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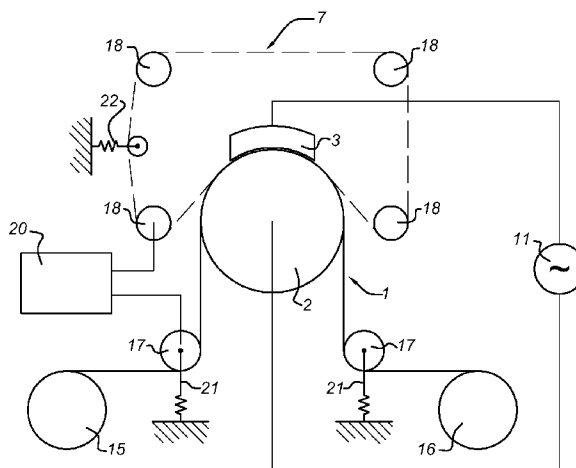
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(54) Title: METHOD AND APPARATUS FOR PLASMA SURFACE TREATMENT OF A MOVING SUBSTRATE

Fig 1



(57) Abstract: Method and plasma treatment apparatus for treatment of a substrate surface (1) using an atmospheric pressure plasma. An atmospheric pressure plasma is provided in a treatment space (5) between a first electrode (2) and a second electrode (3). Furthermore, a substrate (1) and a mask web (7) in contact with the substrate (1) are provided. A plasma generating power is applied to the first and second electrode (2, 3) for treatment of surface areas of the substrate (1) exposed by the mask web (7), in which the substrate (1) and mask web (7) are moved synchronously through the treatment space (5).

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METHOD AND APPARATUS FOR PLASMA SURFACE TREATMENT OF A MOVING SUBSTRATE

Field of the invention

The present invention relates to a method for treatment of a substrate surface using an atmospheric pressure plasma, the method comprising providing an atmospheric pressure plasma in a treatment space between a first electrode and a second electrode, providing a substrate and a mask web in contact with the substrate, and applying a plasma generating power to the first and second electrode for treatment of surface areas of the substrate exposed by the mask web. In a further aspect, the present invention relates to a plasma treatment apparatus for treatment of a surface of a substrate, comprising a discharge electrode structure having a treatment space and comprising a first electrode and a second electrode, a power supply connected to the first electrode and the second electrode for generating an atmospheric pressure plasma in the treatment space, and a transport installation for transporting the substrate through the treatment space.

Prior art

International patent publication WO2004/019381 describes the process of depositing a coating on a substrate in the form of a moving web. A rotating drum is used as one of the electrodes for generating a glow discharge plasma.

European patent publication EP 1 403 902 A1 discloses a method for generating an atmospheric pressure glow discharge plasma using a dielectric barrier discharge electrode configuration. A drum shaped electrode is used, and the substrate film to be treated is guided along a part of the circumference of the drum shaped electrode.

25

Summary of the invention

The present invention seeks to provide an improved substrate treatment method and apparatus, which allow a substrate surface to be patterned in a continuous manner using an atmospheric pressure plasma.

According to the present invention, a method according to the preamble defined above is provided, in which the substrate and mask web are moved synchronously through the treatment space. This allows to efficiently perform a plasma treatment of a

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substrate in the form of a moving substrate or a moving web in a continuous manner, such as in roll-to-roll treatment of webs.

In a further embodiment, the mask web is electrically conductive. This is advantageous in combination with the generated plasma for providing an optimum
5 result (well defined plasma, and well defined mask openings to expose parts of the substrate). Depending on the specific application, the mask web may be grounded, at floating potential or at the same potential as the first electrode.

As mentioned above, the substrate may be a roll to roll substrate, e.g. in the form of a polymer web. Many materials used in various applications as basic material are
10 provided as a roll-to-roll substrate. Using the present method, these may efficiently be plasma treated to obtain a semi-product for further production into a final product.

To obtain an optimal defined pattern on the substrate, the mask web is a roll to roll mask web in a further embodiment. This allows to synchronize the movement of both substrate and mask to obtain as low as possible shifts between substrate and mask
15 during treatment. In a further embodiment, the mask web is a continuous mask web, (endless mask, loop of material), allowing to re-use pattern areas of the mask continuously.

In a further embodiment, the mask web is held in contact with the web by a magnetic force. This furthermore aids in maintaining the mask web and substrate in
20 close contact, resulting in better defined structures on the substrate after treatment.

