



(43) International Publication Date
13 September 2012 (13.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/121401 A2

(51) International Patent Classification:
G03F 7/00 (2006.01) *G03F 7/075* (2006.01)

(21) International Application Number:
PCT/JP2012/056215

(22) International Filing Date:
6 March 2012 (06.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2011-048908 7 March 2011 (07.03.2011) JP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: NANOIMPRINTING METHOD

(57) Abstract: [Objective] To reduce generation of silane coupling agent aggregates in nanoimprinting that includes a step of processing a surface of a substrate by coating the surface with a silane coupling agent. [Constitution] In a nanoimprinting method, a silane coupling agent (3) having 1 or 2 alkyl groups adjacent to an Si atom is coated on the surface of a substrate (2). A curable resin that includes one of isobornyl acrylate, ethylene glycol acrylate, and a silicone monomer compound is coated on the surface which is coated with the silane coupling agent (3) to form a curable resin film (4). A mold is pressed against the curable resin film (4) with a pattern of protrusions and recesses (13) facing the curable resin film (4). The curable resin film (4) is cured, then the mold (1) is separated from the cured resin film (4).



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DESCRIPTION
NANOIMPRINTING METHOD

Technical Field

5 The present invention is related to a nanoimprinting method that employs a mold having a predetermined pattern of protrusions and recesses on the surface thereof.

Background Art

10 There are high expectations regarding utilization of pattern transfer techniques that employ a nanoimprinting method to transfer patterns onto resist coated on objects to be processed, in applications to produce magnetic recording media such as DTM (Discrete Track Media) and BPM (Bit Patterned Media) and
15 semiconductor devices.

 The nanoimprinting method is a development of the well known embossing technique employed to produce optical discs. In the nanoimprinting method, a metal original (commonly referred to as a mold, a stamper, or a template), on which a pattern of protrusions
20 and recesses is formed, is pressed against curable resin coated on an object to be processed. Pressing of the original onto the resist causes the resist to mechanically deform or to flow, to precisely transfer the fine pattern. If a mold is produced once, nano level fine structures can be repeatedly molded in a simple manner.
25 Therefore, the nanoimprinting method is an economical transfer technique that produces very little harmful waste and discharge. Therefore, there are high expectations with regard to application of the nanoimprinting method in various fields.

 Conventionally, it is an important objective to improve the
30 release properties between a mold and resist, from the viewpoint of pattern formation properties on curable resin (the ease with which a pattern of protrusions and recesses can be formed on the curable resin according to design), accompanying the refinement of patterns of protrusions and recesses.

35 Therefore, a method, in which a mold release layer that

includes an organic compound is formed on the surface of a mold to reduce the adhesive force between the mold and curable resin thereby improving the aforementioned release properties, is being utilized.

Another method for improving the release properties is that
5 in which a surface process is administered in advance to the surface of a substrate to be coated with curable resin in advance, as disclosed in Patent Documents 1 and 2. The surface process involves coating a silane coupling agent onto the surface of the substrate to be coated with curable resin. According to this method, the adhesive force
10 between the substrate and the curable resin is increased by the silane coupling layer. Thereby relatively reducing the adhesive force between the mold and the curable resin, and the release properties therebetween can be improved. In this case, trimethoxysilane or trichlorosilane is generally employed as the silane coupling agent,
15 due to the bonding force of the silane coupling agent with respect to the substrate and from the viewpoint of cost.

[Prior Art Documents]

[Patent Document 1]

PCT Japanese Publication No. 2010-526426

20 [Patent Document 2]

Japanese Unexamined Patent Publication No. 2010-152284

However, in the case that a surface processes is administered using trimethoxysilane or trichlorosilane, aggregates of the silane coupling agent are generated on the substrate, and a problem arises
25 that defects D are generated on curable resin films, as illustrated in Figure 3.

The present invention has been developed in view of the foregoing circumstances. It is an object of the present invention to provide a nanoimprinting method that enables reduction of the
30 generation of silane coupling agent aggregates in nanoimprinting that includes a step of processing a surface of a substrate by coating the surface with a silane coupling agent.

Disclosure of the Invention

35 To achieve the above object, the present invention provides

a nanoimprinting method that employs a mold having a fine pattern of protrusions and recesses on the surface thereof, characterized by comprising the steps of:

coating the surface of a substrate with a silane coupling agent
5 represented by Formula 1 below;

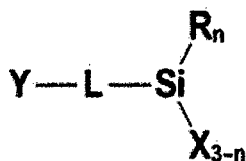
coating a curable resin on the surface coated with the silane coupling agent to form a curable resin film;

pressing the mold against the curable resin film with the pattern of protrusions and recesses facing the curable resin film;

10 curing the curable resin film; and

separating the mold from the cured resin film.

Formula 1:



15 Note that in Formula 1, R represents an alkyl group, X represents an inorganic functional group, Y represents an organic functional group, L represents a linking group or a linking bond that links the Si atom with the organic functional group, and n is either 1 or 2.

