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(71) Applicant *(for all designated States except US)*: **NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK TNO** [NL/NL]; Schoemakerstraat 97, NL-2628 VK Delft (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **YANG, Shangjiong** [NL/NL]; Modaustroom 43, NL-2721 BX Zoetermeer (NL). **VAN DER DONCK, Jacques Cor Johan** [NL/NL]; Lupinesingel 494, NL-2403 EA Alphen aan den Rijn (NL). **DUISTERWINKEL, Antonie Ellert** [NL/NL]; Molukkenstraat 10, NL-2612 EC Delft (NL).

(74) Agent: **JANSEN, C.M.**; Johan de Wittlaan 7, NL-2517 JR Den Haag (NL).

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(54) Title: A METHOD OF CLEANING A SURFACE

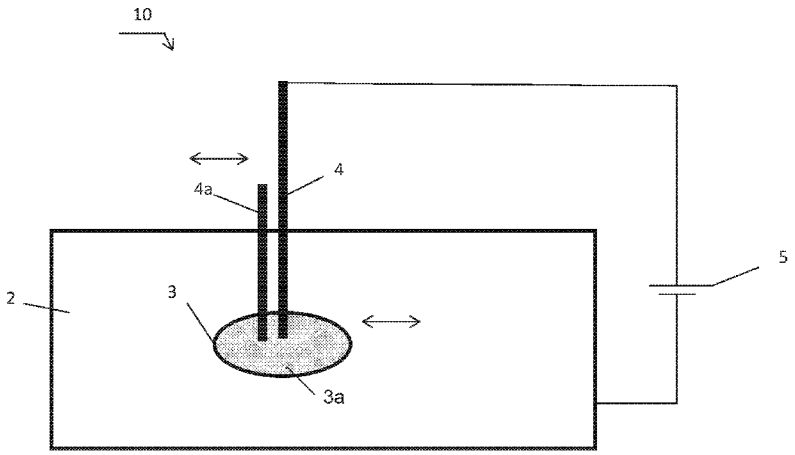

Fig. 1

(57) Abstract: The invention relates to a method of cleaning a surface using continuously generated nanobubbles, comprising the steps of generating a droplet of a liquid forming the nanobubbles on the surface; displacing the droplet over the surface for causing the nanobubbles to remove contaminations from the surface; conducting the liquid away from the surface for removing said contaminations. The invention further relates to a system for enabling cleaning a surface using continuously generated nanobubbles.

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Title: A method of cleaning a surface

FIELD

The invention relates to a method of cleaning a surface using continuously generated nanobubbles.

The invention further relates to a system for enabling cleaning a surface using continuously generated nanobubbles.

BACKGROUND

A method of cleaning a surface using electrochemically generated nanobubbles is known from Z.Wu et al "Cleaning using nanobubbles: defouling by electrochemical generation of bubbles". In the known method a surface conceived to be cleaned is submerged in an electrolyte in which nanobubbles are generated. The nanobubbles interacting with the surface remove (part of) a thin film layer on the surface and by doing so clean the surface.

It is a disadvantage of the known method that a relatively large amount of nanobubble-generating liquid need to be used. In addition, because the surface is submerged, contaminants present in the liquid may deposit on the surface, and the removed materials can re-deoposit. Furthermore, the known method has no control of the location to be cleaned on the surface.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a method of cleaning a surface, for example a wafer, which is more efficient and wherein above disadvantages are mitigated.

To this end the method of cleaning a surface according to the invention comprises the steps of:

- generating a droplet of a liquid which forms the nanobubbles on the surface;

- displacing the droplet over the surface for causing the nanobubbles to remove contaminants from the surface;
- conducting the liquid away from the surface for removing said contaminants.

It is found that when the droplet comprising nanobubbles is moved over the surface particles are removed there from in a controlled and efficient way. By providing suitable means for removing liquid from the droplet, the particles are removed from the surface by the liquid flow.

A method of cleaning a surface is known from JP 2009 101299, wherein nanobubbles homogeneously dispersed in a liquid are used. It is a disadvantage of the known method that the great majority of nanobubbles are generated relatively deep in a volume of the liquid, thereby not reaching the surface to be cleaned. Accordingly, the cleaning efficiency is low.

