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(54) **STEP AND FLASH IMPRINT LITHOGRAPHY**

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(57) **ABSTRACT**

A method of forming a relief image in a structure comprising a substrate and a transfer layer formed thereon comprises covering the transfer layer with a polymerizable fluid composition, and then contacting the polymerizable fluid composition with a mold having a relief structure formed therein such that the polymerizable fluid composition fills the relief structure in the mold. The polymerizable fluid composition is subjected to conditions to polymerize polymerizable fluid composition and form a solidified polymeric material therefrom on the transfer layer. The mold is then separated from the solid polymeric material such that a replica of the relief structure in the mold is formed in the solidified polymeric material; and the transfer layer and the solidified polymeric material are subjected to an environment to selectively etch the transfer layer relative to the solidified polymeric material such that a relief image is formed in the transfer layer.

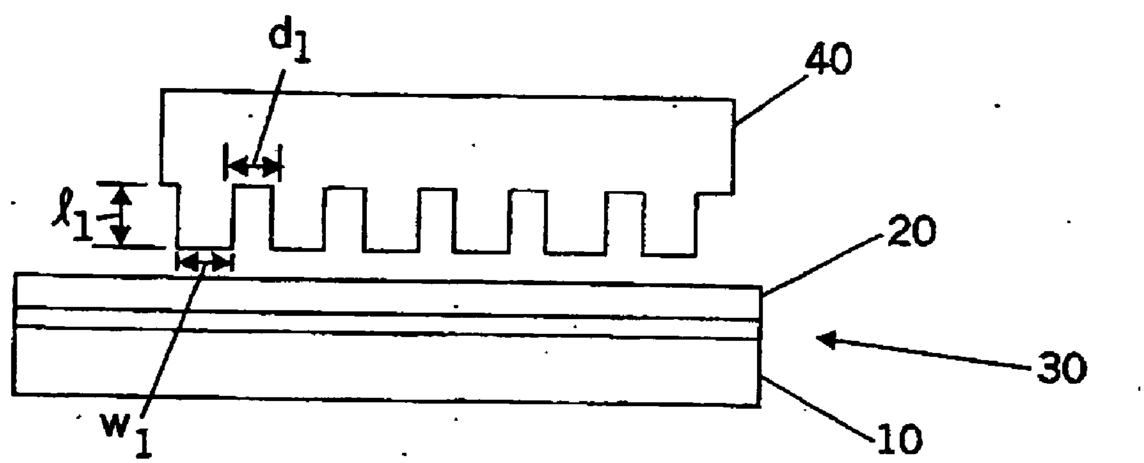


FIG. 1A

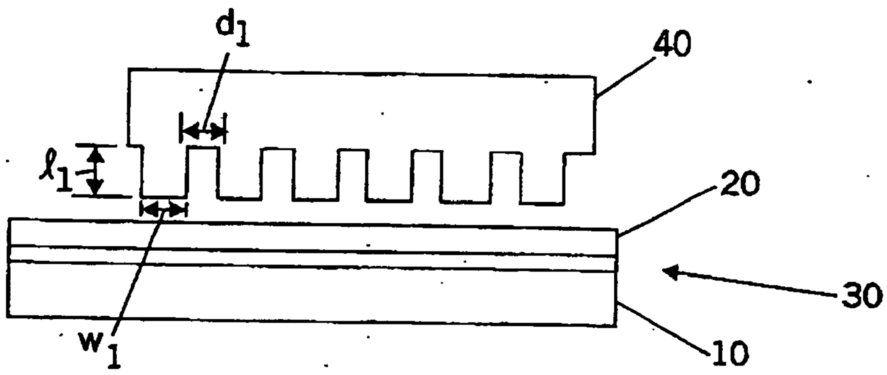


FIG. 1B

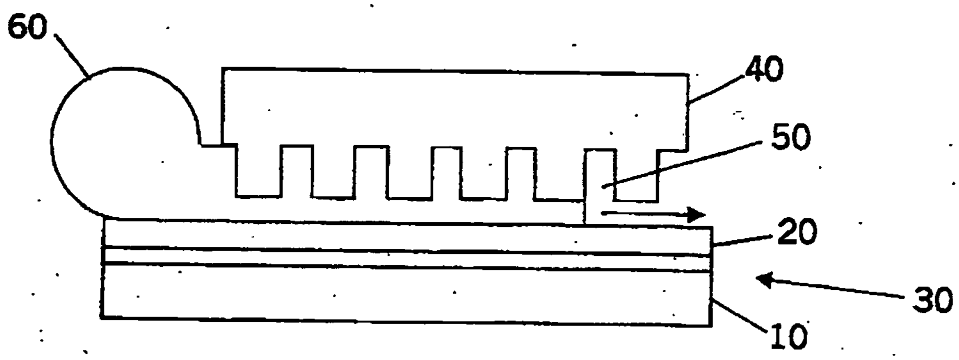


FIG. 1C

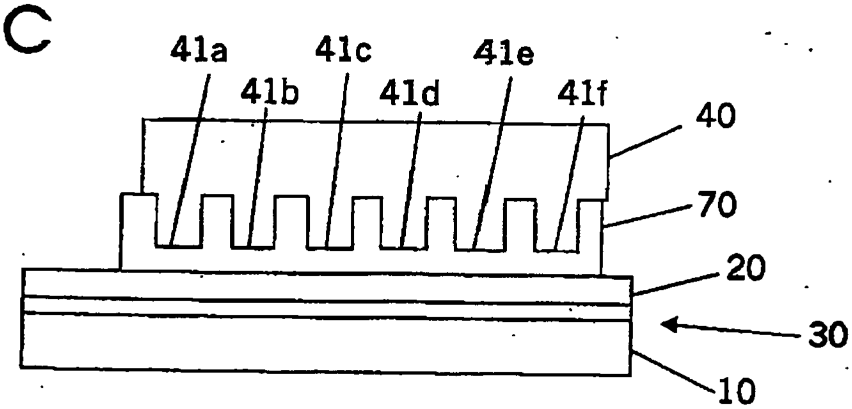
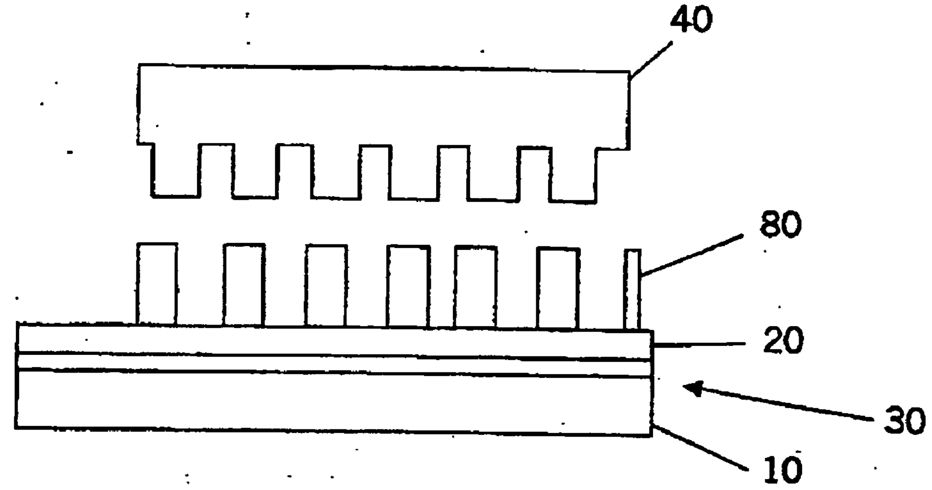


FIG. 1D



STEP AND FLASH IMPRINT LITHOGRAPHY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation of U.S. patent application Ser. No. 10/978,285, filed Oct. 29, 2004, which is a continuation of U.S. patent application Ser. No. 10/806,051, filed Mar. 22, 2004, which is a divisional application of U.S. patent application Ser. No. 09/908,765, now U.S. Pat. No. 6,719,915, which is a continuation patent application of U.S. patent application Ser. No. 09/266,663, now U.S. Pat. No. 6,334,960, all having Carlton Grant Willson and Matthew Earl Colburn listed as inventors.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of MDA-972-97-3-0007 awarded by the Defense Advanced Research Projects Agency (DARPA).

