

Adhesive Sheet suitable for use in the
Preparation of Semiconductor Chips

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FIELD OF THE INVENTION

This invention relates to adhesive sheets and, more particularly, to adhesive sheets which are preferably used in dicing semiconductor wafers into chips.

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BACKGROUND OF THE INVENTION

Semiconductor wafers of silicon, gallium-arsenic, etc., are normally relatively large in diameter when produced, and the wafers are diced into chips, which are then transferred to the subsequent mounting stage. At this time, the semiconductor wafers are subjected, while still applied to the adhesive layer of an adhesive sheet, to such stages as dicing, rinsing, drying, expanding, picking-up and mounting.

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Adhesive sheets which have heretofore been used in the dicing stage of semiconductor wafer manufacture as mentioned above include those which comprise a substrate such as a vinyl chloride or polypropylene film or sheet and thereon an adhesive layer consisting essentially of an adhesive such as an acrylic adhesive or the like. In the adhesive sheets having an acrylic adhesive layer, however, there was involved such a problem that the chips were contaminated on the back side surface thereof with the adhesive which had adhered to and remained thereon.

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In order to solve the problem mentioned above, there has been proposed a process wherein the adhesive applied to the surface of an adhesive sheet is minimized by coating a substrate of the adhesive sheet, not wholly but partly, with the adhesive. According to this

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process, however, there is brought about such a new problem that because of a decrease in adhesion strength between wafer chips and adhesive sheet, the wafer chips peel off from the adhesive sheet during stages

5 subsequent to the dicing stage, such as rinsing, drying and expanding, though the amount of the adhesive used relative to the full number of the chips decreases and thereby lessens contamination of the back side surface of the chips with the adhesive to a certain extent.

10 Adhesive sheets which are intended for use in the processing stage of semiconductor wafer manufacture, from the dicing stage up to pick-up stage, are desired to be such that the adhesive sheets have an adhesion force sufficient to retain wafer chips thereon in the
15 course of the dicing stage up to the expanding stage, but in the pick-up stage they only retain their adhesion force to such an extent that no adhesive sticks to the back side surface of picked-up wafer chips.

International patent application PCT/US80/00822
20 discloses normally tacky and pressure-sensitive adhesives including oxirane rings and an ionic photoinitiator characterized in that the epoxy equivalent value of the adhesive is 400-900, and the ionic photoinitiator is selected from the group
25 consisting of radiation-sensitive aromatic onium salts of Group Va or VIa, onium catalysts of Group Va, VI or VIIa, diaryl halonium salts containing Group Va metal hexafluorides and triaryl sulfonium complex salts, said photoinitiator being present in an amount effective to
30 promote the polymerization of oxirane rings, whereby said adhesive is readily detackified by exposure to actinic radiation.

Further Japanese Patent Laid-Open Publications Nos.196956/1985 and 223139/1985 disclose adhesive sheets
35 which are alleged to satisfy the above-mentioned requirements, said adhesive sheets comprising a substrate having coated on the surface thereof an

adhesive consisting essentially of a low molecular compound having in the molecule at least two photopolymerizable carbon-carbon double bonds and being capable of exhibiting a three-dimensional network on irradiation with light. The low molecular compounds having in the molecule at least two photopolymerizable carbon-carbon double bonds as exemplified in the above-mentioned publications include trimethylolpropane triacrylate, tetramethylolmethane tetraacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol monohydroxy pentaacrylate, dipentaerythritol hexaacrylate, 1,4-butyleneglycol diacrylate, 1,6-hexanediol diacrylate, polyethylene glycol diacrylate, commercially available oligoester acrylates, etc.

We have found that the adhesive sheets comprising a substrate having coated thereon an adhesive layer consisting essentially of such low molecular compounds having in the molecule at least two photopolymerizable carbon-carbon double bonds as exemplified above involve problems as mentioned below.

(1) Such an adhesive sheet as mentioned above can exhibit an excellent performance to a certain extent when a semiconductor wafer to be applied to the adhesive sheet has a fine and smooth surface like a mirror surface. If the wafer surface is rough, however, there is observed such a problem that even when irradiation with such radiation as ultraviolet is effected in the pick-up stage, the adhesion strength between the wafer chips and adhesive sheet does not decrease sufficiently and accordingly the adhesive sticks to and remains on the back side surface of the chips.

(2) Where a semiconductor wafer applied onto the adhesive layer of an adhesive sheet is diced into wafer chips and the diced chips are then picked up, the position of the chip has been detected by means of a photosensor. In the above-mentioned adhesive sheet,

however, there is observed such a problem that because the adhesive sheet reflects the detection beam at the chip's position, the detection operation of the chip cannot be performed with satisfactory accuracy and a failure in the detection operation sometimes occurs.

(3) Where the wafer surface to which the adhesive layer of an adhesive sheet is applied is greyed or blackened for some reason or other, there is involved such a problem that even when the adhesive sheet is irradiated with radiation such as ultraviolet in the pick-up stage of the semiconductor wafer chips, the adhesion force of the portions of the adhesive layer of the adhesive sheet corresponding to the portions of the greyed or blackened portions of wafer does not decrease sufficiently and accordingly the adhesive adheres to and remains on the back side surface of wafer chips.

(4) In the adhesive sheet as mentioned above, there is observed such a problem that the adhesive force certainly decreases but not to the optimum level, thus the larger is the size of chips, the more difficult becomes the pick-up operation.

(5) In the above-mentioned adhesive sheets, there is observed such a problem that because a general-purpose polymer sheet, such as of polyvinyl chloride or polypropylene, is used as a substrate sheet in said adhesive sheets, a tensile force is applied to said adhesive sheets when wafers are applied onto said adhesive sheets or when the thus applied wafers are diced into chips, and the substrate sheet undergoes elongation after the completion of the dicing stage of the wafers, whereby a deflection occurs in the adhesive sheets and the thus deflected adhesive sheets cannot be received by a wafer box for transfer to the subsequent processing operation or the received wafers mutually contact with one another in the wafer box. Furthermore, there is also observed such a problem that when the adhesive sheets, after the completion of the dicing

operation of the wafers applied onto said adhesive sheets, are subjected to irradiation with radiation such as ultraviolet, an elongation or deflection occurs afresh in the irradiated adhesive sheets, or such elongation or deflection which has occurred in the adhesive sheets in the dicing stage of the wafers as mentioned previously is sometimes retained in the irradiated adhesive sheets, and hence said irradiated adhesive sheets cannot be received by a wafer box for transfer to the subsequent pick-up stage, or the received wafers mutually contact with one another in the wafer box.