In the invention, to the contrary, the nanobubbles are generated directly and instantly on the surface to be cleaned within the droplet which is pre-seeded on the surface. This results in a substantial increase of the cleaning efficiency, in particular, for particles up to 20nm in size.

In an embodiment of the method according to the invention the droplet comprises the nanobubbles generated using electrolysis.

It will be understood that in this embodiment the surface or at least a portion of it must be conductive to form a part of the electrolysis electric circuit. Preferably, electrolysis of water is used.

In a suitable embodiment of the electrolysis set-up the droplet is formed by one or more needle-like electrodes. It will be appreciated, however, that a plurality of droplets may be formed at the same time on the surface using a suitable plurality of electrodes.

In a further advantageous embodiment, the one or more needle-like electrodes are adapted to conduct the droplet-forming liquid to the surface.

It is found advantageous to combine the liquid supply functionality and the droplet forming functionality in the needle-like electrode, which for

this purpose may be provided with a suitable conduit for supplying the liquid towards the surface. It will be further appreciated that a great plurality of suitable electrolytes may be used for implementing the method according to the invention. More details on this embodiment will be given with reference to Figure 1.

In a still further embodiment of the method according to the invention the droplet comprises the nanobubbles generated by mixing of two solvent liquids.

It is found then when two suitable solvents are mixed, their interaction may cause formation of nanobubbles, especially when the second liquid solvent has a lower gas solubility with respect to the first liquid solvent. For example, when the first solvent liquid is alcohol and the second solvent liquid is water, nanobubbles may be continuously formed at the surface in the controlled way. Suitable examples of alcohol are ethanol, propanol, methanol, etc. More details on this embodiment will be given with reference to Figure 2.

In a still further embodiment of the method according to the invention the droplet comprising the nanobubbles is a droplet of an electrolyte which is displaced over the surface using an electrowetting matrix, the surface forming a part of the electrowetting matrix.

It is found that the droplet (or droplets) formed on the surface may be efficiently and controllably displaced when the surface acts as a first electrode in the electrowetting set-up. More details on this embodiment will be given with reference to Figure 3.

When applying the electrowetting principle, the droplet may be displaced over the surface by applying a sequence of potentials to electrodes forming the electrowetting matrix.

It will be appreciated that in method according to the invention as is set forth in the foregoing, a further conduit arranged in fluid communication with the droplet may be provided for conducting the liquid away from the

surface. As a result the contaminants accumulated in the droplet are conducted away from the surface.

In a further embodiment of the method according to an aspect of the invention, the said droplet of liquid comprises dissolved gas, the method further comprising the step of maintaining the temperature of the said droplet in the range of 25 – 45 degrees Celsius.

Preferably, the gas is selected from the group consisting of: hydrogen, helium, methane, nitrogen, oxygen, argon, carbon dioxide, air.

It is found that good results for enabling nanobubble generation inside the droplet may be reached when the concentration of the gas is in the range of - 100 – 110%.

The system for enabling cleaning a surface using continuously generated nanobubbles, comprises:

- a body for generating a droplet of a liquid for forming the nanobubbles on the surface;
- means for displacing the droplet over the surface for causing the nanobubbles to remove contaminants from the surface;
- a conduit for conducting the liquid away from the surface for removing said contaminations.

Further advantageous embodiments of the system according to the invention are recited in the dependent claims.

These and other aspects of the invention will be discussed in more detail with reference to drawings, wherein like reference numerals refer to like elements. It will be appreciated that the drawings are presents for illustrative purposes and may not be used for limiting the scope of the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 presents in a schematic way an embodiment wherein water electrolysis is applied for generating nanobubbles and displacing the droplet over the surface.

Figure 2 presents in a schematic way an embodiment wherein two solvents are used for generating nanobubbles and displacing the droplet over the surface.

Figure 2a presents an embodiment wherein continuous cleaning of a surface is enabled.

Figure 3 presents in a schematic way an embodiment wherein an electrowetting matrix is used for generating nanobubbles and displacing the droplet over the surface.

Figure 4 presents in a schematic way an embodiment of the system according to the invention wherein the droplet comprises dissolved gas.

DETAILED DESCRIPTION OF THE DRAWINGS

Figure 1 presents in a schematic way an embodiment 10 wherein water electrolysis is applied for generating nanobubbles and displacing a droplet over the surface. The surface 2 may relate to any suitable surface which has to be made substantially free from surface contaminations. In particular, the surface 2 may relate to a surface of a wafer.

