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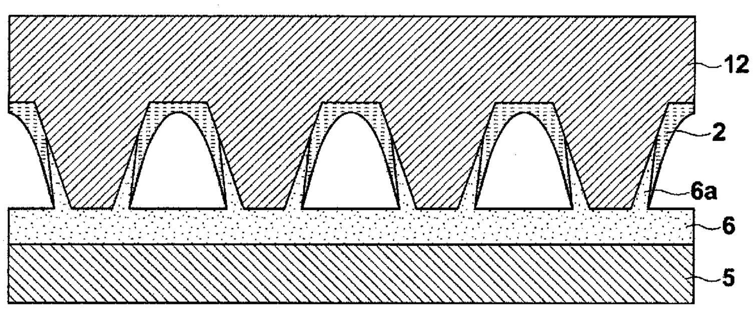
(54) **Title**: MOLD RELEASE PROCESSING METHOD FOR NANOIMPRINTING MOLDS, PRODUCTION METHOD EMPLOYING THE MOLD RELEASE PROCESSING METHOD, NANOIMPRINTING METHOD, AND METHOD FOR PRODUCING PATTERNED SUBSTRATES

FIG.4



(57) **Abstract**: A mold release processing method for a mold (1) includes: preparing a mold release processing substrate (5) coated with a mold release agent (6); causing a mold main body (12) having adsorbed water (2) on the surface thereof and the mold release processing substrate (5) to approach each other until a contact state in which the upper portions of protrusions of pattern (13) of protrusions and recesses are in contact with the mold release agent (6); maintaining the contact state until mold release layer (14), having a thickness distribution in which the thickness of the mold release layer (14) at the side surface (Ss) of the pattern (13) of protrusions and recesses becomes thinner from the top of surfaces (St) of the protrusions toward the bottom surfaces (Sb) of the recesses due to the mold release agent (6) becoming diffused in the adsorbed water (2), is formed; and causing the mold main body (12) and the mold release processing substrate (5) to move away from each other such that the upper portions of the protrusions separate from the mold release agent (6) on the mold release processing substrate (5).

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DESCRIPTION

MOLD RELEASE PROCESSING METHOD FOR NANOIMPRINTING MOLDS, PRODUCTION METHOD EMPLOYING THE MOLD RELEASE PROCESSING METHOD, NANOIMPRINTING METHOD, AND METHOD FOR PRODUCING PATTERNED SUBSTRATES

Technical Field

The present invention is related to a mold having a fine pattern of protrusions and recesses on a surface thereof, a method for producing the mold, a nanoimprinting method, and a method for producing a patterned substrate.

Background Art

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 semiconductor devices.

Specifically, the nanoimprinting method, a mold (commonly referred to as a mold, a stamper, or a template), on which a pattern of protrusions and recesses is formed, is pressed against resist coated on a substrate, which is 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. 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.

In nanoimprinting, mold release processes are administered to form mold release layers, in which mold release agents are bound (including physical bonds and chemical bonds) to the surfaces of mold main bodies, such that residual resist will not remain on the surfaces of the molds when the molds are separated from resist (Patent Documents 1 through 4). More specifically, Patent Document 2 discloses a method for administering a mold release process only on the top surfaces of protrusions of a pattern of protrusions and recesses on a mold. Patent Document 3 discloses a method that causes a large amount of a mold release agent to bind to recesses of a pattern of protrusions and recesses, to cause mold release properties to become non uniform across the entirety of the pattern of protrusions and recesses. Patent Document 4 discloses a method in which the amount of a mold release agent bound to the bottom surfaces of recesses is less than the amount of mold release agent bound to the top surfaces of protrusions.

However, it is known that mold release agents gradually peel away from the surfaces of molds as nanoimprinting operations are repeatedly performed. In these cases, it is preferable to perform mold release processes to form mold release layers on molds every time a predetermined imprinting operations are performed, for example. Further, productivity of nanoimprinting significantly decreases if the mold release processes are performed outside nanoimprinting apparatuses. Therefore, it is preferable for the mold release processes to be performed along with the nanoimprinting processes within the nanoimprinting apparatuses. A transfer technique, in which a pattern of protrusions and recesses of a mold main body is caused to contact a mold release agent coated on a mold release processing substrate (Patent Document 2), is a mold release process that can be performed easily within a nanoimprinting apparatus.

[Prior Art Documents]

[Patent Documents]

[Patent Document 1]

U.S. Patent No. 6,309,580

[Patent Document 2]

Japanese Patent No. 4317375

[Patent Document 3]

Japanese Unexamined Patent Publication No. 2008-179034

[Patent Document 4]

Japanese Unexamined Patent Publication No. 2009-226750

However, only the top surfaces of the protrusions of a pattern of protrusions and recesses undergo the mold release process in the method disclosed in Patent Document 2, and therefore there is a problem that the mold release properties of the other surfaces are poor. This is not an issue in the invention of Patent Document 2 from the viewpoint of the objective thereof, which is to impart a resist pattern with a greater aspect ratio than that of the pattern of protrusions and recesses. However, in general nanoimprinting operations, it is often the case that high mold release properties are desired across the entirety of the surfaces of patterns of protrusions and recesses, from the viewpoint of suppressing the occurrence of defects in resist patterns.

The present invention has been developed in view of the foregoing circumstances. It is an object of the present invention to provide a mold release processing method for molds for use in the production of nanoimprinting molds which is capable of being performed easily within a nanoimprinting apparatus and that improves the mold release properties across the entirety of the surface of a pattern of protrusions and recesses. It is another object of the present invention to provide a method of producing a nanoimprinting mold that employs the mold release processing method.

It is a further object of the present invention to provide a mold that enables precise processing, a nanoimprinting method, and a method for producing a patterned substrate for use in the production of patterned substrates employing nanoimprinting.

Disclosure of the Invention

A mold release processing method of the present invention that achieves the above object is a method for forming a mold release layer on a surface of a mold main body having a fine pattern of protrusions and recesses on the surface, characterized by comprising:

preparing a mold release processing substrate coated with a mold release agent;

causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent;

maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water; and

causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate.

It is preferable for the mold release processing method of the present invention to be executed within a nanoimprinting apparatus.

A method for producing a nanoimprinting mold of the present invention is a method for producing a mold having a mold main body with a fine pattern of protrusions and recesses on a surface thereof and a mold release layer on the surface of the mold main body, characterized by comprising:

preparing a mold release processing substrate coated with a mold release agent;

causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent;

maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water;

and

causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate.

It is preferable for the method for producing a nanoimprinting mold of the present invention to be executed within a nanoimprinting apparatus.

A nanoimprinting mold of the present invention comprises:

a mold main body with a fine pattern of protrusions and recesses on a surface thereof; and

a mold release layer on the surface of the mold main body; and is characterized by:

the mold release layer having a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses.

In the mold of the present invention, the thickness distribution of the mold release layer may be that in which the thickness at the side surfaces decreases from a thickness which is the same thickness as the thickness at the top surfaces to a thickness which is the same thickness as the thickness at the bottom surfaces.

In the mold of the present invention, the thickness distribution of the mold release layer may be that in which the thickness at the top surfaces is within a range from 1nm to 5nm, and the thickness at the bottom surfaces is within a range from 0.1nm to 1nm and 70% of the thickness at the top surfaces or less.

Further, a nanoimprinting method of the present invention is characterized by comprising:

employing a mold as described above;

coating a nanoimprinting substrate with resist;

pressing the mold on the surface of the nanoimprinting substrate which is coated with the resist; and

separating the mold from the nanoimprinting substrate.

It is preferable for the nanoimprinting method of the present invention to be that in which a mold release process being administered on the mold after every predetermined number of pressing steps or according to the degree of wear of the mold release layer, the mold release process comprising:

preparing a mold release processing substrate coated with a mold release agent;

causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent;

maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water; and

causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate.

In the nanoimprinting method of the present invention, it is preferable for the step of pressing the mold against the nanoimprinting substrate and the step of administering the mold release process to both be executed within a nanoimprinting apparatus.

A method for producing a patterned substrate of the present invention is characterized by comprising:

forming a resist film, to which a pattern of protrusions and recesses is transferred, on a substrate to be processed by the nanoimprinting method described above; and

performing etching using the resist film as a mask, to form a pattern of protrusions and recesses corresponding to the pattern of protrusions and recesses transferred onto the resist film.

The mold release processing method and the method for producing a mold of the present invention are characterized by comprising the steps of: preparing a mold release processing substrate coated with a mold release agent; causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent; maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water; and causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate. Thereby, the mold release layer can be formed not only on the top surfaces of the protrusions of the pattern of protrusions and recesses, but also on the side surfaces of the protrusions and the bottom surfaces of the recesses. As a result, the mold release process can be performed easily within a nanoimprinting apparatus and improves the mold release properties across the entirety of the surface of the pattern of protrusions and recesses.

Further, the nanoimprinting mold of the present invention is characterized by having a mold release layer with a thickness distribution in which the thickness of the mold release layer at the side surfaces of a pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses. Because the mold release layer is formed on the entirety of the surface of the pattern of protrusions and recesses, the mold release properties of the entire surface are high. As a result, precise processing is enabled in the production of patterned substrates employing nanoimprinting.

Still further, the nanoimprinting method and the method for producing patterned substrates of the present invention are executed employing the mold of the present invention, which has high mold release properties across the entirety of the surface of the pattern of protrusions and recesses thereof. Therefore, precise processing is enabled in the production of patterned substrates employing nanoimprinting.

Brief Description of the Drawings

Figure 1 is a schematic sectional view that illustrates the structure of a mold.

Figure 2 is a schematic sectional view that illustrates a step of a method for producing the mold.

Figure 3 is a schematic sectional view that illustrates a step of a method for producing the mold.

Figure 4 is a schematic sectional view that illustrates a step of a method for producing the mold.

Figure 5 is a schematic sectional view that illustrates a step of a method for producing the mold.

Figure 6 is a schematic sectional view that illustrates a step of a method for producing the mold.

