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(54) PIN ARRAY ASSEMBLY AND METHOD OF MANUFACTURE

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(52) **U.S. Cl.** **438/109**; 257/48; 438/14; 438/50; 422/100

(58) **Field of Search** 422/100; 257/48; 436/180, 50

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(57) ABSTRACT

An improved pin array assembly and method of manufacture of the pin array assembly are provided. A pin array assembly includes a single crystal silicon wafer. The single crystal silicon wafer is formed to define a base and an array of pins. Each of the pins has a shaft and a tip surface. The pin shaft is hydrophobic and the pin tip surface is hydrophilic. The method of manufacture of the pin array assembly includes the steps of forming an initial shape of a single crystal silicon wafer to define a base and an array of pins. The initial shape of a single crystal silicon wafer is etched and the array of pins is polished. The step of forming an initial shape of a single crystal silicon wafer to define a base and an array of pins includes mechanically sawing the single crystal silicon wafer to define a base and an array of pins. Chemical treatment of the pins is performed to make the shaft of the pins hydrophobic and to make the pin tip surfaces hydrophilic.

17 Claims, 6 Drawing Sheets

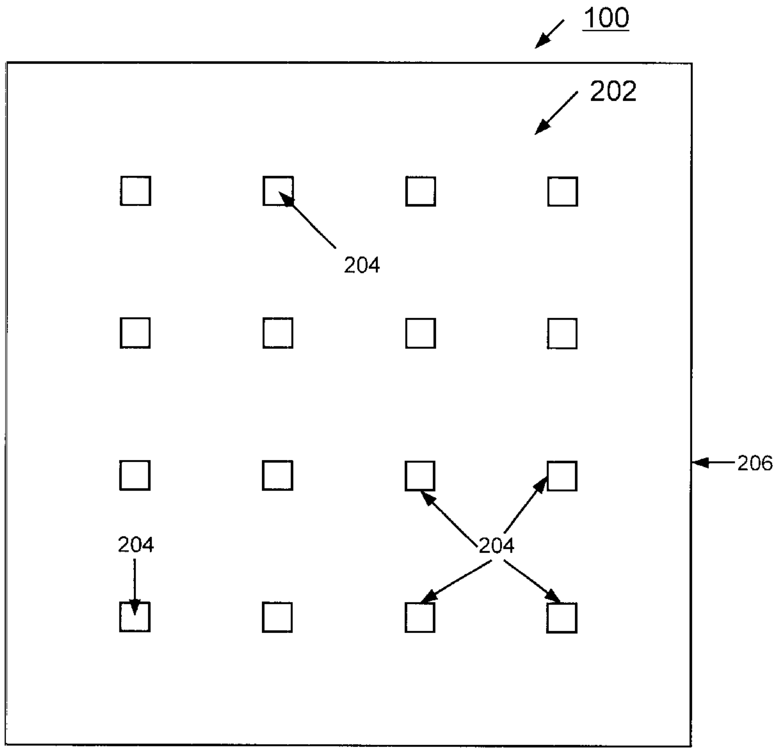


FIG. 1

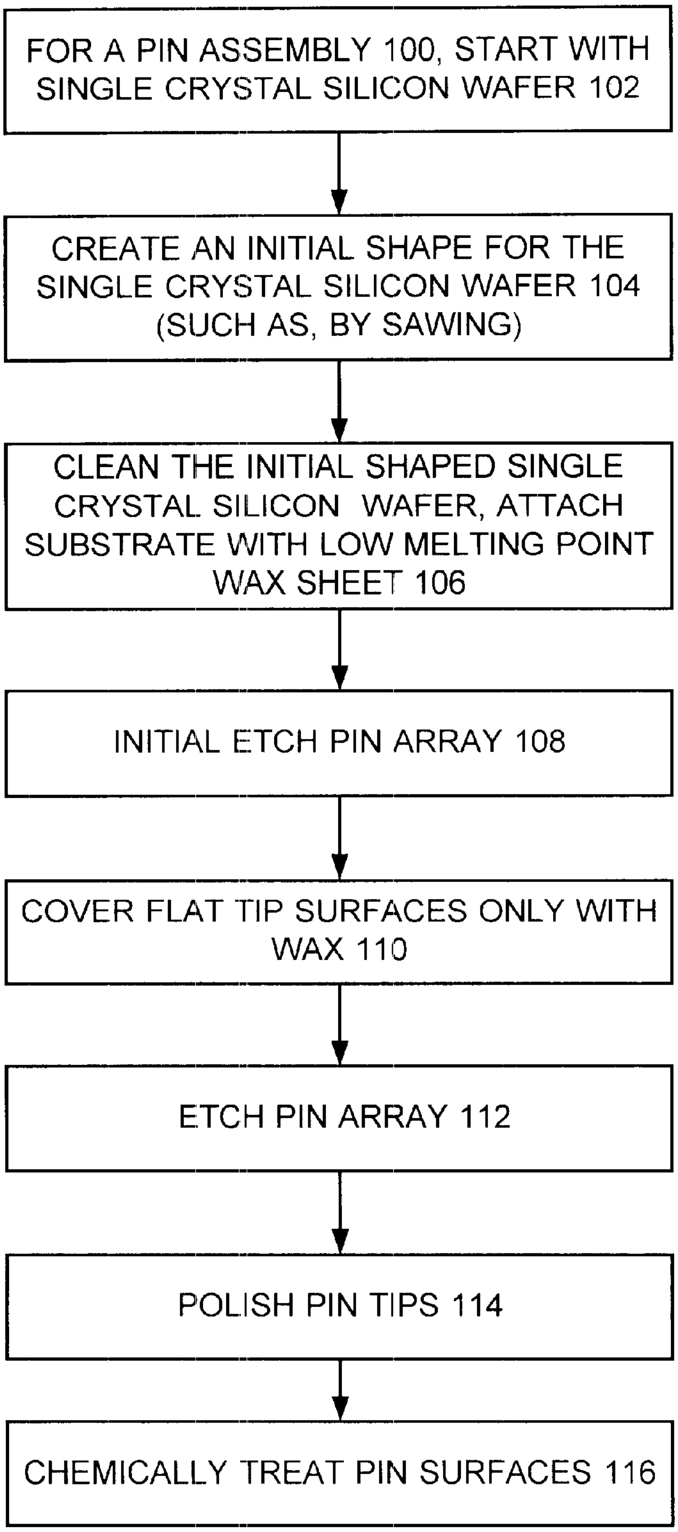
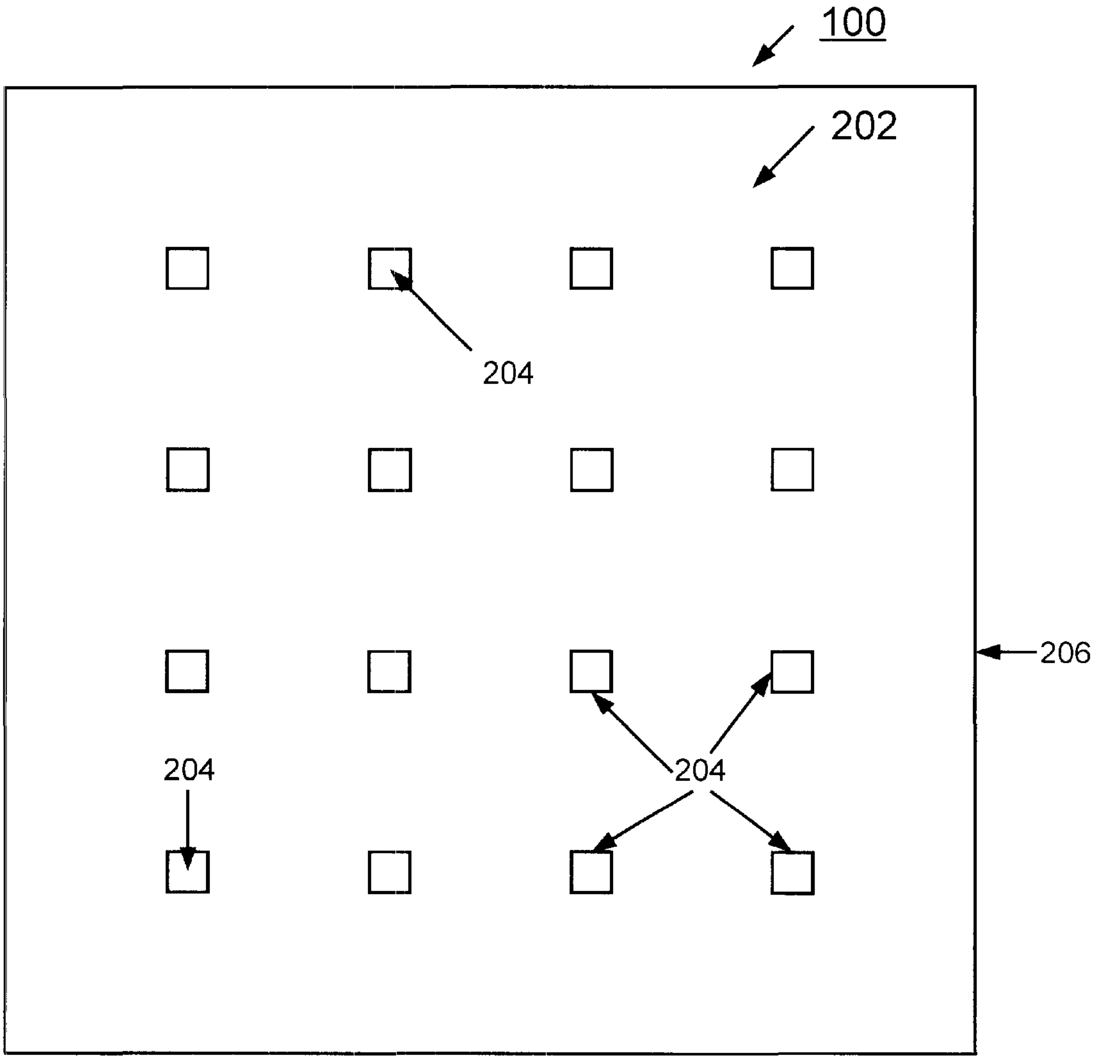

