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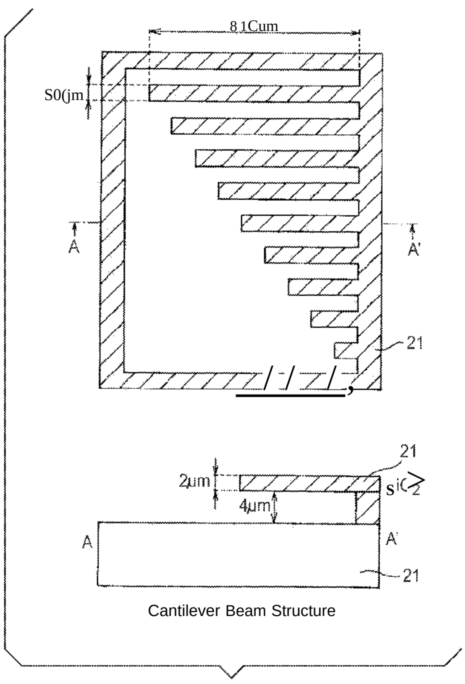
(54) Title: DRYING METHOD FOR SURFACE STRUCTURE BODY



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(57) Abstract: To provide a drying method for a surface structure body in which a first liquid deposited onto the surface structure body is rapidly solidified and that makes possible concurrent drying of multiple surface structure bodies. The present invention provides a drying method for a surface structure body having a first liquid deposited thereon, including the steps of: placing a surface structure part of the surface structure body in a second liquid that is a liquid at a temperature, said temperature being lower than a solidification point of the first liquid; solidifying the first liquid in the second liquid; removing the second liquid from the surface structure part while the first liquid is in a solidified state; and sublimating the solidified first liquid.

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DRYING METHOD FOR SURFACE STRUCTURE BODY

FIELD OF THE INVENTION

The present invention relates to a drying process for surface structures in a manufacturing process for a structure body having fine structures on a surface such as, for example, semiconductor devices, integrated devices such as micro electro mechanical systems (MEMS), and the like.

BACKGROUND

Cleaning and processing rinse liquids such as, for example, water and the like, are known as cleaning liquids that are used in manufacturing processes for structure bodies having fine structures on their surfaces such as, for example, semiconductor devices, integrated devices, and the like. These cleaning liquids are used to remove contaminants from surface structures. However, the cleaning liquids are trapped in irregular patterns of the surface structures and due to the surface tension of the cleaning liquid itself at a time of drying there are problems such as the patterns collapsing or becoming attached.

In order to solve these problems, Japanese Unexamined Patent Application No. H04-242930, for example, describes a drying method in which after droplets deposited on a processed product are cooled and frozen, these frozen droplets are sublimated in vacuo. Additionally, Japanese Unexamined Patent Application No. H06-2241 16 describes a resist development method in which after surfaces of wafers are washed with a rinse liquid, the rinse liquid is frozen and sublimated in vacuo in order to dry said surfaces.

These drying methods solve the problems of patterns collapsing or becoming attached due to surface tension because the state of the cleaning liquid is changed directly from a solid to a gas.

However, with Japanese Unexamined Patent Application No. H04-242930, when solidifying the liquid deposited on the surface structure body, the liquid is solidified by introducing a low-temperature nitrogen gas into a processing chamber in which the processed product is placed. Because nitrogen gas is the gas being used for solidification though, there is a problem in that the solidification takes time.

With Japanese Unexamined Patent Application No. H06-2241 16, a fixed stage is used to cool the wafers and freeze the rinse liquid, but with this method only one wafer can be processed at a time, which leads to problems with productivity. Additionally, with this method, a device having multiple stages with heating/cooling functionality is necessary to simultaneously process multiple wafers, which leads to a problem of extensive equipment being needed.

SUMMARY

The present invention seeks to solve the problems of the conventional technology such as the aforementioned problems and makes possible the rapid solidification of a first liquid deposited on a surface structure body by a second liquid and also makes possible the concurrent drying of multiple surface structure bodies.

