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(54) **A method of cleaning a surface**

(57) The invention relates to a method of cleaning a surface using continuously generated nanobubbles, comprising the steps of generating a droplet of a liquid comprising 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.

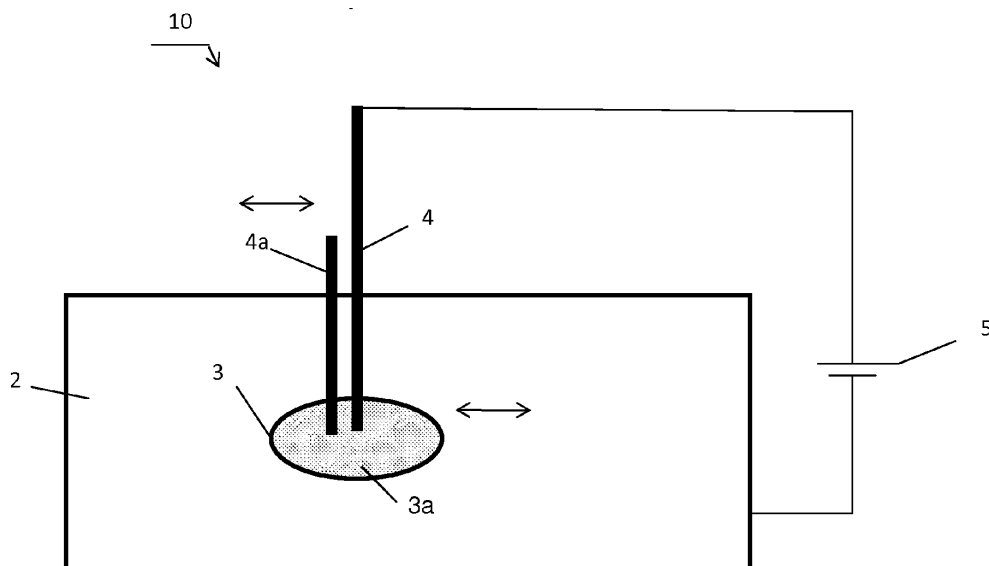


Fig. 1

Description

FIELD

[0001] The invention relates to a method of cleaning a surface using continuously generated nanobubbles.

[0002] The invention further relates to a system for enabling cleaning a surface using continuously generated nanobubbles.

BACKGROUND

[0003] 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.

[0004] 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-deposit. Furthermore, the known method has no control of the location to be cleaned on the surface.

SUMMARY OF THE INVENTION

[0005] 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.

[0006] To this end the method of cleaning a surface according to the invention comprises the steps of:

- generating a droplet of a liquid comprising 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.

[0007] 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.

[0008] In an embodiment of the method according to the invention the droplet comprises the nanobubbles generated using electrolysis.

[0009] 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.

[0010] 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.

[0011] In a further advantageous embodiment, the one or more needle-like electrodes are adapted to conduct the droplet-forming liquid to the surface.

[0012] 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.

[0013] In a still further embodiment of the method according to the invention the droplet comprises the nanobubbles generated by mixing of two solvent liquids.

[0014] 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.

[0015] 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] The system for enabling cleaning a surface using continuously generated nanobubbles, comprises:

- a body for generating a droplet of a liquid comprising 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.

[0020] Further advantageous embodiments of the system according to the invention are recited in the dependent claims.

[0021] 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

[0022]

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

DETAILED DESCRIPTION OF THE DRAWINGS

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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 comprising 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.
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 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.
11. A system for enabling cleaning a surface using continuously generated nanobubbles, comprising:
 - a body for generating a droplet of a liquid comprising 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.
12. The system according to claim 11, wherein the body is further arranged to conduct the liquid towards the surface.
13. The system according to claim 11, wherein the surface and the body form part of an electric circuit.
14. The system according to claim 13, wherein the body is adapted to conduct two different solvents towards the surface.
15. The system according to any one of the preceding claims 11 - 14, further comprising a conduit arranged to remove the liquid comprising contaminations from the surface.