FIELD OF THE INVENTION

[0003] The invention generally relates to using lithography techniques in fabricating various microstructures.

BACKGROUND OF THE INVENTION

[0004] There is currently a strong trend toward fabricating small structures and downsizing existing structures, which is commonly referred to as microfabrication. One area in which microfabrication has had a sizeable impact is in the microelectronic area. In particular, the downsizing of microelectronic structures has generally allowed the structures to be less expensive, have higher performance, exhibit reduced power consumption, and contain more components for a given dimension relative to conventional electronic devices. Although microfabrication has been widely active in the electronics industry, it has also been applied to other applications, such as biotechnology, optics, mechanical systems, sensing devices, and reactors.

[0005] Lithographic techniques are often employed in device microfabrication. See S. Wolf et al., *Silicon Processing for the VLSI Era*, Volume 1-Process Technology, (1986), pp. 407-413. Using microcircuit fabrication as an example, photoresist materials are applied to a substrate. Next, the resist layer is selectively exposed to a form of radiation. An exposure tool and mask are often used to affect the desired selective exposure. Patterns in the resist are formed when the substrate undergoes a subsequent "developing" step. The areas of resist remaining after development protect the substrate regions which they cover. Locations from which resist has been removed can be subjected to a variety of additive (e.g., lift-off) or subtractive (e.g., etching) processes that transfer the pattern onto the substrate surface.

[0006] There is a current move toward developing photolithography techniques that may allow for forming microscale devices with small features. Whiteside et al., *Agnew. Chem. Int. Ed.,* 1998, 37, pp. 550-575 propose various techniques. One proposed technique involves the self-assembly of monolayers. Self-assembled monolayers (SAMs) typically form spontaneously by chemisorption and self-organization of functionalized, long-chain organic molecules onto the surfaces of appropriate substrates. SAMs are usually prepared by immersing a substrate in a solution containing a ligand that is reactive toward the surface, or by exposing the substrate to a vapor of the reactive species. The self-assembly of monolayers is potentially advantageous in that ordered structures may form rapidly.

[0007] An imprint lithography process that teaches producing nanostructures with 10 nm feature sizes is proposed by Chou et al., *Microelectronic Engineering,* 35, (1995), pp. 237-240. In particular, Chou et al. teach pressing a mold having nanostructures formed therein into a thin resist cast that is present on the surface of a substrate. The resist cast is designed to conform to the mold shape. The mold is then removed from the resist cast and the substrate having the resist cast present thereon is etched such that the mold pattern is transferred to the substrate.

[0008] Chou et al. teach using (poly)methyl methacrylate for the resist cast. The use of this material, however, may be disadvantageous in that it is potentially difficult to form some structures in varying pattern densities. Moreover, it is perceived that the etch selectivity may be potentially undesirable for common microelectronic device processing.

[0009] In view of the above, there is a need in the art for an imprint lithography process that allows for the formation of nanostructures having high resolution for a wide range of pattern densities. It would be particularly desirable if the nanostructures could be formed in a more efficient manner relative to prior art processes.

SUMMARY OF THE INVENTION

[0010] The present invention addresses the potential problems of the prior art, and in one aspect provides a method of forming a relief image in a structure that comprises a substrate and a transfer layer formed thereon. The method applies to forming structures with nanoscale patterns. The method comprises covering the transfer layer with a polymerizable fluid composition; contacting the polymerizable fluid composition with a mold having a relief structure formed therein such that the polymerizable fluid composition fills the relief structure in the mold; subjecting the polymerizable fluid composition to conditions to polymerize the polymerizable fluid composition and to form a solidified polymeric material therefrom on the transfer layer; separating the mold from the solidified polymeric material such that a replica of the relief structure in the mold is formed in the solidified polymeric material; and finally subjecting the transfer layer and the solidified polymeric material to an environment that allows for the selective etching of the transfer layer relative to the solidified polymeric material such that a relief image is formed in the transfer layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] **FIGS. 1A through 1D** illustrate a method for forming a relief structure in a substrate in accordance with the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] The present invention now will be described more fully hereinafter with reference to the accompanying drawings and specification in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, the thickness of layers and regions are exaggerated for clarity. Like numbers refer to like elements throughout. It will also be understood that when a layer is referred to as being "on" another layer or substrate, it can be directly on the other layer or substrate, or intervening layers may also be present.