The present invention provides a drying method for a surface structure body having a first liquid deposited thereon, including the steps of: placing a surface structure part of the surface structure body in a second liquid that is a liquid at a temperature, said temperature being lower than a solidification point of the first liquid; solidifying the first liquid in the second liquid; removing the second liquid from the surface structure part while the first liquid is in a solidified state; and sublimating the solidified first liquid.

According to an aspect of the present invention, after cleaning the surface structure body with the first liquid having, for example, strong cleaning power and/or strong rinsing power, the first liquid that is deposited on the surface structure body is solidified by the second liquid. Therefore, the first liquid can be rapidly solidified. Furthermore, concurrent drying of multiple surface structure bodies is facilitated because multiple surface structure bodies can be processed by the first liquid and the second liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG 1 is a phase diagram of a first liquid related to an embodiment of the present invention.

FIG. 2is a schematic view of a cantilever beam structure.

DETAILED DESCRIPTION OF THE INVENTION

The details of an embodiment of the present invention are set forth in the description below. However, the present invention is not limited to the particular embodiment described.

The drying method of the present invention is applied to surface structure bodies having fine surface structures such as semiconductor devices, integrated devices, and the like. Though not particularly limited, the present invention can be particularly preferably used on structure bodies having fine surface structures that are on an order of a few dozen micrometers or smaller.

When processing the surface structure body with a first liquid, the first liquid can be used for, for example, cleaning, rinsing, wet etching, and sacrifice layer etching the surface structures, or the like. Examples of such liquid include water-soluble liquids such as water, aqueous ammonia, aqueous hydrogen peroxide, hydrochloric acid, nitric acid, sulfuric acid, hydrofluoric acid, aqueous potassium hydroxide solutions, aqueous sodium hydroxide solutions, hydroxide tetramethylammonium, and the like; alcohols such as methanol, ethanol, isopropyl alcohol, and the like; and ketones such as acetone and the like. The liquids mentioned may be used singly or in the form of mixtures of two or more thereof.

Additives such as surfactants, chelates, viscosity adjusting agents, oxidizing agents, reductants, anticorrosive agents, surface modification agents, and the like may be added to the first liquid for the purposes of improving cleaning properties, drying properties, and the like. After cleaning, etching or otherwise processing the surface structure body with the first liquid, the surface structure body having the first liquid deposited thereon is placed in a second liquid. The surface structure body is preferably placed in the second liquid prior to the surface structures beginning to collapse and/or becoming attached due to the first liquid.

The second liquid is a liquid at a temperature lower than a solidification point or sublimation point of the first liquid. A solidification point of the second liquid may be at least 10 degrees lower than the solidification point or the sublimation point of the first liquid. If at least 10°C lower, solidification of the first liquid can be performed more efficiently.

A solubility of the first liquid with respect to the second liquid may be from 0 mass% to 1 mass%. If the solubility exceeds 1 mass%, a problem will arise in which the first liquid will be displaced by the second liquid during the time from when the surface structure body having the first liquid deposited thereon is immersed in the second liquid to a completion of the freezing. The solubility is a value that is measured, for example, using a Karl Fischer titration-type moisture meter.

For the second liquid, a liquid having a vapor pressure at 25°C of 1 kPa or higher may be used. If the vapor pressure is less than 1 kPa, excessive time will be required for the step of removing the second liquid from the surface structure part.

Examples of liquids that can be used as the second liquid include fluoro-based solvents such as hydrofluoroethers (HFE), hydrofluorocarbons (HFC), hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC), and the like; hydrocarbon-based solvents such as toluene, xylene, hexane, pentane, and the like; and glycol ester-based solvents such as propylene glycol monomethyl ether acetate (PGMEA), and the like.

FIG. 1 is a drawing that schematically shows a phase diagram of the first liquid. The first liquid can be solidified faster than when using a cold gas because the first liquid is solidified by the cold second liquid.

When placing the surface structure body into the second liquid, the surface structure body may be placed after lowering a temperature of the second liquid to a temperature lower than the solidification point or sublimation point of the first liquid, or the temperature of the second liquid may be lowered after placing the surface structure body into the second liquid.

