

ADHESIVE COMPOSITION FOR RESIN-BONDED WIRE SAW AND METHOD FOR PRODUCING RESIN-BONDED WIRE SAW

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a fixed abrasive grain wire saw to be used for cutting substrates for solar cells and electronics typically including wafers obtained by slicing silicon ingots each having a large diameter, compound semiconductor substrates such as gallium arsenide, alternatively magnetic and optic substrates such as magnetic materials, crystals, glass. More particularly, the present invention relates to a method for producing a fixed abrasive grain wire saw suitable for a precision cutting process in hard and fragile materials and particularly to a method for producing a resin-bonded wire saw (a wire saw obtained by fixing abrasive grains to a wire with a resin adhesive) and an adhesive composition to be used for the production method.

BACKGROUND OF THE INVENTION

[0002] Year after year, silicon ingots for use in TFT (thin-layer transistor) and solar cells have increasingly been having larger diameters. In inner diameter blade abrasive grains (ID blades) which have been conventionally used for cutting a silicon ingot, problems, such as a decrease in processing efficiency and productivity, generation of affected flow layers, a reduction in

precision of cutting dimensions or necessity of large equipment or the like have been pointed out. Therefore, in recent years, cut processing using a wire saw has become actively performed. Cutting works are performed by a wire saw, causing the wire saw to travel while bringing a wire into contact with an object to be cut along with abrasive grains for cutting by pressurizing. A cutting process using a wire saw is easy to deal with a silicon ingot having a large diameter. Unlike inner diameter blade abrasive grains which can obtain only one wafer per one cutting, in the cutting process, multiple cutting for simultaneously fabricating a plurality of wafers is possible.

[0003] Wire saws to be used for such a cutting process include free abrasive grain wire saws and fixed abrasive grain wire saws. In a free abrasive grain wire saw, a wire such as a piano wire which becomes a core is used by applying an abrasive grain liquid in which fine abrasive grains such as diamonds and silicon carbide have been dispersed into water-based slurry or oil and the like. In this case, a cutting process is performed by causing the wire to which the abrasive grain liquid has been applied to travel while adding a tensile strength to the wire (For instance, JP 2008-103690 A). As a result, cutting is gradually performed by abrasive grains intervening in a clearance between the wire and an object to be cut.

[0004] However, this method needs to always continue providing a cutting interface with an appropriate quantity of abrasive grains. Particularly, as a result of subtle fluctuations of viscosity of slurry and oil or the like caused by temperatures or the like, it is especially difficult to control quality of wafers such as irregular thicknesses and swells. In this method, since abrasive grains freely move at the time of cutting wafers, not only wafers but also wire are rubbed. There is, therefore, a limit for making a wire diameter smaller without breaking. Since surfaces of wafers are grinded with the abrasive grains that freely move, it has been pointed out that there are fears that an affected flow layer (damaged layer) having a great thickness relating to light and electricity conversion efficiency may be formed.

[0005] As a method for solving such problems, a fixed abrasive grain wire saw in which diamonds or the like are fixed to a wire has been proposed. Methods for fixing the diamonds include the resin-bonded method and the electrodeposition method or the like.

[0006] The electrodeposition method is performed by fixing diamonds to a piano wire by nickel plating and the like (For instance, JP 04-004105 B, JP 2003-334763 A). This method is a method for embedding diamonds into a nickel layer while precipitating nickel on a surface of the piano wire in a nickel plating liquid to firmly fix the diamonds. Although this method is excellent in strong fixing strength

from a point of cutting ingots, the diameter of the wire becomes gradually greater in a process of nickel plating.
[0007]

In this method, it is preferred to deeply embed diamonds in a plating layer to be physically fixed firmly and fixing strength of diamonds is subject to an amount of a plating film precipitated. Accordingly, this method has such problems that productivity is extremely low and costs are high. Since a wire has a great wire diameter due to nickel, there is a possibility for the wire to easily have a fatigue break when repeatedly rewinding a long wire to a pulley.

[0008] In addition, a fixed abrasive grain wire saw, which is characterized in that a metal layer formed of a brazing material or a solder with a thickness of 5% to 40% of a particle size of diamonds (abrasive grains) is formed on a wire to solidify the diamonds by adhesion in a state where the metal layer is dissolved, is disclosed (For instance, JP 2006-123024 A). In such a method, when a melting point of the solder or the like to configure the metal layer is high, there is a high possibility that the wire may be excessively heated by melting the metal layer, resulting in generation of an anneal of the wire. Consequently, tensile strength of the wire may be lowered, resulting in difficulty in selecting a wire material. Typically, it is not possible to use a piano wire and a hard steel wire each having a lower hardness and tensile strength caused by

annealing of a core wire at a comparatively low temperature as a core wire. Consequently, a stainless steel and a tungsten wire or the like each having an equivalent tensile strength, which are weak for repeated bending due to embrittlement, are used instead. Conversely, when the melting point of solder which constitutes the metal layer is low, heat generation caused by friction at the time of cutting work with the wire saw makes abrasive grains easy to fall off from the wire by the melting of the metal layer by heat generation.