FOR A PIN ASSEMBLY 100, START WITH SINGLE CRYSTAL SILICON WAFER 102
CREATE AN INITIAL SHAPE FOR THE SINGLE CRYSTAL SILICON WAFER 104 (SUCH AS, BY SAWING)
CLEAN THE INITIAL SHAPED SINGLE CRYSTAL SILICON WAFER, ATTACH SUBSTRATE WITH LOW MELTING POINT WAX SHEET 106
INITIAL ETCH PIN ARRAY 108
COVER FLAT TIP SURFACES ONLY WITH WAX 110
ETCH PIN ARRAY 112
POLISH PIN TIPS 114
CHEMICALLY TREAT PIN SURFACES 116

FIG. 2A



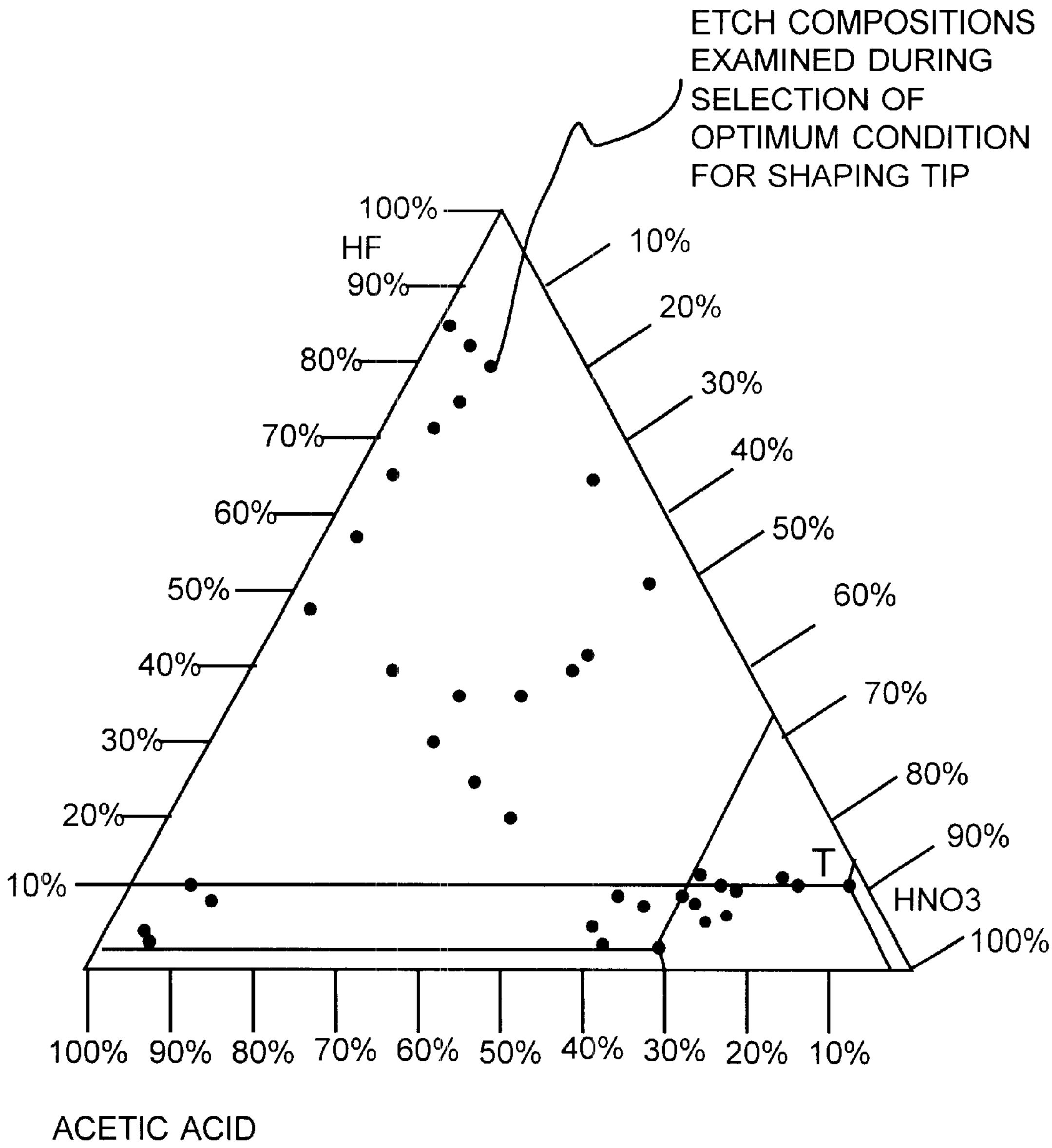

ETCH COMPOSITIONS
EXAMINED DURING
SELECTION OF
OPTIMUM CONDITION
FOR SHAPING TIP
100%
HF
90%
80%
70%
60%
50%
40%
30%
20%
10%
10%
20%
30%
40%
50%
60%
70%
80%
90%
T
HNO3
100%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
ACETIC ACID

