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(54) DUAL-TIP CANTILEVER

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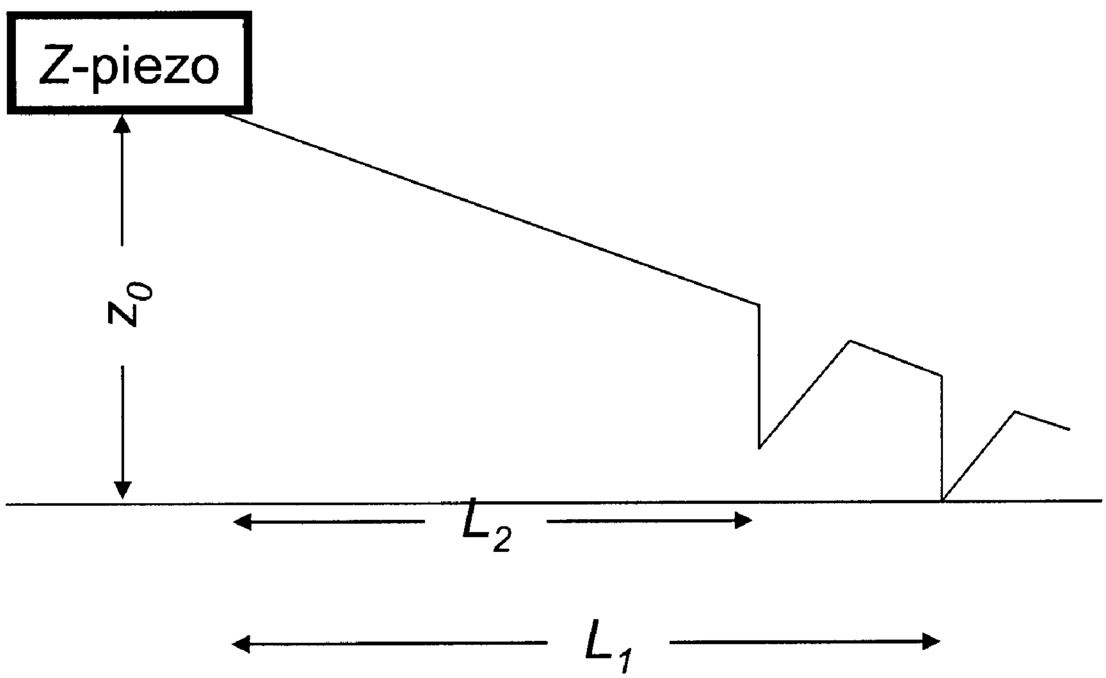
(57) **ABSTRACT**

A device comprising at least one cantilever comprising at least two tips is described, where the tips have substantially the same tip heights. Methods for making and using such a device are also provided. The height of one tip off of the surface can be more easily determined when the two tips have equal height.