[0009] The resin bonding method is a method for performing a heat treatment with an enamel baking furnace or the like by coating a mixture of a resin adhesive such as a phenol resin and abrasive grains such as diamonds on a piano wire using a floating dice (JP 2006-123024 A). This leads to fix diamonds with a cured resin (For instance, JP 2000-263452 A, JP 2000-271872 A, and WO 98/35784). A hot-air drying system is known as an enamel baking furnace (For instance, JP 09-035556 A, JP 2010-267533 A). The resin bonding method is comparatively less expensive and is suitable for manufacturing long wire saws. Since there are effects that vibrations of a wire generated during cutting of ingots are absorbed by a resin such as a phenol resin which is softer than metal, it is possible to cause a wire saw to travel at high speed in cut of the ingots, resulting in stable cutting at high speed. It is possible to obtain a thin wafer. On the other hand, it has been pointed out

that the resin bonding method suffers from such disadvantages that the diamonds fall off one after another during cutting due to low adhesion with a resin, cutting quality is deteriorated and a short life due to a reduction in wire diameter. In addition, when a thermally cured resin adhesive is used, it is impossible to perform curing in a short period of time and when curing is performed at a high temperature, there was a problem that speed up of manufacturing a wire saw was not possible because there were troubles associated with foaming or dissolution of vaporized components caused by a curing agent and reaction.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

- [0010] Patent document 1: JP 2008-103690 A
Patent document 2: JP 04-004105 B2
Patent document 3: JP 2003-334763 A
Patent document 4: JP 2006-123024 A
Patent document 5: JP 2000-263452 A
Patent document 6: JP 2000-271872 A
Patent document 7: WO 98/35784
Patent document 8: JP 09-035556 A
Patent document 9: JP 2010-267533 A

SUMMARY

PROBLEMS TO BE SOLVED

[0011] It is an object of the present embodiments disclosed herein to provide a long-life resin-bonded wire saw which is possible to obtain a smooth wafer with a small thickness of an affected flow layer (damaged layer) of a wafer surface and less irregularity in thickness, utilizing stability in an ingot cutting process of the resin-bonded wire saw and a method for producing a resin-bonded wire saw having high production efficiency. It is another object of the present embodiments disclosed herein to provide a novel adhesive composition for a resin-bonded wire saw suitable for this method.

In one aspect, there is provided an adhesive composition for a resin-bonded wire saw to be used for producing a resin-bonded wire saw, in which abrasive grains are fixed to a surface of a metal core wire by means of a resin bond, the adhesive composition for a resin-bonded wire saw including essential components, comprising:

100 parts by weight of a novolak-type phenol resin;

10 to 30 parts by weight of a resol-type phenol resin;

and

0.1 to 5 parts by weight of an amine-based silane coupling agent.

In another aspect, there is provided a paste for a resin-bonded wire saw, comprising:

the adhesive composition as defined above;

a solvent for the adhesive composition;

abrasive grains; and

a filler made of inorganic particles.

In another aspect, there is provided a method for producing a resin-bonded wire saw, comprising the steps of:

preparing the paste as defined above and a metal core wire;

applying the paste to a surface of the metal core wire; and

heating the applied paste by infrared rays including near-infrared rays to cause the adhesive composition to produce a cross-linking reaction.

MEANS FOR SOLVING THE PROBLEMS

[0012] As a result of intensive study to solve the above-described problems, the inventors of the present invention have found a composition system thermally cured efficiently in a short period of time by infrared heating with a combination of a resol-type phenol resin and a novolak-type phenol resin at a specific ratio as a resin for an adhesive and effective production of a long-life resin-bonded wire saw with less fall of diamond abrasive grains capable of obtaining wafers each having a small thickness of the damaged layer of each wafer surface by cutting, which is smooth, to achieve the present invention.

[0013] The summary of the present invention is described as below.

In a first preferred embodiment, there is provided an adhesive composition for a resin-bonded wire saw to be used

for producing a resin-bonded wire saw according to the present invention, in which abrasive grains are fixed to a surface of a metal core wire by means of a resin for an adhesive, which includes essential components: 100 parts by weight of a novolak-type phenol resin; 10 to 30 parts by weight of a resol-type phenol resin; and 0.1 to 5 parts by weight of an amine-based silane coupling agent.

[0014] In a second preferred aspect, the adhesive composition for a resin-bonded wire saw may further include 5 to 20 parts by weight of a novolak-type phenol resin curing agent.

[0015] In a third preferred aspect, a paste for a resin-bonded wire saw which includes the adhesive composition; a solvent for the adhesive composition; abrasive grains; and a filler made of inorganic particles.

[0016] In a fourth preferred aspect, there is provided a method for producing a resin-bonded wire saw which includes the steps of: preparing for a paste and a metal core wire; applying the paste to a surface of the metal core wire; and heating the applied paste by infrared rays including near-infrared rays to cause the adhesive composition to produce a cross-linking reaction.

[0017] In a fifth preferred aspect, the method for producing a resin-bonded wire saw may further include the steps of: winding up a wire obtained in the heating step to obtain a winding body; and re-heating the winding body.