FIG. 2B

FIG. 3

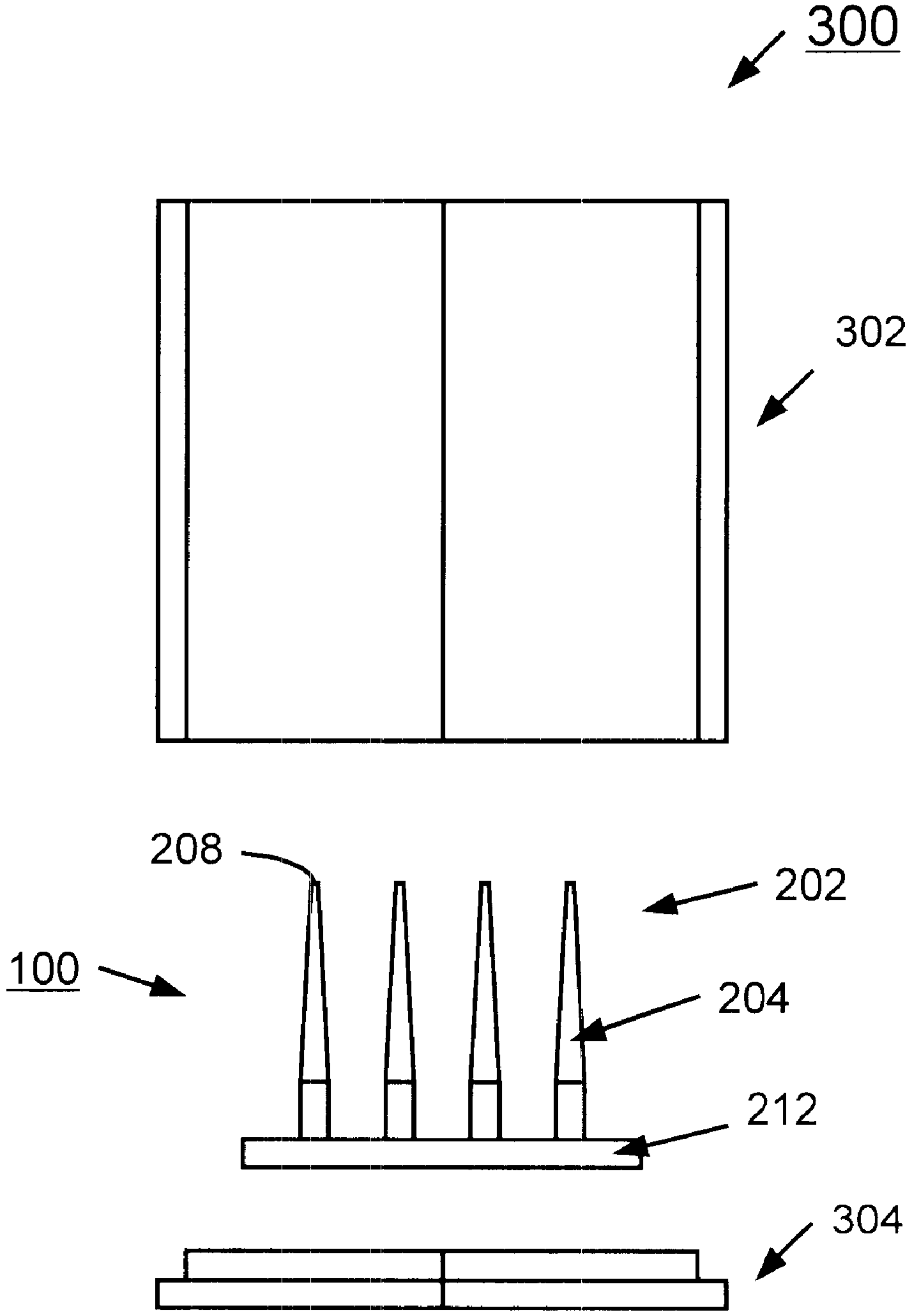


FIG. 4

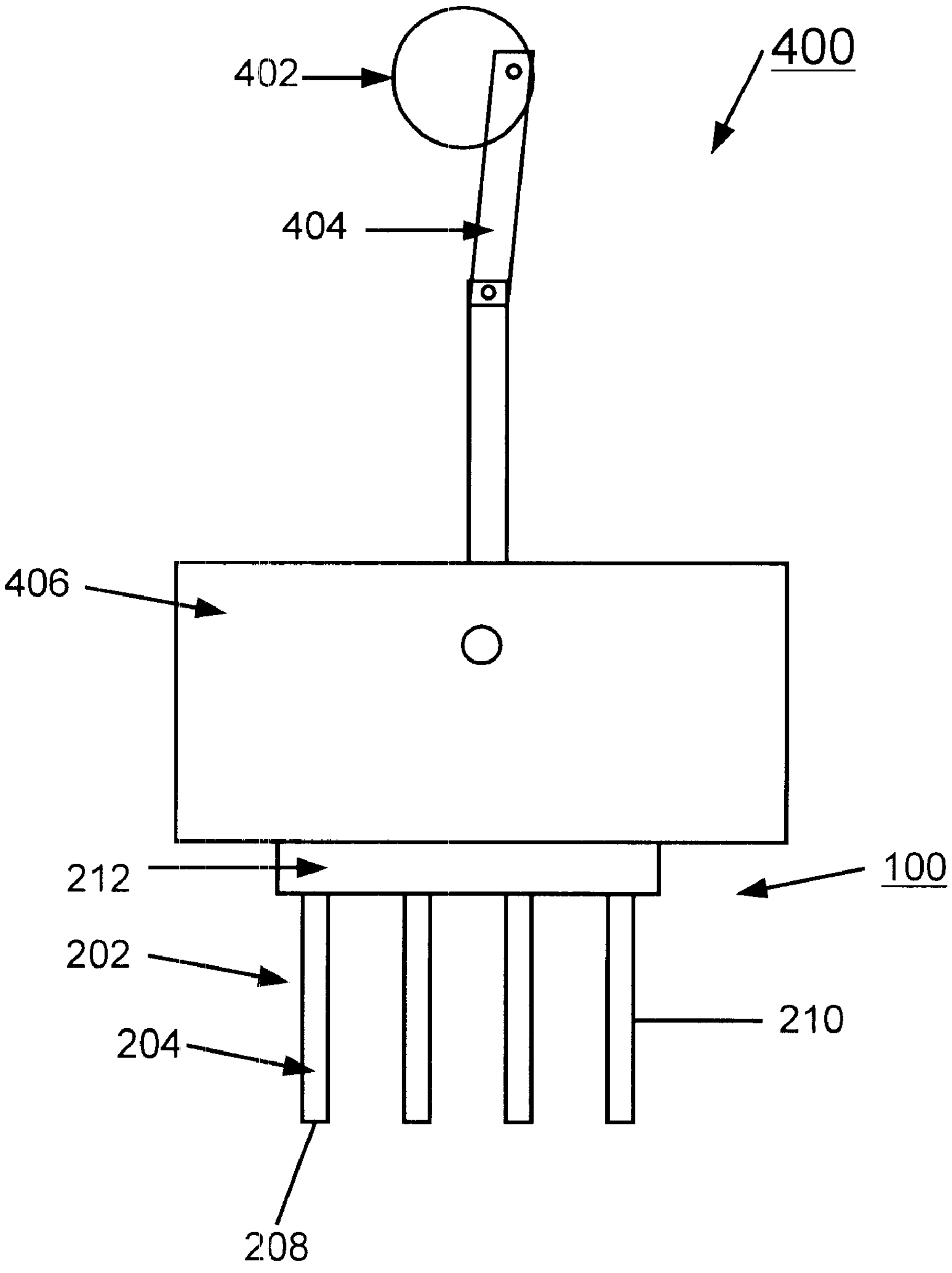
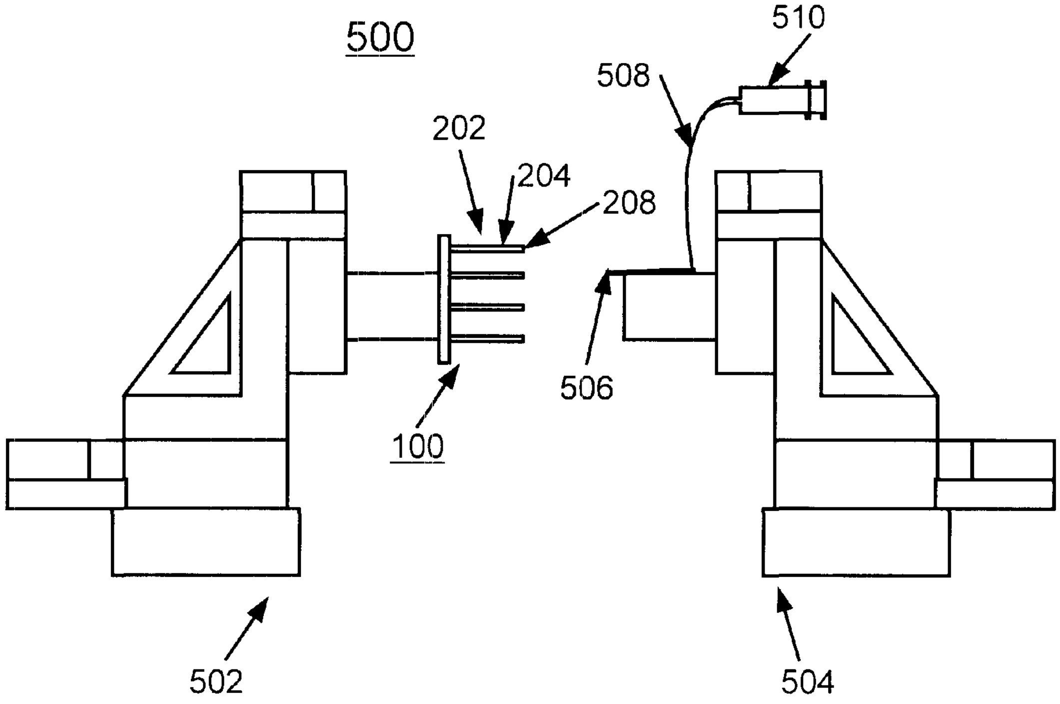


FIG. 5



PIN ARRAY ASSEMBLY AND METHOD OF MANUFACTURE

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the United States Government and Argonne National Laboratory.