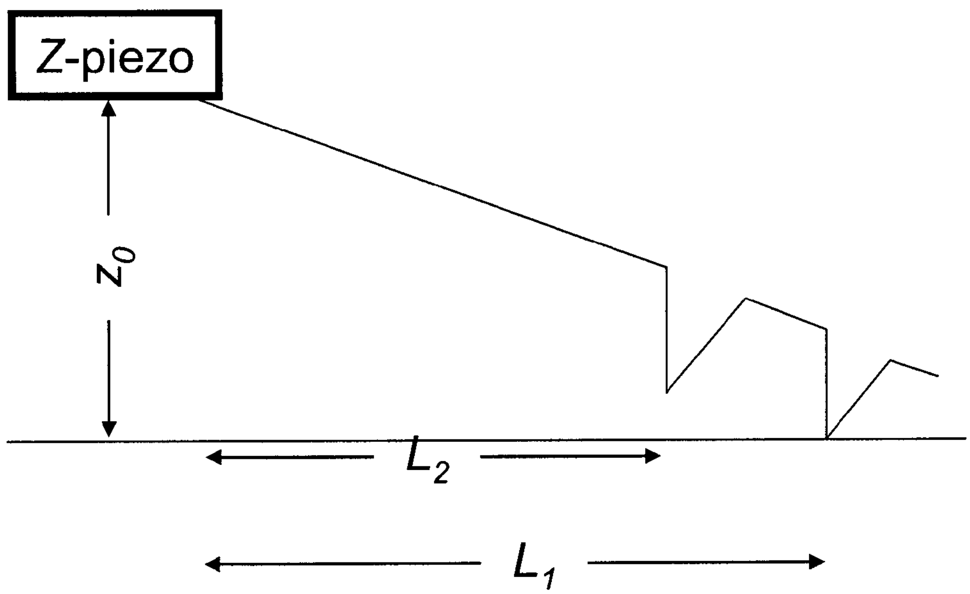


Figure 1

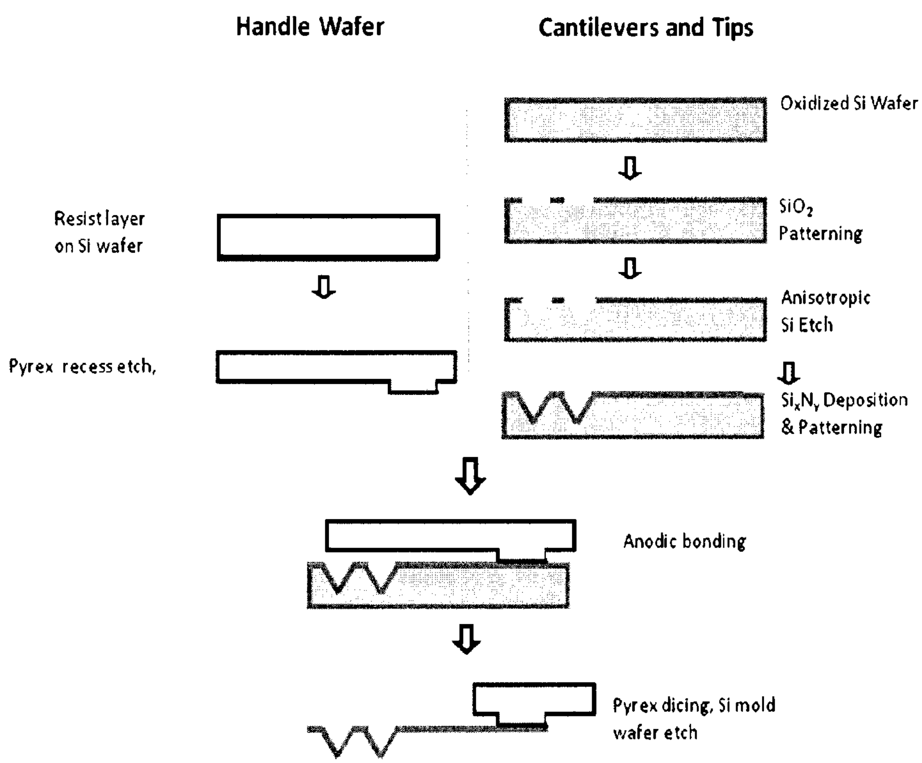

Handle Wafer
Cantilevers and Tips
Oxidized Si Wafer
Resist layer
on Si wafer
SiO_2
Patterning
Anisotropic
Si Etch
Pyrex recess etch,
Si_xN_y Deposition
& Patterning
Anodic bonding
Pyrex dicing, Si mold
wafer etch

Figure 2

DUAL-TIP CANTILEVER

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Applications No. 61/052,864, filed May 13, 2008, and U.S. Provisional Application No. 61/167,853, filed Apr. 8, 2009, each of which are incorporated by reference in their entirety.

BACKGROUND

[0002] A need exists to develop better devices and methods to create small scale structures including microstructures and nanostructures, particularly for commercial operation.

SUMMARY

[0003] Provided herein are devices, apparatuses, compositions, methods of making same, and methods of using same.

[0004] One embodiment provides a device comprising at least one cantilever comprising at least two tips, where the cantilever's largest dimension is about 1000 μm and the tips comprise substantially equal tip heights. In some embodiments, at least one cantilever comprises silicon carbide or silicon nitride. In some embodiments, the tips have substantially equal tip heights. In some embodiments, at least one cantilever has a spring constant that is not spatially uniform. In some embodiments, the spring constant of at least one cantilever between two of its tips differs from its spring constant between an attached actuator and the tip closest to the actuator.