20 In the nanoimprinting method of the present invention, it is preferable for the alkyl group to be a methyl group and/or an ethyl group, and particularly preferable for the alkyl group to be a methyl group.

In the nanoimprinting method of the present invention, it is
25 preferable for the silane coupling agent to be
3-acryloxypropyl-dimethylmethoxysilane,
3-acryloxypropyl-methylbis (trimethylsiloxy) silane,
3-acryloxypropyl-methyldichlorosilane, or
3-acryloxypropyl-methyldimethoxysilane.

30 In the nanoimprinting method of the present invention, it is preferable for the curable resin to contain one of isobornyl acrylate, ethylene glycol diacrylate, and a silicone monomer compound.

In the nanoimprinting method of the present invention, it is preferable for the silane coupling agent to be coated by a micro contact printing method.

5 The nanoimprinting method of the present invention employs the silane coupling agent represented by Formula 1 as the silane coupling agent to be coated on the surface of the substrate, onto which the curable resin is to be coated. Thereby, the frequency at which the silane coupling agent bonds with itself decreases. As a result, the generation of defects in the curable resin film due to
10 aggregates of the silane coupling agent can be reduced in nanoimprinting that includes a step of processing the surface of a substrate with a silane coupling agent.

Brief Description of the Drawings

15 Figure 1A is a sectional diagram that schematically illustrates a step of a nanoimprinting method that includes a step of coating a silane coupling agent by the micro contact method.

Figure 1B is a sectional diagram that schematically illustrates a step of a nanoimprinting method that includes a step
20 of coating a silane coupling agent by the micro contact method.

Figure 1C is a sectional diagram that schematically illustrates a step of a nanoimprinting method that includes a step of coating a silane coupling agent by the micro contact method.

Figure 1D is a sectional diagram that schematically
25 illustrates a step of a nanoimprinting method that includes a step of coating a silane coupling agent by the micro contact method.

Figure 1E is a sectional diagram that schematically illustrates a step of a nanoimprinting method that includes a step of coating a silane coupling agent by the micro contact method.

30 Figure 2A is a sectional diagram that illustrates a mold utilized for nanoimprinting.

Figure 2B is a partial magnified view that illustrates a cross section of a patterned region of the mold of Figure 2A.

Figure 3 is a diagram that illustrates defects in a curable
35 resin film on a substrate, the surface of which has been processed

with a conventional silane coupling agent.

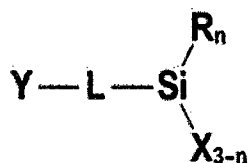
Best Mode for Carrying Out the Invention

Hereinafter, an embodiment of the present invention will be described with reference to the attached drawings. However, the present invention is not limited to the embodiments to be described below. Note that the dimensional scale ratios, etc. of the constituent elements within the drawings are not necessarily as the actual scale ratios in order to facilitate visual understanding.

Figures 1A through 1E are schematic sectional diagrams that illustrate the steps of a nanoimprinting method according to the present embodiment. Figure 2A is a schematic sectional diagram that illustrates a mold, and Figure 2B is a magnified view that illustrates a portion of a cross section of a patterned region of the mold of Figure 2A.

As illustrated in Figures 1A through 1E, the nanoimprinting method of the present embodiment is a nanoimprinting method that employs a mold 1 having a fine pattern 13 of protrusions and recesses on the surface thereof. A silane coupling agent 3 represented by Formula 1 below is coated on the surface of a substrate 2 (Figure 1A and Figure 1B). A photocurable resin that includes one of isobornyl acrylate, ethylene glycol diacrylate and a silicone monomer compound is coated on the surface coated with the silane coupling agent 3 to form a photocurable resin film 4 (Figure 1C). The mold 1 is pressed against the photocurable resin film 4 with the fine pattern 13 of protrusions and recesses facing the photocurable resin film 4 (Figure 1D). The photocurable resin film 4 is exposed and cured. Thereafter, the mold 1 is separated from the cured photocurable resin film 4 (Figure 1E).

Formula 1:



In Formula 1, R represents an alkyl group, X represents an inorganic functional group, Y represents an organic functional group, L represents a linking group or a linking bond that links the Si atom with the organic functional group, and n is either 1 or 2.

(Mold)

The mold 1 is constituted by a support portion 12 and the fine pattern 13 of protrusions and recesses 13 formed on a surface of the support portion 12 as illustrated in Figure 2A and Figure 2B, for example.

The material of the support portion 12 may be: a metal, such as silicon, nickel, aluminum, chrome, steel, tantalum, and tungsten; oxides, nitrides, and carbides thereof. Specific examples of the material of the mesa type substrate 10 include silicon oxide, aluminum oxide, quartz glass, Pyrex™, glass, and soda glass.