ADVANTAGES OF THE INVENTION

[0018] According to the present invention, a method for producing a long-life resin-bonded wire saw, in which any of irregularity in thicknesses of wafers, deviation of thicknesses in the wafers, and irregularity in deviation of thicknesses is small and a damaged layer caused by cutting each formed on a surface of each wafer has a small thickness, is provided. Further, according to the present invention, an adhesive composition for a resin-bonded wire saw suitable for the above-mentioned method is provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

FIG. 1 is an explanatory view illustrating an embodiment of the present invention to collect emitted radiation from a luminous body with a half-cylinder-type concave mirror;

FIG. 2 shows one example of luminescence emission spectrum of a stick-type lamp that has filled a tungsten filament in a quartz glass tube to be used in the present invention;

FIG. 3 is a graph showing distribution of thicknesses of wafers; and

FIG. 4 is a graph showing distribution of deviation in thicknesses in wafers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] An adhesive composition of the present invention is used for producing a resin-bonded wire saw obtained by fixing abrasive grains to a surface of a metal core wire (hereinafter referred to as a core wire) through a resin bond (resin adhesive) and has the following essential components:

Novolak-type phenol resin: 100 parts by weight

Resol-type phenol resin: 10 to 30 parts by weight

Amine-based silane coupling agent: 0.1 to 5 parts by weight

[0021] A novolak-type phenol resin is a resin obtained by condensation reaction of phenol compounds such as phenol, cresol, bisphenol A, and aldehyde such as formaldehyde in the presence of an acidified medium. A resol-type phenol resin is a resin obtained by condensing a phenol compound such as phenol, cresol, and bisphenol A and an aldehyde such as formaldehyde with a basic catalyst.

[0022] The adhesive composition of the present invention may further include a novolak-type phenol resin curing agent. The novolak-type phenol resin curing agent is preferably contained in the adhesive composition of the present invention 5 to 20 parts by weight relative to 100 parts by weight of a phenol resin.

[0023] In the case where the adhesive composition of the present invention includes a novolak-type phenol resin curing agent, when the compounding ratio of the curing agent is over 20 parts by weight relative to 100 parts by weight of the novolak-type phenol resin, a gas generated by

the dissolution of the curing agent may cause bulges and cracks and the like. When the compounding ratio of the curing agent is less than 5 parts by weight relative to 100 parts by weight of the novolak-type phenol resin, there are fears that curing of novolak resins may be insufficient when the compounding ratio of the resol-type phenol resin is rather little. At this time, although a resol-type phenol resin may be preferably added appropriately, it is further preferable to appropriately set the quantity of the novolak-type phenol resin curing agent to be compounded in the range of the aforementioned compounding ratio (5 to 20 parts by weight) according to the compounded quantity of the resol-type phenol resin.

[0024] Examples of the novolak-type phenol resin curing agent typically include hexamethylenetetramine, methylol melamine, methylol urea and the like. Among them, hexamethylenetetramine is preferable because the curing time thereof is short.

[0025] The adhesive composition of the present invention may further include typically 5 to 15 parts by weight of a phenol compound such as phenol, cresol, and bisphenol A. The adhesive composition of the present invention may further include a small amount of aldehyde such as formaldehyde (for example, 1 part by weight or smaller) and a small amount of a basic catalyst and water.

[0026] Since the adhesive composition for a resin-bonded wire saw of the present invention contains 10 to 30 parts

by weight of a resol-type phenol resin relative to 100 parts by weight of a novolak-type phenol resin, it is possible to obtain a dense three-dimensional mesh structure by cross-linking of phenol resins. This makes it possible to realize a firm joining with abrasive grains. When the resol-type phenol resin is by 30 parts by weight greater than 100 parts by weight of the novolak-type phenol resin, viscosity of a paste to be mentioned later becomes lower. Accordingly, when the resol-type phenol resin is by 30 parts by weight greater than 100 parts by weight of the novolak-type phenol resin, it is impossible to obtain viscosity suitable for applying a paste by causing a core wire to rapidly travel. When the resol-type phenol resin is by 10 parts by weight smaller than 100 parts by weight of the novolak-type phenol resin, the cross-linking rate of the adhesive composition becomes slower. As a result, when the resol-type phenol resin is by 10 parts by weight smaller than 100 parts by weight of the novolak-type phenol resin, it becomes difficult to cure the paste in a short period of time while causing the core wire to travel. This makes it impossible to produce a high quality resin-bonded wire saw. To cure the paste in a short period of time, it is further preferable to appropriately add a novolak-type phenol resin curing agent at a rate mentioned above.

[0027] In the adhesive composition for a resin-bonded wire saw of the present invention, 0.1 to 5 parts by weight of an amine-based silane coupling agent is contained relative

to 100 parts by weight of the novolak-type phenol resin. This leads to increase adhesive strength among the abrasive grains and the core wire and the adhesive. When the compounding ratio of the amine-based silane coupling agent is less than 0.1 part by weight relative to 100 parts by weight of the novolak-type phenol resin, sufficient adhesion between the phenol resin and the abrasive grains coated with nickel is not obtainable. In such a case, cutting capacity of the resin-bonded wire saw is inferior to the resin-bonded wire saw produced by using an adhesive composition compounded at the aforementioned compounding ratio of the amine-based silane coupling agent. When the compounding ratio of the amine-based silane coupling agent is by 5 parts by weight greater than 100 parts by weight of the novolak-type phenol resin, bubbles are generated by thermal decomposition and the curing of the novolak-type phenol resin is affected. This makes it impossible to obtain sufficient adhesion between the phenol resins and the abrasive grains. In such a case, the cutting capacity of the resin-bonded wire saw becomes smaller.

[0028] Examples of the amine-based coupling agent include 3-aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropylmethyldimethoxysilane, 3-aminopropyltriethoxysilane and the like.