OBJECTS OF THE INVENTION

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The present invention is intended to solve such technical problems associated with the prior art as mentioned above and its objects are as in the following.

A first object of the invention is to provide adhesive sheets which are suitable for use in semiconductor wafer dicing operations, said adhesive sheets being such that even if the wafer surface to be applied onto an adhesive layer of the adhesive sheets is rough, the adhesion force of the adhesive layer sufficiently decreases when the adhesive sheets are subjected in the pick-up stage of semiconductor wafer chip manufacture to irradiation with such radiation as ultraviolet and accordingly no adhesive sticks to and remains on the back side surface of wafer chips as picked up.

A second object of the invention is to provide adhesive sheets which are suitable for use in semiconductor wafer dicing operations, said adhesive sheets being such that when wafer chips are picked up from the adhesive sheets, the detection of the chips by means of a photosensor can be performed with satisfactory accuracy and accordingly no failure in

operation for positioning the wafer chips occurs, moreover, the adhesive layer of the adhesive sheets has a sufficient adhesive force before ultraviolet irradiation of the adhesive sheets but retains a sufficiently decreased adhesion force after the irradiation such that no adhesive sticks to the back side surface of the wafer and, furthermore, an operator supervising the dicing operation can easily ascertain whether or not the adhesive sheets have been irradiated, thereby preventing possible troubles in operation before they happen.

A third object of the invention is to provide adhesive sheets which are suitable for use in semiconductor wafer dicing operations, said adhesive sheets being such that even when the wafer surface to which an adhesive layer of the adhesive sheets is applied is greyed or blackened for some reason or other, the adhesion force of the adhesive layer at the portions thereof corresponding to the greyed or blackened portions of the wafers sufficiently decreases in the pick-up stage of semiconductor wafer chip manufacture where the adhesive sheets are subjected to irradiation with radiation such as ultraviolet and accordingly no adhesive sticks to and remains on the wafer chip surface and, moreover, said adhesive layer has a sufficient adhesion force before the ultraviolet irradiation of the adhesive sheets.

A fourth object of the invention is to provide adhesive sheets which are such that in the wafer dicing stage, no elongation or deflection occurs in a substrate sheet of the adhesive sheets onto which the wafers have been applied, no elongation or deflection occurs afresh in the adhesive sheets having the diced wafer chips thereon even when said adhesive sheets are irradiated and, moreover, even when a slight elongation or slight deflection occurs in the substrate sheet in the dicing stage, said deflection disappears by virtue of passing

the adhesive sheets through the irradiation operation and the resulting adhesive sheets can be received with accuracy by a receiving box.

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SUMMARY OF THE INVENTION

The adhesive sheets of the present invention comprise a substrate having coated on the surface thereof an adhesive layer which layer comprises an acrylate or methacrylate polymer-based adhesive and a radiation polymerizable compound, said radiation polymerizable compound being a urethane acrylate oligomer having a molecular weight of 3,000-10,000, preferably 4,000-8,000.

15 A further feature of the adhesive sheets of the invention is that they may contain a radiation color developable compound, whereby the radiation color developable compound may be incorporated in the adhesive layer, or the substrate may be coated at least on one side thereof with the radiation color developable compound, or the radiation color developable compound may be incorporated in the substrate.

20 Another feature of the adhesive sheets of the invention is that they may contain a light scattering inorganic powder compound incorporated in the adhesive layer.

25 A still further feature of the adhesive sheets of the invention is that the substrate may be a crosslinked film.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 2 are sectional views of the adhesive sheets of the present invention, and Figs. 3-6 are illustrations showing said adhesive sheets used in the course of semiconductor wafer manufacture from the dicing stage up to the pick-up stage of diced wafers. Fig. 7

is an illustration showing said adhesive sheet used in the course of masking for coated products.

DETAILED DESCRIPTION OF THE INVENTION

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The adhesive sheets of the present invention are illustrated below in detail with reference to the accompanying drawings.

10 As can be seen from its sectional view shown in Fig. 1, the present adhesive sheet is composed of a substrate 2 and an adhesive layer 3. Before use of this adhesive sheet, it is preferable to tentatively apply a strippable sheet 4 as shown in Fig. 2 in order to protect the adhesive layer 3.

15 The present adhesive sheet may be shaped into any forms such as a tape-like, label-like or other form. Suitable as the substrate 2 are materials which are low in electrical conductivity and excellent in water resistance as well as in heat resistance, and on this
20 view, synthetic resin films are particularly useful. As will be stated later, the present adhesive sheet is, when used, irradiated with such radiation as EB or UV, and hence the substrate 2 is not required to be transparent when said adhesive sheet is subjected to EB
25 irradiation but must be transparent when said adhesive sheet is subjected to UV irradiation.

Practically speaking, usable as the substrate 2 are films of such synthetic resins as polyethylene, polypropylene, polyvinyl chloride, polyethylene
30 terephthalate, polybutylene terephthalate, polybutene, polybutadiene, polyurethane, polymethyl pentene, ethylene vinyl acetate, etc.

Where the present adhesive sheet requires, after the dicing of semiconductor wafers, an expansion
35 treatment, it is preferable to use as a substrate in the conventional manner a synthetic resin film of polyvinyl chloride, polypropylene or the like which has

extensibility in the machine and cross machine directions. However, any substrates having no extensibility are also usable in the case of the treatment processing of semiconductors, automobile body masking or the like where no such expanding treatment is needed.