[0013] In one aspect, the invention relates to at least one method of forming a relief image in a structure comprising a substrate and a transfer layer formed thereon. The method comprises covering the transfer layer with a polymerizable fluid composition. The polymerizable fluid composition is then contacted by a mold having a relief structure formed therein such that the polymerizable fluid composition fills the relief structures in the mold. The polymerizable fluid composition is then subjected to conditions so as to polymerize the polymerizable fluid composition and to form a solidified polymeric material therefrom on the transfer layer. Stated differently, the polymerizable fluid composition becomes chemically crosslinked or cured so as to form a thermoset material (i.e., solidified polymeric material). The mold is then separated from the solidified polymeric material such that a replica of the relief structure in the mold is formed in the solidified polymeric material. The transfer layer and the solidified polymeric material are then subjected to an environment such that the transfer layer is selectively etched relative to the solidified polymeric material. As a result, a relief image is formed in the transfer layer. The method of the invention is advantageous in that a number of devices may be fabricated therefrom utilizing processes known to one skilled in the art, such as, but not limited to, microelectronic devices, information storage devices, printed wiring boards, flat panel displays, micromachines, and charge couple devices.

[0014] The substrate used in the above invention may comprise a number of different materials, such as, but not limited to, silicon, plastics, gallium arsenide, mercury telluride, and composites thereof. The transfer layers are formed from materials known in the art, such as, for example, thermoset polymers, thermoplastic polymers, polyepoxies, polyamides, polyurethanes, polycarbonates, polyesters, and combinations thereof. The transfer layer is fabricated in such a manner so as to possess a continuous, smooth, relatively defect-free surface that may exhibit excellent adhesion to the polymerizable fluid. As appreciated by one skilled in the art, the term "transfer layer" refers to a layer containing material that may be etched so as to transfer an image to the underlying substrate from the polymerizable fluid composition as described in detail herein.

[0015] The polymerizable fluid composition that is polymerized and solidified in accordance with the methods of the invention typically comprises a polymerizable material, a diluent, and other materials employed in polymerizable fluids, such as, but not limited to, to initiators and other materials. Polymerizable (or crosslinkable) materials which may be used in the methods of the invention preferably encompass various silicon-containing materials that are often present themselves in the forms of polymers. The silicon-containing materials include, but are not limited to, silanes, silyl ethers, silyl esters, functionalized siloxanes, silsesquioxanes, and mixtures thereof. Silicon-containing materials which are employed preferably are organosilicons. The silicon-containing materials preferably contain the element silicon in an amount greater than about 8 percent based on the weight of the polymerizable fluid composition, and more preferably greater than about 10 weight percent.

[0016] The polymers which may be present in the polymerizable fluid composition preferably include various reactive pendant groups. Examples of pendant groups include, but are not limited to, epoxy groups, ketene acetyl groups, acrylate groups, methacrylate groups, and combinations of the above. Although not wishing to be bound by any theory, it is believed that the polymerizable fluid composition may react accordingly to a variety of reaction mechanisms, such as, but not limited to, acid catalysis, free radical catalysis, or 2+2 photocycloaddition.

[0017] The mold used in the methods of the invention may be formed from various conventional methods. Typically, the materials are selected such that the mold is transparent which allows the polymerizable fluid composition covered by the mold to be exposed to an external radiation source. For example, the mold may comprise materials, such as, but not limited to, quartz, silicon, organic polymers, siloxanes polymers, borosilicate glass, fluorocarbon polymers, metal, and combinations of the above. Preferably, the mold comprises quartz. To facilitate release of the mold from the solid polymeric material, the mold may be treated with a surface modifying agent. Surface modifying agents which may be employed include those which are known in the art. An example of a surface modifying agent is a fluorocarbon silylating agent. These surface modifying agents or release materials my be applied, for example, from plasma sources, a Chemical Vapor Deposition method (CVD), such as analogs of paralene, or a treatment involving a solution.