The shape of the fine pattern 13 of protrusions and recesses is not particularly limited, and may be selected as appropriate according to the intended use of the nanoimprinting mold. An example of a typical pattern is a line and space pattern as illustrated in Figure 2A and Figure 2B. The length of the protrusions, the width W1 of the protrusions, the distance W2 among the protrusions, and the height H of the protrusions from the bottoms of the recesses (the depth of the recesses) are set as appropriate in the line and space pattern. For example, the width W1 of the lines is within a range from 10nm to 100nm, more preferably within a range from 20nm to 70nm, the distance W2 among the lines is within a range from 10nm to 500nm, more preferably within a range from 20nm to 100nm, and the height H of the protrusions is within a range from 10nm to 500nm, more preferably within a range from 30nm to 100nm. The fine pattern 13 of protrusions and recesses may alternatively be that in which dots having rectangular, circular, or oval cross sections are arranged therein.

(Mold Release Layer)

It is preferable for a mold release layer to be provided on

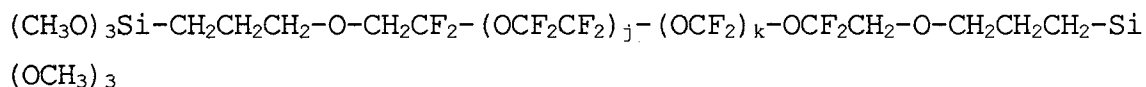
the surface of the mold 1 having the 13 thereon, in order to improve the release properties of the mold 1 with respect to the photocurable resin film 4. It is preferable for the mold release layer to include a fluorine compound. It is preferable for the fluorine compound to be a perfluoropolyether. Examples of preferred fluorine compounds include those represented by Formula 2 and Formula 3 below.

Formula 2:



In Formula 2, p is an integer 1 or greater that represents a degree of polymerization.

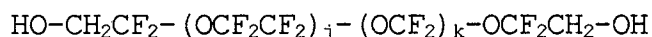
Formula 3:



In Formula 3, j and k are integers 1 or greater that represent degrees of polymerization.

The compound of Formula 3 may be produced, for example, by employing Fomblin ZDOL by Aujimont (presently Solvay Solexis). Fomblin ZDOL is a compound represented by Chemical Formula 3-1 below.

Formula 3-1:



In Formula 3-1, j and k are integers 1 or greater that represent degrees of polymerization. The number average molecular weight of the compound is approximately 2000.

For example, the compound represented by Formula 3 can be obtained by the following steps. First, NaH (sodium hydride) is caused to react with Fomblin ZDOL represented by Formula 3-1 to cause the ends of the hydroxyl group to become sodium oxide. Then, aryl bromide is caused to react with the sodium oxide at the ends to arylate the hydroxyl groups at the ends. Thereafter, hydrosilylation is performed on the unsaturated compound using trichlorosilane (SiHCl_3). Finally, methanol is employed to substitute chlorine atoms on silicon with methoxy.

The mold release layer is formed by exposing the mold to a

fluorine compound. Specifically, the formation process is performed as follows.

Perfluoropolyether is diluted with a fluorinated inert solvent to a concentration within a range from 0.01% by weight to 10% by weight, preferably a concentration within a range from 0.01% by weight to 1% by weight, and more preferably a concentration within a range from 0.01% by weight to 0.2% by weight. That is, it is preferable for the mold release layer to be formed by immersing the mold 1 into such a diluted solution. Examples of the fluorinated inert solvent include: perfluorohexane; perfluoromethylcyclohexane; perfluoro-1,3-dimethylcyclohexane; and dichloropentafluoropropane (HCFC-225). The temperature during immersion is not particularly limited, and may be within a range from 0°C to 100°C. The amount of time required for immersion varies according to the temperature during immersion. However, generally, 10 minutes or less is favorable, and approximately 1 minute is sufficient.

Alternatively, the mold release layer may be formed by exposing the mold 1 to perfluoropolyether vapor under decreased pressure conditions. The pressure in this case is not particularly limited, as long as it is less than 1 atmosphere and 0.1 atmosphere or greater. In order to expose the mold 1 to the perfluoropolyether vapor, the mold 1 may be left in an environment in which the diluted perfluoropolyether solution is heated and vaporized. Alternatively, the perfluoropolyether vapor may be blown onto the mold 1. In this case, the temperature of the vapor may be within a range from 100°C to 250°C.

The degree of coating of the mold release layer including the sparsity and density of the layer can be set as appropriate by adjusting the amount of time that the mold 1 is exposed to the diluted fluorine compound solution or by adjusting the concentration of the diluted solution.