The method, in a further embodiment, further comprises depositing a material on the treated substrate. E.g., the material is an ink selected from the group consisting of a water based ink, a conductive ink, a gel based ink. Using the present method
25 embodiments, a substrate may be treated with a mask with very fine details, after which material may be deposited using the changed characteristics of the substrate after treatment. For ink treatment, e.g. use can be made of hydrophobic/hydrophilic areas on the treated substrate.

In a further aspect, the present invention relates to a plasma treatment apparatus according to the preamble defined above, in which the first electrode is arranged to
30 receive, in operation, the substrate to be treated and a mask web in contact with the substrate, in which the transport installation is arranged to move the substrate and the mask web synchronously through the treatment space. This apparatus is suitable for implementing the method according to the various embodiments of the present

invention. E.g. in further apparatus embodiments, the transport installation comprises a roll to roll assembly for the substrate, and/or the transport installation comprises an endless web assembly for the mask web. Furthermore, the transport installation may comprise a control unit for controlling the speed of the substrate and the speed of the mask web in the treatment space. Even further, the web mask comprises a paramagnetic material and the plasma treatment apparatus further comprises a magnetic layer provided in the first electrode, in order to obtain close contact between mask and substrate. For this, e.g., the mask web has a magnetic permeability of at least 1 Tm/A, e.g. equal to or larger than 5 Tm/A.

10 In even further aspects, the present invention also relates to use of the method according to any one of the present embodiments for providing a surface of a substrate with a predefined pattern, or to use of the method according to the present embodiments for providing a hydrophobic substrate with a predefined hydrophilic pattern. Sharp defined transitions may e.g. be provided between hydrophobic and
15 hydrophilic areas of the substrate, in which a transition length is less than 10 microns, e.g. less than 2 micron or even less than 0.2 micron. Furthermore, the present invention relates to use of the method according to any of the present embodiments for etching a surface of a substrate with a predefined pattern, or to the use of the method according to any of the present embodiments for depositing material in a predefined pattern on a
20 surface of a substrate.

Short description of drawings

25 The present invention will be discussed in more detail below, using a number of exemplary embodiments, with reference to the attached drawings, in which

Fig. 1 shows a schematic diagram of an embodiment of a plasma treatment apparatus according to the present invention;

Fig. 2 shows a schematic diagram of a further embodiment according to the
30 present invention, illustrating details of a straightened electrode section in which a mask is held to a substrate using magnetic forces;

Fig. 3 shows a graph of a measurement of a water contact angle of a substrate treated using the present invention embodiments.

Detailed description of exemplary embodiments

In Fig. 1 a schematic embodiment is shown of a plasma treatment apparatus for the treatment of a substrate 1 in the form of e.g. a polymeric web. The substrate 1 is a long web, which is transported from a first roll 15 to a second roll 16, e.g. using intermediate rollers 17 to keep the substrate 1 under tension.

The plasma is generated using two electrodes 2, 3 in a dielectric barrier discharge (DBD) configuration, which as such is known to the skilled person. In this embodiment, a first electrode 2 has the form of a cylinder electrode connected to a plasma generation unit 11. A second electrode 3 is formed by a flat curved electrode following the curvature of the cylindrical surface of the first electrode 2 at a predetermined distance, which also is connected to the plasma generation unit 11. The width of the second electrode 3 substantially corresponds to the width of the web 1 to be treated, or is somewhat wider.

A mask web 7 is also put in motion, synchronous with the movement of the web 1, and is brought into contact with the web 1 on the first electrode 2, just before entering the treatment space 5 between electrodes 2, 3. As a result, two different materials are transported over the drum shaped first electrode 2, e.g. a polymeric film as substrate or web 1, covered by a metallic mask web 7. This allows the use of a (flexible) mask web 7 to pattern the surface of the web 1 in a continuous roll to roll mode. By having the substrate 1 and mask web 7 to move synchronously, damage to the substrate 1 is prevented.

The mask web in this embodiment is an endless loop, running over rollers 18. An additional tensioning unit 22 may also be included in the pathway of the mask web 7 in order to make sure a sufficient high tension is maintained in the mask web 7.

In a further embodiment, the mask web 7 may be of finite dimension, and may, like the web 1, be transported from a first to a second roll to hold the mask web 7.

The transport of the substrate 1 and the mask web 7 through the treatment space 5 is implemented by a transport installation, comprising various parts. In the embodiment shown in Fig. 1, the transport installation comprises the rollers 18 for the mask web 7, and the first, second and intermediate rollers 15, 16, 17 for the substrate 1. Other embodiments and constituents of the transport installation are possible.