[0005] Another embodiment provides a device comprising at least one cantilever comprising at least two tips, where the cantilever's largest dimension is about 1000 μm and the tips comprise substantially equal tip heights, where the device comprises at least one microscope tip, atomic microscope tip, scanning microcope tip, or nanoscope tip.

[0006] Yet another embodiment provides a method comprising providing an oxidized silicon wafer with a silicon dioxide layer, patterning the silicon dioxide layer to form a mask with at least two holes, etching the silicon dioxide layer to form two or more pits in the wafer, stripping the silicon dioxide layer, oxidizing the silicon wafer, and depositing silicon nitride on the wafer to form a cantilever comprising two or more tips. In some embodiments, an e-beam is used for patterning. In some embodiments, the holes are square. In some embodiments, the pits are pyramidal.

[0007] Still another embodiment provides a method comprising providing a device comprising an actuator attached to a cantilever comprising two tips, moving the actuator to bring the first tip into contact with a surface, and determining the height of the second tip. In some embodiments, the two tips have substantially the same tip height. In some embodiments, the height is determined using the distances of the tips from the actuator. In some embodiments, the height is determined using the ratio of the distances of the tips from the actuator. In some embodiments, the height is determined using the elevation of the actuator above the surface.

[0008] At least one advantage of at least one embodiment includes improved height sensing for a dual tip system.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. **1** provides a schematic of a cantilever comprising dual tips with substantially equal height.

[0010] FIG. **2** provides schematics of a flow chart of a dual-tip cantilever fabrication process.

DETAILED DESCRIPTION

[0011] All references cited herein are incorporated by reference in their entirety.

Introduction

[0012] For practice of the various embodiments described herein, lithography, microlithography, and nanolithography instruments, pen arrays, active pens, passive pens, inks, patterning compounds, kits, ink delivery, software, and accessories for direct-write printing and patterning can be obtained from NanoInk, Inc., Skokie, Ill. Instrumentation includes, for example, the NSCRIPTOR and DPN5000. Software includes, for example, INKCAD software (NanoInk, Chicago, Ill.), providing user interface for lithography design and control. E-Chamber can be used for environmental control. Dip Pen Nanolithography® and DPN® are trademarks of NanoInk, Inc.

[0013] The following patents and co-pending applications related to direct-write printing with use of cantilevers, tips, and patterning compounds, and related instrumentation, are hereby incorporated by reference in their entirety and can be used in the practice of the various embodiments described herein, including inks, patterning compounds, software, ink delivery devices, and the like:

[0014] U.S. Pat. No. 6,635,311 to Mirkin et al., which describes fundamental aspects of DPN printing including inks, tips, substrates, and other instrumentation parameters and patterning methods;

[0015] U.S. Pat. No. 6,827,979 to Mirkin et al., which further describes fundamental aspects of DPN printing including software control, etching procedures, nanoplotters, and complex and combinatorial array formation.

[0016] U.S. patent publication number 2002/0122873 A1 published Sep. 5, 2002 ("Nanolithography Methods and Products Produced Therefore and Produced Thereby"), which describes aperture embodiments and driving force embodiments of DPN printing.

[0017] U.S. Pat. No. 7,279,046 to Eby et al. ("Methods and Apparatus for Aligning Patterns on a Substrate"), which describes alignment methods for DPN printing.

[0018] U.S. Pat. No. 7,060,977 to Dupeyrat et al. ("Nanolithographic Calibration Methods"), which describes calibration methods for DPN printing.

[0019] U.S. Patent Publication 2003/0068446, published Apr. 10, 2003 to Mirkin et al. ("Protein and Peptide Nanoarrays"), which describes nanoarrays of proteins and peptides.

[0020] U.S. Pat. No. 7,361,310 to Mirkin et al. ("Direct-Write Nanolithographic Deposition of Nucleic Acids from Nanoscopic Tips"), which describes nucleic acid.

[0021] U.S. Pat. No. 7,273,636 to Mirkin et al. ("Patterning of Solid State Features by Direct-Write Nanolithographic Printing"), which describes reactive patterning and sol gel inks (now published Aug. 28, 2003 as 2003/0162004).

[0022] U.S. Pat. Nos. 6,642,129 and 6,867,443 to Liu et al. ("Parallel, Individually Addressable Probes for Nanolithography"), describing active pen arrays.