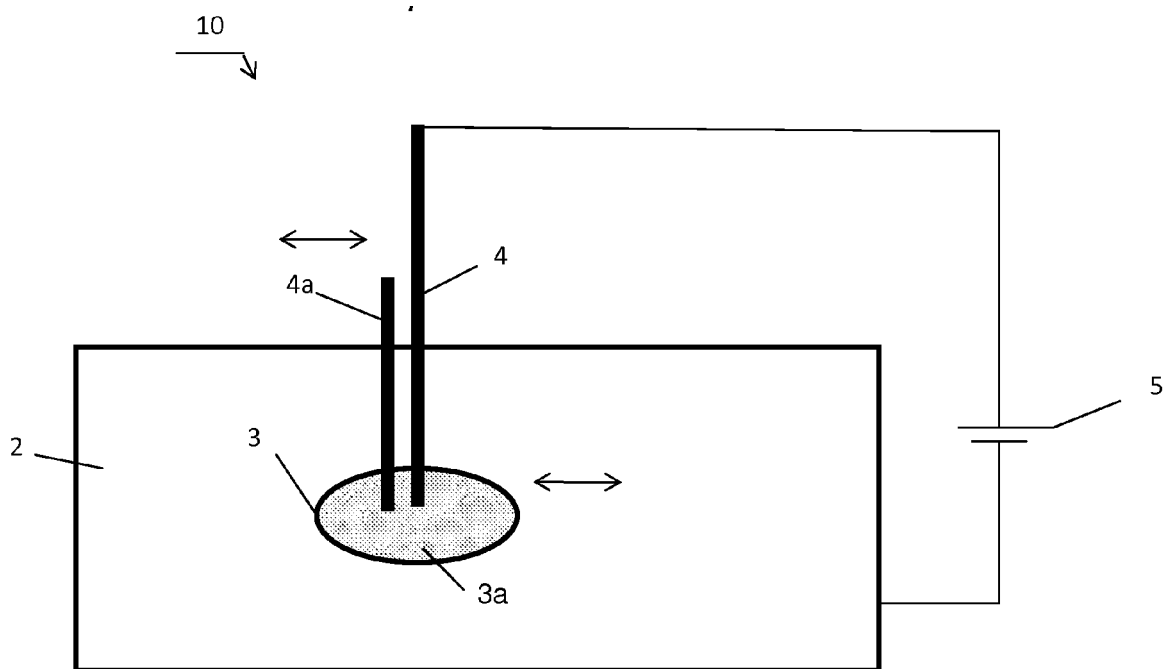


Fig. 1

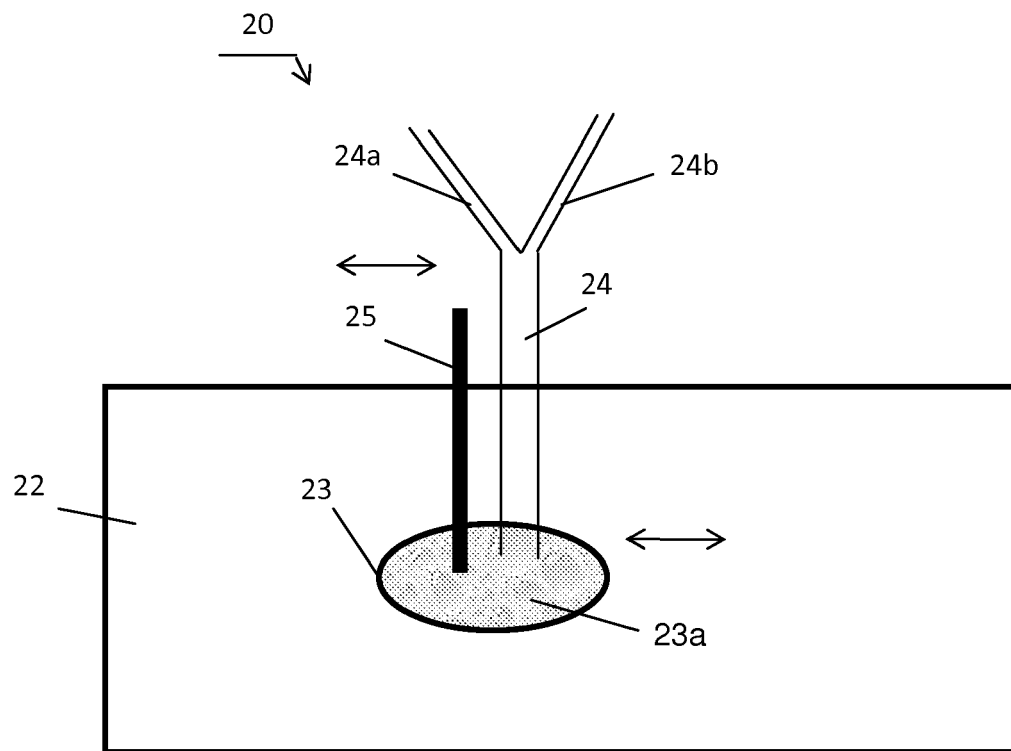


Fig. 2

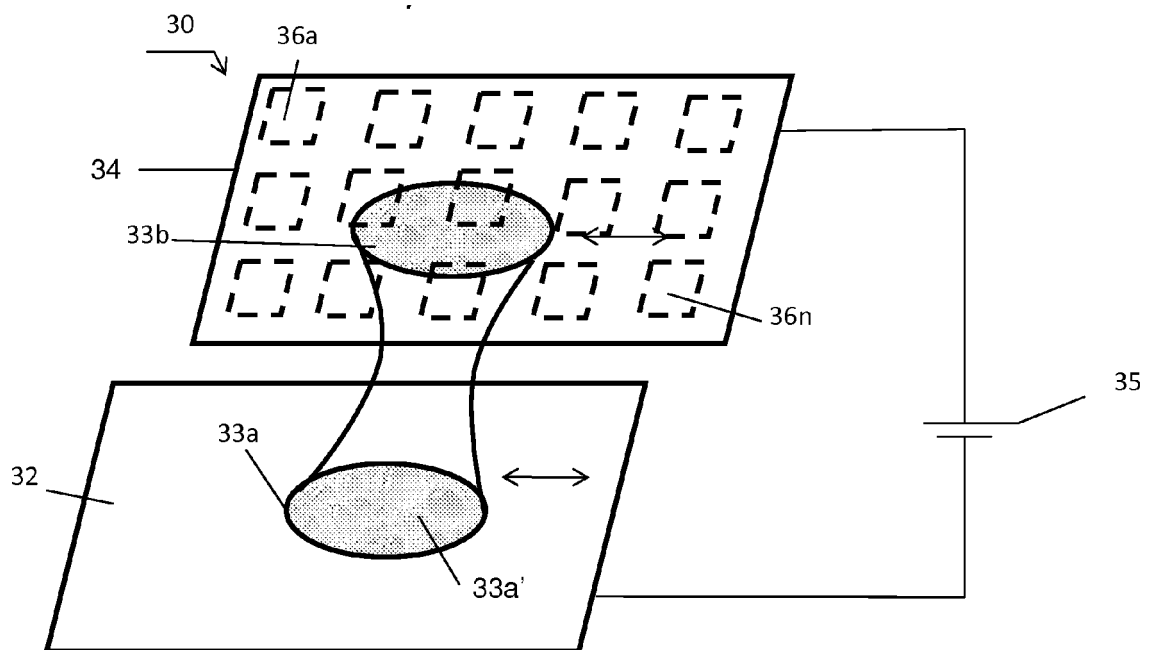


Fig. 3



EUROPEAN SEARCH REPORT

Application Number
EP 11 15 9171

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 2009 101299 A (FUJI XEROX CO LTD) 14 May 2009 (2009-05-14)	1,10-12, 15	INV. C25F1/00
Y	* abstract *	2,7-9,13	B08B3/10
E	* paragraphs [0027], [0046]; claim 3 * -& US 2011/168210 A1 (TABATA KAZUAKI [JP] ET AL) 14 July 2011 (2011-07-14) * paragraph [0064] - paragraph [0067]; claim 3 * * paragraph [0101] *	1,10-12, 15	
Y	----- WU Z H ET AL: "Cleaning using nanobubbles: Defouling by electrochemical generation of bubbles", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS, NEW YORK, NY, US, vol. 328, no. 1, 1 December 2008 (2008-12-01), pages 10-14, XP025589341, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2008.08.064 [retrieved on 2008-09-09] * paragraph [02.2]; figure 6 *	2,7-9,13	TECHNICAL FIELDS SEARCHED (IPC)
Y	----- Yang, Shangjiong: "Manipulating surface nanobubbles", University of Twente Dissertation, 9 October 2008 (2008-10-09), XP002656895, Twente, NL Retrieved from the Internet: URL:http://dx.doi.org/10.3990/1.9789036527286 [retrieved on 2011-08-16] * page 72 - page 74 *	2,7-9,13	C25F B08B
A	----- US 2009/120460 A1 (HEKMAN FREDERICK A [US] ET AL) 14 May 2009 (2009-05-14) * the whole document *	1,2, 7-13,15	
----- The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 16 August 2011	Examiner Hammerstein, G
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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EPO FORM 1503 03.82 (P04C01)



Application Number

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