In order to maintain a synchronous movement of web 1 and mask web 7 in the treatment space 5 between electrodes 2, 3, the system may also comprise a web control unit 20, which is connected to at least one of the rollers 17 in the pathway of the web 1, and at least one of the rollers 18 in the pathway of the mask web 7, for driving the rollers 17, 18 (e.g. using an internal or external drive device such as an electric motor). These rollers 17, 18 may also be provided with sensors measuring the speed of the web 1 and mask web 7, respectively, which feed back these signals to the web control unit 20. As a result it is possible to ensure that the web 1 and the mask web 7 have the same line speed in the treatment space 5 between first and second electrode 2, 3, as a result of which any possible scratching of the web 1 is prevented.

The plasma control unit 11 e.g. comprises a power supply and associated control circuitry as described in the pending international patent application PCT/NL2006/050209, and European patent applications EP-A-1381257, EP-A-1626613 of applicant, which are herein incorporated by reference. The mask device 7 can be either on a floating potential, be grounded, or be on the same potential as the first (bottom) electrode 2. Depending on the type of material used for the mask device 7 and the substrate 1, and the type of application, these alternatives may provide an optimum result.

The plasma generation unit 11 is arranged to generate a uniform atmospheric pressure glow discharge plasma in the treatment space 5 between first and second electrode 2, 3. With this APG plasma, the parts of the surface of the web 1 may be treated which are exposed by the metallic mask web 7. This may e.g. be applied in the manufacturing of printed electronics as one of the processing steps, e.g. to make parts of the surface of the web 1 hydrophilic or hydrophobic. Also, with appropriate gas supply means, the local plasma in the treatment space 5 may be used to deposit substances on the exposed parts of the surface of the web 1.

Using the APG plasma, the treatment space 5 may be supplied with various gasses and compounds. These include, but are not limited to N₂, NH₃, O₂, CO₂ for hydrophilic treatment of a substrate 1, or CF₄ / H₂ or plasma polymerized HMDSO (ppHMDSO) for hydrophobic treatment of a substrate 1.

Although the embodiment described above mentions the use of a DBD electrode structure for generating an atmospheric pressure glow discharge plasma, any plasma

may be used to treat the surface of the web 1 as desired, e.g. using an inductively coupled plasma (ICP) generation.

In a further embodiment, a better contact between web 1 and mask web 7 is ensured by using magnetic forces. For this, the first electrode 2 is provided with a magnetized layer 6, as e.g. shown in the schematic diagram of Fig. 2, in which the area of the treatment space 5 (including first and second electrode 2, 3) is shown straightened. This is specifically advantageous when the patterns in the mask web 7 are complicated and may tend to lift off from the polymeric web 1.

The DBD structure of the apparatus according to Fig. 1 is enhanced by using a further dielectric barrier 4 on the surface of the second electrode 3 directed towards the treatment space 5. This will enhance the generation of a stable plasma in the treatment space 5 and may help in providing a stable and uniform glow discharge plasma in case this is needed.

In an embodiment, the mask web 7 is used on top of the surface of web 1, which in its turn is positioned on top of a magnetic layer 6, which interacts with the mask web 7. The mask web 7 may be made of conductive material, e.g. a metal mask web 7. To secure intimate contact between mask web 7 and the surface of web 1, the mask web 7, which has a predetermined magnetic permeability, can be held in close contact with the web 1 using the magnetic layer 6. For the best results, there is basically no space between the mask web 7 and the web 1, and if there would be a space at all, the distance between mask web 7 and web 1 should be e.g. less than 1 micrometer. The material to be treated (surface of web 1) is sandwiched between the mask web 7 and magnetic layer 6. Main advantages are that the bulk plasma ignites at normal low breakdown voltages and the gas supply to the holes 10 in the mask device 7 towards the surface of the web 1 is by diffusion from the bulk plasma in treatment space 5.

The magnetic layer 6 is positioned on top of the first electrode 2, e.g. in the form of a magnetic layer 6. As an alternative, the magnetic layer 6 is arranged as part of the first electrode 2. The mask web 7 is made of a thin material, in which a pattern is provided as holes or openings 10 in the material for patterning the surface of the web 1. As a result, the web 1 is sandwiched between the mask web 7 and the magnetic layer 6.