When a crosslinked film is used, particularly as the substrate 2, there are obtained such great advantages that no extension or deflection occurs in the adhesive sheet having wafers thereon when the wafers are diced, no deflection occurs afresh in the adhesive sheet when said adhesive sheet is irradiated with radiation and moreover, even when a slight deflection occurs in the adhesive sheet in the wafer dicing stage, said slight deflection diminishes on irradiation of the substrate sheet with radiation and accordingly the adhesive sheet bearing the diced wafers thereon can assuredly be received by a receiving box wherein no mutual contact of the adhesive sheets is observed. Moreover, when the diced wafer chips are picked up after irradiation, the substrate sheet sufficiently extends at the time of expanding, and hence the wafer chips can be picked up with accuracy.

The crosslinked films which are preferably used, particularly as the substrate in the present invention are those which have been obtained by irradiating synthetic resin films having crosslinking sites with radiation or those which have been obtained by incorporating crosslinking-reaction-initiators into starting polymers which are then chemically crosslinked. Usable as the crosslinked films as mentioned above are films of crosslinked polyolefin, crosslinked polydiene, crosslinked ethylene-vinyl acetate copolymers or crosslinked polyolefin-polydiene copolymers.

Such crosslinked films used as the substrates in the present invention are subjected to expanding treatment at the time when diced wafer chips are picked

up, and these films have extensibility sufficient to meet the expanding treatment, whereby the wafer chips can be picked up with accuracy.

In addition synthetic resin films having a carboxyl group-containing monomer as a principal constituent monomer unit are preferably used as the substrate 2. Such synthetic resin films having a carboxyl group-containing monomer as a principal constituent monomer unit include ethylene (meth)acrylic acid copolymer and ethylene-vinyl acetate- (meth)acrylic acid copolymer. In addition, a laminate film comprising a synthetic resin film having a carboxyl group-containing monomer as a principal constituent monomer unit and a general synthetic resin film such as polyethylene, ethylene-vinyl acetate copolymer, polypropylene, polybutene, polybutadiene, polyvinylchloride, polyurethane, polymethyl pentene may be used.

On the substrate 2 as illustrated above is provided the adhesive layer 3 which is composed of an adhesive and a radiation polymerizable compound.

Acrylic and methacrylic adhesive are used as the adhesives in the present invention, and contain acrylic and methacrylic polymers conveniently selected from homopolymers and copolymers comprising acrylic esters as principal constitutive monomer units, copolymers of acrylic esters and other functional monomers, and mixtures thereof. The preferred polymers are those containing, as acrylic ester monomers, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate, 2-hydroxyethyl methacrylate, etc., and the above-mentioned monomers containing acrylic acid esters instead of methacrylic acid esters are also preferred.

Furthermore, in order to enhance miscibility with the oligomers which will be mentioned later, the above-mentioned polymers may be those obtained by copolymerization of such monomers as (meth)acrylic acid,

acrylonitrile and vinyl acetate. The above-mentioned (meth)acrylic type polymers used as the adhesives in the present invention conveniently have a molecular weight of up to 10.0×10^5 , preferably 4.0×10^5 to 8.0×10^5 .

5 In the present invention urethane acrylate oligomers are used as the radiation polymerizable compound. The molecular weight of the urethane acrylate oligomer is 3,000-10,000, preferably 4,000-8,000. The molecular weight referred to above is a value as an
10 average molecular weight of polystyrene as measured by gel permeation chromatography (GPC).

The urethane acrylate oligomers are obtained by reacting terminal isocyanate urethane prepolymers obtained by the reaction of polyester or polyether type
15 polyol compounds with polyvalent isocyanate compounds, for example, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,4-xylylene diisocyanate and diphenylmethane 4,4'-diisocyanate, with (meth)acrylates having hydroxyl groups, for example, 2-hydroxyethyl
20 (meth)acrylate, 2-hydroxypropyl (meth)acrylate, polyethylene glycol (meth)acrylate, etc. The urethane acrylate oligomers as obtained above are radiation polymerizable compounds having in the molecule at least one carbon-carbon double bond.

25 It is not preferable to use the urethane acrylate oligomers having a molecular weight of less than 3000. This is because, though no serious problem is brought about when semiconductor wafers used have a fine or smooth surface, when the wafers have a rough surface,
30 the adhesion strength between the wafer chips and adhesive sheet does not decrease sufficiently even when the adhesive sheet is irradiated with radiation and the adhesive sometimes adheres to and remains on the back side surface of the wafer chips when they are picked up.
35 The fact that when the urethane acrylate oligomer having a molecular weight of less than 3000 is used the adhesive adheres to the back side surface of wafer chips

when the wafer has a rough surface is considered ascribable to the following reason. That is, the rough surface of the wafer means that a large number of fine grooves are present on the wafer surface, and when the urethane acrylate oligomer is brought into contact with the rough surface of the wafer, said oligomer intrudes into these fine grooves if said oligomer is low in molecular weight. On that account, it is considered that even when such oligomer is sufficiently cured by irradiation with radiation, the adhesion strength is kept at a high level by the anchoring effect of the adhesive and accordingly the adhesive adheres to and remains on the back side surface of wafer chips when the chips are picked up.

Thus, we found first the above-mentioned problem concerning the molecular weight of urethane acrylate oligomers, and it is almost a truism to say that all compounds concretely disclosed, for example, in the aforementioned Japanese Patent Laid-Open Publications Nos. 196956/1985 or No. 223139/1985, as the low molecular compounds having in the molecule at least two photopolymerizable carbon-carbon double bonds have a molecular weight of less than about 1500. The fact that these compounds low in molecular weight have heretofore been used is considered accountable for poor coatability of the compounds having excessively high molecular weights or deterioration in the surface gloss of coatings formed from such high molecular compounds.

In this connection, the urethane acrylate oligomers used in the present invention possess markedly excellent properties, as compared with low molecular compounds having in the molecule at least two photopolymerizable carbon-carbon double bonds as disclosed in Japanese Patent Laid-Open Publications Nos. 196956/1985 and 223139/1985. For instance, adhesive sheets prepared by the use of the present urethane acrylate oligomers show that the adhesive layer of the thus prepared adhesive

1 sheets has a sufficient adhesion force before
irradiation of said sheets with radiation but after the
irradiation the adhesion force decreases to such a level
that the adhesive does not adhere and hence the chips
5 can simply be picked up. In contrast thereto, adhesive
sheets prepared by the use of dipentaerythritol
monohydroxy pentaacrylate as disclosed in the examples
of Japanese Patent Laid-Open Publication No. 196956/1985
show that the adhesive layer of the thus prepared
10 adhesive sheets exhibits a sufficient adhesion force
before irradiation of said sheets with radiation but
does not decrease in adhesion force sufficiently even
after irradiation and the adhesive adheres to and
remains on the back side surface of wafer chips when the
15 chips are picked up.