Best Mode for Carrying Out the Invention

Hereinafter, embodiments 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 in the drawings, the dimensions of the constitutive elements are drawn differently from the actual dimensions thereof, in order to facilitate visual recognition thereof.

[Mold Release Processing Method for a Nanoimprinting Mold, Method for Producing a Nanoimprinting Mold, and Nanoimprinting Mold]

Figure 1 is a schematic sectional view that illustrates the structure of a mold 1 according to an embodiment of the present invention. Figure 2 through Figure 6 are schematic sectional diagrams that illustrate the step of a method for producing the mold 1.

A mold release process for the mold 1 of the present embodiment includes the steps of: preparing a mold main body 12 having a pattern 13 of protrusions and recesses; preparing a mold release processing substrate 5 coated with a mold release agent 6 (Figure 2); causing the mold main body 12 having adsorbed water 2 on the surface thereof and the mold release processing substrate 5 to approach each other until a contact state in which the upper portions of protrusions of the pattern 13 of protrusions and recesses are in contact with the mold release agent 6 (Figure 3); maintaining the contact state until a mold release layer 14, having a thickness distribution in which the thickness of the mold release layer 14 at the side surfaces Ss of the pattern 13 of protrusions and recesses becomes thinner from the top surfaces St of the protrusions toward the bottom surfaces Sb of the recesses due to the mold release agent 6 becoming diffused in the adsorbed water 2, is formed (Figure 5); and causing the mold main body 12 and the mold release processing substrate 5 to move away from each other such that the upper portions of the protrusions separate from the mold release agent 6 on the mold release processing substrate 5 (Figure 6).

Note that the mold 1 is completed when the mold release layer 14 is formed on the mold main body 12. Therefore, the mold release processing method is practically the same as a method for producing the mold 1.

The mold 1 of the present embodiment which is obtained by the mold release processing method and the method for producing a mold described above is equipped with: the mold main body 12 having the fine pattern 13 of protrusions and recesses on the surface thereof; and the mold release layer 14 which is formed on the entirety of the surface of the mold main body 12, as illustrated in Figure 1. The mold release layer 14 has a thickness distribution in which the thickness of the mold release layer 14 at the top surfaces St of the protrusions is greater than the thickness thereof at the bottom surfaces Sb of the recesses, and the thickness of the mold release layer 14 at the side surfaces Ss of the pattern 13 of protrusions and recesses becomes thinner from the top surfaces St toward the bottom surfaces Sb.

(Mold Main Body)

The material of the mold main body 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 support portion 12 include silicon oxide, aluminum oxide, quartz glass, Pyrex™, glass, and soda glass.

The shape of the 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 1. The length of the protrusions of the line and space pattern, 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 lines is within a range from 10nm to 500nm, more preferably within a range from 30nm to 100nm. In addition, the shapes of the protrusions that constitute the pattern 13 of protrusions and recesses may be dots having rectangular, circular, or elliptical cross sections.

The mold main body 12 described above may be produced by the following procedures, for example. First, a silicon substrate is coated with a photoresist having acrylic resin, such as a PHS (polyhydroxy styrene) type chemically amplified resist, a novolac resin, or PMMA (polymethyl methacrylate) as its main component by the spin coat method or the like, to form a resist layer. Next, a laser beam (or an electron beam) is irradiated onto the silicon substrate while being modulated according to a desired pattern of protrusions and recesses, to expose the pattern on the surface of the photoresist layer. Then, the photoresist layer is developed to remove the exposed portions. Finally, selective etching is performed by RIE (reactive ion etching) or the like, using the photoresist layer after the exposed portions are removed as a mask, to obtain the mold main body having a predetermined pattern of protrusions and recesses. In the case that a mesa type mold main body 12 having a mesa portion and a flange portion is obtained, a base material having a stepped outer peripheral portion is employed, and a pattern of protrusions and recesses is formed on the mesa portion by the steps described above.

(Water Adsorbed on the Surface of the Mold Main Body)

The adsorbed water 2 which is adsorbed on the surface of the mold main body 12 is important in the present invention. More specifically, the phenomenon that meniscuses (liquid bridges formed in fine spaces between objects) are formed by the capillary action of the adsorbed water 2 is utilized to diffuse the mold release agent 6 on the surface of the pattern 13 of protrusions and recesses, as will be described later. The "adsorbed water" refers to water molecules included in the environment about the mold main body 12 which are adhered onto the surface of the mold main body 12 in the liquid phase.

In the present embodiment, the environment about the mold main body 12 is adjusted as necessary such that the adsorbed water 2 adheres to the surface of the mold main body 12. The thickness of the layer formed by the adsorbed water 2 (adsorbed water layer) is set as appropriate according to the thickness of the mold release layer 14 to be formed. Specifically, relationship between the thickness of the adsorbed water layer and the thickness of the mold release layer 14 is set such that the thickness of the adsorbed water layer is approximately half the thickness of the mold release layer to be formed. In the present invention, it is preferable for the thickness of the adsorbed water layer to be within a range from 0.3nm to 3nm, and more preferable for the thickness to be within a range from 1nm to 2nm. The reason why the above upper limit is set is because the probability that condensation will occur is high in an environment in which the thickness of the adsorbed water layer will exceed 3nm. If condensation occurs, it becomes difficult for a uniform adsorbed water layer to be formed. The reason why the above lower limit is set is because the diffusion efficiency of the mold release agent 6 significantly decreases if the thickness of the adsorbed water layer is less than 0.3nm. It is effective to arrange conditions under which adhesion of the adsorbed water 2 to the surface of the mold main body 12 is facilitated, in order to increase the coating rate of the mold release agent 6 or to reduce the mold release processing time. Examples of methods for arranging such conditions include: administering surface processes onto the surface of the mold main body 12 to modify the properties thereof such that the surface becomes hydrophilic; and increasing the relative humidity of the environment in which imprinting is executed. Surface processing methods for modifying the properties of the surface of the mold main body 12 such that the surface becomes hydrophilic include: wet cleansing methods that employ chemical agents; dry cleansing methods that employ plasma or UV ozone; and methods that combine the wet and dry cleansing methods. The preferable range of relative humidity is from 20% to 90%, and more preferably within a range from 40% to 90%, from the viewpoint of setting the thickness of the adsorbed water layer to be within the range described above. There are cases in which the relative humidity satisfies the above conditions without intentional control being exerted. Alternatively, it is possible to control the relative humidity to be a desired value by supplying dry air or moist air to adjust the environment about the mold main body 12. The adsorbed water 2 will reach an equilibrium state (a state in which the amount of water molecules that become adsorbed and the amount of water molecules that vaporize are equal) depending on the hydrophilic properties of the surface of the mold main body 12, the humidity of the environment, the temperature of the environment, etc. The adsorbed water layer will maintain a constant thickness on the surface of the mold main body 12 in the equilibrium state.

Alternatively, the adsorbed water 2 may be caused to adhere to the surface of the mold main body 12 by coating the surface with water. In this case, the mold main body 12 and the mold release agent

6 are caused to contact each other at the stage when the adsorbed water 2 which is coated on the surface of the mold main body 12 reaches an equilibrium state, or at a stage prior to the equilibrium state being reached (that is, a stage in which vaporization of water molecules is predominant). In the case that the surface of the mold main body 12 is coated with water, it is preferable to cause the mold main body 12 and the mold release agent 6 to contact each other at the stage when the adsorbed water 2 which is coated on the surface of the mold main body 12 reaches the equilibrium state. This is because it is difficult for the thickness of the adsorbed water layer to be controlled to be uniform across the entirety of the surface of the mold main body 12 in the case that the mold main body 12 and the mold release agent 6 are caused to contact each other at a stage prior to the equilibrium state being reached. It is difficult for the thickness of the adsorbed water layer to become uniform because amounts of adsorbed water differ at the protrusions and recesses that constitute the pattern 13 of protrusions and recesses. Particularly in the case that the surface of the mold main body 12 has hydrophilic properties, the adsorbed water collects in the recesses but does not collect on the protrusions. In contrast, fluctuations in the thickness of the adsorbed water layer caused by the aforementioned factors are reduced when the adsorbed water 2 which is coated on the surface of the mold main body 12 reaches the equilibrium state. As a result, an adsorbed water layer having a uniform thickness can be realized in cases that the mold main body 12 and the mold release agent 6 are caused to contact each other at a stage when the adsorbed water 2 on the surface of the mold main body 12 reaches the equilibrium state.

(Mold Release Agent)

It is preferable for the mold release agent 6 to be a fluorine compound. It is preferable for the fluorine compound to be a fluorine series silane coupling agent. Commercially available mold release agents such as Optool DSX by Daikin Industries K.K. and Novec EGC-1720 by Sumitomo 3M K.K. may be utilized.

Alternatively, other known fluorine resins, hydrocarbon series lubricants, fluorine series lubricants, fluorine series silane coupling agents, etc., may be utilized.

An example of a fluorine series resin is PTFE (polytetrafluoroethylene).

Examples of hydrocarbon series lubricants include: carboxylic acids such as stearic acid and oleic acid; esters such as stearic acid butyl; sulfonic acids such as octadecylsulfonic acid; phosphate esters such as monooctadecyl phosphate; alcohols such as stearyl alcohol and oleyl alcohol; carboxylic acid amides such as stearic acid amide; and amines such as stearyl amine.

Examples of fluorine series lubricants include lubricants in which a portion or the entirety of the alkyl groups of the aforementioned hydrocarbon series lubricants are replaced with fluoroalkyl groups or perfluoropolyether groups. The perfluoropolyether groups may be perfluoromethylene oxide polymers, perfluoroethylene oxide polymers, perfluoro-n-propylene oxide polymers $(CF_2CF_2CF_2O)_n$, perfluoroisopropylene oxide polymers $(CF(CF_3)CF_2O)_n$, copolymers of the aforementioned polymers, etc. Here, the subscript n represents the degree of polymerization.