(Substrate)

The shape, structure, size, material, etc. of the substrate

2, which is the target of processing, is not particularly limited in the case that the mold 1 has light transmissive properties, and may be selected as appropriate according to intended use. The surface of the substrate 2 onto which the pattern is transferred is the surface onto which the curable resin is coated. For example, in the case that the substrate 2 is for producing a data recording medium, the shape of the substrate 2 will generally be that of a disc. With respect to the structure of the substrate, a single layer substrate may be employed, or a laminated substrate may be employed. With respect to the material of the substrate, the material may be selected from among known materials for substrates, such as silicon, tantalum, nickel, aluminum, oxides and nitrides of these metals, glass such as quartz, and resin. These materials may be utilized singly or in combination. Note that silicon, silicon oxide, silicon nitride, and quartz are preferred as the material of the substrate, and silicon is particularly preferred. The thickness of the substrate is not particularly limited, and may be selected according to intended use. However, it is preferable for the thickness of the substrate to be 0.05mm or greater, and more preferably 0.1mm or greater. If the thickness of the substrate is less than 0.05mm, there is a possibility that the substrate will flex during close contact with the mold, resulting in a uniform close contact state not being secured. Meanwhile, in the case that the mold 1 does not have light transmitting properties, a quartz substrate is employed to enable exposure of the photocurable resin film 4. The quartz substrate is selected as appropriate according to intended use from among those that have light transmissive properties and thicknesses of 0.3mm or greater. If the thickness of the quartz substrate is less than 0.3mm, it becomes likely to be damaged during handling or by pressure during imprinting. Note that it is preferable for the quartz substrate to be formed by fused quartz.

It is preferable for the substrate 2 to have a mask layer that includes at least one layer on the surface to be coated with the curable resin, as illustrated in Figure 1A, etc. In this case, the substrate 2 is constituted by a support substrate 2a and a mask layer

2b. The mask layer 2b functions to prevent structures beneath residual film, that is, the substrate 2, from being etched after the residual film is removed in a residual film etching step. The material of the mask layer 2b is selected such that the etching selectivity ratio of the mask layer 2b with respect to the photocurable resin film 4 becomes low. Metals such as chrome, tungsten, titanium, nickel, silver, platinum, and gold, oxides, and nitrides of these metals are preferred as the material of the mask layer 2b. Further, it is preferable for the mask layer 2b to include at least one layer that includes chrome, chrome oxide, or chrome nitride.

(Silane Coupling Agent)

The silane coupling agent functions to increase the adhesive force between the substrate and the curable resin. The silane coupling agent utilized in the present invention is that represented by Formula 1, that is, a silane coupling agent having 1 or 2 alkyl groups adjacent to an Si atom.

It is preferable for the carbon number of the alkyl group R to be within a range from 1 to 6. It is more preferable for the alkyl group R to be a methyl group or an ethyl group. It is particularly preferable for the alkyl group R to be a methyl group. This is because long carbon chains of the alkyl group will become three dimensional obstructions to bonds with the substrate. In the case that $n=2$, one of the alkyl groups may be a methyl group, and the other may be an ethyl group.

The inorganic functional group X is a functional group that reacts with inorganic materials. Examples of the inorganic functional group X mainly include: hydrolysable groups such as alkoxy groups (such as methoxy groups and ethoxy groups), acyloxy groups (such as acetoxy groups and propanoyloxy groups); and halogen atoms (fluorine atoms, chlorine atoms, bromine atoms, and iodine atoms).

The organic functional group Y is a functional group that reacts with organic materials. Examples of the organic functional group Y mainly include: amino groups; carboxyl groups; hydroxyl

groups; aldehyde groups; thiol groups; isocyanate groups; isothiocyanate groups; epoxy groups; cyano groups; dimethyl amino groups; diethyl amino groups; hydrazyno groups; hydrazyde groups; vinyl sulfone groups; vinyl groups; and alkoxy groups.

5 The linking group L is selected from: an alkylene group (preferably with a carbon number within a range from 1 to 20); -O-; -S-; an arylene group; -CO-; -NH-; -SO₂-; -COO-; -CONH-; or combinations of these groups. An alkylene group is preferred as the linking group L. Meanwhile, in the case that L is a linking bond,
10 Y and Si are directly linked in Formula 1.

It is particularly preferable for the silane coupling agent to be 3-acryloxypropyl-dimethylmethoxysilane, 3-acryloxypropyl-methylbis (trimethylsiloxy) silane, 3-acryloxypropyl-methyldichlorosilane, or
15 3-acryloxypropyl-methyldimethoxysilane.

(Method for Coating the Silane Coupling Agent)

The method for coating the silane coupling agent is not particularly limited, and the dip method, the spin coat method, etc.
20 may be employed. Figure 1A and Figure 1B illustrate a case in which the silane coupling agent is coated by the micro contact printing method (μ CP method) that employs a stamp 5. A rubber like plastic stamp having a fine pattern of protrusions and recesses on the surface thereof is prepared in the μ CP method. Molecules are attached to
25 the surfaces of the peaks of the protrusions of the pattern on the surface of the stamp. The upper surfaces of the peaks are caused to closely contact the substrate, to form a molecular film having a pattern corresponding to the pattern of protrusions and recesses on the substrate. In the case that the μ CP method is employed,
30 material consumption can be suppressed to a minimum.