In the adhesive layer of the adhesive sheet in
accordance with the present invention, the acrylic
adhesive and the urethane acrylate oligomer are used
preferably in the proportion of 100 to 50-900 parts by
20 weight. In that case, the adhesive sheet obtained is
high in initial adhesion force and, moreover, the
initial adhesion force greatly decreases after
irradiation of said sheet with radiation and hence the
wafer chips can readily be picked up from the adhesive
25 sheet.

In another embodiment of the adhesive sheet of the
present invention, the adhesive layer 3 contains therein
a radiation colour developable compound in addition to
the acrylic adhesive and radiation polymerizable
30 compound mentioned above, or the substrate 2 of the
above-mentioned adhesive sheet is coated at least on one
side thereof with a radiation colour developable layer
containing a radiation colour developable compound.
Under certain circumstances, a radiation colour
35 developable compound may be incorporated in the
substrate 2.

The radiation colour developable layer containing the radiation colour developable compound may be formed on the side of the substrate 2 on which the adhesive layer 3 is not formed, or may be formed between the substrate 2 and the adhesive layer 3.

The radiation colour developable compounds used in the present invention are compounds which are colourless or pale-coloured before irradiation but develop colour on irradiation with radiation, and preferred examples of such compounds are leuco dyes. Preferably usable as the leuco dyes are those which are conventionally used compounds such as triphenyl methane, fluoran, phenothiazine, Auramine, and spiropyrane compounds. These compounds include, for example, 3-[N-(p-tolylamino)]-7-anilinofluoran, 3-[N-(p-tolyl)-N-methylamino]-7-anilinofluoran, 3-[N-(p-tolyl)-N-ethylamino]-7-anilinofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, crystal violet lactone, 4,4',4"-trisdimethylaminotriphenyl methanol, 4,4',4"-trisdimethylaminotriphenyl methane, etc.

Developers preferably usable in combination with the above-mentioned leuco dyes are those which have heretofore conventionally been used, such as initial polycondensation products of phenol-formalin resins, aromatic carboxylic acid derivatives and electron

acceptors such as activated clay, and further when the developed colour is intended to vary in colour tone, various known colour formers can also be used in combination therewith.

5 The radiation colour developable layer containing the radiation colour developable compound mentioned above can be formed at least on one side of the substrate 2 by coating a solution of said compound in an organic solvent either on one side or both sides of the
10 substrate 2.

 The radiation colour developable layer may be formed by incorporating the radiation colour developable compound in a subbing composition and then coating the subbing composition at least on one side of the
15 substrate 2. Though suitably selected according to the type of the substrate 2 used, the subbing compositions mentioned above include those consisting essentially of vinyl acetate-vinyl chloride copolymers, polyurethane resins, polyester resins, polyamide resins or epoxy
20 resins.

 In another aspect, the above-mentioned solution of the radiation colour developable compound in an organic solvent may be incorporated in the substrate 2 by using said solution at the time when the material for the
25 substrate 2 is formed into a sheet-like product. Under certain circumstances, the radiation colour developable compound may also be incorporated in the form of fine powder into the substrate 2.

 By virtue of incorporating the radiation colour
30 developable compound into the adhesive layer 3, or coating said compound at least on one side of the substrate 2, or by incorporating said compound into the substrate 2 in the manner now described, the adhesive sheet 1 is sufficiently coloured on irradiation with
35 radiation, whereby the detection accuracy is enhanced at the time of detecting wafer chips by means of a photosensor and a possible failure in the operation to

pick up the wafer chips from the adhesive sheet 1 is prevented.

By coating the radiation colour developable compound at least on one side of the substrate 2, there is also obtained such an advantage that in comparison with the case of incorporation in the adhesive layer 3 of said compound, there is no possibility of exerting an adverse effect on the expected decrease in adhesion force of the adhesive layer 3 by irradiation with radiation.

In another embodiment of the adhesive sheet of the present invention, the adhesive layer 3 preferably contains therein powder of a light scattering inorganic compound in addition to the adhesive and the radiation polymerizable compound.

The light scattering inorganic compounds being referred to above are such compounds as are capable of irregular reflection of ultraviolet (UV) or electron beam (EB) radiation, which concretely include, for example, silica powder, alumina powder, silica alumina powder or mica powder. The light scattering inorganic compounds are preferably those which reflect such radiation as mentioned above almost perfectly, but those which absorb the radiation to a certain extent are of course usable.

Preferably, the light scattering inorganic compounds are in the form of powder and have a particle diameter of 1-100 μm , preferably about 1-20 μm . In the adhesive layer, this light scattering inorganic compound is desirably used in an amount of 0.1-10%, preferably 1-4% by weight. The use of this light scattering inorganic compound in an amount exceeding 10% by weight is not preferable since the compound may then sometimes reduce the adhesion force and, on the other hand, the

use of said compound in an amount less than 1% by weight is also not preferable since the adhesive layer does not sufficiently lower the adhesion force even when radiation is applied to the portions of the adhesive layer corresponding to the greyed or blackened portions of the semiconductor wafer surface, if any, and the adhesive adheres to and remains on the wafer chip surface when the chips are picked up from the adhesive sheet.