[0029] A method for producing a resin-bonded wire saw using the adhesive composition of the present invention includes

the steps of: preparing a paste which includes the adhesive composition, a solvent for dissolving the adhesive composition and adjusting viscosity of the paste, abrasive grains, and a filler including inorganic particles; preparing a metal core wire; applying the paste to a surface of the metal core wire; and heating the applied paste with infrared rays to allow the adhesive composition to produce a cross-linking reaction accompanied by dehydration.

[0030] The adhesive composition is rapidly dehydrated and condensed by this heating step to form a precise three-dimensional cross-linking structure.

[0031] It is possible to continuously apply a paste to a surface of a metal core wire from a nozzle with a small diameter using the dispenser (syringe) method for applying the paste to the traveling core wire by squeezing the paste or the floating dice method and the like. The application quantity of the paste is preferably set so that the degree of concentration of the abrasive grains may be 50 to 120. The degree of concentration is an index value of a percentage of an area of the abrasive grains that occupies a project area of an outer surface of the wire saw. In this specification, when the project area of the abrasive grains that accounts for the total project area is 15%, the degree of concentration is set at 100. For instance, when the project area of the abrasive grains that accounts for the total projection area is 30%, the degree of

concentration is set at 200. And when the projection area of the abrasive grains occupies the total projection area is 7.5%, the degree of concentration is set at 50.

[0032] In the case where the paste is continuously applied to the traveling core wire, it is preferable to adjust viscosity of the paste to 3 to 6 Pa.s by adding the solvent to the adhesive composition to obtain the appropriate and unified application quantity. For instance, the solvent is preferably set in the range of 100 to 200 parts by weight relative to 100 parts by weight of the adhesive composition. While the solvent to adjust the viscosity of the paste is not particularly limited, among o-, m-, and p-isomers, o-cresol having a low boiling point is preferable.

[0033] While it is not particularly limited, only if abrasive grains for a fixed abrasive grain wire saw are used as abrasive grains to be used in the present invention, examples of the abrasive grains include diamond abrasive grains, cubic-based BN abrasive grains, alumina abrasive grains, and silicon carbide abrasive grains.

[0034] Among them, diamond abrasive grains have extremely high thermal conductivity, so that temperatures rapidly rise also in a shadow portion of irradiation to the abrasive grains by heating in a short period of time. This makes it possible to rapidly perform a chemical reaction relating to uniform fixing, which is preferable to use the diamond abrasive grains. The size of the abrasive grains is selected in accordance with purpose or the diameter of

the core wire. The size of the abrasive grains is, however, preferably some microns to 25 microns from a point of a cut of a silicone ingot having less cutting allowance. Further, the abrasive grains to be used in the present invention may be diamonds coated with a metal such as nickel or titanium except for copper (in the case where copper remains as an impurity, since a deep level is created in a silicon band gap in the heat treatment step, power generation efficiency is lowered when using the abrasive grains as a solar battery). In the case where diamonds coated with nickel are used, it is possible for the resin-bonded wire saw obtained by the present invention to realize slicing which can obtain silicon wafers having fewer warps and saw marks than a diamond abrasive grain fixed wire saw by electroplating (electrodeposition) such as nickel and extremely smooth surfaces.

[0035] The abrasive grains need to be appropriately fixed in a dispersed state on the core wire on the scale referred to as the aforementioned degree of concentration to avoid clogging caused by silicon wastes created at the time of slicing. Further, it is preferable to contain 50 to 120 parts by weight of the abrasive grains relative to 100 parts by weight of the adhesive composition.

[0036] A steel wire is preferably used as the core wire to be used in the present invention. While the wire diameter is not particularly limited, the wire diameter is preferably 0.3 mm to 0.5 mm. Examples of the steel wire

include a wire rod obtained by thermal treated spring steel such as high-carbon steel and medium carbon low-alloy steel, a wire rod created by processed spring steel such as a hard steel wire, a piano wire, a stainless wire, a cold-rolled steel wire or an oil temper wire, a low alloy steel, a medium alloy steel, high alloy steel, a steel wire rod with high-toughness and high fatigue strength such as maraging steel.

[0037] A paste is continuously applied to the traveling core wire to continuously heat the core wire to which the paste has been applied while causing the core wire to travel. This allows the applied paste to be cured by heating. The heating is performed by irradiating infrared rays to the applied paste. When the paste is heated by hot air with a conventional enamel furnace and the like, thermal curing occurs from an outer surface of the paste. Then an epidermal membrane is created, so that water generated by dehydration reaction is trapped inside, bubbles are easily generated in the adhesive accompanied by gasification of this water. In contrast, when heating the paste by infrared rays using a lamp and the like, dehydration reaction is performed in a short period of time to complete cross-linked polymer because near-infrared rays with a wavelength of appropriately 1 μm are effectively absorbed. Since water is excited to be evaporated in a short period of time, bubbles are not easily generated in the adhesive. The infrared rays preferably have one or a