In the present embodiment, the stamp 5 has a pattern of protrusions and recesses that complements the pattern of protrusions and recesses on the mold 1, in order to increase the adhesive force between the protrusions of the pattern of protrusions and recesses
35 which is transferred onto the photocurable film 4. That is, the

protrusions and recesses in the pattern of the stamp 5 are the inverses (refer to Figure 1A) of the protrusions and recesses in the pattern of the mold. Polydimethylsiloxane is preferable as a resin material of the stamp 5. In the case that the μ CP method is executed employing a stamp 5 constituted by polydimethylsiloxane, approximately 10 continuous coating operations for coating the silane coupling agent become possible for each application of the silane coupling agent onto the stamp 5. The details of the μ CP method are described in Japanese Unexamined Patent Publication No. 2010-080865, for example.

(Curable Resin Film)

In the present embodiment, the curable resin film is formed by a photocurable material. However, the present invention is not limited to such a configuration, and a thermally curable material maybe employed as an alternative. The nanoimprinting method of the present invention is effective regardless of the type of curable resin which is employed. Further, the nanoimprinting method of the present invention is more effective with respect to curable resins that include one of isobornyl acrylate, ethylene glycol diacrylate, and a silicone monomer compound. For example, bulk materials that constitute photocurable resin include: isobornyl acrylate; n-hexyl acrylate; ethylene glycol diacrylate; and a photocuring resist X that includes 2-hydroxy-2-methyl-1-phenyl-propane-1-on. Note that a surfactant may be added as appropriate.

It is preferable for isobornyl acrylate (IBOA) as an acrylate component to constitute approximately 47% by weight of the bulk material, but may be adjusted within a range from 20% by weight to 80% by weight. As a result, the mechanical properties of the resist are mainly borne by IBOA. Sartomer Company, Inc., located in Exton, Pennsylvania, is a supplier of IBOA, under the product name SR506.

It is preferable for n-hexyl acrylate (n-HA) to constitute approximately 25% by weight of the bulk material, but may be adjusted within a range from 0% by weight to 50% by weight. In the case that it is desired to impart more pliable properties to the resist, n-HA is utilized to decrease and adjust the viscosity of the resist to

be within a range from 2cP to 9cP. Aldrich Chemical Company, located in Milwaukee, Wisconsin, is a supplier of n-HA.

It is preferable for ethylene glycol diacrylate (EGDA), which is a bridging component, to constitute approximately 25% by weight of the bulk material, but may be adjusted within a range from 10% by weight to 50% by weight. EGDA contributes to increased elasticity and rigidity, and further functions to promote bridging between n-HA and IBOA when the bulk material is polymerized.

It is preferable for 2-hydroxy-2-methyl-1-phenyl-propane-1-on, which is a polymerization initiator, to constitute approximately 3% by weight of the bulk material, but may be adjusted within a range from 1% by weight to 5% by weight. The chemical rays that the polymerization initiator is responsive to are wide band ultraviolet rays emitted by a medium pressure mercury lamp. The polymerization initiator facilitates bridging and polymerization of each component of the bulk material. Ciba Specialty Chemicals, located in Tarrytown, New York, is a supplier of 2-hydroxy-2-methyl-1-phenyl-propane-1-on, which is available under the product name DAROCUR™ 1173.

(Mold Pressing Step)

The amount of residual gas is reduced by pressing the mold 1 against the substrate 2 after depressurizing the atmosphere between the mold 1 and the substrate 2, or by causing the atmosphere between the mold 1 and the substrate 2 to be a vacuum. However, there is a possibility that the photocuring resin will volatilize before curing in a vacuum environment, causing difficulties in maintaining a uniform film thickness. Therefore, it is preferable to reduce the amount of residual gas by causing the atmosphere between the substrate 1 and the mold 2 to be a He atmosphere or a depressurized He atmosphere. He passes through the quartz substrate, and therefore the amount of residual gas (He) will gradually decrease. As the passage of He through the quartz substrate takes time, it is more preferable for the depressurized He atmosphere to be employed.

The mold 1 is pressed against the substrate 2 at a pressure

within a range from 100kPa to 10MPa. The flow of the resin is promoted, the residual gas is compressed, the residual gas dissolves into the photocuring resin, and the passage of He through the quartz substrate is promoted at greater pressures, resulting in improved production efficiency. However, if the pressure is excessive, there is a possibility that the mold and the substrate will be damaged if a foreign object is interposed between the mold 1 and the substrate 2 when the mold 1 contacts the substrate 2. Accordingly, it is preferable for the pressure to be within a range from 100kPa to 10MPa, more preferably within a range from 100kPa to 5MPa, and most preferably within a range from 100kPa to 1MPa. The reason why the lower limit of the pressure is set to 100kPa is that in the case that the space between the mold and the substrate is filled with liquid when performing imprinting within the atmosphere, the space between the mold and the substrate is pressurized by atmospheric pressure (approximately 101kPa).