Even when semiconductor wafers having the surface greyed or blackened for some reason or other are applied to adhesive sheets having an adhesive layer containing a powder of the above-mentioned light scattering inorganic polymerizable compound, the adhesion force of this adhesive layer sufficiently decreases even at the portions corresponding to the greyed or blackened portions of the wafer surface when irradiated with radiation, and the reason for this is considered to be probably found in the following discussion. That is, the adhesive sheet 1 of the present invention has thereon the adhesive layer 3, and when this adhesive layer 3 is irradiated with radiation, the radiation polymerizable compound contained in the adhesive layer 3 comes to cure and this adhesive layer 3 decreases in adhesion force. In that case, however, the semiconductor wafers to be applied to the adhesive layer 3 have sometimes on the surface thereof portions greyed or blackened for some reason or other. In that case, when the adhesive layer is irradiated with radiation, the radiation passes through the adhesion layer to reach the wafer surface, however, if the wafers have greyed or blackened portions, the radiation is absorbed by said portions and does not reflect. On that account, it follows that the radiation which is to be utilized to cure the adhesive layer 3 is absorbed by the portions corresponding to the greyed or blackened portions of the

wafer surface, and this adhesive layer 3 does not cure sufficiently and does not sufficiently decrease in adhesion force. Accordingly, it is considered that the adhesive adheres to and remains on the back side surface of wafer chips when the chips are picked up from the adhesive sheet.

When powder of the light scattering inorganic compound is incorporated into the adhesive layer 3, however, the radiation as irradiated comes into irregular reflection and is altered in its direction before reaching the wafer surface. On that account, even if greyed or blackened portions are present in the wafer chip surface, the irregularly reflected radiation sufficiently permeates into the upper region of the portions of the adhesive layer corresponding to said greyed or blackened portions and accordingly the corresponding portions of the adhesive layer cure sufficiently. By virtue of incorporating the light scattering inorganic compound powder into the adhesive layer, even when portions greyed or blackened for some reason or other are present in the semiconductor wafer surface, the adhesive layer does not cure insufficiently at its portions corresponding to the greyed or blackened portions of the wafer chip surface and accordingly the adhesive will not adhere to and remain on the chip surface when the chips are picked up from the adhesive sheet.

Furthermore, the initial adhesive force of the above-mentioned adhesive layer can be altered to any desired level by incorporating an isocyanate type hardener into said adhesive layer. Usable as the isocyanate type hardeners in the above case are polyvalent isocyanate compounds, for example, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 3-methyl-diphenylmethane

diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, dicyclohexyl-methane-4,4'-diisocyanate, dicyclohexylmethane-2,4'-diisocyanate and lysine isocyanate.

5 Furthermore, the above-mentioned adhesive layer may be incorporated with a UV curing initiator when said layer is subjected to UV irradiation, thereby shortening the polymerization curing time by U.V. irradiation and minimizing the amount of UV irradiation.

10 Concrete examples of such U.V. curing initiators include, for example, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzyl diphenyl sulfide, tetramethylthiuram monosulfide, azobisisobutyronitrile, dibenzyl, diacetyl, β -
15 chloroanthraquinone, etc.

The adhesive sheet of the present invention is illustrated below with respect to the method of use thereof (reference numbers refer to the accompanying drawings).

20 Where the strippable sheet 4 is provided on the adhesive sheet 1, said sheet 4 is first removed and the adhesive sheet 1 is placed, turning the adhesive layer 3 upward. On the face side of this adhesive layer 3 is applied the semiconductor wafer A to be subjected later
25 to dicing. The wafer A is subjected in this state to such processing operations as dicing, rinsing, drying and expanding. In that case, the wafer chips will not fall off from the adhesive sheet 1 during each operation because the wafer chips are sufficiently attached to and
30 held on the adhesive sheet 1 by means of the adhesive layer 3.

Subsequently, the wafer chips are picked up from the adhesive sheet 1 and mounted on a given support substrate. In that case, before the pick-up operation
35 or at the time when the pick-up operation is carried out, the adhesive layer 3 of the adhesive sheet 1 is irradiated with an electrodisassociative radiation such as

ultraviolet light (UV) or an electron beam (EB) to cure the radiation polymerizable compound contained in the adhesive layer 3. When the radiation polymerizable compound contained in the adhesive layer 3 is

5 polymerized to cure by irradiating the adhesive layer 3 with radiation, the adhesion force of the adhesive contained in the adhesive layer 3 greatly decreases, leaving only a slight adhesion force.

The irradiation to the adhesive sheet 1 is
10 preferably effected from the side of the substrate 2 on which the adhesive layer 3 is not formed. Accordingly, as mentioned previously, the substrate 2 must be light transmittable when UV is used but the substrate 2 need not always be light transmittable when EB is used.

15 In the manner now described, the portions of the adhesive layer 3 on which the wafer chips A_1 , A_2 ... are provided is irradiated with radiation B to lower the adhesion force of the adhesive layer 3. Thereafter, the adhesive sheet 1 having this adhesive layer 3 is
20 transferred to a pick-up station (not shown) wherein the chip A_1 ... is pushed up according to the usual way from the back side of the substrate 2 by means of a pushing rod 5, and the pushed-up wafer chips A_1 , A_2 ...
... are picked up by picking up means 6, for example by
25 means of an air pincette, and are mounted on a given support substrate. By picking up the wafer chips A_1 , A_2 ...
... in this manner, all the wafer chips can be simply picked up without any adhesion of the adhesive to the back side surface of every wafer chip, thereby
30 obtaining chips of good quality free from contamination. Furthermore, the irradiation may be effected in the pick up station, as well.

The irradiation need not always be to effected at once on the whole surface of the wafer A, and may be
35 effected partially in several times; for instance, only the portion of the substrate 2 corresponding to each of the wafer chips A_1 , A_2 ... is irradiated from the

back side of the substrate 2 by means of an irradiating tube to lower the adhesion force of the adhesive corresponding to the irradiated portion of the substrate 2, and thereafter the wafer chips A_1 , A_2 ... are pushed up by means of the pushing rod 5 and then the pushed-up chips are successively picked up from the adhesive sheet 1. Fig. 6 shows a modification of the above-mentioned irradiation method, wherein the pushing rod 5 is made hollow in the interior thereof and a radiation source 7 is provided in the hollow portion of the pushing rod 5 so that the irradiation and pick up operations can be effected at the same time, thus the apparatus can be simplified and, at the same time, the time necessary for the pick-up operation can be shortened.

In the above-mentioned treatment of semiconductor wafers, the wafer chips A_1 , A_2 ... may be subjected to pick-up treatment immediately after dicing, rinsing, and drying without effecting an expanding operation.