It is preferable for the other fluorine series silane coupling agents to have at least one and preferably one to 10 alkoxy silane groups and chloro silane groups in each molecule, and to have a molecular weight within a range from 200 to 10,000. $-Si(OCH_3)_3$ and $-Si(OCH_2CH_3)_3$ are examples of the alkoxy silane group. Meanwhile, examples of the chloro silane groups include $-Si(Cl)_3$. Specific examples of the fluorine series silane coupling agents include: heptadecafluoro-1,1,2,2-tetra-hydrodecyltrimethoxysilane; pentafluorophenylpropyldimethylchlorosilane; tridecafluoro-1,1,2,2-tetra-hydrooctyltriethoxysilane; and tridecafluoro-1,1,2,2-tetra-hydrooctyltrimethoxysilane.

(Mold Release Processing Substrate)

The mold release processing substrate 5 is a substrate on which the mold release agent 6 is coated in advance to administer the mold release process on the mold main body 12. The shape, structure, size, material, etc. of the mold release processing substrate 5 are not particularly limited. However, a substrate having high level of flatness is preferred. The mold release processing substrate 5 may be of a single layer structure or a laminated structure. The material of the mold release processing substrate 5 may be selected as appropriate from among known materials. Examples of such materials include: silicon, nickel, aluminum, glass, and resin. These materials may be used singly or in combinations of two or more. The mold release processing substrate 5 may be produced, or a commercially available substrate may be utilized. The thickness of the mold release processing substrate 5 is not particularly limited. However, it is preferable for the thickness of the mold release processing substrate 5 to be 0.05mm or greater, and more preferably 0.1mm or greater. The reason why the lower limit is set as described above is because the mold release processing substrate 5 will flex when the top surfaces St of the protrusions of the mold main body 12 and the mold release agent 6 contact each other if the thickness of the mold release processing layer 5 is less than 0.05mm, and there is a possibility that a uniform contact state cannot be secured.

The method by which the mold release agent 6 is coated onto the mold release processing substrate 5 is not particularly limited. Examples of coating methods include: the vapor deposition method; the spin coat method+ the dip coat method; the spray coat method; and the ink jet method. It is preferable for the film thickness of the mold release agent 6 on the mold release processing substrate 5 in a coated state to be within a range from 1nm to 100nm, more preferably within a range from 2nm to 50nm, and most preferably within a range from 3nm to 30nm.

(Contact Step between Main Mold Body and Mold Release Agent)

After the mold release agent 6 is coated on the mold release processing substrate 5, the mold main body 12 is caused to approach the mold release processing substrate 5 such that a contact state, in which only the upper portions of the protrusions of the pattern 13 of protrusions and recesses are in contact with the mold release agent 6, is achieved. The "upper portions of the protrusions" refers to portions of the protrusions that include the top surfaces St of the protrusions, and portions of the protrusions within a predetermined distance from the top surfaces St. This is because it becomes difficult to control the film thickness of the mold release layer 14 if the protrusions contact the mold release agent 6 such that the entireties of the protrusions are immersed in the mold release agent 6. Therefore, it is preferable for a configuration to be designed such that the total volume of the mold release agent 6 is smaller than the total volume of a space that corresponds to the recesses, such that only the portions in the vicinity of the top surfaces St contact the mold release agent 6. If such a configuration is designed, spaces will remain in the recesses even if the mold main body 12 and the mold release processing substrate 5 approach each other and are pressed against each other, and therefore the entireties of the protrusions will not be immersed in the mold release agent 6. Alternatively, in the case that the total volume of the mold release agent 6 is not designed in advance, the distance between the mold main body 12 and the mold release processing substrate 5 may be adjusted to cause only the upper portions of the protrusions of the pattern 13 of protrusions and recesses to contact the mold release agent 6. The film thickness of the mold release layer 14 on the side surfaces Ss of the protrusions is enabled to be controlled over a wide range by achieving contact state, in which only the upper portions of the protrusions of the pattern 13 of protrusions and recesses are in contact with the mold release agent 6.

The mold main body 12 and the mold release processing substrate 5 are caused to contact each other after they are aligned to have a predetermined relative positional relationship. Alignment marks may be employed to align the mold main body 12 and the mold release processing substrate 5. Pressure may be applied as necessary after the contact state is achieved.

The amount of time that the mold main body 12 and the mold release agent 6 are maintained in contact is set as appropriate according to conditions such as the type of the mold release agent 6, the amount of the mold release agent 6 coated on the mold release processing substrate 5, the shape of the pattern on the mold main body 12, the amount of adsorbed water 2 on the mold main body 12, and relative humidity. The amount of time that the mold main body 12 and the mold release agent 6 are maintained in contact is preferably within a range from 1 second to 1 hour, more preferably within a range from 10 seconds to 10 minutes, and still more preferably within a range from 1 minute to 5 minutes.

(Diffusion of Mold Release Agent)

Diffusion of the mold release agent 6 due to the meniscus phenomenon will be described. Figure 3 illustrates the manner in which the top surfaces St of the protrusions of the pattern 13 of protrusions and recesses of the mold main body 12 are in contact with the surface of the mold release agent 6. In such a case, meniscuses are formed in the spaces between the side surfaces Ss of the protrusions and the surface of the mold release agent 6. Then, the mold release agent 6 diffuses across the surface of the pattern 13 of protrusions and recesses, as illustrated in Figure 4 (denoted by reference numeral 6a in Figure 4). The amount of the mold release agent 6a which is diffused depends on the amount of time that the top surfaces St of the protrusions and the surface of the mold release agent 6 are maintained in contact, the amount of the adsorbed water 2, etc. The diffusion of the mold release agent continues during the time that the mold main body 12 and the mold release agent 6 are in contact, and the mold release agent 6 ultimately diffuses to the bottom surfaces Sb of the recesses of the pattern 13 of protrusions and recesses. The mold release agent 6a on the pattern 13 of protrusions and recesses binds with the surface thereof, to constitute the mold release layer 14.

The diffusion of the mold release agent 6 processes form the top surfaces St of the protrusions of the pattern of protrusions and recesses to the bottom surfaces Sb of the recesses. Therefore, it is possible to impart a distribution to the thickness of the mold release layer 14 from the top surfaces St to the bottom surfaces Sb. In the case that the mold main body 12 and the mold release agent 6 are caused to be in contact for a long period of time, the amount of the diffused mold release agent 6a will become saturated. Therefore, it is also possible to form the mold release layer 14 to have a uniform thickness. Diffusion of the mold release agent 6 is a physical phenomenon that proceeds regardless of the widths of the recesses of the pattern 13 of protrusions and recesses. Accordingly, even if the pattern of protrusions and recesses includes recesses having different widths, the mold release layer 14 can be formed to have a uniform thickness at the bottom surfaces of all of the recesses, simply by maintaining the contact state for an amount of time that enables the mold release agent 6 to become sufficiently diffused at the bottom surfaces of the recesses having larger widths.

(Mold Release Layer)

The mold release process administered on the surface of the mold is completed and the mold release layer 14 is formed by separating the mold main body 12 from the mold release processing substrate 5 after the mold main body 12 is caused to contact the mold release agent 6 for a predetermined amount of time.

It is preferable for the thickness of the mold release layer 14 to be within a range from 1nm to 5nm. In the case that a distribution is imparted onto the thickness of the mold release layer, the thickness distribution may be that in which the thickness at the top surfaces is within a range from 1nm to 5nm, and the thickness at the bottom surfaces is within a range from 0.1nm to 1nm and 70% of the thickness at the top surfaces or less. Note that the "thickness" of the mold release layer 14 is the average thickness at the top surfaces St or the bottom surfaces Sb.

The difference between the thickness of the mold release agent at the top surfaces St of the protrusions and the bottom surfaces Sb of the recesses and the percentage of the thickness at the bottom surfaces Sb with respect to the thickness at the top surfaces St are measured by the following method. First, a line and space pattern for measuring thickness, of a size that enables the tip of a probe of an AFM (Atomic Force microscope) to reach the bottom surface Sb of the recesses thereof, is formed on the mold main body 12 separately from the pattern 13 of protrusions and recesses. The AFM measures the shape of the pattern of protrusions and recesses using the probe, and designates data obtained by measurement as reference data. Next, the same measurements are performed with respect to the mold 1 on which the mold release process has been administered, and data regarding the heights of the steps are compared against the reference data. Thereby, the difference in the thicknesses of the mold release agent at each of the top surface St of the protrusions and the bottom surface Sb of the recesses can be calculated. Next, the thickness of the mold release layer 14 is measured at a flat region of the mold main body 12 without any protrusions or recesses by an ellipsometer. The thickness of the mold release layer at the flat region corresponds to the thickness of the mold release layer at the top surfaces St of the protrusions. The percentage of the thickness at the bottom surfaces Sb of the recesses with respect to the thickness at the top surfaces St of the protrusions can be calculated based on the difference in thicknesses between the mold release agent at the top surfaces St and the bottom surfaces Sb, and the thickness of the mold release agent at the top surfaces St, which are obtained by the methods described above.

The thickness distribution on the side surfaces Ss of the protrusions from the top surfaces St of the protrusions to the bottom surfaces Sb of the recesses is measured by the following method. First, resist patterns formed by imprinting employing a mold main body 12 on which the mold release process has not been administered and employing a mold main body 12 on which the mold release process has been administered are prepared. Then, the cross sectional shapes of the patterns of protrusions and recesses in each of the resist patterns are measured by a scanning electron microscope. The angles of inclination and the widths of the protrusions are obtained from the measured cross sectional shapes, and comparisons are made between the case in which the mold release process has been administered and the case in which the mold release process has not been administered. Thereby, the thickness distribution of the mold release layer 14 on the side walls Ss from the top surfaces St of the protrusions to the bottom surfaces Sb of the recesses can be calculated.

Hereinafter, the operational effects of the present invention will be described. The mold release processing method of the present invention can be performed within a general nanoimprinting apparatus, by providing the mold release processing substrate in the nanoimprinting apparatus instead of a nanoimprinting substrate. The trouble of removing the mold 1 from the interior of the nanoimprinting apparatus and processing it in a separate apparatus for performing the mold release process is obviated by executing the mold release processing method within the nanoimprinting apparatus, thereby improving the productivity of nanoimprinting operations. In addition, the risk of foreign matter adhering to the mold 1 while the mold is removed and conveyed can also be avoided.