[0023] U.S. Patent Publication 2003/0007242, published Jan. 9, 2003 to Schwartz ("Enhanced Scanning Probe Microscope and Nanolithographic Methods Using Same").

[0024] U.S. Patent Publication 2003/0005755, published Jan. 9, 2003 to Schwartz ("Enhanced Scanning Probe Microscope").

[0025] U.S. Pat. No. 7,093,056 to Demers et al., describing catalyst nanostructures and carbon nanotube applications.

[0026] U.S. Pat. No. 7,199,305 to Cruchon-Dupeyrat et al., and U.S. Pat. No. 7,102,656 to Mirkin et al., describing printing of proteins and conducting polymers respectively.

[0027] U.S. Pat. No. 7,005,378 to Crocker et al., describing conductive materials as patterning compounds.

[0028] U.S. patent application Ser. No. 10/689,547 filed Oct. 21, 2003, now published as 2004/0175631 on Sep. 9, 2004, describing mask applications including photomask repair.

[0029] U.S. Pat. No. 7,034,854 Cruchon-Dupeyrat et al., describing microfluidics and ink delivery.

[0030] U.S. patent application Ser. No. 10/788,414 filed Mar. 1, 2004, now published as 2005/0009206 on Jan. 13, 2005 describing printing of peptides and proteins.

[0031] U.S. Pat. No. 7,326,380 to Mirkin et al., describing ROMP methods and combinatorial arrays.

[0032] U.S. Pat. No. 7,491,422 to Zhang et al., describing stamp tip or polymer coated tip applications.

[0033] U.S. patent application Ser. No. 11/065,694 filed Feb. 25, 2005, now published as 2005/0235869 on Oct. 27, 2005, describing tipless cantilevers and flat panel display applications.

[0034] US Patent publication 2006/001,4001 published Jan. 19, 2006 describing etching of nanostructures made by DPN methods.

[0035] WO 2004/105046 to Liu & Mirkin published Dec. 2, 2004 describes scanning probes for contact printing.

[0036] US patent application "Active Pen Nanolithography," Ser. No. 11/268,740 to Shile et al. filed Nov. 8, 2005 describes for example thermcompression bonding and silicon handle wafers.

[0037] DPN methods are also described in Ginger et al., "The Evolution of Dip-Pen Nanolithography," *Angew. Chem. Int. Ed.* 2004, 43, 30-45, including description of high-throughput parallel methods. See also Salaita et al., "Applications of Dip-Pen Nanolithography," Nature Nanotechnology, 2007, Advanced On-line publication (11 pages).

[0038] Direct write methods, including DPN printing and pattern transfer methods, are described in for example *Direct-Write Technologies, Sensors, Electronics, and Integrated Power Sources*, Pique and Chrisey (Eds), 2002.

[0039] The direct-write nanolithography instruments and methods described herein are of particular interest for use in preparing bioarrays, nanoarrays, and microarrays based on peptides, proteins, nucleic acids, DNA, RNA, viruses, biomolecules, and the like. See, for example, U.S. Pat. No. 6,787,313 for mass fabrication of chips and libraries; U.S. Pat. No. 5,443,791 for automated molecular biology laboratory with pipette tips; U.S. Pat. No. 5,981,733 for apparatus for the automated synthesis of molecular arrays in pharmaceutical applications. Combinatorial arrays can be prepared. See also, for example, U.S. Pat. Nos. 7,008,769; 6,573,369; and 6,998,228 to Henderson et al.

[0040] Scanning probe microscopy is reviewed in Bottomley, *Anal. Chem.*, 1998, 70, 425R-475R. Also, scanning probe microscopes are known in the art including probe exchange mechanisms as described in, for example, U.S. Pat. No. 5,705,814 (Digital Instruments).

[0041] Microfabrication methods are described in for example Madou, *Fundamentals of Microfabrication*, 2nd Ed., 2002, and also Van Zant, *Microchip Fabrication*, 5th Ed., 2004.

[0042] See for example U.S. Pat. No. 6,827,979 to Mirkin et al. is also incorporated by reference in its entirety.

[0043] US Patent Publication 2003/0022470 and Publication 2006/0228873 to Liu et al. describe cantilever fabrication methods.

[0044] US Patent Publication 2006/0040057 to King, Sheehan et al. describes thermal DPN printing methods.