FIELD OF THE INVENTION

The present invention generally relates to a pin array assembly and method of manufacture; and more particularly relates to a single crystal silicon pin array assembly and method of manufacture of the single crystal silicon pin array assembly.

DESCRIPTION OF THE RELATED ART

Current pin array assemblies used to transfer material from a reservoir to another surface substrate such as a membrane or a lay out of gel micro matrices are subject to deformation during the loading process. As a result of bending of the individual pins, problems with the solution transfer result. A need exists for very precise solution transfer and that the resulting geometry of the solutions on the substrate will be uniform. In addition to spacing requirements of the pins in the pin assembly, there are also certain chemical characteristics that are very important. For example, it is necessary that the pin ends that come in contact with the solutions, are hydrophilic; while the sides of each pen must be hydrophobic. These requirements restrict the drop of solution to the end of the pin, so that there is no danger that the drop of solution will roll down the sides of a pin in the array.

A principal object of the present invention is to provide an improved pin array assembly and method of manufacture of the pin array assembly.

It is another object of the present invention to provide such an improved pin array assembly and method of manufacture of the pin array assembly where the potential for bending of individual pins is minimized.

It is another object of the present invention to provide such an improved pin array assembly and method of manufacture of the pin array assembly enabling very precise solution transfer and generally uniform geometry of the solutions on the pin array assembly.

It is another object of the present invention to provide such an improved pin array assembly and method of manufacture of the pin array assembly where pin ends are hydrophilic while pin sides are hydrophobic.

It is another object of the present invention to provide such an improved pin array assembly and method of manufacture of the pin array assembly where the pin array assembly is generally easy to make.

SUMMARY OF THE INVENTION

In brief, an improved pin array assembly and method of manufacture of the pin array assembly are provided. A pin array assembly includes a single crystal silicon wafer. The single crystal silicon wafer defines a base and an array of pins. Each of the pins has a shaft and a tip surface. The pin shaft is hydrophobic and the pin tip surface is hydrophilic.

The method of manufacture of the pin array assembly includes the steps of forming an initial shape of a single crystal silicon wafer to define a base and an array of pins. The initial shape of a single crystal silicon wafer is etched and the array of pins is polished.

In accordance with features of the invention, the step of forming an initial shape of a single crystal silicon wafer to define a base and an array of pins includes mechanically sawing the single crystal silicon wafer to define a base and an array of pins. Potting of the pin array in wax allows all pins to be made the same length and also allows the plane of the tips of the pins to be made coplanar with the base. Chemical treatment of the pins is performed to make the shaft of the pins hydrophobic and to make the tip surfaces hydrophilic.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention together with the above and other objects and advantages may best be understood from the following detailed description of the preferred embodiments of the invention illustrated in the drawings, wherein:

FIG. **1** is a flow diagram illustrating sequential steps of a method of manufacture of a pin array assembly of the preferred embodiment;

FIG. **2**A is a diagram illustrating a pin array assembly of the preferred embodiment;

FIG. **2**B is a diagram illustrating etch solutions tested in accordance with the preferred embodiment;

FIG. **3** is a diagram illustrating a form used to pot the pin array assembly of the preferred embodiment;

FIG. **4** is a diagram illustrating a fixture for dipping the pin array assembly of the preferred embodiment into an etch solution; and

FIG. **5** is a diagram illustrating exemplary apparatus for chemically treating pin surfaces in accordance with the preferred embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Having reference now to the drawings, in FIG. **1** there are shown sequential steps of a method of manufacture of a pin array assembly **100** of the preferred embodiment. Referring also to FIGS. **2**A, **3** and **4**, the pin array assembly **100** of the preferred embodiment is illustrated.

In accordance with features of the invention, the pin array assembly **100** includes an array **202** of pins **204** constructed from single crystal silicon wafer **206**. Each pin **204** has a generally flat hydrophilic tip **208** and a hydrophobic shaft **210**. Pins **204** extend from a base **212**. A motor driven fixture **400** is illustrated in FIG. **4** for dipping the pin array **202** into an etch solution. Motor driven fixture **400** includes a motor **402** attached to a crank **404**. A pin array holder **406** attached to the crank **404** receives the pin array assembly **100**. The ends **208** of the pins **204** are dipped into the etch solution during a taper etch step of manufacture of a pin array assembly **100**.

Two 4×4 square arrays **202** of cylindrical pins **204** with flat hydrophilic tips **208** and hydrophobic shafts **210** were constructed from single crystal silicon for the precise robotic application of small liquid volumes of approximately 1 nL. The dimension of each pin **204** was 11 mm in total length with a diameter of about 200 μm at the tip and extending down the pin about 3 mm which then widened to 500 μm at the base **212**. The pins were 3 mm apart and extended from a 15 mm square base **212**, 2 mm thick. A 4 inch diameter, 13 mm thick, <110>, polished one side, silicon wafer **206** was chosen as the substrate. Silicon was specified as the preferred material due to its high thermal conductivity, allowing close control of the array temperature. The <110> orientation was chosen because the fracture line along the <111>

plane are either at an angle perpendicular or at 35.26 degrees to the longitudinal axis of the pins which was believed would decrease pin breakage. The <110> orientation also allows anisotropic chemical etching of deep grooves, with vertical sidewalls, with the longitudinal axes running in the <111> and <111> directions. The grooves would have vertical sidewalls due to the slow etching <111> planes perpendicular to the surface of these wafers.