In the mold release processing method of the present invention, it is possible to form the mold release layer 14 such that the thickness thereof gradually becomes thinner from the upper surfaces St of the protrusions toward the bottom surfaces Sb of the recesses. By utilizing this ability, it is possible for the mold release processing method of the present invention to cause the taper angle of the pattern 13 of protrusions and recesses of the mold main body to approach 90 degrees, although the degree of this effect will vary according to processing conditions. In addition, the thickness distribution of the mold release layer 14 practically improves the rectangularity of the pattern 13 of protrusions and recesses of the mold 1 coated by the mold release layer 14, thereby further increasing the height of the pattern.

Specifically, the shape of a resist pattern obtained by imprinting a resist film becomes more advantageous in steps for processing substrates following the imprinting step as the rectangularity thereof is greater. However, as the line width of patterns of protrusions and recesses becomes narrower, it becomes difficult to form patterns of protrusions and recesses having high rectangularity when producing molds. As a result, the shapes of patterns of protrusions and recesses on molds will become tapered and narrow at the tips thereof. Resist patterns which are formed using such molds will necessarily be shaped as tapers as well. In such cases, there is a problem that the processing precision of substrates will deteriorate. Therefore, it is desired to correct tapered patterns of protrusions and recesses on molds to increase the rectangularity thereof in a step following formation of the patterns. According to the mold release processing method of the present invention, the mold release layer 14 that gradually becomes thinner from the top surfaces St of the protrusions to the bottom surfaces Sb of the recesses can be formed. Therefore, it is possible to realize such a correction step.

The mold release processing method of the present invention utilizes diffusion of the mold release agent 6 within the adsorbed water 2. Therefore, the mold release layer 14 can be formed such that it gradually becomes thinner from the top surfaces St of the protrusions to the bottom surfaces Sb of the recesses at the same ratio, regardless of the widths of the protrusions and recesses of the pattern 13 of protrusions and recesses.

Use of solvents other than water to diffuse the mold release agent 6 may be considered. However, the use of water is preferable for the following reasons. In the case that a solvent other than water is utilized to diffuse the mold release agent 6, it is necessary to achieve an equilibrium state between a gas phase component of the solvent in the environment and a liquid phase component on the surface of the mold main body, in the same manner as in the case that water is utilized as described above. Accordingly, it is necessary for the affinity of the surface of the mold main body with respect to organic solvents to be improved, in order for the organic solvents to become adsorbed on the surface of the mold main body. However, it is often the case that the properties of the surfaces of mold main bodies, which are generally constituted by materials such as silicon, metal, oxides, quartz, are modified to become hydrophilic after a cleansing step prior to the mold release process. That is, because the surface of the mold main body is hydrophilic after being cleansed, organic solvents will volatilize easily. Therefore, it is extremely difficult for organic solvents to remain on the surface of the mold as adsorbed solvents, and also to form meniscuses of the organic solvents on the surface of the mold main body having low affinity thereto.

A thickness distribution can be imparted to the mold release layer from the top surfaces St of the protrusions to the bottom surfaces Sb of the recesses in the case that a chemical vapor deposition method is employed as an alternative method. However, in the case that the chemical vapor deposition method is employed, the thickness of the mold release layer will become greater as the openings of the recesses are larger. Accordingly, the chemical vapor deposition method is effective in cases that molds have patterns of protrusions and recesses with recesses having openings of a uniform size. However, in cases that molds have patterns of protrusions and recesses with recesses having openings of various sizes, coating of the mold release layer may become insufficient at portions where the openings are small. In addition, if deposition conditions suited for the thickness of the mold release layer at portions where the openings of the recesses are small, the thickness of the mold release layer will become excessive at portions where the openings are large. Such problems do not occur in the mold release processing method of the present invention. Therefore, the mold release processing method of the present invention is effective as a method that imparts a thickness distribution thickness distribution to the mold release layer from the top surfaces St of the protrusions to the bottom surfaces Sb of the recesses.

[Nanoimprinting Method Employing the Mold of the Present Invention]

Hereinafter, an embodiment of a nanoimprinting method that employs the mold of the present invention will be described.

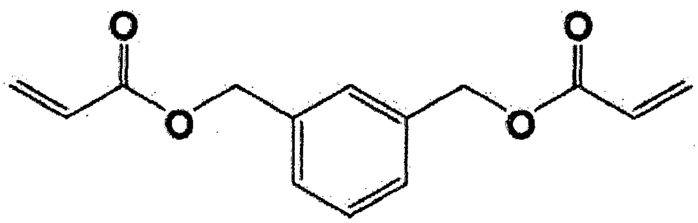
The nanoimprinting method of the present embodiment employs a mold 1 such as that illustrated in Figure 1. A nanoimprinting substrate formed by quartz is coated with a photocurable resist. Next, the mold 1 is pressed against the surface of the nanoimprinting substrate on which the resist is coated. Then, ultraviolet light is irradiated from the back surface of the nanoimprinting substrate to cure the resist, and the mold 1 is separated from the resist.

(Resist)

The resist is not particularly limited. In the present embodiment, a resist prepared by adding a photopolymerization initiator (2% by mass) and a fluorine monomer (0.1% by mass to 1% by mass) to a polymerizable compound may be employed. An antioxidant agent (approximately 1% by mass) may further be added as necessary. The resist produced by the above procedures can be cured by ultraviolet light having a wavelength of 360nm. With respect to resist having poor solubility, it is preferable to add a small amount of acetone or acetic ether to dissolve the resin, and then to remove the solvent. Note that the resist is a photocurable material in the present embodiment. However, the present invention is not limited to such a configuration, and a heat curable material may alternatively be employed.

Examples of the polymerizable compound include: benzyl acrylate (Viscoat #160 by Osaka Organic Chemical Industries, K.K.), ethyl carbitol acrylate (Viscoat #190 by Osaka Organic Chemical Industries, K.K.), polypropylene glycol diacrylate (Aronix M-220 by TOAGOSEI K.K.), and trimethylol propane PO denatured triacrylate (Aronix M-310 by TOAGOSEI K.K.). In addition, a compound A represented by Chemical Formula 1 below may also be employed as the polymerizable compound.

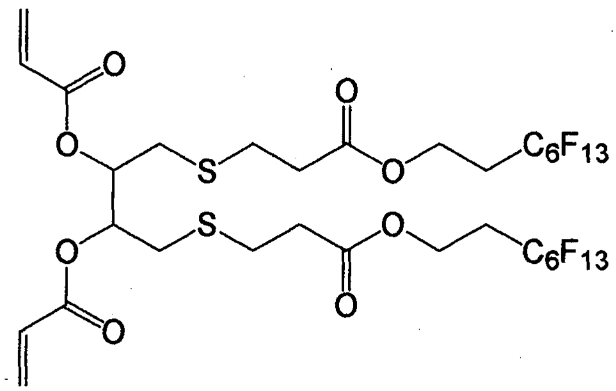
[Chemical Formula 1]



Examples of the photopolymerization initiating agent include alkyl phenone type photopolymerization initiating agents, such as 2-(dimethyl amino)-2-[(4-methylphenyl) methyl]-1-[4-(4-morpholinyl) phenyl]-1-butanone (IRGACURE 379 by Toyotsu Chemiplas K.K.)

In addition, a compound B represented by Chemical Formula 2 below may be employed as the fluorine monomer.

[Chemical Formula 2]



In the case that the resist is coated by the ink jet method, it is preferable for a photocurable resist formed by mixing the compound A represented by Chemical Formula 1, Aronix M-220, Irgacure 379, and the Compound B represented by Chemical Formula 2 at a mass ratio of 48:48:3:1 to be utilized.

In the present invention, the viscosity of the resist material is within a range from 8cP to 20cP, and the surface energy of the resist material is within a range from 25mN/m to 35mN/m. Here, the viscosity of the resist material was measured by a RE-80L rotating viscosity meter (by Touki Industries K.K.) at 25±0.2C°. The rotating speeds during measurements were: 100rpm at viscosities greater than or equal to 0.5cP and less than 5cP; 50rpm at viscosities greater than or equal to 5cP and less than 10cP; 20rpm at viscosities greater than or equal to 10cP and less than 30cP; and 10rpm at viscosities greater than or equal to 30cP and less than 60cP. The surface energy of the resist material was measured using the technique disclosed in H. Schmitt et al, "UV nanoimprint materials: Surface energies, residual layers, and imprint quality", J. Vac. Sci. Technol. B., Vol. 25, Issue 3, pp. 785-790, 2007. Specifically, the surface energies of Si substrates that underwent UV ozone processes and the surface of which were treated with Optool DSX (by Daikin Industries K.K.) were measured, then the surface energy of the resist material was calculated from the contact angles thereof with respect to the substrates.

(Nanoimprinting substrate)

In the case that the mold 1 has light transmissive properties, the Nanoimprinting substrate is not limited with regard to the shape, the structure, the size or the material thereof, and may be selected according to intended use. The expression "light transmissive properties" refers to a degree of light transmissivity that enables sufficient curing of the resin film when light enters the side of the substrate opposite that on which the resin film is formed. The surface of the nanoimprinting substrate which is the target of pattern transfer is the surface on which the resist is coated. With respect to the shape of the substrate, a substrate having a discoid shape may be utilized in the case that a data recording medium is to be produced, for example. 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, nickel, aluminum, glass, and resin. These materials may be utilized singly or in combination. 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 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 transmissive properties, it is preferable for a quartz substrate to be employed as the nanoimprinting substrate to enable the resist to be exposed to light. The quartz substrate is not particularly limited as long as it has light transmissive properties and a thickness of 0.3mm or greater, and may be selected as appropriate according to intended use. With respect to the light transmissive properties, a light transmissivity of at least 5% with respect to light having wavelengths of 200nm or greater from the side of the substrate opposite that on which the resin film is formed to the side of the substrate on which the resin film is formed is sufficient. A quartz substrate having a surface coated with a silane coupling agent may be employed. Further, a quartz substrate having a metal layer formed by chrome, tungsten, tantalum, titanium, nickel, silver, platinum, gold, etc., and/or a metal oxide layer formed by CrO_2, WO_2, TiO_2, etc. laminated thereon may be employed. It is preferable for the thickness of the metal layer or the metal oxide layer to be 30nm or less, and more preferably 20nm or less. If the thickness of the mask layer exceeds 30nm, UV transmissivity deteriorates, and resist curing failures become more likely to occur. Note that the surface of the laminated layer may be coated with a silane coupling agent. It is preferable for the thickness of the quartz substrate to be 0.3mm or greater. If the thickness of the quartz substrate is less than 0.3mm, it is likely to become damaged during handling or due to pressure during imprinting.