[0045] U.S. Provisional Applications No. 61/052,864, filed May 13, 2008, and U.S. Provisional Application No. 61/167,853, filed Apr. 8, 2009, are also both incorporated by reference in their entireties.

[0046] Companion US applications "Piezoresistor Height-Sensing Cantilever" and "Heated Cantilever", both filed May 13, 2009 as Ser. No. ______ and Ser. No. ______ respectively, are both incorporated by reference in their entireties.

Cantilevers

[0047] Some embodiments comprise devices comprising one or more cantilevers. Some cantilevers may be of microscopic dimension. Some cantilevers may be of nanoscopic dimension. Some cantilevers may be used in such devices as atomic microscopes, scanning microscopes, or nanoscopes. Some cantilevers may be used to deposit materials on surfaces, measure local heights of surfaces, and the like.

[0048] In some embodiments, cantilevers may comprise silicon nitride. Alternatively, they may comprise silicon carbide. These materials are tough polycrystalline ceramics, having high wear resistances. Both silicon nitride and silicon carbide are electrical insulators. Cantilevers made from these materials can show different properties compared to silicon cantilevers. Because these materials are also chemically inert, cantilevers made from them may also be used with biological materials. Silicon nitride may be more readily commercially available than silicon carbide.

[0049] Some cantilevers may be configured into arrays. Such arrays may be one-dimensional. Some arrays may have more than one dimension. In some embodiments, cantilevers are configured into two-dimensional arrays.

Tips

[0050] Some cantilevers may comprise two or more tips. Some tips may comprise the same materials as the rest of their cantilevers. In some embodiments, tips may comprise different materials than the rest of their cantilevers.

[0051] Some tips may extend below the rest of their cantilevers. Such tips may contact a surface below their cantilevers. Some tips may take up substances from surfaces or deposit substances to surfaces.

[0052] Some tips may be scanning tips. Scanning can be done over the X-Y plane of a surface, and tips can be used to image or deposit materials. Such tips may be used to detect features of surfaces or substances on surfaces below their cantilevers. Such features may include local physical dimensions such as height, local chemical compositions, and the like.

[0053] Some tips may be microscope tips, such as atomic microscope tips. Some tips may be nanoscopic tips. Other variants will be understood by those skilled in the art.

[0054] Some embodiments comprise cantilevers with two or more tips having substantially equal tip heights. A tip may be characterized by its tip height, which refers to the distance from the point of the tip to the base of the tip, measured perpendicularly to the cantilever. Two tip heights are said to be substantially equal if the shorter tip height is no less than about 90% of the longer tip height, preferably no less than about 95% of the longer tip height, and more preferably no less than about 99% of the longer tip height. Two or more tip heights are said to be substantially equal if each of the tip heights is substantially equal to the longest tip height.

Sensing Height

[0055] Two fundamental activities associated with cantilevers are positioning tips over specific locations on a surface and determining the vertical displacements (heights) of the tips with respect to the surface. Both activities can involve knowledge of positions of the tips relative to the actuators that direct the cantilevers' movements.

[0056] A dual tip cantilever can have a proximal tip and a distal tip. Herein, one can know the height of a proximal tip relative to the surface when a distal tip is touching, while using the existing z-height sensing equipment of an instrument like an AFM.

[0057] One source of uncertainty is the fact that materials expand and contract in response to changes in temperature. Materials' responses are characterized by their coefficients of thermal expansion, which may differ according to composition. Where different materials are used, for example in cantilevers and their tips, this uncertainty is compounded.

[0058] In some embodiments, it is possible to determine the vertical height of tips above a surface. For example, consider embodiments comprising a cantilever with two or more tips having substantially equal tip heights. In such cases, geometry can be used to determine the actual vertical heights of each the tips above a surface. For example, FIG. **1** depicts a dual-tip cantilever attached to a z-piezo actuator located a distance Z_o above a surface. One of the two tips is just contacting the surface. In such a case, the distance of the second pen is given by:

$$Z_2 = Z_0\left(1 - \frac{L_2}{L_1}\right) \tag{1}$$

where L_1 and L_2 are the horizontal displacements of the respective tip points from the actuator. Note that the effects of thermal expansion or contraction do not affect this relationship, provided the materials of the tips are identical, because the lengths L_1 and L_2 appear as a ratio in Equation 1. This principle can be extended to three or more tips in a similar manner.