It will be appreciated, however, that the method of the invention is suitable for cleaning other surfaces, plain or patterned. In particular, extreme ultraviolet lithography reticles, glass plates, and other substrates, especially for semiconductor industry: integrated circuit, light emitting diode, flat panel display, photovoltaics, and nanotechnology-produced items may be successfully cleaned.

In accordance with the invention on the surface 2 a liquid droplet 3 comprising nanobubbles 3a is generated. In this particular embodiment for providing the droplet 3 comprising continuously generated nanobubbles 3a an electrolysis set-up is used. The electrolysis set-up comprises a voltage source 5 adapted to generate voltage between the surface 2 and a working electrode 4. The working electrode may be needle formed. It will be appreciated that for

realization of the electrolysis set-up the surface 2 should be electrically conductive.

For the working liquid water may be used. The water may be supplied by a suitable conduit (not shown), or, alternatively, the working electrode 4 may be provided with a conduit for supplying water to the surface 2.

When the working voltage is applied between the surface 2 and the electrode 4, the droplet of a suitable liquid, for example, water, will be generating nanobubbles which interact with the surface 2. As a result the surface 2 will be subject to cleaning.

For displacing the droplet 3 comprising continuously generated nanobubbles 3a over the surface, the working electrode 4 may be suitably displaced. Preferably, the displacement pattern is pre-programmed.

In order to conduct the particles and contaminations removed from the surface a further conduit 4a is provided. The further conduit is displaceable in cooperation with the electrode 4. When the contaminated droplets are removed, the new clean droplets may be generated and the cleaning procedure may be resumed. It will be appreciated that a plurality of individual droplets comprising nanobubbles may be generated and displaced in this way.

Figure 2 presents in a schematic way an embodiment 20 wherein two solvents are used for generating nanobubbles, displacing the droplet over the surface. This particular embodiment is based on the insight that when two solvent liquids having different gas solubility are mixed in a droplet 23, generation of nanobubbles 23a will occur.

In accordance with the present embodiment, a conduit 24 may be provided which comprises a suitable bifurcation for conducting a first solvent liquid, such as alcohol, and a second solvent liquid, such as water towards the surface 22 conceived to be cleaned. It will be appreciated that the two liquids have to mix when they are in contact with the surface. Therefore, using this

configuration local cleaning or cleaning of successive locations can be achieved. Using separate needles of application of liquids enables a continuous movement over the substrate. This embodiment is schematically presented in Figure 2a.

For example, the first solvent liquid may be conducted using the arm 24a and the second solvent liquid may be conducted using the arm 24b. For removing particles from the surface a further conduit 25 is provided. The supply conduit 24 and the further conduit 25 are movable in accordance with each other over the surface 22. It will be appreciated that a plurality of individual droplets comprising nanobubbles may be generated and displaced in this way.

Figure 2a presents in a schematic way an alternative embodiment allowing for continuous cleaning of the surface. The embodiment 200 is in general similar to the embodiment 20 shown in Figure 2, except that in the present embodiment separate conduits 240a, 240b are provided for each liquid. The liquids exiting from a distal portion of each respective conduit 240a, 240b mix directly in the droplet 23. This improves the efficiency of nanobubble formation at the surface as the interaction between the two liquids takes place substantially at the surface. For enabling the continuous movement, the conduits 240a and 240b are being synchronously moved with respect to the surface 22. It will be appreciated that, in principle, either the conduits may be moved or the surface may be moved.

Figure 3 presents in a schematic way an embodiment 30 wherein an electrowetting matrix is used for generating nanobubbles and displacing a droplet over the surface. This particular embodiment is based on the insight that electrowetting principle may be used for displacing the droplet over the surface 32, which is conceived to be cleaned.

Accordingly, for the droplet a suitable electrolyte, such as diluted ammonia may be selected. When applying a suitable voltage sequence using the voltage source 35 to the surface 32 and the electrowetting matrix 34, the

droplet having surface portions 33a, 33b and comprising nanobubbles 33a', formed between the surface 32 and the matrix 34 may be displaced. The matrix 34 may comprise a suitable number of electrode portions 36a, ... 36n which can be energized separately by the voltage pulses. It will be also appreciated that a plurality of individual droplets may be generated and displaced over the surface 32 in this way.