The adhesive sheet 1 of the present invention is preferably used in the processing of semiconductor wafer, from dicing operation up to pick-up operation, as illustrated hereinbefore. This adhesive sheet 1 may also be used in masking an object to be coated with coating materials. As shown in Fig. 7, in the case of an object 8 to be coated, for example, an automobile body, onto the surface 9 not to be coated with a coating material is applied the adhesive sheet 1 of the present invention, and a coating 10 is formed on the object 8 to be coated, as it is. Thereafter, the adhesive sheet 1 is irradiated from upside with radiation B to lower the adhesion force of said adhesive sheet 1, followed by peeling off the irradiated adhesive sheet 1 from the object 8 to be coated. In this way, there is obtained such an excellent effect that no adhesive will remain on or deposit on the surface of the object 8 to be coated.

The present invention is illustrated below by means

of examples, but it should be construed that the invention is in no way limited to those examples. Parts are given by weight.

5 Example 1

 An adhesive layer forming composition was prepared from a mixture comprising 100 parts of an acrylic adhesive (a copolymer of n-butyl acrylate and 2-ethylhexyl acrylate), 100 parts of a urethane acrylate oligomer having a molecular weight of about 7000 (a product of Dainich Seika Kogyo, K.K., sold under the trade name SEIKABEAM PU-4), 10 parts of a hardener (a diisocyanate type hardener) and 4 parts of a UV curing initiator (a benzophenone type initiator).

15 The composition thus prepared was coated on one side of a polypropylene film substrate of 80 μm in thickness in such a manner that an adhesive layer to be formed thereon may have a thickness of 10 μm , and the thus coated substrate was then heated at 100°C for 1 minute to prepare an adhesive sheet.

 Onto the adhesive layer surface of the adhesive sheet thus obtained was applied a silicon wafer having a fairly rough surface of $R_a=0.27$ as measured in the manner as will be explained below, and the adhesion strength between the wafer and adhesive sheet was measured according to JIS-Z-0237 (180° Peeling Method, 300 mm/min peeling speed, 25 mm wide test specimen, measurement in a chamber at 23°C and 65% RH) whereupon the adhesion strength as measured was 410 g/25 mm.

25 Surface roughness of the silicon wafer was represented in terms of a centerline average roughness R_a (μm) according to JIS B0601-1976, and the measurement thereof was conducted using "Universal Surface Profile Tester" Model SE-3A manufactured and sold by K.K. Kosaka Seisakusho.

30 Subsequently, the adhesive layer of this adhesive sheet was irradiated during second with ultraviolet ray

(UV) from an air-cooling high pressure mercury lamp (80 W/cm, irradiation distance 10 cm). After the irradiation, the adhesion strength between the silicon wafer and this adhesive sheet was measured, whereupon the adhesion strength as measured decreased to 24 g/25 mm.

So far as a visual inspection was conducted, there was not observed at all any adhesive which had adhered to and remained on the back side surface of the silicon wafer peeled after the irradiation from the adhesive sheet.

The silicon wafer applied onto the adhesive layer of this adhesive sheet was diced into chips of 5 mm square and, after the UV irradiation, the chips were then picked up, whereupon 100 chips out of 100 chips were picked up.

Example 2

An adhesive layer forming composition was prepared from a mixture comprising 100 parts of an acrylic adhesive (a copolymer of 2-ethylhexyl acrylate and acrylonitrile), 200 parts of a urethane acrylate oligomer having a molecular weight of about 7000 (a product of Dainichi Seika Kogyo K.K. sold under the trade name SEIKABEAM PU-4), 10 parts of a hardener (a diisocyanate type hardener) and 4 parts of a UV curing initiator (a benzophenone type initiator).

The composition thus prepared was coated on one side of a polypropylene film substrate of 80 μm in such a manner that an adhesive layer to be formed thereon may have a thickness of 10 μm , and the thus coated substrate was then heated at 100°C for 1 minute to prepare an adhesive sheet.

Onto the adhesive layer surface of the adhesive sheet thus obtained was applied a silicon wafer having a rough surface of $R_a=0.27$, and the adhesion strength between the wafer and adhesive sheet was measured before

and after UV irradiation in the same manner as in Example 1.

5 The adhesion strength as measured before the UV irradiation was 230 g/25mm, and after the UV irradiation was 21 g/25mm.

10 So far as a visual inspection was conducted, there was not observed at all any adhesive which had adhered to and remained on the back side surface of the silicon wafer peeled after the irradiation from the adhesive sheet.

15 The silicon wafer applied onto the adhesive layer of this adhesive sheet was diced after the UV irradiation into chips of 5 mm square, and the chips were then picked up, whereupon 100 chips out of 100 chips were picked up.

Comparative Example 1

20 An adhesive sheet was prepared in the same manner as in Example 2 except that in place of the urethane acrylate oligomer, 100 parts of pentaerythritol acrylate having a molecular weight of about 580 was used as a radiation polymerizable compound, and the adhesion strength between a silicon wafer of Ra=0.27 applied onto the adhesive layer surface of the thus prepared adhesive sheet and this adhesive sheet was measured before and after a UV irradiation.

25 The adhesion strength as measured before the UV irradiation was 700 g/25 mm, and after the UV irradiation was 100 g/25 mm.

30 The silicon wafer applied onto the adhesive layer surface of this adhesive sheet was diced after the UV irradiation into chips of 5 mm square, and the chips were then picked up, whereupon, even 1 chip out of 100 chips could not be picked up.

35

Example 3

Example 1 was repeated except that a silicon wafer

having a fine smooth surface of $Ra=0.04$ was used instead, and the adhesion strength between the wafer and adhesive sheet was measured in like manner before and after UV irradiation.

- 5 The adhesion strength as measured before the UV irradiation was 150 g/25 mm, and after the UV irradiation was 6 g/25mm.

Example 4

- 10 Example 2 was repeated except that a silicon wafer having a fine smooth surface of $Ra=0.04$ was used instead, and the adhesion strength between the wafer and adhesive sheet was measured in like manner before and after UV irradiation.

- 15 The adhesion strength as measured before the UV irradiation was 50 g/25 mm, and after the UV irradiation was 4 g/25mm.