[0059] This method may be used in conjunction with tip tracking methods, such as those based on strain gauges, laser fluorometry and the like.

Fabricating Cantilever and Tips

[0060] In preparing the cantilever, one embodiment provides a cantilever comprising two or more tips, wherein the cantilever is prepared by: (i) providing an oxidized silicon wafer comprising a silicon dioxide layer on silicon, (ii) patterning the silicon dioxide layer to generate etch openings adapted for formation of at least two tips per cantilever, (iii) etching the silicon wafer anisotropically, (iv) depositing and patterning silicon nitride to form the cantilever, and (v) optionally bonding the cantilever to a handle wafer.

[0061] Fabrication of the pen can be carried out with adapted process flows developed by Quate's group during the 1990's (1,2). In one embodiment, this process starts with a highly accurate e-beam written mask to pattern two or more square openings onto an oxidized silicon surface, which will become two or more tips. The openings can be of any size. For example, they can be between about 1 micron to about 60 microns, such as between about 2 microns to about 50 microns. The size of the two or more openings can be the same or different from one another.

[0062] Subsequently, the wafer can be immersed in a KOH etch solution to etch anisotropically pyramidal pits into the silicon wafer to form the basic tip mold(s). The masking oxide can then be stripped and the wafers re-oxidized at 950° C. for 360 minutes to grow about 3900 Å of silicon oxide. At this time and temperature, the oxide at the bottom of the pit is hindered with respect to growth, and thus when a cast film is deposited in this pit, the tip sharpness can approach a 10 nm tip radius or smaller. No maximum limit of the tip size need to be imposed. For instance, the tip size can be increased by increasing the pit size.

[0063] Silicon nitride with low stress gradient can then be deposited onto the mold wafer to form a cantilever. In one embodiment, the nitride thickness is about 600 nm. Accordingly, with this thickness and a width of 25 um and a length of 200 um, a rectangular cantilever in this embodiment can have a spring constant of about 0.04 N/m. While this is a value that is commonly used for contact mode AFM probes and can work well for DPN, other spring constants may also be obtained and used. Not to be bound by any particular theory, the spring constant changes linearly with width w and with the third power of length L such that for a given thickness t, a wide range of spring constants K can be obtained: $K=Ewt^3/4L^3$, where E will depend on the materials of construction. In one alternative embodiment, the thickness of the nitride may also be changed on a batch basis to have a larger variation in spring constant. For example, nitride thicknesses from 400 nm to 1000 nm for cantilevers (with spring constant ranging from 0.0015 to over 1 N/m) have been used by Nanolnk for different applications.

[0064] In some embodiments, the spring constant may vary from one location to another along the cantilever. Such variation in spring constants may be effected by using different cantilever widths or thicknesses at the different locations. For cantilevers with two tips, some embodiments provide a spring constant between the tips that differs from the spring constant between the actuator and the tip nearest the actuator.

[0065] The nitride can be oxidized, patterned, and etched to form the cantilevers. See FIG. **2**. See also, (1) T. R. Albrecht, S. Akamine, T. E. Carver, and C. F. Quate, "Microfabrication of cantilever styli for the atomic force microscope," *J. Vac. Sci. Technol. A, Vac. Surf. Films* (*USA*), 1990; (2) S. Akamine, and C. F. Quate, "Low temperature oxidation sharpening of microcast tips," *J. Vac. Sci. Technol B., vol.* 10, No. 5, September/October 1992.

Non-Limiting Working Example #1

[0066] 1) Starting material

2) Clean

3) Oxidation

4) Clean

[0067] 5) Tip lithography

6) Descum

7) Oxide Etch

8) Strip Resist/Clean

9) Tip Etch

10) Clean

11) Strip Oxide

12) Clean

13) Oxidize

14) Sharpen Lithography

15) Inspect

16) Oxide Etch

17) Strip Resist/Clean

18) Deposit Silicon Nitride

19) Cantilever Lithography

[0068] 20) Frontside etch

21) Backside Lithography

22) Backside Etch

23) Strip Resist/Clean

24) Actuator Lithography

25) Descum

26) Clean

27) Etch

Non-Limiting Working Example #2

[0069] The procedure of Example #1 was repeated, with the following changes: (1) Steps 14-17 were not used, and (2) prior to Step 18, wet oxidation was performed.