plurality of spectrum peaks in a band of the near-infrared rays of 0.7 μm to 2.5 μm . Particularly, heating by the near-infrared rays having a wavelength of about 1 μm (the range of 0.9 μm to 1.3 μm) is preferable to prevent the adhesive after curing from bubbling by controlling bubbles of the adhesive accompanied by gasification of water generated by dehydration reaction as well as promotion of dehydration and cross-linking of the adhesive composition. [0038] As a method for heating the applied paste during traveling of the core wire that have been applied with the paste, a method as shown in FIG. 1 is a typical example. A half-cylindrical concave mirror 2 and a luminous body 4 that emits infrared rays are used in this system. In this system, the half-cylindrical concave mirror 2 is so arranged that emitted radiation from the luminous body 4 arranged linearly parallel to a longitudinal direction of the concave mirror 2 may be collected at a travelling route of the core wire in a size of about 10 mm ϕ with the core wire 3 applied with the paste traveling in the longitudinal direction of the concave mirror 2 (an orthogonal direction to a paper surface seen from drawings). Reference numeral 8 is a reflecting surface of the concave mirror 2. The concave mirror 2 and the luminous body 4 become a pair and a plurality of pairs of the concave mirrors 2 and the luminous bodies 4 may be arranged in combination with a travel route of the core wire being the center of symmetry. An infrared lamp may be preferably used as the luminous

body 4 in effective heating in a short period of time. The temperature of a collecting portion 6 is preferably 500°C to 800°C when measuring with a sheath-type thermocouple having a diameter of 1.0 mm. The length of the collecting portion 6 is decided according to the size and the number of the luminous bodies 4 and the concave mirrors 2. It is possible to heat the applied paste with infrared rays during traveling of the core wire with the paste applied by employing the collecting portion 6 as a heating zone. The heating zone may be constituted using an infrared ray lamp. When using an infrared ray lamp, the length of the collecting portion 6 may be typically 400 mm to 1,000 mm. The heating zone may be formed by arranging a plurality of infrared ray lamps in series in a traveling direction of the core wire.

[0039] An infrared ray lamp having a peak of light-emitting spectrum in a band of near-infrared rays is preferably used as the luminous body 4. Examples of a preferable infrared ray lamp include a Short-arc Xenon Lamp and a stick-shaped lamp in which a tungsten filament is contained in a quartz glass tube.

[0040] In the present invention, such a heating method makes it possible to cure the adhesive in a short period of time without generation of bubbles under a high speed of the travel speed of the 1,000 mm/sec to 2,000 mm/sec for the core wire to which the paste has been applied.

[0041] A filler made of inorganic particles is contained in

the paste. 20 parts by weight to 100 parts by weight of the filler is preferably contained relative to 100 parts by weight of the adhesive composition. 30 parts by weight to 60 parts by weight of the filler is further preferably contained. While particulates of diamonds (about 2 μm to 3 μm) may be used as a filler, inorganic materials with various shapes and hardness may be used. For one example, silicon carbide particles are used. The mixture of the filler has effects to inhibit thermal expansion and heat shrinkage of the resin to decrease the loss of abrasive grains during cutting of ingots.

[0042] In the present invention, it is rather more possible to obtain a resin-bonded wire saw having more stable performance by reheating the heated wire (the core wire to which paste has been applied) with the aforementioned infrared heating. This reheating is performed for the purpose of removing thermal strain that resin layers and the core wire have received, which repeat expansion and shrinkage caused by curing for a short period of time with the aforementioned infrared heating. In the case where the wire (the core wire to which the paste has been applied) is wound up to a bobbin with a predetermined tensile force, i.e., about 10N to reheat the winding body, such troubles arise that the wire is conglutinated in neighboring portions thereof, resulting in impossibility of disentangling the wire or peeling off of the adhesive when the wire is forcibly disentangled. Consequently, it is

principally preferable for the adhesive composition to substantially complete curing in infrared heating.

[0043] Reheating is preferably performed at 100°C to 200°C for 1 hour to 5 hours. Even when it takes time to reheat, there is no possibility that productivity is significantly lowered as a whole production process of the resin-bonded wire saw because it is possible to reheat a great number of winding bodies at one time. As mentioned above, in the present invention, it is possible to improve productivity of the resin-bonded wire saw by a combination of rapid heating of the wire and reheating of the winding body to effectively produce the resin-bonded wire saw.

[0044] Conventionally, in such a reheating system of the winding body, when heating the wire under high speed travel, such troubles arouse that the wire is conglutinated in neighboring portions thereof when reheating, resulting in impossibility of disentangling the wire or peeling off of the adhesive when disentangling the wire. In the present invention, however, the use of the aforementioned adhesive composition and near-infrared heating has made it possible to substantially perfectly cure the adhesive composition by rapidly heating the wire without such a trouble that bubbles are formed. As a result, in the present invention, it is possible to remove thermal strain by reheating without such a trouble that the wire is conglutinated in the neighboring portions thereof.

[0045] The resin-bonded wire saw obtained by the present

invention has a slit depth greater than the slit depth of the conventional resin-bonded wire saw. This slit depth is a slit depth at the time when a piece which is an object to be cut in a predefined shape is pushed to the wire saw to cut into until the wire saw cuts by a back-and-forth motion of the wire saw. The cut of the wire saw at this time is mainly evoked by the loss of abrasive grains. As a result, the resin-bonded wire saw obtained by the present invention has a significant improvement in fixing strength to the core wire of the abrasive grains, which leads to a long life. Since the resin-bonded wire saw obtained by the present invention has a high fixing strength to the core wire of the abrasive grains, any of irregularity in thicknesses of wafers, deviation of the thicknesses in the wafers, and irregularity in deviation of thicknesses is smaller than the resin-bonded wire saw produced by conventional methods. Further, it is possible to obtain smooth silicon wafers by the resin-bonded wire saw obtained by the present invention. Moreover, it is possible to obtain wafers each having a thin affected flow layer formed on a surface by the resin-bonded wire saw obtained by the present invention. In addition, as is shown from measuring results of three-point bending stress, there is few origination of destruction caused by the affected flow layer, it is possible to obtain wafers with high bending strength.