(Mold Release Step)

After the mold 1 is pressed against the substrate 2 and a pattern of protrusions and recesses is formed on the photocuring resin film 4, the mold 1 is separated from the photocuring resin film 4. As an example of a separating method, the outer edge portion of one of the mold 1 and the substrate 2 may be held, while the rear surface of the other of the mold 1 and the substrate 2 is held by vacuum suction, and the held portion of the outer edge or the held portion of the rear surface may be relatively moved in a direction opposite the pressing direction. When this step is performed, the width of the protrusions in the pattern on the curable resin is the same as the interval W2 between adjacent protrusions in the fine pattern 13 of protrusions and recesses of the mold 1.

Hereinafter, the operation of the present invention will be described. The defects D illustrated in Figure 3 are generated in curable resin films because the silane coupling agent bonds with itself and generates silane coupling agent aggregates on the substrate. It is believed that the defects D occur due to curable

resin being bounced off by the aggregates. Accordingly, it is necessary to decrease the frequency at which the silane coupling agent bonds with itself in order to suppress generation of the defects D in the curable resin film. Bonding of the silane coupling agent with itself occurs when inorganic functional groups X of each molecule of the silane coupling agent become detached, and Si atoms bond with each other via O atoms. Therefore, the present invention utilizes a silane coupling agent in which one or two of the linking bonds of the Si atom are substituted by an alkyl group R, to inhibit bonding among Si atoms with each other.

As described above, the nanoimprinting method of the present invention employs the silane coupling agent represented by Formula 1 as the silane coupling agent to be coated on the surface of the substrate, onto which the curable resin is to be coated. Thereby, the frequency at which the silane coupling agent bonds with itself decreases. As a result, the generation of defects in the curable resin film due to aggregates of the silane coupling agent can be reduced in nanoimprinting that includes a step of processing the surface of a substrate with a silane coupling agent.

[Examples]

Examples of execution of the nanoimprinting method of the present invention will be described below.

<Example 1>

<Preparation of Photocurable Resin>

The aforementioned photocurable resin was prepared as the photocurable resin to be utilized in nanoimprinting. The specific components of the photocurable resin are as follows.

Photocurable Resin:

Isobornyl acrylate (47% by weight of the entire weight of bulk materials)

n-hexyl acrylate (25% by weight of the entire weight of bulk materials)

Ethylene glycol diacrylate (25% by weight of the entire weight

of bulk materials)

2-hydroxy-2-methyl-1-phenyl-propane-1-ol (3% by weight of the entire weight of bulk materials)

5 ZONYL™ (fluorine surfactant, less than 1% by weight of the entire weight of bulk materials)

<Substrate Surface Process>

3-acryloxypropyl-dimethylmethoxysilane was utilized as the silane coupling agent. A solution, in which 1g of the silane coupling agent was diluted in 99g of propylene glycol monomethyl ether acetate (PGMEA), was coated on the substrate by the spin coat method, in order to process the surface of a Si substrate.

<Production of Photocurable Resin Film>

15 First, the photocurable resin was coated onto the processed surface of the Si substrate by the spin coat method. Then, the photocurable resin was baked for 10 minutes at a substrate temperature of 100°C, to form a photocurable resin film having a film thickness of 80nm.

<Evaluation Method>

20 Whether defects were present in the photocurable resin film was confirmed with an Atomic Force Microscope (Nanoscope 3 by Digital Instruments) within a 10μm·10μm field of view. If defects were present, the number of defects was counted.

<Example 2>

25 A photocurable resin film was produced by the same steps as those described with respect to Example 1 except that 3-acryloxypropyl-methyl bis (trimethylsiloxy) silane was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed in the same manner as that described with respect to Example 1.

30 <Example 3>

A photocurable resin film was produced by the same steps as those described with respect to Example 1 except that 3-acryloxypropyl-methyldichlorosilane was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed in the same manner as that described with

respect to Example 1.

<Example 4>

A photocurable resin film was produced by the same steps as those described with respect to Example 1 except that
5 3-acryloxypropyl-methyldimethoxysilane was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed in the same manner as that described with respect to Example 1.

<Comparative Example 1>

10 A photocurable resin film was produced by the same steps as those described with respect to Example 1 except that 3-acryloxypropyl-trimethoxysilane was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed in the same manner as that described with
15 respect to Example 1.

<Comparative Example 2>

A photocurable resin film was produced by the same steps as those described with respect to Example 1 except that
20 3-acryloxypropyl-trichlorosilane was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed in the same manner as that described with respect to Example 1.

<Comparative Example 3>

A photocurable resin film was produced by the same steps as
25 those described with respect to Example 1 except that 3-acryloxypropyl-tris (trimethylsiloxy) silane was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed in the same manner as that described with respect to Example 1.