As shown in (11) of FIG. 1, the surface structure body is left for a short time in the cold second liquid, and after the first liquid is solidified, the second liquid is removed from the surface structure part while the first liquid is in a solidified state. A liquid having a surface tension lower than that of the first liquid may be used as the second liquid. By using a liquid having a low surface tension, the irregular patterns of the surface structures collapsing or becoming attached can be prevented.

When using, as the first liquid, a liquid such as water or the like that does not sublimate under atmospheric pressure, as shown in (12) of FIG. 1, a pressure of a system in which the aforementioned surface structure body is placed is reduced before or after removing the second liquid. Next, the pressure is either further reduced (13) or the temperature is raised (13') to sublimate the first liquid and remove the first liquid from the surface structures.

Because the concept of liquid surface tension is absent during the sublimation step, there is no problem of the fine surface structure parts collapsing or becoming attached.

EXAMPLES

The present invention is described below based on Examples, but the present invention is not limited by these Examples.

Example 1

Silicone dioxide was used on a silicone substrate (22) to produce a chip having cantilever beams (21) shown in the structure of FIG. 2. An electron microscope (VE-9800, manufactured by Keyence Corporation) was used to confirm that in an initial state, beams of all lengths were neither collapsed nor attached.

A glass beaker was filled with ultrapure water (first liquid) and the chip was immersed in the ultrapure water for 10 minutes. Immediately after removing the chip from the ultrapure water, the chip was immersed in another glass beaker filled with HFE (Novec™ HFE-7100, manufactured by Sumitomo 3M Limited; second liquid) cooled to -20°C for three minutes and the ultrapure water was frozen. A vacuum container (Kan'i Vacuum Oven KVO-300, manufactured by AS ONE Corporation) was attached to a rotary pump (PD-52, manufactured by ULVAC, Inc.) and a vacuum environment was made. Immediately after removing the chip having ice deposited thereon from the HFE, the chip was placed in this vacuum environment and left to sit for two hours. A display of a vacuum meter attached to the vacuum equipment was checked and pressure was confirmed to be -0.1 MPa. After visually confirming that the ice deposited on the chip had disappeared, the chip was removed from the vacuum equipment.

A scanning electron microscope (VE-9800, manufactured by Keyence Corporation; SEM) was used to observe the pattern of the chip and it was confirmed that the cantilever beams (21) were not attached to the substrate (22).

Example 2

Aside from using a different HFE (AE-3000, manufactured by Asahi Glass Co., Ltd.) as the second liquid, the surface structure body was dried according to the same conditions as described in Example 1. None of the cantilever beams (21) were attached to the substrate (22).

Example 3

Aside from using a different HFE (Novec™ HFE-7200, manufactured by Sumitomo 3M Limited) as the second liquid, the surface structure body was dried according to the same conditions as described in Example 1. None of the cantilever beams (21) were attached to the substrate (22).

Example 4

Aside from using an HFC (Vertrel™ XF, manufactured by Du Pont-Mitsui Fluorochemicals Company, Ltd) as the second liquid, the surface structure body was dried according to the same conditions as described in Example 1. None of the cantilever beams (21) were attached to the substrate (22).

Example 5

Aside from using a toluene (special grade, manufactured by Wako Pure Chemical Industries, Ltd.) in place of an HFE as the second liquid, the surface structure body was dried according to the same conditions as described in Example 1. None of the cantilever beams (21) were attached to the substrate (22).

Comparative Example 1

Aside from placing the chip in a -20°C freezer for one hour and freezing the ultrapure water immediately after removing the chip from the ultrapure water, the same procedures were carried out as in Example 1. It was confirmed that the cantilever beams (21) were not attached to the substrate (22), but it took one hour for the ultrapure water to freeze.

Comparative Example 2

The same procedures were carried out as in Example 1, up to the point of immersing the chip in ultrapure water for ten minutes. After removing the chip from the ultrapure water, the chip was left for 30 minutes at room temperature (25°C) to air dry. The SEM was used to observe the pattern as in Example 1 and it was confirmed that all 9 cantilever beams (21) were attached to the substrate (22).

Reference Example 1

The following experiment was conducted in order to confirm the difference in the speed of solidification of water in a gas phase and a liquid phase.