EXAMPLES

[0046] A resin-bonded wire saw was produced by using an adhesive composition for a resin-bonded wire saw with the following combination, adjusting a paste at the compounding ratio indicated below, and employing a production line of the wire saw indicated below.

[Example 1]

[0047] Compounding ratio of an adhesive composition for a resin-bonded wire saw

Novolak-type phenol resin composition (Product name: Shonol BRP-5417): 80 parts by weight; content: 86 weight % of novolak-type phenol resin ($(\text{C}_6\text{H}_6 \cdot \text{CH}_2\text{O})_n$); 5 weight % of phenol; 9 weight % of hexamethylenetetramine; resol-type phenol resin composition (Product name: Shonol BRL-131): 20 parts by weight; content: 80 weight % of resol-type phenol resin ($(\text{C}_6\text{H}_6 \cdot \text{CH}_2\text{O})_n$), 5.9 weight % of phenol, 0.6 weight % of formaldehyde, 1.2 weight % of NaOH, 12.2 weight % of moisture, 0.1 weight % of other auxiliary agent; and 1 part by weight of an amine-based silane coupling agent (Product name: Sila-Ace S330).

(Note: The amount of the contained novolak-type phenol resin is 80 parts by weight $\times 0.86 = 68.8$ parts by weight and the amount of the contained resol-type phenol resin is 20 parts by weight $\times 0.80 = 16$ parts by weight. Accordingly, in Example 1, when converting into a ratio relative to 100 parts by weight of the novolak-type phenol resin, about

23.2 parts by weight of the resol-type phenol resin is contained.)

Compounding ratio of a paste

100 parts by weight of an adhesive composition; 80 parts by weight of diamond abrasive grains coated with nickel (average particle diameter: 10 μm to 20 μm); 50 parts by weight of a filler (silicon carbide powder; #8000); and 150 parts by weight of a solvent (o-cresol).

[Example 2]

[0048] Compounding ratio of an adhesive composition for a resin-bonded wire saw

90 parts by weight of a novolak-type phenol resin composition (Product name: Shonol BRP-5417); 10 parts by weight of a resol-type phenol resin composition (Shonol BRL-131); and 1 part by weight of an amine-based silane coupling agent (Product name: Sila-Ace S330).

Compounding ratio of a paste

100 parts by weight of an adhesive composition; 80 parts by weight of diamond abrasive grains coated with nickel (average particle diameter: 10 μm to 20 μm); 50 parts by weight of a filler (silicon carbide powder; #8000); and 170 parts by weight of a solvent (o-cresol).

(Note: In Example 2, when converting into a ratio relative to 100 parts by weight of a novolak-type phenol resin, about 10.3 parts by weight of a resol-type phenol resin is contained.)

[Comparative Example 1]

[0049] Compounding ratio of an adhesive composition for a resin-bonded wire saw

93 parts by weight of a novolak-type phenol resin composition (Product name: Shonol BRP-5417); 7 parts by weight of a resol-type phenol resin composition (Shonol BRL-131); and 1 part by weight of an amine-based silane coupling agent (Product name: Sila-Ace S330).

Compounding ratio of a paste

100 parts by weight of an adhesive composition; 80 parts by weight of diamond abrasive grains coated with nickel (average particle diameter: 10 μm to 20 μm); 50 parts by weight of a filler (silicon carbide powder; #8000); and 180 parts by weight of a solvent (o-cresol).

(Note: in Comparative Example 1, when converting into a ratio relative to 100 parts by weight of a novolak-type phenol resin, about 7 parts by weight of a resol-type phenol resin is contained.)

[Comparative Example 2]

[0050] Compounding ratio of an adhesive composition for a resin-bonded wire saw

70 parts by weight of a novolak-type phenol resin composition (Product name: Shonol BRP-5417); 30 parts by weight of a resol-type phenol resin composition (Shonol BRL-131); and 1 part by weight of an amine-based silane

coupling agent (Product name: Sila-Ace S330).

Compounding ratio of a paste
100 parts by weight of an adhesive composition; 80 parts by weight of diamond abrasive grains coated with nickel (average particle diameter: 10 μm to 20 μm); and 50 parts by weight of a filler (silicon carbide powder; #8000).
(Note: In Comparative Example 2, when converting into a ratio relative to 100 parts by weight of a novolak-type phenol resin, about 40 parts by weight of a resol-type phenol resin is contained.)

[Comparative Example 3]

[0051] Compounding ratio of an adhesive composition for a resin-bonded wire saw
80 parts by weight of a novolak-type phenol resin composition (Product name: Shonol BRP-5417); and 20 parts by weight of a resol-type phenol resin composition (Shonol BRL-131).