1. A device comprising at least one cantilever comprising at least two tips, said at least one cantilever further comprising a length, a width, and a thickness, and said at least two tips comprising at least two tip heights,

wherein the largest of said length, said width, and said thickness is less than about 1000 μm, and

wherein said at least two tip heights are substantially equal.

2. The device according to claim **1**, wherein said at least one cantilever comprises silicon nitride or silicon carbide.

3. (canceled)

4. The device according to claim **1**, wherein the at least one cantilever is one of an array of cantilevers.

5-**9**. (canceled)

10. The device according to claim **1**, wherein at least two tips are atomic force microscope tips.

11. The device according to claim **1**, wherein at least one tip is a nanoscopic tip.

12. The device according to claim **1**, wherein said at least one cantilever comprises two tips.

13. The device according to claim **1**, wherein said at least two tip heights comprise a longest tip height, wherein said at least two tip heights are no less than about 95% of said longest tip height.

14. (canceled)

15. The device according to claim **1**, wherein said at least one cantilever is attached to an actuator, said at least one cantilever further comprising a first tip and a second tip, said at least one cantilever further comprising a first spring constant between said actuator and said first tip and a second spring constant between said first tip and said second tip, wherein said first spring constant and said second spring constant are not the same.

16. A device comprising a cantilever comprising a first tip and a second tip, said cantilever further comprising a length, a width, and a thickness, said first tip comprising a first tip height, and said second tip comprising a second tip height,

wherein the largest of said length, said width, and said thickness is less than about 1000 μm, and

wherein said first tip height and said second tip height are substantially equal.

17. A method comprising:

(i) providing a first oxidized silicon wafer comprising a first silicon dioxide layer and a silicon substrate, wherein said first silicon dioxide layer is disposed on said silicon substrate,

(ii) patterning said silicon dioxide layer with a mask to form a masked silicon dioxide layer, said mask comprising a first two or more openings,

(iii) etching said masked silicon dioxide layer to form a second two or more openings in said masked silicon dioxide layer and to form two or more pits in said silicon substrate,

(iv) stripping said masked silicon dioxide layer,

(v) oxidizing said silicon substrate to form a mold wafer,

(vi) depositing silicon nitride onto said mold wafer to form a cantilever comprising two or more tips in the pits.

18. (canceled)

19. The method according to claim **17**, wherein said first two or more openings are square.

20.-**22**. (canceled)

23. The method according to claim **17**, wherein said first two or more openings comprise at least two lengths and at least two widths, wherein said at least two lengths are substantially equal and wherein said at least two widths are substantially equal.

24. (canceled)

25. The method according to claim **17**, wherein said etching is anisotropic.

26. The method according to claim **17**, wherein said two or more pits are pyramidal.

27-**28**. (canceled)

29. A method comprising:

(i) providing a device and a surface, said device comprising an actuator attached to a cantilever, wherein said cantilever comprises a first tip and a second tip,

(ii) moving said actuator to contact said first tip with said surface.

(iii) determining height of said second tip above said surface, wherein said first tip comprises a first tip height and said second tip comprises a second tip height, wherein said first tip height and said second tip height are substantially equal.

30. The method according to claim **29**, wherein said height of said second tip is determined using a first distance from said actuator to said first tip and a second distance from said actuator to said second tip.

31. The method according to claim **29**, wherein said height of said second tip is determined using a ratio of a first distance from said actuator to said second tip to a second distance from said actuator to said first tip.

32. The method according to claim **29**, wherein said height of said second tip is determined using an elevation of said actuator above said surface, a first distance from said actuator to said first tip, and a second distance from said actuator to said second tip.

33. The method according to claim **29**, wherein said height of said second tip is determined using an elevation of such actuator above said surface and a ratio of a first distance from said actuator to said second tip to a second distance from said actuator to said first tip.

34. The method according to claim **29**, wherein said height of said second tip Z_2 is determined using an elevation of such actuator above said surface Z_o, a first distance from said actuator to said first tip L_1, and a second distance from said actuator to said second tip L_2 according to the formula:

$$Z_2 = Z_0\left(1 - \frac{L_2}{L_1}\right).$$

* * * * *