The sequential steps for manufacturing the pin array assembly **100** start with a single crystal silicon wafer **206** as indicated in a block **102**. As indicated in a block **104**, an initial shape for the single crystal silicon wafer **206** is created, for example, by sawing. For example, the initial shape was made by sawing a 15 mm square piece from the wafer **206** and sawing many 11 mm deep cuts with a wide, coarse diamond blade to rough form the array **202** of square posts **204**. This left a 2 mm thick base **212**. Then a fine diamond blade was used to trim the posts to 500 μm square. This work was performed by Precision Surface Technology, Allentown, Pa.

Referring to FIG. **2B** there is shown a diagram illustrating etch solutions tested. In FIG. **2B** percentages of Acetic Acid are indicated along the horizontal axis, percentages of HF and HNO_3 respectively are shown relative to the left and right sides of the chart. The points in FIG. **2B** show various solution concentrations that were tested. The concentration indicated with a T was used for the taper etch.

Next the initial shaped single crystal silicon wafer is cleaned, then a substrate is attached with a low melting point wax sheet as indicated in a block **106**. Then an initial etching of the array **202** is provided as indicated in a block **108**. For example, prior to etching the array **202** was cleaned with 1 part H_2SO_4 (96%), to 3 parts H_2O_2 (30%) by volume for 5 minutes, and then attached to a 33 mm×60 mm Al_2O_2 substrate, such as manufactured and sold by Coors Ceramics Company, Golden, Colo., with a low melting-point, such as 80° C., wax sheet. This was done to protect the base **212** and maintain a smooth, flat surface. The array **202** was then etched in a 2 parts HF (49%), 38 parts HNO_3 (70%), 17 parts CH_3COOH (99.5%), by volume, isotropic etching solution, for 15 minutes to remove saw damage and form an initial taper. After this, the pins **204** retained a square cross-section with some rounding of the tip edges. The dimensions of the pins **204** were approximately 400 μm square.

Next the pin tips **208** are optionally covered with a wax as indicated in a block **110**. Then a taper etch of the pin array **202** is performed as indicated in a block **112**. For the next etch the flat tip surfaces **208** only, were covered with black wax, for example, of a type sold by Apiezon W, Apiezon Products, Manchester, United Kingdom, to minimize shortening of the pins **204**. The array **202** was attached to the motor driven fixture **400** illustrated in FIG. **4**, that dipped the ends **208** of the pins **204** into an etch solution of 1 part CH_3COOH (99.5%), 4 parts HF (49%), 35 parts HNO_3 (70%) and this solution contains an FC-99 surfactant. Pins **204** were dipped to a depth of 5 mm at a rate of 40 dips/minute for 12 minutes. Pins **204** showed a "waist" effect, the pin narrowed to a very thin, rectangular cross-section near the tip **208** and then widened to nearly the original tip width. The pins also showed a pronounced rippling where they had been dipped in the etch solution. After etching the array **202** and the Al_2O_3 substrate were heated to separate them. The black wax was removed by soaking the pin array **202** in toluene at 80° C. for 20 minutes followed by soaking in Summa Clean supplied by Ashland Chemical, Columbus, Ohio, at 80° C. for 5 minutes. To eliminate the rippling of the pins **204**, a surfactant was added to the etch solution. The surfactant was FC-99 that was sold by the 3M Company of St. Paul, Minn., a fluoropolymer solution that does not break down in strong acids. The FC-99 surfactant has been discontinued by the 3M Company; however, various other surfactants can be used. Etch solution was 2 parts FC-99 (25%), 5 parts CH_3COOH (99.5%), 20 parts HF (49%), 175 parts HNO_3 (70%). This is the maximum effective concentration. Lesser concentrations were ineffective.

Next the pin tips **208** are polished as indicated in a block **114**. In order to make all pins **204** uniform in length with flat tips the array was potted in wax, such as a generic investment casting wax and the tips **208** polished.

Referring also to FIG. **3**, a form **300** used to pot pin array **202** in wax is illustrated. Potting is performed by placing the array **202** in a plastic cylindrical form **302** with a stepped cap **304** that is press fit into one end of the form **302**. The pin array **202** was polished by hand with a sequence of abrasive papers, such as silicon carbide and aluminum oxide abrasive papers, sold by 3M Abrasive Systems Division, St. Paul, Minn. Polishing was performed with water and detergent solution on the abrasive paper, this reduced loading of the abrasive paper with wax. After polishing was finished the potted pin array **202** was placed on a support in a shallow dish in an oven at 200° C. until the wax had melted and flowed off the pin array **202**. The remaining wax film was removed by soaking the pin array **202** in toluene at 80° C. for 20 minutes followed by soaking in Summa Clean at 80° C. for 5 minutes.

Next the pin surfaces **208** and **210** are chemically treated as indicated in a block **116**. To make the shaft **210** of the pins **204** hydrophobic, the pin array **202** was etched in Buffered Oxide Etch, 10:1 NH_4F:HF, sold by Ashland Chemicals, Columbus, Ohio, for 5 minutes to expose the silicon. The tip surfaces **208** were made hydrophilic by applying a drop of HNO_3 (70%) to the flat surface of the tip to form a thin oxide layer. The HNO_3 drop was left in contact with the tip **208** for 30 seconds and then rinsed with deionized water.