Comparative Example 2

- 20 Comparative Example 1 was repeated except that a silicon wafer having a fine smooth surface of $Ra=0.04$ was used instead, and the adhesion strength between the wafer and adhesive sheet was measured in like manner before and after UV irradiation. The adhesive strength
25 as measured before the UV irradiation was 490 g/25 mm, and after the UV irradiation was 15g/25 mm.

- 30 There was observed the adhesive which had adhered to and remained on the back side surface of the silicon wafer peeled after the UV irradiation from the adhesive sheet.

Comparative Example 3

- 35 An adhesive layer forming composition was prepared from a mixture comprising 100 parts of an acrylic adhesive (a copolymer of n-butyl acrylate and 2-ethylhexyl acrylate), 100 parts of a urethane acrylate oligomer (a product of Dainichi Seika Kogyo K.K., sold

under a trade name of EX 808) having an average molecular weight of about 1100 which is estimated by the calibration curve using standard polystyrene molecular weight as measured by gel permeation chromatography (GPC), 10 parts of a hardener (a diisocyanate type hardener) and 4 parts of a UV curing initiator (a benzophenone type initiator).

An adhesive sheet was prepared using this composition in the same manner as in Example 1, the adhesion strength before and after UV irradiation between a silicon wafer having a fairly rough surface of $R_a=0.27$ and the adhesive sheet thus prepared was measured.

The adhesion strength as measured before the UV irradiation was 320 g/25 mm, and after the UV irradiation was 75 g/25 mm.

The silicon wafer applied onto the adhesive layer surface of this adhesive sheet was diced into chips of 5 mm square, and after the UV irradiation the chips were picked up, whereupon only 30 chips out of 100 chips were picked up.

Example 5

To 100 parts by weight of an undercoating composition comprising a vinyl acetate-vinyl chloride copolymer as a principal ingredient was added 5 parts by weight of 4,4',4"-trisdimethylaminophenylmethane as a UV irradiation colour developable leuco dye. The resulting undercoating composition was coated and dried on one side of a polyethylene terephthalate film substrate of 50 μm in thickness in such a manner that an undercoat layer to be formed thereon may have a dry thickness of 1-2 μm .

On the undercoat layer thus formed was coated an dried, a mixture comprising 100 parts by weight of an acrylic adhesive (a copolymer of n-butyl acrylate and acrylic acid), 100 parts by weight of a urethane

acrylate oligomer having a molecular weight of 3,000-10,000, 25 parts by weight of a hardener (a diisocyanate type hardener) and 10 parts by weight of a UV irradiation curing initiator (a benzophenone type initiator) so as to form an adhesive layer having a dry thickness of 10 μm , and the thus coated substrate was heated at 100°C for 1 minute to obtain an adhesive sheet of a triple layer structure according to the present invention.

10 The adhesive layer of the adhesive sheet thus obtained was irradiated for 2 seconds with ultraviolet radiation (UV) from an air-cooling high pressure mercury lamp (80W/cm, irradiation distance 10 cm). By virtue of the UV irradiation, the adhesive sheet which had been
15 transparent assumed a bluish purple colour. The colour difference $E(L^*a^*B^*)$ of the adhesive sheet at the time of UV irradiation was measured by means of an SM Color Computer (manufactured and sold by Suga Testers K.K.). whereupon the colour difference as measured was 21.6.

20 Furthermore, a silicon wafer applied onto the adhesive layer surface of this adhesive sheet was diced into wafer chips and then subjected to UV irradiation under the conditions mentioned above to effect detection of the wafer chips by means of a photo-sensor, whereupon
25 the wafer chips could easily be detected. The wafer chips were then picked up while using the photosensor, whereupon no error in the picking-up performance was observed at all.

30 Comparative Example 4

 An adhesive sheet was prepared in the same manner as in Example 5 except that an undercoat layer capable of coloration on UV irradiation was formed on the substrate, and the colour difference of the adhesive
35 sheet which is due to UV irradiation was measured. The colour difference $E(L^*a^*B^*)$ of the adhesive sheet as measured before and after the UV irradiation was less

than 2.0, thus no coloration due to the UV irradiation was observed.

Further, a silicon wafer applied onto the adhesive layer surface of this adhesive sheet was diced into
5 wafer chips and then subjected to UV irradiation to effect detection of the wafer chips by means of a photo-sensor, whereupon the detection could not be performed sufficiently in some cases.

Furthermore the wafer chips were picked up while
10 using the photosensor, whereupon error in the picking-up performance was observed in some cases.

Example 6

An adhesive layer forming composition was prepared
15 from a mixture comprising 100 parts of an acrylic adhesive (a copolymer of n-butyl acrylate and 2-ethylhexyl acrylate), 100 parts of a urethane acrylate oligomer having a molecular weight of about 7000 (a product of Dainichi Seika Kogyo K.K. sold under a trade
20 name of SEIKABEAM PU-4), 1 part of a hardener (a diisocyanate hardener) and 3 parts of a UV curing initiator (a benzophenone type initiator) said mixture additionally containing 2.5 parts of silica fine particles (produced and sold by Degsa Co., OK-412).

25 The composition thus prepared was coated on one side of a polypropylene film substrate of 80 μm in thickness in such a manner that an adhesive layer to be formed thereon may have a thickness 10 μm , and the thus coated substrate was heated at 100°C for 1 minute to
30 prepare an adhesive sheet.

Onto the adhesive layer surface of the adhesive sheet thus prepared was applied a black melamine plate, as an imaginary silicon wafer, having approximately the same diameter and thickness as in the silicon wafer, and
35 the adhesion strength between the melamine plate and adhesive sheet was measured according to JIS-Z-0237 (180° Peeling Method, peeling speed 300 mm/min, width of

the test specimen 25 mm, measurement in a chamber at 23°C and 65% RH), whereupon the adhesion strength as measured was 1500 g/25 mm.

Subsequently, the adhesive layer surface of this adhesive sheet was irradiated for 1 second with ultraviolet radiation (UV) from an air-cooling high pressure mercury lamp (80 W/cm, irradiation distance 10 cm). The adhesion strength between the black melamine plate and adhesive sheet was measured after the UV irradiation, whereupon the adhesion strength as measured decreased to 15-20 g/25 mm.

When the back side surface of the melamine plate peeled from the adhesive layer was visually inspected, there was not observed at all any adhesive which had adhered to and remained on said surface.