30 <Comparative Example 4>

A photocurable resin film was produced by the same steps as those described with respect to Example 1 except that bis (trimethoxy) silylethylene was utilized as the silane coupling agent. Whether defects were present and the number of defects was confirmed
35 in the same manner as that described with respect to Example 1.

<Results>

Table 1 below shows the evaluation results for Examples 1 through 4 and Comparative Examples 1 through 4. These evaluation results confirmed that generation of silane coupling agent aggregates can be reduced and that more uniform curable resin films can be produced in the case that the surfaces of substrates, onto which the curable resin film is coated, are processed by being coated with the silane coupling agent represented by Formula 1.

TABLE 1

	Number of Defects in Resin Film
Example 1	2
Example 2	12
Example 3	10
Example 4	3
Comparative Example 1	40
Comparative Example 2	35
Comparative Example 3	52
Comparative Example 4	60

<Example 5>

A stamp constituted by polydimethylsiloxane and having a pattern complementary to that of the mold was produced. Next, a silane coupling agent was attached to the surfaces of the peaks of the protrusions of the pattern of the stamp. Thereafter, the silane coupling agent was continuously coated on a plurality of substrates by causing the surfaces of the peaks to come into close contact with the plurality of substrates, without additionally attaching the silane coupling agent.

<Results>

The silane coupling agent was coated according to the pattern of the stamp, even on the 10th substrate that was coated.

CLAIMS

1. A nanoimprinting method that employs a mold having a fine pattern of protrusions and recesses on the surface thereof, characterized by comprising the steps of:

5 coating the surface of a substrate with a silane coupling agent represented by Formula 1 below;

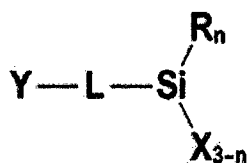
coating a curable resin on the surface coated with the silane coupling agent to form a curable resin film;

10 pressing the mold against the curable resin film with the pattern of protrusions and recesses facing the curable resin film;

curing the curable resin film; and

separating the mold from the cured resin film.

Formula 1:



15 (In Formula 1, R represents an alkyl group, X represents an inorganic functional group, Y represents an organic functional group, L represents a linking group or a linking bond that links the Si atom with the organic functional group, and n is either 1 or 2.)

20 2. A nanoimprinting method as defined in Claim 1, characterized by:

the alkyl group being a methyl group and/or an ethyl group.

3. A nanoimprinting method as defined in Claim 2, characterized by:

25 the alkyl group being a methyl group.

4. A nanoimprinting method as defined in Claim 1, characterized by:

the silane coupling agent being 3-acryloxypropyl-dimethylmethoxysilane.

30 5. A nanoimprinting method as defined in Claim 1, characterized by:

the silane coupling agent being 3-acryloxypropyl-methylbis

(trimethylsiloxy) silane.

6. A nanoimprinting method as defined in Claim 1, characterized by:

the silane coupling agent being
5 3-acryloxypropyl-methyldichlorosilane.

7. A nanoimprinting method as defined in Claim 1, characterized by:

the silane coupling agent being
3-acryloxypropyl-methyldimethoxysilane.