Figure 4 presents in a schematic way an embodiment of the system according to the invention wherein the droplet comprises dissolved gas. A suitable substrate 41 comprising a surface to be cleaned may be adapted to be movable in the direction schematically indicated by arrow 48. It will be appreciated that any type of linear or planar movement of the substrate may be envisaged.

In order to clean the surface of the substrate 41 a droplet of liquid 46 is provided on the surface. It will be appreciated that the droplet according to the invention is capable to carry-out local cleaning or, alternatively, may be used for cleaning ultimately the whole surface. For the latter the substrate 41 may be displaced with respect to a supply conduit 42 from which the droplet is provided.

The supply conduit 42 may be arranged to combine an inflow of a suitable gas 43 and an inflow of a suitable liquid 44. Alternatively, the supply 42 may be arranged to conduct a liquid suitably saturated with gas. It is found that good results may be achieved when the concentration of a gas is about 100 -110%. It is also found that provided the temperature of the droplet is about 25 – 45 degrees Celsius, the nanobubble generation inside the droplet is optimal.

In order to maintain the temperature of the droplet for effectuating due nanobubble generation, either gas or liquid may be heated by a controller 45, or the substrate 41 may be heated with the controller 47. It will be appreciated that the controller may be adapted to operate a suitable heater (not shown).

When the droplet is suitably heated, the gas dissolved in the liquid is nucleated leading to production of nanobubbles on the surface. Suitable gasses to be used in the system according to the present aspect of the invention are: hydrogen, helium, methane, nitrogen, oxygen, argon, carbon dioxide, or air.

It will be further appreciated that the surface cleaning method according to the aspects of the invention set forth in the foregoing is specifically suitable for removing particles of about 20 nm from a surface. Good results for local and extended cleaning are obtained. Preferably, in order to improve cleaning efficiency, the liquid is frequently or continuously freshened, the contaminated liquid being conducted away from the surface to a suitable container. It will be still further appreciated that the method of cleaning the surface according to the aspects of the invention is suitable not only for cleaning a surface, but may also be used in a groove, a depletion, or in an area between two substrates. The latter makes the method of the invention particularly versatile for industrial applications, in particular in semiconductor industry.

It will be appreciated that while specific embodiments of the invention have been described above, that the invention may be practiced otherwise than as described. In particular, it will be appreciated that still different methods may be used for generating nanobubbles, e.g., heating up the substrate, pressurize the liquid, etc. Accordingly, the invention is not limited to the methods described with reference to particular embodiments. In addition, isolated features discussed with reference to different figures may be combined.

Claims

1. A method of cleaning a surface using continuously generated nanobubbles, comprising the steps of:
   - generating a droplet of a liquid which forms nanobubbles on the surface;
   - displacing the droplet over the surface for causing the nanobubbles to remove contaminants from the surface;
   - conducting the liquid away from the surface for removing said contaminants.

2. The method according to claim 1, wherein the droplet comprises the nanobubbles generated using electrolysis.

3. The method according to claim 1, wherein the droplet comprises the nanobubbles generated by mixing of two solvent liquids.

4. The method according to claim 3, wherein the first solvent liquid has higher gas solubility than the second solvent, preferably wherein alcohol is used as the first solvent, and water is used as the second solvent.

5. The method according to claim 1, wherein the droplet comprising the nanobubbles is a droplet of an electrolyte which is displaced over the surface using an electrowetting matrix, the surface forming a part of the electrowetting matrix.

6. The method according to claim 5, wherein the droplet is displaced over the surface by applying a sequence of potentials to electrodes forming the electrowetting matrix.

7. The method according to claim 2, wherein the surface to be cleaned is part of the electrolysis electric circuit.

8. The method according to claim 7, wherein the droplet is being formed by one or more needle-like electrodes.

9. The method according to claim 8, wherein the one or more needle-like electrodes are adapted to conduct the droplet-forming liquid to the surface.

10. The method according to claim 1, wherein the said droplet of liquid comprises dissolved gas, the method further comprising the step of maintaining the temperature of the said droplet in the range of 25 – 45 degrees Celsius.