The nanoimprinting substrate may have a mesa type structure.

(Resist Coating Step)

A method that can arrange droplets of a predetermined amount at predetermined positions, such as the ink jet method and the dispensing method, is employed to coat the nanoimprinting substrate with resist. When the droplets of the resist are arranged on the nanoimprinting substrate, an ink jet printer or a dispenser may be used according to desired droplet amounts. For example, in the case that a droplet amount is less than 100nl, the ink jet printer may be selected, and in the case that a droplet amount is 100nl or greater, the dispenser may be selected.

Examples of ink jet heads that expel the resist from nozzles include the piezoelectric type, the thermal type, and the electrostatic type. From among these, the piezoelectric type of ink jet head, in which the droplet amount (the amount of resist in each arranged droplet) and the expelling speed are adjustable, is preferable. The amount of droplet amount and the expelling speed are set and adjusted prior to arranging the droplets of the resist onto the nanoimprinting substrate. For example, it is preferable for the droplet amount to be adjusted to be greater at regions at which the spatial volume of the pattern of protrusions and recesses of the mold is large, and to be smaller at regions at which the spatial volume of the pattern of protrusions and recesses of the mold is small. Such adjustments are controlled as appropriate according to droplet expulsion amounts (the amount of resist in each expelled droplet). Specifically, in the case that the droplet amount is set to 5pl, an ink jet head having a droplet expulsion amount of 1pl is controlled to expel droplets onto the same location 5 times. In the present invention, the droplet amount is within a range from 1pl to 10pl. The droplet amount is obtained by measuring the three dimensional shapes of droplets arranged on a substrate under the same conditions with a confocal microscope or the like, and by calculating the volumes of the droplets from the shapes thereof.

After the droplet amount is adjusted as described above, the droplets are arranged on the nanoimprinting substrate according to a predetermined droplet arrangement pattern.

In the case that the spin coat method or the dip coat method is employed, the resist is diluted with a solvent such that a predetermined thickness will be achieved. In the case of the spin coat method, the rotating speed is controlled, and in the case of the dip coat method, the pull up speed is controlled, to form a uniform coated film on the nanoimprinting substrate.

(Imprinting Step)

Prior to the mold and the resist being placed in contact, residual gas is reduced by depressurizing the atmosphere between the mold and the substrate, or by causing the atmosphere between the mold and the substrate to be a vacuum. However, there is a possibility that the resist 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 and the mold 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. It is preferable for the pressure of the depressurized He atmosphere to be within a range from 1kPa to 90kPa, and more preferably a range from 1kPa to 10kPa.

The mold and the substrate, which is coated with the resist, are caused to contact each other after they are aligned to have a predetermined positional relationship. It is preferable for alignment marks to be employed to perform the aligning operation. The alignment marks are formed by patterns of protrusions and recesses which can be detected by an optical microscope or by the Moire interference technique. The positioning accuracy is preferably 10μm or less, more preferably 1μm or less, and most preferably 100nm or less.

The mold is pressed against the substrate at a pressure within a range from 100kPa to 10MPa. The flow of the resist is promoted, the residual gas is compressed, the residual gas dissolves into the resist, and the passage of He through the quartz substrate is promoted as the pressure is greater. 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 and the substrate when the mold contacts the substrate. 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).

After the mold is pressed against the nanoimprinting substrate and the resist film is formed, the mold is separated from the resist film. As an example of a separating method, the outer edge portion of one of the mold and the nanoimprinting substrate may be held, while the rear surface of the other of the mold and the nanoimprinting substrate is held by vacuum suction, and the held portion of the outer edge or the held portion of the rear surface is relatively moved in a direction opposite the pressing direction.

(Repeated Mold Release Process)

In nanoimprinting, the mold release agent 6 on the surface of the mold 1 wears as imprinting operations are repeated. Therefore, it is preferable for the mold release process to be administered on the mold after every predetermined number of pressing steps or according to the degree of wear of the mold release layer (decrease in the coating rate by the mold release agent). The mold release process following imprinting operations is the same as the mold release process described above, which is administered when producing the mold 1. A large amount of the adsorbed water 2 is present at portions of the surface of the mold 1 where the mold release agent 6 has become thin, and particularly at portions where the mold main body 12 is exposed. In the case that the mold release agent 6 is diffused utilizing the meniscuses of the adsorbed water 2 are utilized, the mold release agent 6 will become concentrated at the portions where the mold release agent 6 has become thin. Thereby, the mold release layer 14 can be mended while maintaining the thickness distribution of the mold release layer 14 from the top surfaces St of the protrusions to the bottoms surfaces Sb of the recesses.

[Method for Producing Patterned Substrates]

Next, an embodiment of a method for producing a patterned substrate of the present invention will be described. The present embodiment employs the nanoimprinting method described above to produce a patterned substrate.

First, a resist film, on which a pattern has been formed by the nanoimprinting method described above, is formed on a surface of a substrate to be processed. Then, etching is performed using the resist film having the pattern formed thereon as a mask, to form a pattern of protrusions and recesses corresponding to the pattern of protrusions and recesses of the resist film. Thereby, a patterned substrate (copy) having a predetermined pattern is obtained.

In the case that the substrate to be processed is of a layered structure and includes a mask layer on the surface thereof, a resist film, on which a pattern has been formed by the nanoimprinting method described above, is formed on a surface of a substrate to be processed having the mask layer. Next, dry etching is performed using the resist film as a mask, to form a pattern of protrusions and recesses corresponding to the pattern of protrusions and recesses of the resist film in the mask layer. Thereafter, dry etching is further performed with the mask layer as an etching stop layer, to form a pattern of protrusions and recesses in the substrate. Thereby, a patterned substrate having a predetermined pattern is obtained.

The dry etching method is not particularly limited as long as it is capable of forming a pattern of protrusions and recesses in the substrate, and may be selected according to intended use. Examples of dry etching methods that may be employed include: the ion milling method; the RIE (Reactive Ion Etching) method; the sputter etching method; etc. From among these methods, the ion milling method and the RIE method are particularly preferred.

The ion milling method is also referred to as ion beam etching. In the ion milling method, an inert gas such as Ar is introduced into an ion source, to generate ions. The generated ions are accelerated through a grid and caused to collide with a sample substrate to perform etching. Examples of ion sources include: Kauffman type ion sources; high frequency ion sources; electron bombardment ion sources; duoplasmatron ion sources; Freeman ion sources; and ECR (Electron Cyclotron Resonance) ion sources.

Ar gas may be employed as a processing gas during ion beam etching. Fluorine series gases or chlorine series gases may be employed as etchants during RIE.

As described above, the method for producing patterned substrates of the present invention is executed employing the mold of the present invention, which has high old release properties across the entire surface of the pattern of protrusions and recesses thereof. Therefore, highly precise processing becomes possible in the production of patterned substrates using nanoimprinting.

In addition, the method for producing patterned substrates of the present invention performs dry etching using the resist film having the pattern of protrusions and recesses with high rectangularity formed by the nanoimprinting method described above as a mask. Therefore, substrates can be processed with high precision and high yields.

[Examples]

Examples of the present invention and Comparative Examples will be described below.

<Example 1>

(Production of Mold)

First, a Si substrate was coated with a resist liquid having a PHS (polyhydroxy styrene) series chemically amplified resist as a main component by the spin coat method, to form a resist layer. Thereafter, an electron beam, which was modulated according to a line pattern having a line width of 30nm and a pitch of 60nm, was irradiated onto the resist layer while the Si substrate was scanned on an XY stage, to expose a straight linear pattern of protrusions and recesses on the entirety of a 0.5mm square range of the resist layer.

Thereafter, the photoresist layer underwent a development process and the exposed portions were removed. Finally, selective etching was performed to a depth of 60nm by RIE using the resist layer, from which the exposed portions were removed, as a mask, to obtain a Si mold having the straight linear pattern of protrusions and recesses. The taper angle of the pattern of protrusions and recesses was 85 degrees.

The surface of a main body of the Si mold was cleansed by a UV ozone processing apparatus, to modify the properties of the surface of the Si mold main body to be hydrophilic.

(Mold Release Processing Substrate)

A 0.525mm thick Si wafer was employed as the mold release processing substrate. First, the surface of the Si wafer was cleansed by a UV ozone processing apparatus. Next, Optool DSX, which is a mold release agent by Daikin Industries K.K., was dissolved in HD-ZV, which is a fluorine series specialized solvent by Daikin

Industries K.K., to prepare a mold release processing liquid containing Optool DSX at 0.1w%. The Si wafer was immersed in the mold release processing liquid for 1 minute, then pulled up at a constant speed of 5mm/sec to dip coat the mold release agent onto the Si wafer. The film thickness of the mold release agent was 5nm.

(Mold Release Processing Method)

The Si mold main body and the Si wafer were placed in a nanoimprinting apparatus. The Si mold main body and the Si wafer were caused to contact each other under the conditions: room temperature 25°C; and 80% relative humidity. The contact state was maintained for 5 minutes, and then the Si mold main body was separated from the Si wafer. A mold release layer having a thickness distribution in which the thickness at the top surfaces of the protrusions is 3nm, the thickness at the bottom surfaces of the recesses is 1nm, and the thickness at the side surfaces of the protrusions continuously changes from 3nm to 1nm from the top surfaces to the bottom surfaces was formed by the method described above. The Si mold was obtained by the above steps.