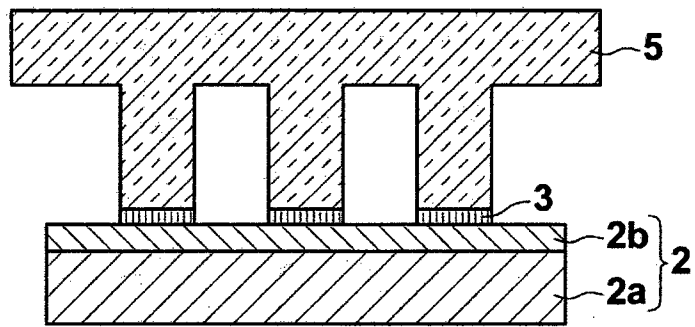
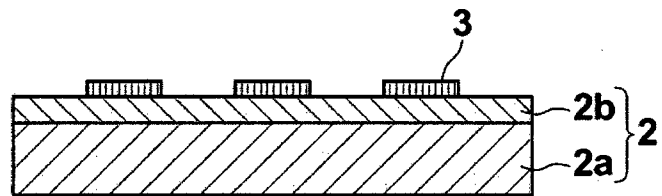
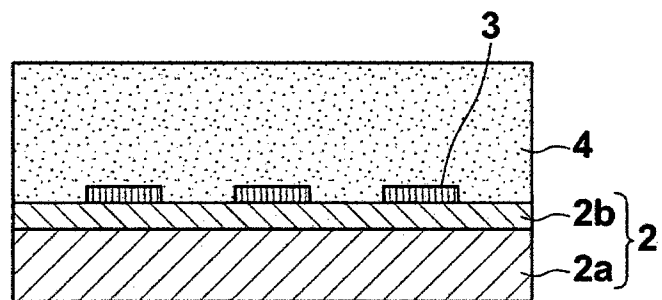
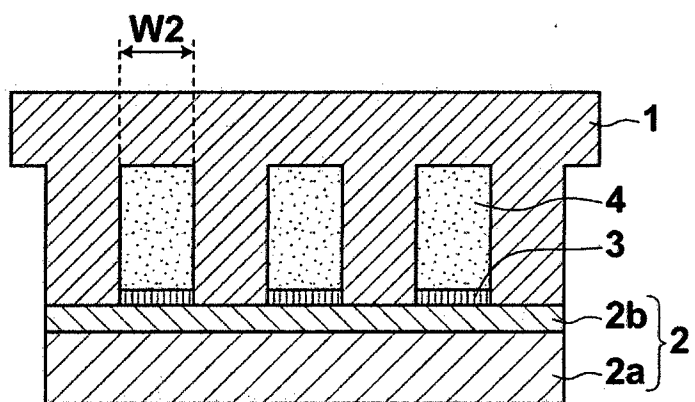
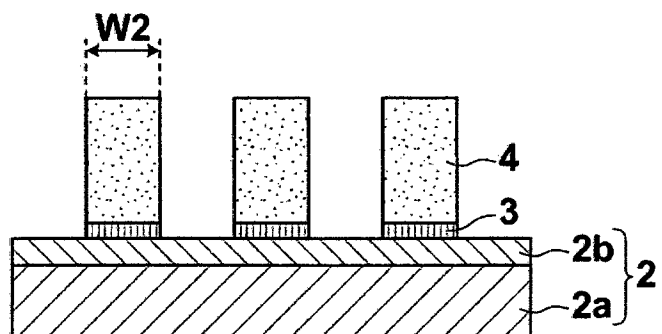
10 8. A nanoimprinting method as defined in any one of Claims 1 through 7, characterized by:

the silane coupling agent being coated by a micro contact printing method.

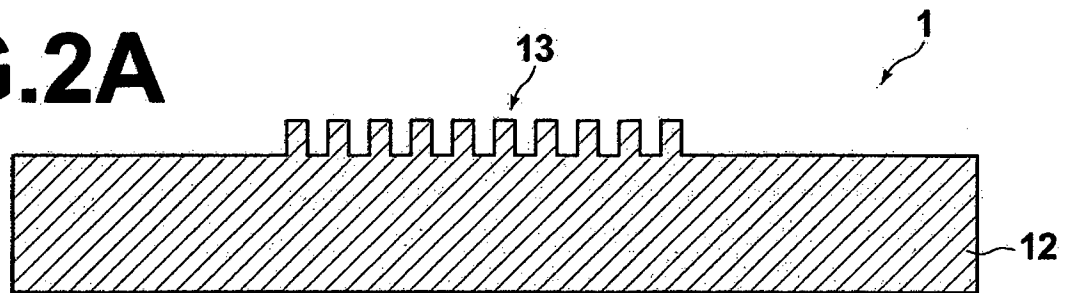
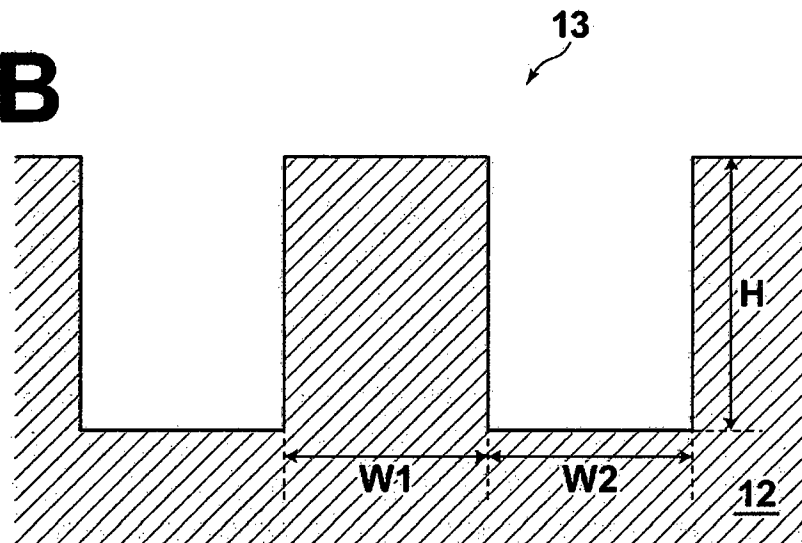
15 9. A nanoimprinting method as defined in any one of Claims 1 through 8, characterized by:

the curable resin containing one of isobornyl acrylate, ethylene glycol diacrylate, and a silicone monomer compound.

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FIG.1A**FIG.1B****FIG.1C****FIG.1D****FIG.1E**

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FIG.2A**FIG.2B****FIG.3**