A 25 mm x 10 mm size silicone sample of a thermal oxide film (thickness = 100 nm) was prepared and immersed in distilled water. The silicone sample was removed from the distilled water, immersed in an HFE (Novec™ HFE-7100, manufactured by Sumitomo 3M Limited) cooled to -20°C, and the time required for the distilled water deposited on the silicone sample to solidify was measured. It took 50 seconds from immersion to solidify. Whether solidification had taken place or not was determined visually. As water turns white when it solidifies rapidly, solidification was determined to be complete when all of the water had turned white.

Reference Example 2

After immersing the silicone sample in distilled water as in Reference Example 1, the time required for the distilled water deposited on the silicone sample to solidify at a temperature of -20°C was measured. It took nine minutes from introduction to the -20°C environment to solidify. In cases when solidification took time, a portion of the distilled water dried before solidifying, thus working in a disadvantageous direction against preventing the fine structures from collapsing or becoming attached.

Claims

1. A drying method for a surface structure body having a first liquid deposited thereon, comprising the steps of:

placing a surface structure part of the surface structure body in a second liquid that is a liquid at a temperature, said temperature being lower than a solidification point of the first liquid;

solidifying the first liquid in the second liquid;

removing the second liquid from the surface structure part while the first liquid is in a solidified state; and

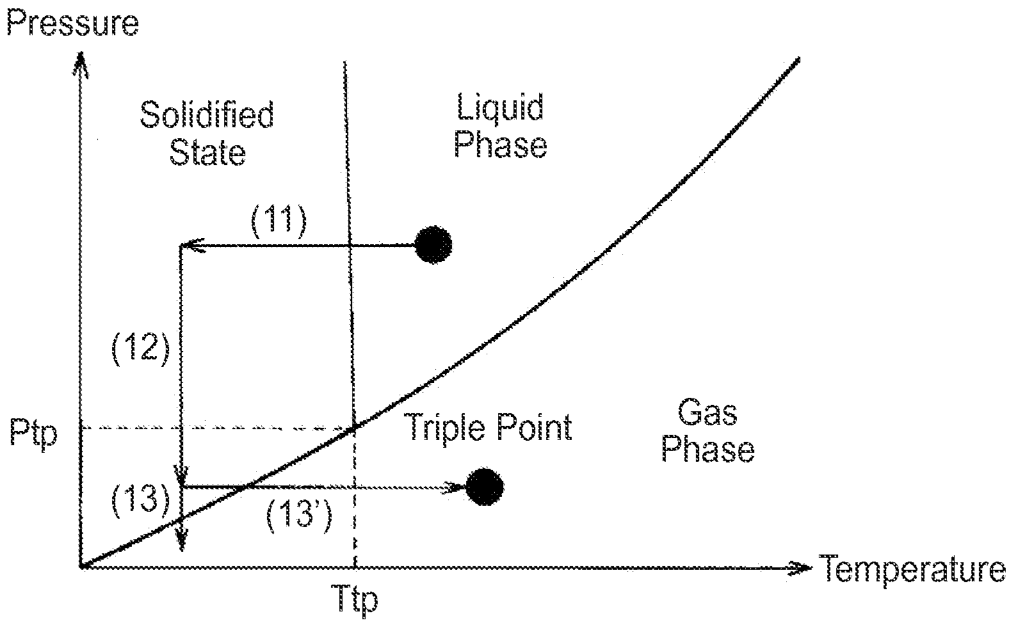
sublimating the solidified first liquid.

2. The drying method for a surface structure body according to claim 1, wherein a solubility of the first liquid with respect to the second liquid is from 0 mass% to 1 mass%.

3. The drying method for a surface structure body according to claim 1 or 2, wherein a solidification point of the second liquid is at least 10°C lower than the solidification point or the sublimation point of the first liquid.

4. The drying method for a surface structure body according to any one of claims 1 to 3, wherein a vapor pressure of the second liquid at 25°C is 1 kPa or higher.

5. The drying method for a surface structure body according to any one of claims 1 to 4, wherein the second liquid is a fluorine-based solvent.