(Nanoimprinting Substrate)

A 0.525mm thick quartz substrate was employed as a substrate. The surface of the quartz substrate was processed with KBM-5103 (by Shin-Etsu Chemical Industries, K.K.), which is a silane coupling agent having superior close contact properties with respect to the resist. The KBM-5103 was diluted to 1% by mass using PGMEA, and coated on the surface of the substrate by the spin coat method. Thereafter, the coated substrate was annealed for 5 minutes at 150°C on a hot plate, causing the silane coupling agent to bond to the surface of the substrate.

(Resist)

A resist containing the compound A represented by Chemical Formula 1 at 48w%, Aronix M220 at 48w%, IRGACURE 379 at 3w%, and the compound B represented by Chemical Formula 2 at 1w% was prepared as the resist.

(Resist Coating Step)

DMP-2831, which is an ink jet printer of the piezoelectric type by FUJIFILM Dimatix, was utilized. DMC-11610, which is a dedicated 10pl head, was utilized as an ink jet head. Ink expelling conditions were set and adjusted in advance such that the amount of resist in each droplet was 10pl. After the droplet amount was adjusted in this manner and adjustments were made such that a residual film thickness will become 10nm, droplets were arranged on the substrate according to a predetermined droplet arrangement pattern.

(Imprinting Step)

The Si mold and the quartz substrate were caused to approach each other such that the gap therebetween was 0.1mm or less, and positioning was performed from the rear surface of the quartz substrate such that the positions of the alignment marks on the quartz substrate matched the positions of the alignment marks on the Si mold. The space between the Si mold and the quartz substrate was replaced with a gas which is 99% He by volume or greater. Then, depressurization was performed to 20kPa or less. The mold was caused to contact the droplets of resist under the depressurized He conditions. After contact, a pressure of 1MPa was applied for one minute, and ultraviolet light including a wavelength of 360nm as irradiated at a dosage of 300mJ/cm^2, to cure the resist. Thereafter, the back surfaces of the quartz substrate and the Si mold were held by suction. Then, the quartz substrate or the Si mold was relatively moved in a direction opposite the pressing direction to separate the Si mold.

(Si Mold Copy Production Step)

Dry etching was performed as described below using the resist film, on which the pattern of protrusions and recesses is transferred, as a mask. Thereby, shapes of protrusions and recesses based on the pattern of protrusions and recesses of the resist film were formed on the quartz substrate. First, the residual film present at the recesses of the pattern was removed by oxygen plasma etching, to expose the quartz substrate at the recesses of the pattern. At this time, conditions were set such that the amount of etching is capable of removing the thickest residual film within the region of the pattern of protrusions and recesses. Next, RIE using a fluorine series gas was administered on the quartz substrate, using the protrusions of the pattern as a mask. The RIE conditions were set such that the depth of etching was 60nm. Finally, the residue of the protrusions of the pattern was removed by oxygen plasma etching. As a result, a copy mold having a predetermined pattern of protrusions and recesses was obtained.

The quartz mold, which is a copy of the Si mold, was produced by the above copy production step.

<Example 2>

The same steps as those performed in Example 1 were executed except that the mold release process was executed employing a chemical vapor deposition method as described below.

The mold release process employing the chemical vapor deposition method was executed by depressurizing the interior of a container having a mold therein to 10kPa or less, heating a mold release agent to vaporize it, introducing a gas that includes the mold release agent into the container while controlling the amount of flow thereof, and exposing the surface of the mold to an atmosphere that includes the mold release agent in a gaseous state. A mold release layer having a thickness distribution in which the thickness at the top surfaces of the protrusions is 3nm, the thickness at the bottom surfaces of the recesses is 1nm, and the thickness at the side surfaces of the protrusions continuously changes from 3nm to 1nm from the top surfaces to the bottom surfaces was formed on the surface of a mold main body by the method described above.

<Example 3>

The same steps as those performed in Example 1 were executed except that an electron beam, which was modulated according to a line pattern having a line width of 30nm and a pitch of 60nm and a line pattern having a line width of 300nm and a pitch of 600nm, was irradiated onto the resist layer while the Si substrate was scanned on an XY stage, to expose a straight linear pattern of protrusions and recesses with recesses having different widths within a 5mm square range of the resist layer.

<Comparative Example 1>

A mold having a mold release layer only on the protrusions thereof was produced. The steps other than the mold release processing step were the same as those executed for Example 1.

(Mold Release Processing Method)

A Si mold main body and a mold release processing substrate were placed in a nanoimprinting apparatus. The Si mold main body and the mold release processing substrate were caused to contact each other under the conditions: room temperature 25°C; and 20% relative humidity. The contact state was maintained for 1 minute, and then the Si mold main body was separated from the mold release substrate. Diffusion of a mold release agent by meniscuses was suppressed by the low humidity and the short contact time. A mold release layer having a thickness distribution in which the thickness at the top surfaces of the protrusions is 3nm, the thickness at the bottom surfaces of the recesses is 0nm, and the thickness at the side surfaces of the protrusions is less than 3nm was formed on the surface of the Si mold main body by the method described above.

<Comparative Example 2>

The same steps as those performed in Example 1 were executed except that a mold release process was administered employing the dipping method as described below.

The mold release process employing the dipping method was performed by immersing a Si mold body in a solution, in which a mold release agent was dissolved at a concentration of 0.1% by weight, for 1 hour. A mold release layer having a thickness distribution in which the thickness at the top surfaces of the protrusions is 1nm, the thickness at the bottom surfaces of the recesses is 1nm, and the thickness at the side surfaces of the protrusions is uniform was formed on the surface of the Si mold main body by the method described above.

<Comparative Example 3>

The same steps as those performed in Example 2 were executed except that an electron beam, which was modulated according to a line pattern having a line width of 30nm and a pitch of 60nm and a line pattern having a line width of 300nm and a pitch of 600nm, was irradiated onto the resist layer while the Si substrate was scanned on an XY stage, to expose a straight linear pattern of protrusions and recesses with recesses having different widths within a 5mm square range of the resist layer. Note that the mold release layer was adjusted to have a desired thickness within the region having the line pattern with the line width of 30nm and the pitch of 60nm. That is, the mold release layer was formed to have a thickness distribution in which the thickness at the top surfaces of the protrusions is 3nm, the thickness at the bottom surfaces of the recesses is 1nm, and the thickness at the side surfaces of the protrusions continuously changes from 3nm to 1nm from the top surfaces to the bottom surfaces was formed in the region of the line pattern with the line width of 30nm and the pitch of 60nm. As a result, the mold release layer in the region of the line pattern with the line width of 300nm and the pitch of 600nm became that without a thickness distribution, in which the thickness at the top surfaces of the protrusions is 2nm, the thickness at the bottom surfaces of the recesses is 2nm, and the thickness at the side surfaces of the protrusions is approximately 2nm.

<Evaluation Method>

Hereinafter, the specific evaluation methods and evaluation results with respect to the pattern formability of resist patterns, the durability of molds, the number of increased defects at the time of repeated mold release processing, and the productivity of nanoimprinting operations will be described.

Evaluations of the pattern formability of resist patterns were performed by cutting the resist patterns formed by nanoimprinting operations in the vertical direction, and by measuring the cross sectional shapes thereof by an AFM and/or a scanning electron microscope. Measurements were performed using the angles of inclination of the protrusions within the regions of patterns of protrusions and recesses having line widths of 30nm and pitches of 60nm as an index. In addition, with respect to Example 3 and Comparative example 3 only, difference values of average values of the depths in pattern regions having different line widths and pitches, to perform evaluations of the uniformity of the depths. The angles of inclinations and the difference values of the Examples and the Comparative Examples are as shown in Table 1.

TABLE 1

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Inclination Angle of Protrusions	87 degrees	87 degrees	87 degrees	85 degrees	85 degrees	87 degrees
Difference in Depths	n/a	n/a	0.5nm	n/a	n/a	2nm

Evaluations of the durability of the molds were performed by observing the surfaces of the molds with an optical microscope, a scanning electron microscope, and an atomic force microscope after 100 nanoimprinting operations were performed. The number of foreign objects adhered to the surfaces were employed as indices of durability. When comparing the evaluation results, the numbers of foreign objects of the Examples and the Comparative Examples were calculated as relative values in the case that the number of foreign objects adhered to the mold of Example 1 was designated as 100. The numbers of adhered foreign objects for each of the Examples and Comparative Examples are as shown in Table 2.

TABLE 2

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Number of Foreign Objects	100	98	108	188	121	102

Evaluations of the number of increased defects at the time of repeated mold release processing were performed by administering mold release processes again after 100 nanoimprinting operations were performed, and observing the surfaces of the molds with an optical microscope, a scanning electron microscope, and an atomic force microscope prior to and following the mold release processes. Increases in the number of foreign objects adhered to the surfaces (increases in the number of defects) were employed as indices for the evaluations. When comparing the evaluation results, the increases in the numbers of defects of the Examples and the Comparative Examples were calculated as relative values in the case that the increase in the number of defects in the mold of Example 1 was designated as 100. The increase in the number of defects for each of the Examples and Comparative Examples are as shown in Table 3.

TABLE 3

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Increase in Number of Defects	100	105	101	98	162	99

Evaluations of the productivity of nanoimprinting operations were performed, employing the total amounts of time required for the mold release processes (including conveyance and placement of molds from a mold release processing apparatus to a nanoimprinting apparatus) as indices. When comparing the evaluation results, the total times for the Examples and the Comparative Examples were calculated as relative values in the case that the total time for the mold of Example 1 was designated as 100. The total times for each of the Examples and Comparative Examples are as shown in Table 4.