[0018] It should be appreciated that one skilled in the art may select the substrate, the mold, the polymerizable fluid composition, the surface modifying agent, as well as any other materials, such that the method of the invention optimally functions according to the specific needs of the end user.

[0019] The methods of the invention will now be described in greater detail to the accompanying drawings in which a preferred embodiment of the invention is shown. **FIG. 1A** illustrates a step-by-step sequence for carrying out the method of the invention. A structure **30** is present which includes a substrate **10** having a transfer layer **20** positioned thereon. As shown, a mold **40** is aligned over transfer layer **20** such that a gap **50** is formed between mold **40** and transfer layer **20**. Mold **40** has a nanoscale relief structure formed therein having an aspect ratio preferably ranging from about 0.1 to about 10, and more preferably from about 0.5 to about 2. Specifically, the relief structures in mold **40** preferably have a width w_1 ranging from about 10 nm to about 5000 μm. The relief structures are separated from each other by a distance d_1, preferably ranging from about 10 nm to about 5000 μm.

[0020] A polymerizable fluid composition **60** then contacts transfer layer **20** and mold **40** so as to fill gap **50**

therebetween, as shown in **FIG. 1B**. Polymerizable fluid composition **60** may have a low viscosity such that it may fill gap **50** in an efficient manner. Preferably, the viscosity of polymerizable fluid composition **60** ranges from about 0.01 cps to about 1000 cps measured at 25° C., and more preferably from about 0.01 cps to about 1 cps measured at this same temperature.

[**0021**] Referring now to **FIG. 1C**, mold **40** is then moved closer to transfer layer **20** to expel excess polymerizable fluid composition **60** such that edges **41***a* through **41***f* of mold **40** come into contact with transfer layer **20**. Polymerizable fluid composition **60** is then exposed to conditions to sufficiently polymerize the fluid. Preferably, polymerizable fluid composition **60** is exposed to radiation sufficient to polymerize the fluid composition and to form a solidified polymeric material, represented by **70** in **FIG. 1C**. More specifically, polymerizable fluid composition **60** is exposed to ultraviolet light, although other means for polymerizing the fluid may be employed, such as, for example, heat or other forms of radiation. The selection of a method of initiating the polymerization of the fluid composition is known to one skilled in the art, and typically depends on the specific application which is desired.

[**0022**] Mold **40** then leaves solidified polymeric material **70** on transfer layer **20**, as shown in **FIG. 1D**. Transfer layer **20** is then selectively etched relative to solidified polymeric material **70** such that a relief image **80** corresponding to the image in mold **40** is formed in transfer layer **20**. The etching step is depicted in **FIG. 1C**. The etching selectivity of transfer layer **20** relative to solidified polymeric material **70** preferably ranges from about 1.5 to about 100. As an example, the selective etching or the ion milling may be carried out by subjecting transfer layer **20** and solidified polymeric material **70** to an environment, such as, but not limited to, an argon ion stream, an oxygen-containing plasma, a reactive ion etching gas, a halogen-containing gas, a sulfur dioxide-containing gas, and combinations of the above.

[**0023**] Residual material, denoted as **90**, which may be in the form of (1) a portion of polymerizable fluid composition **60**; (2) a portion of solidified polymeric material **70**; or (3) combinations of (1) and (2) might be present in the gaps within in relief image **80**. The method of the invention therefore may further comprise the step of subjecting residual material **90** to conditions such that residual material **90** is removed (e.g., a clean-up etch). The clean-up etch may be carried out using known techniques. Additionally, it should be appreciated that this step may be carried out during various stages of the method of the invention. For example, the removal of the residual material may be carried out prior to the step of subjecting the transfer layer and the solidified polymeric material to an environment wherein the transfer layer is selectively etched relative to the solidified polymeric material. Various environments may be employed during the clean-up etch, such as, for example, argon ion milling, fluorine-containing plasma, reactive ion etch gas, and combinations thereof.