Comparative Example 5

An adhesive sheet was prepared in the same manner as in Example 6 except that no silica fine particles were incorporated in the adhesive layer forming composition, and the adhesion strength between the black melamine plate and adhesive sheet before and after UV irradiation was measured.

The adhesion strength as measured before the UV irradiation was 1,700 g/25mm, and after the UV irradiation was 500-1,000 g/25mm.

The back side surface of the black melamine plate peeled after the UV irradiation from the adhesive sheet retained large amounts of the adhesive which had adhered to and remained thereon.

Example 7

Example 6 was repeated except that a white melamine plate was used as an imaginary silicon wafer, and the adhesion strength between the white melamine plate and adhesive sheet before and after UV irradiation was measured in like manner.

The adhesion strength as measured before the UV irradiation was 1700 g/25 mm, and after the UV irradiation was 6 g/25 mm.

5 When visually inspected, no adhesive which had adhered to and remained on the back side surface of the melamine plate peeled after the UV irradiation from the adhesive sheet was observed at all.

Comparative Example 6

10 Comparative Example 5 was repeated except that a white melamine plate was used as an imaginary silicon wafer, and adhesion strength between the white melamine plate and adhesive sheet before and after UV irradiation was measured in like manner.

15 The adhesion strength as measured before the UV irradiation was 1700 g/25 mm in the same way as in Comparative Example 5, and after the UV irradiation was 9 g/25 mm.

Example 8

20 An adhesive layer forming composition was prepared from a mixture comprising 100 parts by weight of an acrylic adhesive (a copolymer of n-butyl acrylate and acrylic acid), 100 parts by weight of a urethane
25 acrylate oligomer having a molecular weight of 3,000-10,000, 25 parts by weight of a hardener (a diisocyanate type hardener) and 10 parts by weight of a UV curing initiator (a benzophenone type initiator).

30 The adhesive forming composition thus prepared was coated on one side of an electron radiation crosslinked polyethylene substrate of 50 μm in thickness in such a manner that an adhesive layer to be formed on the substrate may have a dry thickness of 10 μm , and the thus coated substrate was heated at 100°C for 1 minute
35 to prepare an adhesive sheet.

Onto the adhesive layer surface of the adhesive sheet thus obtained was applied a silicon wafer and

diced, thereafter the state of the adhesive sheet was visually inspected, whereupon a deflection or the like was not observed in the sheet. The adhesive sheets prepared in the manner now described could all be
5 received smoothly by a container box. After having been received by the container box, no contact between the sheets was observed. Even after having been irradiated with ultraviolet radiation, no deflection was observed in the sheets in which the adhesion strength between the
10 silicon wafer and adhesive sheet was decreased, no deflection was observed likewise and the sheets were received by the container box smoothly without causing contact between the sheets. Furthermore, at the time of the subsequent picking-up of the wafer chips, the sheets
15 were assuredly expanded and the accurate positioning of the wafer chips was performed by a sensor, whereby the wafer chips were picked up smoothly.

Comparative Example 7

20 An adhesive sheet was prepared in the same manner as in Example 8 except that the polyethylene substrate used was not electron radiation crosslinked. A silicon wafer was applied onto the adhesive layer surface of the adhesive sheet thus prepared and diced into wafer chips,
25 followed by UV irradiation, whereupon the substrate underwent deflection after each step of the dicing and UV irradiation and trouble was caused by mutual contact of the adhesive sheets when they were received by the container box. Furthermore, when the wafer chips were
30 picked up, there was observed an error in the picking-up performance which is considered ascribable to deflection of the substrate.

Attention is directed to the inventions claimed in our divisional applications nos. 2221468, 2221469 and 2221470.



CLAIMS

1. An adhesive sheet comprising a substrate having coated on the surface thereof an adhesive layer which layer comprises an acrylate or methacrylate polymer-based adhesive and a radiation polymerizable compound, said compound being a urethane acrylate oligomer having a molecular weight of 3000-10000.
2. An adhesive sheet according to claim 1 wherein the urethane acrylate oligomer has a molecular weight of 4000-8000.
3. An adhesive sheet according to claim 1 or claim 2 wherein a radiation color developable compound has been incorporated in the adhesive layer.
4. An adhesive sheet according to any preceding claim wherein a radiation color developable compound has been coated on at least one side of the substrate.
5. An adhesive sheet according to any preceding claim wherein a radiation color developable compound has been incorporated in the substrate.
6. An adhesive sheet according to any of claims 3 to 5 wherein the radiation color developable compound is a leuco dye.
7. An adhesive sheet according to claim 6 wherein the leuco dye is 4,4',4''-trisdimethylamino-triphenylmethane.
8. An adhesive sheet according to any preceding claim wherein a light scattering inorganic powder compound has been incorporated in the adhesive layer.



9. An adhesive sheet according to claim 8 wherein the light scattering inorganic compound is silica powder, alumina powder, silica-alumina powder or mica powder.

5

10. An adhesive sheet according to any preceding claim wherein the substrate is a crosslinked film.

11. An adhesive sheet according to claim 10 wherein
10 the crosslinked film is a crosslinked polyolefin film.

12. An adhesive sheet according to claim 11 wherein
15 the crosslinked polyolefin film is a crosslinked polyethylene film.

13. An adhesive sheet according to any of claims
1 to 9 wherein the substrate is a synthetic resin
film having a carboxyl group-containing monomer
20 as a principal constituent monomer unit.

14. An adhesive sheet according to claim 13 wherein
the synthetic resin film is an ethylene-(meth)acrylic
acid copolymer film.

25

15. A method for attaching an adhesive sheet
to a surface, wherein the sheet is readily released
from the surface following irradiation of the adhesive,
which comprises using as the sheet an adhesive
30 sheet as claimed in any preceding claim.

16. A method for preparing semiconductor chips
from a semiconductor wafer which comprises
a) attaching the said wafer to an adhesive sheet
35 as claimed in any of claims 1 to 14;
b) processing the said wafer to form semiconductor
chips; and



- c) irradiating the adhesive layer of the said sheet whereby the semiconductor chips may readily be released from the said sheet.
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