Compounding ratio of a paste
100 parts by weight of an adhesive composition; 80 parts by weight of diamond abrasive grains coated with nickel (average particle diameter: 10 μm to 20 μm); 50 parts by weight of a filler (silicon carbide powder; #8000); and 150 parts by weight of a solvent (o-cresol).

[0052] Steel wires used in Examples and Comparative Examples: $\phi 100$ μm of steel wires

[0053] Production lines of wire saws in Examples and

Comparative Examples

Core wire feeder→ coating equipment→ heating apparatus→ winder...→ reheating furnace

Core wire feeder: a general feeder configured to feed a core wire in the shape of wound up.

Coating equipment: a paste was homogeneously applied to a surface of the core wire by a dice in the shape of a water jet.

Heating apparatus: an apparatus configured to heat the core wire to which the paste has been applied. Three infrared ray gold image furnaces, model No. RHL-E410-N (heating length: 265 mm, maximum output: 4kw) produced by Ulvac-riko, Inc. using a stick-type lamp, in which a tungsten filament is capsulated into a quartz glass tube, were used in series as the apparatus. FIG. 2 shows energy spectral distribution of the stick-type lamp.

Winder: a general winder configured to wind up the wire saw.

Image furnace: Setting temperature 725°C to 750°C

Travel speed of the core wire: 1,200 mm/sec

Quantity of the paste applied: 0.01 g/m

Reheating furnace: a heating furnace configured to store and heat the wire wound up by the winder (with an adhesive and abrasive grains)

Heating in the reheating furnace: 180°C × 2 hours

[0054] In comparative Example 1, the curing rate of the adhesive composition is slow and the curing of the adhesive composition is imperfect after passing through the image

furnace, resulting in impossibility of disentangling the wire (winding) because the wire was conglutinated in neighboring portions thereof after heating with the reheating furnace. In Examples 1 and 2, the wire was not conglutinated after heating with the reheating furnace, which led to smooth disentangling of the wire (winding). [0055] In Comparative Example 2, although a solvent for adjusting viscosity was not used, the paste had a viscosity as low as 2 Pa·S. As a result, the target applied quantity (0.01 g/m) (in travel speed of the core wire: 120 mm/sec) was not obtainable.

[0056] Cutting performance of a resin-bonded wire saw (a1) obtained in Example 1, and a resin-bonded wire saw (a2) obtained in Example 2 were compared with cutting performance of the resin-bonded wire saw (b1) using an optical curable resin as an adhesive and the resin-bonded wire saw (b2) obtained in Comparative Example 3.

Cutting performance test

1 cm of a cubic multi-crystal silicon piece was set downward the wire that was horizontally pulled to be moved downward to measure cutting depths.

Cutting conditions

Wire movement: amplitude 80 mm, speed: reciprocation of 400 mm/min

Cutting time: until disconnection

Downward speed of the piece: 0.9 mm/min

Table 1 shows results of a cutting performance test.

[0057] [Table 1]

Sample	(a1)	(a2)	(b1)	(b2)
Cutting depth (mm)	6.5	6.5	3.5	4.8

[0058] As shown in table 1, results that cutting depths of resin-bonded wire saws (a1) and (a2) obtained in Examples 1 and 2 were deeper than cutting depths of a resin-bonded wire saw (b1) using an optical curable resin and a resin-bonded wire saw (b2) obtained in Comparative Example 3 were obtained.

[0059] FIGS. 3 and 4 respectively indicate distribution of thicknesses of wafers, deviation of thicknesses in wafers (difference between the maximum thickness and the minimum thickness) at the time when a great number of wafers have been cut from a silicon ingot by cutting (A1) using the resin-bonded wire saw (a1) obtained in Example 1, cutting (B) using a wire saw (c) obtained by the electrodeposition method (abrasive grains: diamond particles coated with nickel, core wire diameter: 100 μ m). Vertical axes in FIGS. 3 and FIG. 4 are each the number of wafers. The horizontal axis in FIG. 3 indicates thicknesses of wafers and the horizontal axis in FIG. 4 indicates deviation of thicknesses in wafers.

Cutting conditions:

Apparatus: Multi-wire saw apparatus: Model No. PV500D
produced by Komatsu NTC Ltd.

Speed of wire saw wire line: 1,000 m/min

Slit speed (the slit depth of the wire slit into a silicon ingot per unit time): 0.5 mm/min

Work: Multi-crystal silicon ingot: an angle of 156 mm

As shown from FIGS. 3 and 4, when using the resin-bonded wire saw (a1), it turned out that production that was stable in quality was possible because all of irregularity of the thicknesses of the wafers, deviation of the thicknesses in the wafers, and irregularity of deviation of the thicknesses at the time of cutting a great number of wafers were smaller than those of the wire saw (c) obtained by the electrodeposition method.

[0060] Table 2 shows arithmetic mean surface roughness (Ra) and the maximum heights (Ry) in accordance with the JIS B 0601 of the wafers when cutting the wafers (set a pitch equivalent to 170 μm) from a silicon ingot, by cutting (A1) using the resin-bonded wire saw (a1) obtained in Example 1, cutting (A2) using the resin-bonded wire saw (a2) obtained in Example 2, cutting (B) using a wire saw (c) obtained by the electrodeposition method [abrasive grains: diamond particles with nickel plated (particle size: 10 μm to 20 μm)], core wire diameter 100 μm), cutting (C) by free abrasive grain method (use of SiC abrasive grains #5000). Numerical values in Table 2 are averages of measured values of three places. Cutting conditions are similar to the cutting conditions in FIGS. 3 and 4.

