.0 % and not more than 50.0 %.

[Claim 13]

The polishing pad according to Claim 9, wherein the isocyanate-terminated prepolymer contains a constituent unit derived from a polyisocyanate compound and a constituent unit derived from a high molecular weight polyol,

wherein the constituent unit derived from the high molecular weight polyol contains a constituent unit derived from a polyester diol and a constituent unit derived from a PTMG.

[Claim 14]

The polishing pad according to Claim 13, wherein a number average molecular weight of the polyester diol forming the constituent unit derived from the polyester diol is not less than 600 and not more than 2500.

[Claim 15]

The polishing pad according to Claim 13, wherein the constituent unit derived from the PTMG is not less than 30 % by weight and not more than 80 % by weight relative to the total weight of the constituent unit derived from the high molecular weight polyol.

[Claim 16]

The polishing pad according to Claim 13, wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the PTMG, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the PTMG is not less than 400 and not more than 500.

[Claim 17]

The polishing pad according to Claim 13, wherein the polyurethane resin foam is prepared from at least two isocyanate-terminated prepolymers as raw materials, and

wherein at least one of the at least two isocyanate-terminated prepolymers contains the constituent unit derived from the polyester diol, and

wherein an NCO equivalent of the isocyanate-terminated prepolymers containing the constituent unit derived from the polyester diol is not less than 550 and not more than 700.