TABLE 4

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Total Time	100	150	100	20	1500	150

<Evaluation Results>

The evaluation results related to Example 2 will be discussed. In the mold release process that employs the chemical vapor deposition method, it is necessary to utilize a dedicated vapor deposition apparatus different from the nanoimprinting apparatus. Accordingly, the productivity thereof was slightly poor compared to Example 1, but the decrease in productivity was within an acceptable range. The pattern formability of the resist pattern was equivalent to that of Example 1, because it is possible to control the thickness of the mold release layer such that the thickness at the bottom surfaces of the recesses is possible. The durability of the mold and the number of increased defects at the time of repeated mold release processing were equivalent to those of Example 1.

The evaluation results related to Example 3 will be discussed. There were slight fluctuations in the depths of the recesses because the pattern on the Si mold had recesses with different widths, and therefore the pattern formability deteriorated slightly. However, the deterioration in pattern formability was within an acceptable range. The durability of the mold, the number of increased defects at the time of repeated mold release processing, and the productivity of nanoimprinting were equivalent to those of Example 1.

The evaluation results related to Comparative Example 1 will be discussed. The pattern formability was poor compared to Example 1, because the mold release agent was only present on the top surfaces of the protrusions. In addition, the number of imprinting defects due to clogging, defects in the resist pattern, peeling, etc., was greater than that of Example 1 because the mold release agent was not present on the bottom surfaces of the recesses. The increase in the number of defects at the time of repeated mold release processing was equivalent to that of Example 1, and the productivity of nanoimprinting was greater than that of Example 1.

The evaluation results related to Comparative Example 2 will be discussed. The pattern formability was poor compared to Example 1, because the mold release process that employs the dipping method uniformly coats the entirety of the pattern of protrusions and recesses with the mold release agent. In addition, the increase in the number of defects at the time of repeated mold release processing was greater than that of Example 1, because foreign objects that adhere to the back and side surfaces of the mold within the nanoimprinting apparatus or during conveyance become adhered to the surface during immersion. In addition, the productivity of nanoimprinting was poor compared to that of Example 1, because it is necessary to utilize a dedicated dipping apparatus outside the nanoimprinting apparatus. The durability of the mold was equivalent to that of Example 1.

The evaluation results related to Comparative Example 3 will be discussed. In the mold release process that employs the chemical vapor deposition method, the thickness of the mold release layer at the bottom surfaces of the recesses will become greater at recesses having greater widths if a pattern having recesses with different widths is present on the Si mold main body. Accordingly, the uniformity of pattern depth deteriorated, and the pattern formability was poor compared to that of Example 3. It became difficult to impart a thickness distribution to the mold release layer on the side surfaces as the line width of the recesses became greater and/or the aspect ratio became smaller, with a line width of approximately 100nm and an aspect ratio of 1 as the boundary. In addition, in the mold release process that employs the chemical vapor deposition method, it is necessary to utilize a dedicated vapor deposition apparatus outside the nanoimprinting apparatus. Therefore, the productivity of nanoimprinting became slightly poor compared to that of Example 1. However, the decrease in productivity of nanoimprinting was within an allowable range. The durability of the mold and the number of increased defects at the time of repeated mold release processing were equivalent to those of Example 1.

Table 5 summarizes the evaluation results related to the Examples and the Comparative Examples.

TABLE 5

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Formability of Resist Pattern	Good	Good	Good	Poor	Poor	Poor
Durability of Mold	Good	Good	Good	Poor	Good	Good
Increase in Number of Defects at Repeated Mold Release Processing	Good	Good	Good	Good	Poor	Good
Productivity of Nanoimprinting	Good	Good	Good	Good	Poor	Good

The indications of Table 5 are as follows.

In the row related to formability of the resist pattern, cases in which the angle of inclination of the protrusions was greater than 85 degrees (this is the taper angle when the Si mold main body is produced) were evaluated as being "Good", and cases in which the angle was 85 degrees or less were evaluated as being "Poor". However, even if the angle of inclination of the protrusions was greater than 85 degrees, the formability of the resist pattern was evaluated as being "Poor" if the difference in average values of the depths in the evaluation of uniformity of depths was 1nm or greater.

In the row related to durability of the mold, cases in which the number of foreign objects was less than 150 were evaluated as being "Good", and cases in which the number was 150 or greater were evaluated as being "Poor".

In the row related to the increase in the number of defects at the time of repeated mold release processing, cases in which the increase in the number of defects was 150 or less were judged as having a small increase in the number of defects, and evaluated as being "Good", while cases in which the increase in the number of defects was greater than 150 were evaluated as being "Poor".

In the row related to the productivity of nanoimprinting, cases in which the total time was 150 or less were evaluated as being "Good", and cases in which the total time was greater than 150 were evaluated as being "Poor".

As can be understood from Table 5, the molds of the present invention, that is, the molds of Examples 1 through 3, exhibited superior performance in the formability of resist patterns, the durability of the molds, the increase in the number of defects at the time of repeated mold release processing, and productivity of nanoimprinting. It can be understood from the results related to Comparative Example 3 that problems arose in the formability of the resist pattern, particularly the uniformity of depth, in the mold having a pattern including different line widths and pitches, even if the chemical vapor deposition method, which yielded favorable results in Example 2, is employed. As indicated by the evaluation results related to Example 3, the uniformity of depth was improved, and superior performance was exhibited for all evaluated items. In comparisons with Examples 1 through 3, non of Comparative Examples 1 through 3 were equivalent or greater with respect to all evaluated items. The superiority of the present invention was confirmed by the above results.

CLAIMS

1. A mold release processing method for forming a mold release layer on a surface of a mold main body having a fine pattern of protrusions and recesses on the surface, characterized by comprising:

preparing a mold release processing substrate coated with a mold release agent;

causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent;

maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water; and

causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate.

2. A mold release processing method as defined in Claim 1, characterized by:

the mold release processing method being executed within a nanoimprinting apparatus.

3. A method for producing a nanoimprinting mold having a mold main body with a fine pattern of protrusions and recesses on a surface thereof and a mold release layer on the surface of the mold main body, characterized by comprising:

preparing a mold release processing substrate coated with a mold release agent;

causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent;

maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water; and

causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate.

4. A method for producing a nanoimprinting mold as defined in Claim 3, characterized by:

the method for producing a nanoimprinting mold being executed within a nanoimprinting apparatus.

5. A nanoimprinting mold comprising:

a mold main body with a fine pattern of protrusions and recesses on a surface thereof; and

a mold release layer on the surface of the mold main body; characterized by:

the mold release layer having a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses.

6. A nanoimprinting mold as defined in Claim 5, characterized by:

the thickness distribution of the mold release layer being that in which the thickness at the side surfaces decreases from a thickness which is the same thickness as the thickness at the top surfaces to a thickness which is the same thickness as the thickness at the bottom surfaces.

7. A nanoimprinting mold as defined in either one of Claim 5 or Claim 6, characterized by:

the thickness distribution of the mold release layer being that in which the thickness at the top surfaces is within a range from 1nm to 5nm, and the thickness at the bottom surfaces is within a range from 0.1nm to 1nm and 70% of the thickness at the top surfaces or less.

8. A nanoimprinting method, characterized by comprising:

employing a mold as defined in any one of Claims 5 through 7;

coating a nanoimprinting substrate with resist;

pressing the mold on the surface of the nanoimprinting substrate which is coated with the resist; and

separating the mold from the nanoimprinting substrate.

9. A nanoimprinting method as defined in Claim 8, characterized by a mold release process being administered on the mold after every predetermined number of pressing steps or according to the degree of wear of the mold release layer, the mold release process comprising:

preparing a mold release processing substrate coated with a mold release agent;

causing the mold main body having adsorbed water on the surface thereof and the mold release processing substrate to approach each other until a contact state in which the upper portions of the protrusions of the pattern of protrusions and recesses are in contact with the mold release agent;

maintaining the contact state until the mold release layer is formed such that it has a thickness distribution in which the thickness of the mold release layer at the side surfaces of the pattern of protrusions and recesses becomes thinner from the top surfaces of the protrusions toward the bottom surfaces of the recesses due to the mold release agent becoming diffused in the adsorbed water; and

causing the mold main body and the mold release processing substrate to move away from each other such that the upper portions of the protrusions separate from the mold release agent on the mold release processing substrate.

10. A nanoimprinting method as defined in Claim 9, characterized by:

the step of pressing the mold against the nanoimprinting substrate and the step of administering the mold release process both being executed within a nanoimprinting apparatus.

11. A method for producing a patterned substrate, characterized by comprising:

forming a resist film, to which a pattern of protrusions and recesses is transferred, on a substrate to be processed by a nanoimprinting method as defined in any one of Claims 8 through 10; and

performing etching using the resist film as a mask, to form a pattern of protrusions and recesses corresponding to the pattern of protrusions and recesses transferred onto the resist film.