[0061] [Table 2]

Samples	Ra (μm)	Ry (μm)
A1	0.19	2.02
A2	0.22	2.33
B	0.31	2.97
C	0.39	3.50

[0062] As shown in table 2, it is possible to obtain smoother wafers than the wafers obtained by cutting using the electrodeposition method and cutting using the free abrasive grain method when using the resin-bonded wire saw (a1) and the resin-bonded wire saw (a2).

[0063] Next, Table 3 shows measuring results using scanning electron microscopy cross-sectional observation in terms of thicknesses of damaged layers (affected flow layers) of wafer surfaces having been cut by cutting (A1), cutting (A2), cutting (B), and cutting (C) on the similar cutting conditions to the cutting conditions in Table 2.

[0064] [Table 3]

Samples	Thicknesses of damaged layers (μm)
A1	4-7
A2	4-7
B	6-8
C	11-15

[0065] As shown in table 3, when the resin-bonded wire saw (a1) and the resin-bonded wire saw (a2) are used, there is less damage of the wafers caused by heat accompanied by cutting and stress strain or the like than the cutting using the electrodeposition method and the cutting using

the free abrasive grain method. As a result, wafers each having a small thickness of the damaged layer are obtainable.

[0066] Such a characteristic also relates to achievement of high power generation efficiency of solar cells. That is, perfect removal of the damaged layers (affected flow layers) proceeding accompanied by brittle fracture is an essential work in view of long life of electrons or holes (carriers). And it was confirmed that the resin-bonded wire saw obtained by the present invention contributed to reduce the number of processes before the cell process and increase the power generation efficiency by 0.12% to 0.15% from a point that there were few damaged layers (affected flow layers).

[0067] Table 4 shows measuring results of bending strengths of three points of wafers having been cut by cutting (A1), cutting (A2), and cutting (B) on the similar conditions to the cutting conditions in table 2. It should be noted that an ingot of a monocrystal silicon as a silicon ingot and cutting directions of measured samples were overlapped to cross each other.

Measuring conditions

Sample: Five-ply of wafers

Bending span length: 30 mm

Crosshead speed: 5 mm/min

[0068] [Table 4]

Sample	Bending strength (MPa)
A1	58
A2	58
B	52

[0069] As shown in table 4, when the resin-bonded wire saw (a1) and the resin-bonded wire saw (a2) are used, it is possible to obtain wafers each having a higher bending strength than the wafers obtained by the cutting using the electrodeposition method and the cutting using the free abrasive grain method.

INDUSTRIAL APPLICABILITY

[0070] The resin-bonded wire saw obtained by the present invention is an essential tool for effectively cutting wafers to be used for substrates for a thin film transistor, substrates for solar cells, and compound semiconductor substrates or the like from monocrystal or multi-crystal ingots such as silicon, gallium arsenide, copper-indium-selenium (CIS). Further, the resin-bonded wire saw obtained by the present invention is an essential tool for effectively cutting wafers to be used for substrates for optical equipment and substrates for electronic apparatuses from magnetic materials, crystals, glass, and sapphire and the like.

CLAIMS

1. An adhesive composition for a resin-bonded wire saw to be used for producing a resin-bonded wire saw, in which abrasive grains are fixed to a surface of a metal core wire by means of a resin bond, the adhesive composition for a resin-bonded wire saw including essential components, comprising:

100 parts by weight of a novolak-type phenol resin;

10 to 30 parts by weight of a resol-type phenol resin;

and

0.1 to 5 parts by weight of an amine-based silane coupling agent.

2. The adhesive composition for a resin-bonded wire saw according to claim 1, further comprises 5 to 20 parts by weight of a novolak-type phenol resin curing agent.

3. A paste for a resin-bonded wire saw, comprising:
the adhesive composition according to claim 1 or claim 2;

a solvent for the adhesive composition;

abrasive grains; and

a filler made of inorganic particles.

4. A method for producing a resin-bonded wire saw, comprising the steps of:

preparing the paste according to claim 3 and a metal core wire;
applying the paste to a surface of the metal core wire; and
heating the applied paste by infrared rays including near-infrared rays to cause the adhesive composition to produce a cross-linking reaction.

5. The method for producing a resin-bonded wire saw according to claim 4, further comprising the steps of:
winding up a wire obtained in the heating step to obtain a winding body; and
re-heating the winding body.

ADHESIVE COMPOSITION FOR RESIN-BONDED WIRE SAW AND
METHOD FOR PRODUCING RESIN-BONDED WIRE SAW

ABSTRACT

There are provided an adhesive composition to be used for producing a resin-bonded wire saw, in which abrasive grains are fixed to a surface of a metal core wire, which includes essential components: 100 parts by weight of a novolak-type phenol resin; 10 to 30 parts by weight of a resol-type phenol resin; and 0.1 to 5 parts by weight of an amine-based silane coupling agent and a method for producing the resin-bonded wire saw which includes the steps of: applying a paste including the adhesive composition, the abrasive grains, and a solvent for dissolving the adhesive composition to a surface of the metal core wire; and heating the applied paste by infrared rays including near-infrared rays to cause the adhesive composition to produce a cross-linking reaction.

[Selected drawing] FIG. 4