[**0024**] In the drawings and specification, there have been disclosed typical preferred embodiments of the invention, and although specific terms are employed, they are used in a generic and descriptive sense only and not for the purposes of limitation. The scope of the invention being set forth in the following claims.

What is claimed is:

1. A method of forming a layer on a surface, said method comprising:

flowing a polymerizable composition between said surface and a mold in contact with said polymerizable composition by providing said polymerizable composition with a viscosity in a range 0.01 to 100 centipoise at 250 Celsius so that said polymerizable composition conforms to a shape of said mold;

solidifying said polymerizable composition, defining a solidified composition; and

increasing a distance between said solidified composition and said mold.

2. The method as recited in claim 1 wherein flowing further includes providing said polymerizable composition with a viscosity in a range of 1 to 5 centipoise, inclusive, at 25° Celsius.

3. The method as recited in claim 1 wherein flowing further includes applying said polymerizable composition to said surface and placing said mold proximate to said polymerizable fluid composition.

4. The method as recited in claim 1 wherein flowing further includes applying said polymerizable composition to said surface and pressing a side of said mold into said polymerizable fluid composition, with said side including a plurality of trenches, with solidifying further including providing said solidified material with a pattern complementary to a shape of said side.

5. The method as recited in claim 1 wherein flowing further includes applying said polymerizable composition to said surface and pressing a side of said mold into said polymerizable fluid composition, with said side including a plurality of trenches, and solidifying further includes providing said solidified material with a pattern complementary to a shape of said side and further including providing a substrate having a transfer layer disposed thereon, with said transfer layer defining said surface, and transferring said pattern into said transfer layer.

6. The method as recited in claim 5 further including transferring said pattern into said substrate.

7. A method of forming a layer on a surface, said method comprising:

placing a mold proximate to a surface with a polymerizable composition being disposed therebetween, said mold having a side with a plurality of trenches formed therein;

flowing said polymerizable composition between said surface and said mold to have said polymerizable composition fill said trenches conforming to a shape of said side by providing said polymerizable composition with a viscosity in a range 0.01 to 100 centipoise at 250° Celsius;

solidifying said polymerizable composition, defining a solidified composition having a solidified shape complementary to said shape of said side; and

increasing a distance between said solidified composition and said mold.

8. The method as recited in claim 7 wherein flowing further includes providing said polymerizable composition with a viscosity in a range of 1 to 5 centipoise, inclusive, at 25° Celsius.

9. The method as recited in claim 7 wherein flowing further includes applying said polymerizable composition to said surface and pressing said side into said polymerizable fluid composition.

10. The method as recited in claim 7 wherein flowing further includes applying said polymerizable composition to said surface and pressing said side of said mold into said polymerizable fluid composition, and further including providing a substrate having a transfer layer disposed thereon, with said transfer layer defining said surface, and transferring said pattern into said transfer layer.

11. The method as recited in claim 10 further including transferring said pattern into said substrate.

12. A composition, comprising:

a polymerizable material having a viscosity in a range of 0.01 to 100 centipoise at 25° Celsius.

13. The composition as recited in claim 12 wherein said polymerizable material has a viscosity in a range of 1 to 5 centipoise, inclusive, at 25° Celsius.

14. The composition as recited in claim 12 wherein said polymerizable material further includes organosilicons.

15. The composition as recited in claim 12 wherein said polymerizable material further includes silicon-containing material in an amount greater than about 8 to 10 percent by weight.

16. The composition as recited in claim 12 wherein said polymerizable composition further includes silicon-containing materials selected from a set of materials consisting essentially of silanes, silyl ethers, silyl esters, functionalized siloxanes, silsesquioxanes.

17. The composition as recited in claim 12 wherein said polymerizable material further includes components selected from a set consisting essentially of epoxy groups, ketene acetyl groups, acrylate groups and methacrylate groups.

18. The composition as recited in claim 12 wherein said polymerizable material further includes an initiator component to facilitate solidification of said polymerizable material in response to predetermined radiation.

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