FIG.1

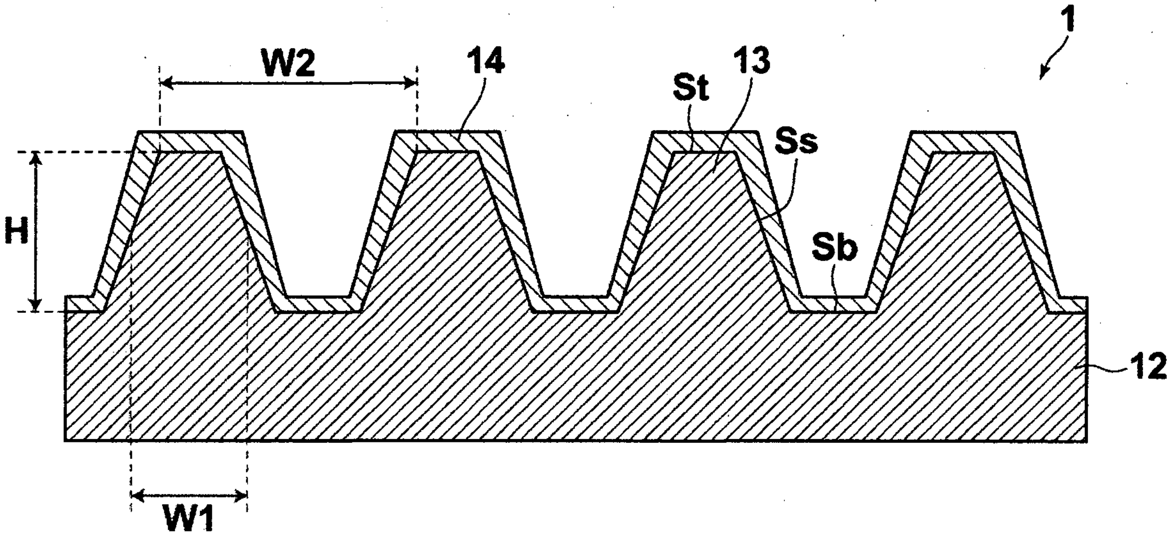


FIG.2

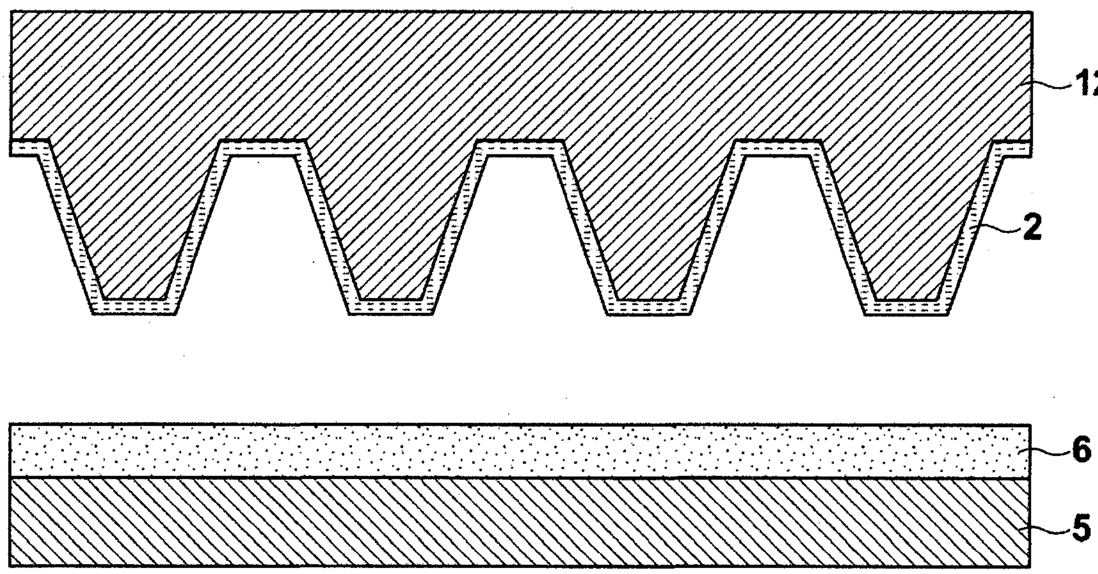


FIG.3

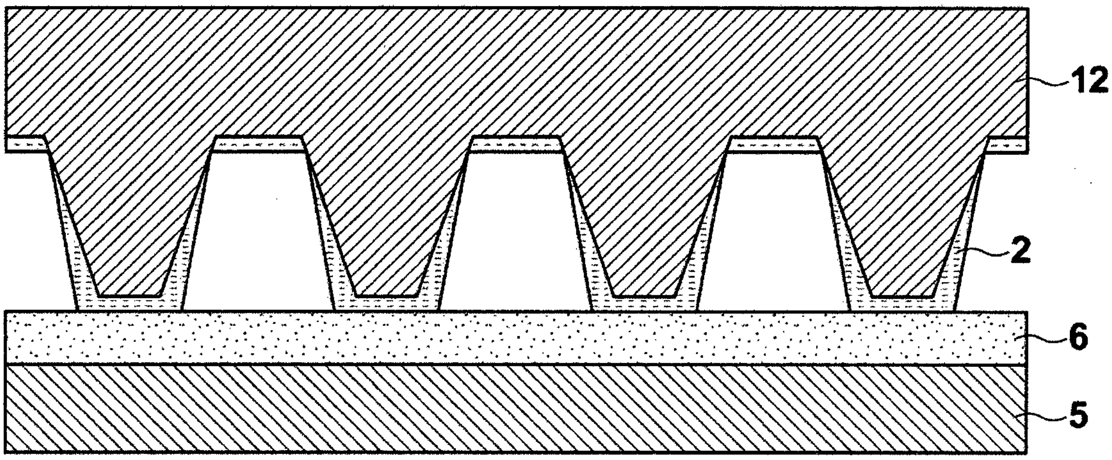


FIG.4

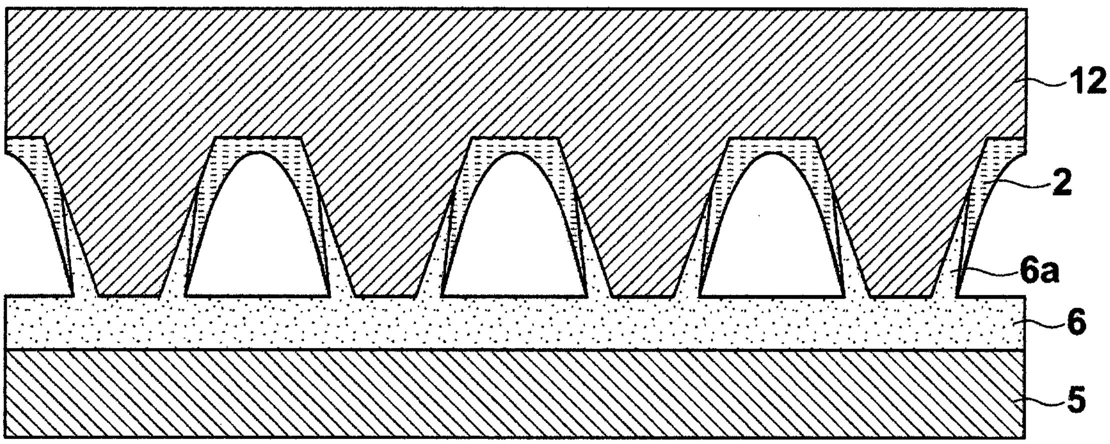


FIG.5

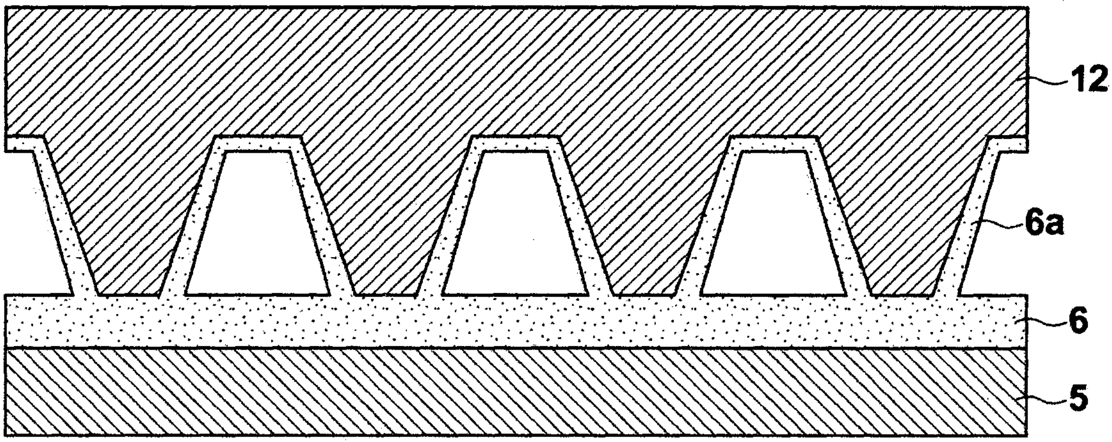
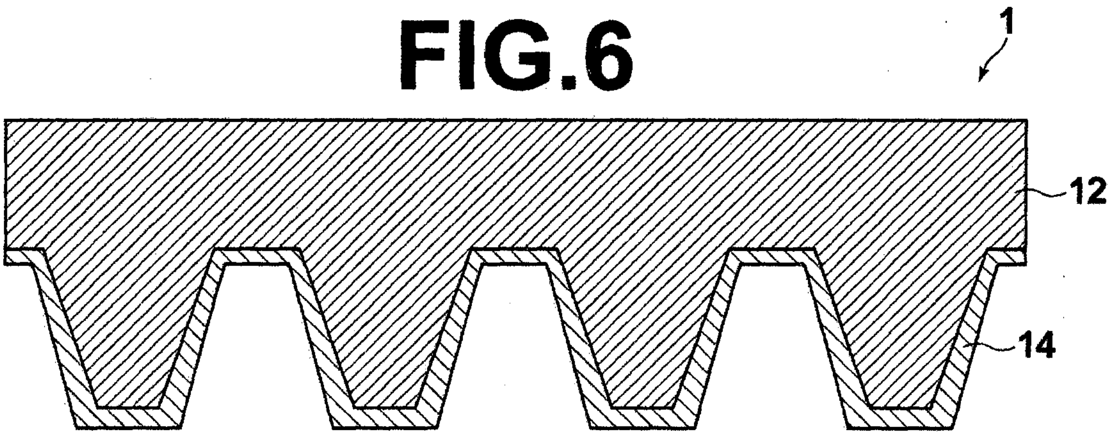


FIG.6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/070577

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B29C33/38(2006.01)i, B29C33/58(2006.01)i, B29C59/02(2006.01)i, H01L21/027(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. B29C33/00-33/76, B29C59/00-59/18, B29C39/00-39/44, B29C43/00-43/58, H01L21/027

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2012
Registered utility model specifications of Japan 1996-2012
Published registered utility model applications of Japan 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2010/0308496 A1 (Shinji UCHIDA) 2010.12.09, [0067]～[0072], FIG.2A～FIG.2G & JP 2010-284814 A	5,6,8,11 1-4,7,9,10
A	US 2004/0182820 A1 (Shigehisa MOTOWAKI) 2004.09.23, whole document & JP 2004-288783 A	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26.11.2012	04.12.2012

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