2, 7-9, 13(completely); 1, 10-12, 15(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

EP 11 15 9171

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 2, 7-9, 13(completely); 1, 10-12, 15(partially)

Claims 2, 7-9 and 13 are directed towards a method and a system for cleaning a surface, comprising generating and displacing a droplet comprising nanobubbles and conducting the liquid away from the surface, further comprising generating the nanobubbles by electrolysis.

2. claims: 3, 4, 14(completely); 1, 10-12, 15(partially)

Claims 3, 4 and 14 are directed towards a method and a system for cleaning a surface, comprising generating and displacing a droplet comprising nanobubbles and conducting the liquid away from the surface, further comprising generating the nanobubbles by mixing of two solvent liquids.

3. claims: 5(completely); 1, 10-12, 15(partially)

Claim 5 is directed towards a method for cleaning a surface, comprising generating and displacing a droplet comprising nanobubbles and conducting the liquid away from the surface, further comprising displacing the droplet over the surface using an electrowetting matrix.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 11 15 9171

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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16-08-2011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2009101299 A	14-05-2009	JP 2009101299 A	14-05-2009
		US 2011168210 A1	14-07-2011

US 2011168210 A1	14-07-2011	JP 2009101299 A	14-05-2009
		US 2011168210 A1	14-07-2011

US 2009120460 A1	14-05-2009	AU 2008323730 A1	14-05-2009
		CN 101909503 A	08-12-2010
		EP 2219507 A2	25-08-2010
		US 2009120460 A1	14-05-2009
		WO 2009062154 A2	14-05-2009