A Phase Diagram of First Liquid

FIG. 1

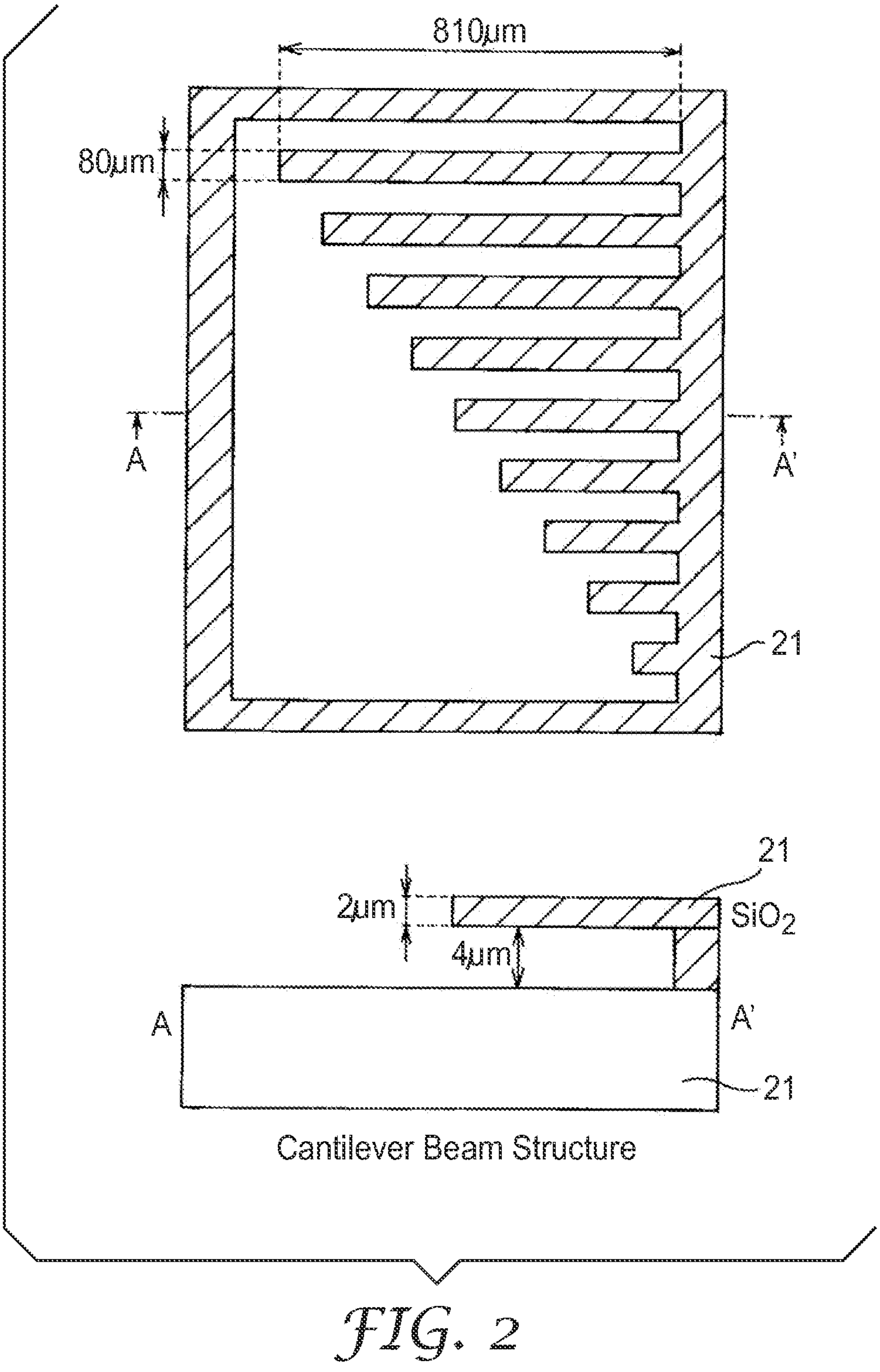

810µm
80µm
A
A'
21
21
2µm
SiO2
4µm
A
A'
21
Cantilever Beam Structure

FIG. 2