Referring also to FIG. **5**, apparatus **500** for applying HNO_3 to the pin tips **208** is illustrated. Applying HNO_3 to the pin tips **208** was done by clamping the pin array assembly **100** in a micropositioner **502** with the pins **204** of pin array **202** disposed horizontally. A second micropositioner **504** held a 100 μl pipette tip **506** horizontally which was attached with tubing **508** to a syringe **510**. Under magnification, such as 20× magnification, a drop of HNO_3 was formed at the pipette tip **506** and the drop and pin tip **208** were brought together. When done correctly the drop wets only the tip **208** of the pin **204**.

In brief summary, silicon pin arrays **202** with 11 mm deep silicon features were successfully fabricated by a combination of mechanical sawing, chemical etching, and mechanical polishing. A novel dipping apparatus **400** was designed, built, and used successfully to create a tapered etch profile. FC-99 is a surfactant that is able to withstand concentrated acids and is an effective method to reduce surface irregularities when etching silicon. It is possible to make the pin tips **208** hydrophilic by oxidation with HNO_3 (70%). Although all literature examined to date describes HF, HNO_3 mixtures to etch all silicon crystal orientations isotropically, it was discovered that a well known "isotropic" etch solution has distinct anisotropic properties.

While the present invention has been described with reference to the details of the embodiments of the invention shown in the drawing, these details are not intended to limit the scope of the invention as claimed in the appended claims.

What is claimed is:

1. A method of manufacture of a pin array assembly comprising the steps of:

forming an initial shape of a single crystal silicon wafer to define a base and an array of pins;

etching said initial shape of a single crystal silicon wafer to form a taper;

dipping said pin array into a second etch solution; and

polishing said array of pins.

2. A method of manufacture of a pin array assembly as recited in claim **1** wherein the step of forming an initial shape of a single crystal silicon wafer to define a base and an array of pins includes the step of mechanically sawing said single crystal silicon wafer to define said base and said array of pins.

3. A method of manufacture of a pin array assembly as recited in claim **1** further includes the step of cleaning said formed base and said array of pins.

4. A method of manufacture of a pin array assembly as recited in claim **3** further includes the step of attaching an Al_2O_3 substrate to said formed base.

5. A method of manufacture of a pin array assembly as recited in claim **1** wherein the step of etching said array of pins to form a taper includes the step of etching said array of pins in a 2 parts HF (49%), 38 parts HNO_3 (70%), 17 parts CH_3COOH (99.5%), by volume, isotropic etching solution, for a predefined period of time.

6. A method of manufacture of a pin array assembly as recited in claim **5** wherein said predefined period of time is about 15 minutes.

7. A method of manufacture of a pin array assembly as recited in claim **1** wherein the step of dipping said pin array into a second etch solution includes the step of dipping the ends of the pins into an etch solution of 1 part CH_3COOH (99.5%), 4 parts HF (49%), 35 parts HNO_3 (70%).

8. A method of manufacture of a pin array assembly as recited in claim **7** wherein the step of dipping the ends of the pins into an etch solution of 1 part CH_3COOH (99.5%), 4 parts HF (49%), 35 parts HNO_3 (70%) includes the step of dipping said pin array to a selected depth at a set rate for a predefined time period.

9. A method of manufacture of a pin array assembly as recited in claim **8** wherein said selected depth at a set rate for a predefined time period includes a depth of about 5 mm at a rate of about 40 dips/minute for about 12 minutes.

10. A method of manufacture of a pin array assembly as recited in claim **1** wherein the step of dipping said pin array into a second etch solution includes the step of utilizing a motor driven pin array holder for dipping said pin array to a selected depth at a set rate for a predefined time period.

11. A method of manufacture of a pin array assembly as recited in claim **1** wherein the step of polishing said array of pins includes the steps of potting said array of pins in wax and polishing tips of said pins.

12. A method of manufacture of a pin array assembly as recited in claim **11** wherein the step of polishing tips of said pins includes the step of polishing with water and detergent solution on an abrasive paper.

13. A method of manufacture of a pin array assembly as recited in claim **1** further includes the step of chemically treating said polished pins.

14. A method of manufacture of a pin array assembly as recited in claim **13** wherein the step of chemically treating said polished pins includes the step of making shafts of said pins hydrophobic.

15. A method of manufacture of a pin array assembly as recited in claim **14** wherein the step of making shafts of said pins hydrophobic includes the step of etching said shafts in a Buffered Oxide Etch, 10:1 NH_4F:HF for a set time period to expose the silicon material.

16. A method of manufacture of a pin array assembly as recited in claim **13** wherein the step of chemically treating said polished pins includes the step of making a tip surface of said pins hydrophilic.

17. A method of manufacture of a pin array assembly as recited in claim **14** wherein the step of making said tip surface of said pins hydrophilic includes the steps of applying a drop of HNO_3 (70%) to said tip surface to form a thin oxide layer; and rinsing with de-ionized water.

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