11. The method according to claim 10, wherein the gas is selected from the group consisting of: hydrogen, helium, methane, nitrogen, oxygen, argon, carbon dioxide, air.

12. The method according to any one of the preceding claims, further comprising a conduit arranged in fluid communication with the droplet for conducting the liquid away from the surface.

13. A system for enabling cleaning a surface using continuously generated nanobubbles, comprising:

- a body for generating a droplet of a liquid forming the nanobubbles on the surface;
- means for displacing the droplet over the surface for causing the nanobubbles to remove contaminations from the surface;
- a conduit for conducting the liquid away from the surface for removing said contaminations.

14. The system according to claim 13, wherein the body is further arranged to conduct the liquid towards the surface.

15. The system according to claim 13, wherein the surface and the body form part of an electric circuit.

16. The system according to claim 15, wherein the body is adapted to conduct two different solvents towards the surface.

17. The system according to claim 13, further comprising a dispenser for dispensing a droplet of liquid provided with a dissolved gas and a controller for controlling the temperature of the droplet in the range of 25 – 45 degrees Celsius.

18. The system according to any one of the preceding claims 13 – 17, further comprising a conduit arranged to remove the liquid comprising contaminations from the surface.

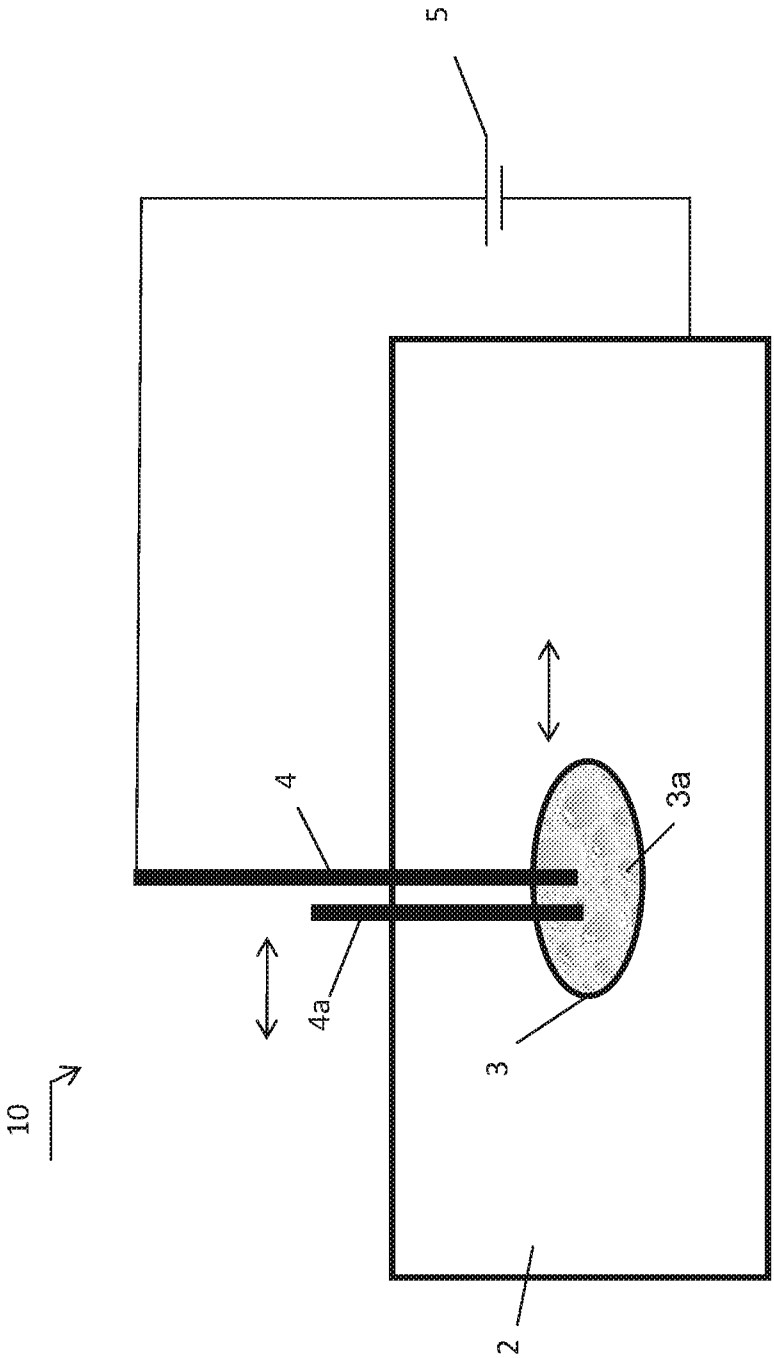

Fig. 1

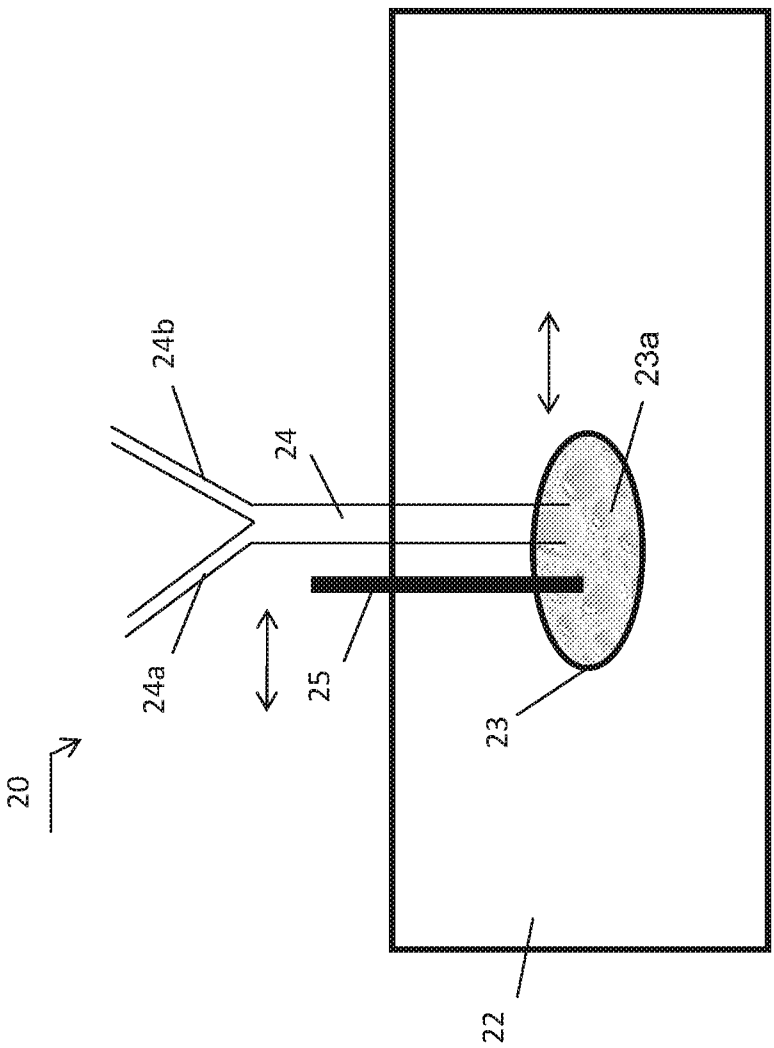

Fig. 2

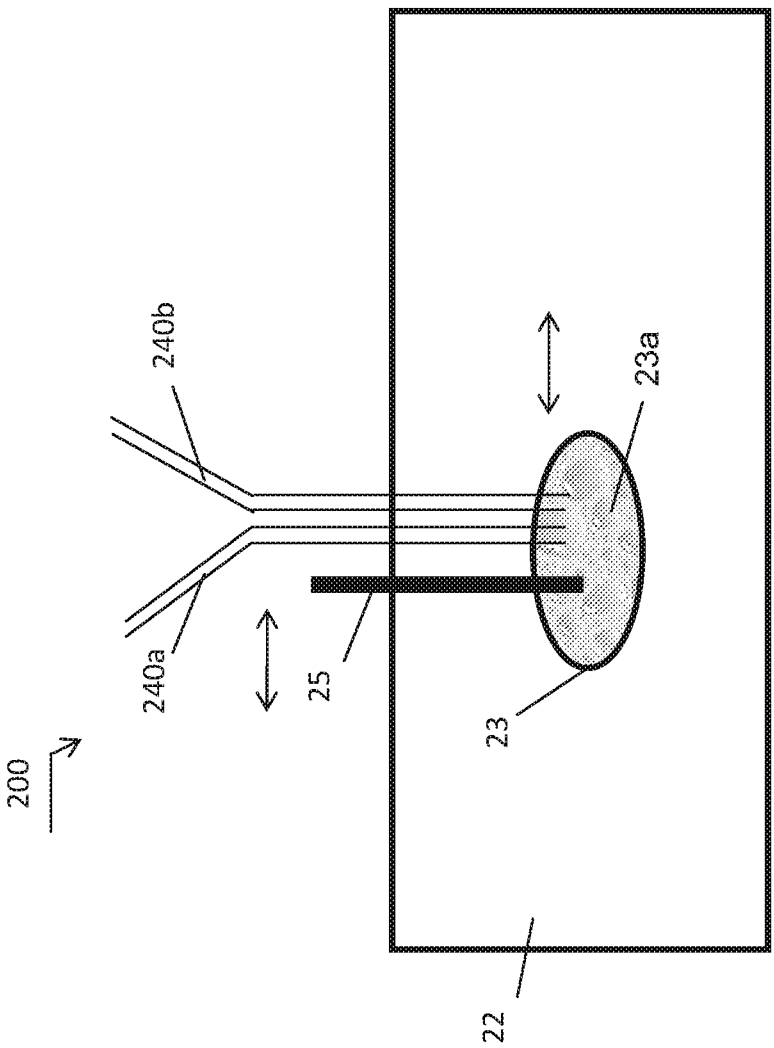

Fig. 2a

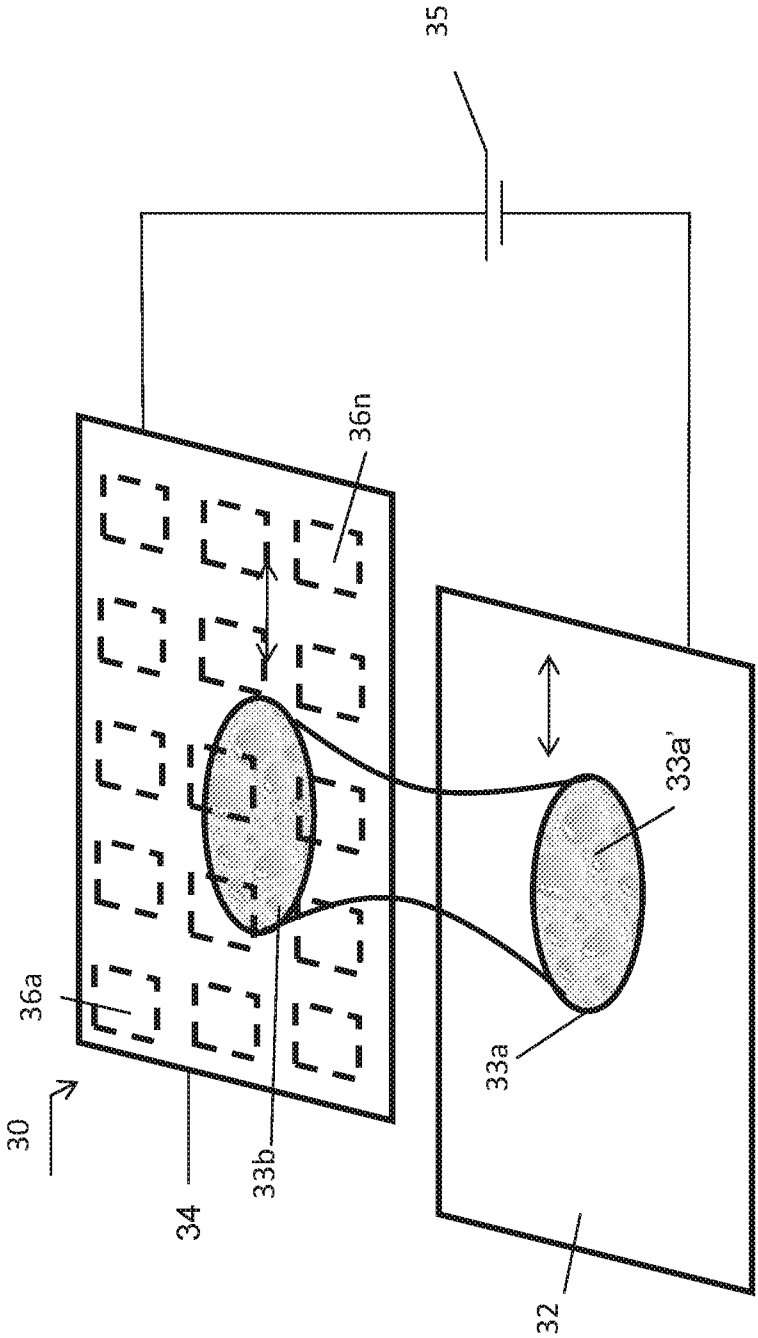

Fig. 3

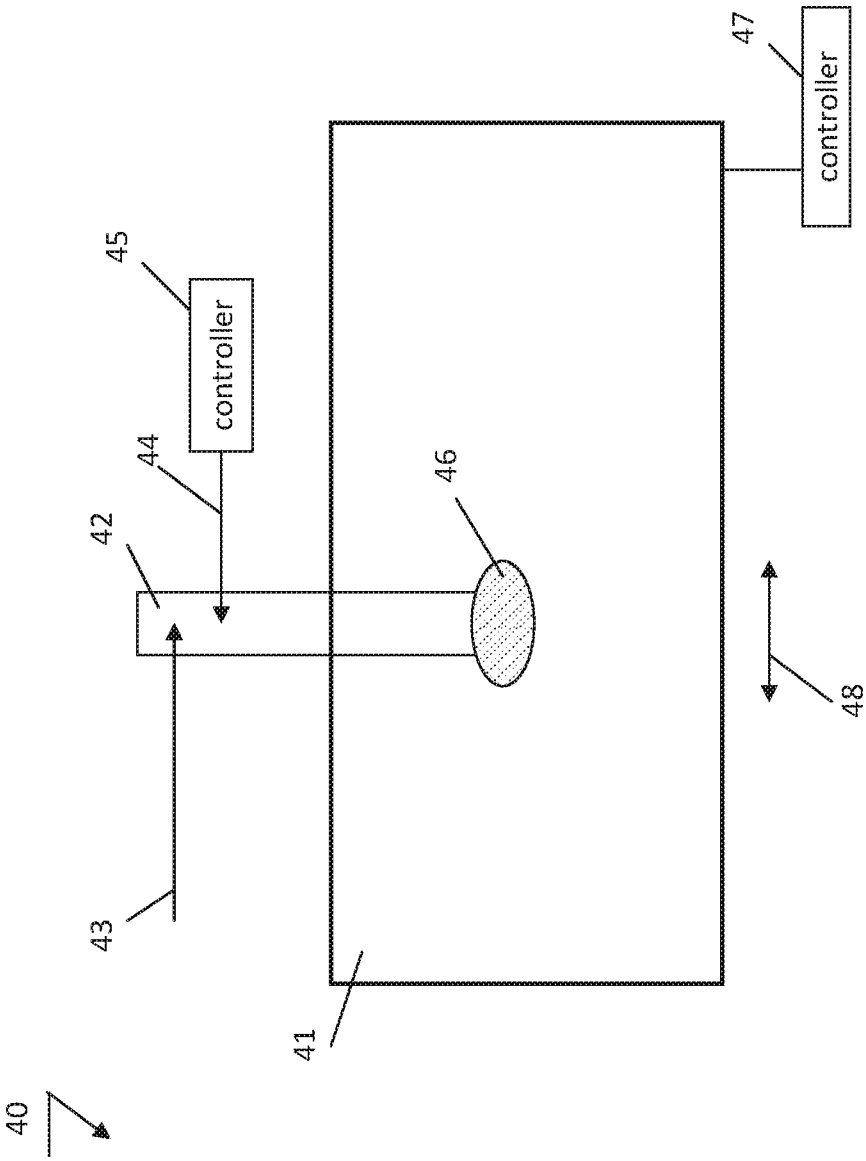

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2012/050174

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25F1/00 B08B3/10
ADD.

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)
C25F B08B

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2009 101299 A (FUJI XEROX CO LTD) 14 May 2009 (2009-05-14) abstract paragraphs [0027], [0046]; claim 3	1-18
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 August 2012	24/08/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Hammerstein, G

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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