In one embodiment, the magnetic layer 6 e.g. comprises small line shaped alternating north and south poles as shown in the cross sectional view of Fig. 2 which have good interaction with the mask device 7. The magnetic layer 6 can either be

conductive or non-conductive. In an example, a magnetic layer 6 was used obtainable from Bakker Magnetics, available under the name 'Natural Magnetic foil', which comprises a semi-anisotropic magnetic layer. This flexible foil comprises alternating magnetic poles at a predefined pitch distance (see e.g. the embodiment shown in Fig. 2)

- 5 Also other flexible magnetic layers from other suppliers may be used. In another magnetic layer 6 which may be used, the magnetic layer e.g. comprises randomly oriented alternating magnetic poles. The thickness of the foil 6 used is as low as possible in order not to interfere with the generation of the glow discharge plasma in the treatment space 5. The thickness of the magnetic layer 6 is e.g. less than 1 mm, e.g.
- 10 0.75 or 0.5 mm In another embodiment also foils 6 may be used with a thickness of more than 1 mm, for example 1.5 or 2 mm or even more. The magnetic layers 6 suitable for use in this invention have as a fundamental property, that the magnetic field extends through the web 1 into the mask web 7 to allow a sufficiently strong attraction force. In order to have this sufficient attractive force the magnetic force should be
- 15 evenly distributed over the surface of the magnetic layer 6 and exerts a magnetic force of between 5 and 100 g/cm², e.g. 19 or 41 g/cm². A higher magnetic force will allow to use a thinner mask web 7 (less material to attract).

- The mask web 7 is made of a material which may have a magnetic permeability of at least 1 Tm/A, e.g. equal to or larger than 5 Tm/A. Very good results are obtained
- 20 with the mask device having a magnetic permeability of 100, or 500 or 1000 Tm/A or any value in between. Material having such magnetic permeability can be selected from ferromagnetic material, or martensitic or austenitic material having ferromagnetic properties. It is furthermore known, that the attraction between a magnetic material and a material attractive for magnetic force is dependant on the thickness of an intermediate
- 25 layer (i.c. the web 1) and the mask web 7. In further embodiments, the thickness of the mask web 7 is chosen as small as possible in order to have a good interaction with the magnetic layer 6 and as little as possible interference with the generation of the plasma in the treatment space 5. For this, the thickness of the mask web 7 is less than 1 mm, e.g. less than 0.4 mm, e.g. 0.1 or 0.05 mm.

- 30 In an embodiment where a glow discharge plasma may be used advantageously the formation of a glow discharge plasma may be stimulated by controlling the displacement current using a plasma control unit 11 connected to the electrodes 2, 3 (see Fig. 1 and 2), and by controlling the distance between electrodes 2, 3, the glow

discharge plasma formation can be promoted even into the small holes 10 in the mask device 7, leading to a uniform activation of the (unmasked) surface of substrate 1.

Example(s)

- 5 A cyclic olefin polymer (COP) substrate roll 1 (optical grade Topas 0.1 mm thick and 17.8 cm width) was used in the surface treatment line as shown in Fig.1 to pattern small hydrophilic spots. The total working length of the plasma discharge in the treatment space 5 is typically 20 cm.

- 10 A flexible mask 7 (open squares with a pitch distance of 0.4 mm) 0.10 mm thick and 18 cm width (AISI 301) was brought as an endless loop in the line as shown in Fig.1 and run with a line speed of 1.0 m/min. The pitch distance is defined as the distance from the centre point of each square to its direct neighbour square centre point

- Gas mixture of Ar 8slm, N₂ 2 slm and O₂ 0.5 slm was used. The sine pulse period applied was 200 micro seconds. Excitation frequency of the plasma was typically 140
15 kHz.. In order to control the stability of the APG plasma in the treatment space a displacement current control was applied (dynamic matching).

- The water contact angle (WCA) was measured using a Krüss DSA 10 Micron contact angle meter, dispensing droplets of 50 pl. First the quality of the plasma surface treatment was classified on COP substrate without using a moving mask according to
20 the reproducibility of the spot to spot treatment, judging in total 10 spots per treated sample. The effective treatment time in the treatment space was influenced by varying the duty cycles (DC). Less than 5% average WCA variation was judged as good (O), more than 5% (Δ) as moderate and more than 20% as bad (X). Table 1 shows its result and points out that at least a duty cycle of 2 % is needed and preferably above 10% in
25 order to give an effective plasma treatment.

Table 1: Relation DC and effective treatment time on COP substrate

<i>DC%</i>	<i>Δt [s]</i>	<i>Classification Ar/N2</i>
<i>1</i>	<i>0.12</i>	<i>Δ</i>
<i>2</i>	<i>0.24</i>	<i>Δ</i>
<i>10</i>	<i>1.2</i>	<i>O</i>
<i>20</i>	<i>2.4</i>	<i>O</i>
<i>40</i>	<i>4.8</i>	<i>O</i>

Non treated COP has a typical WCA of 110°. After treatment the hydrophilicity has increased dramatically.

5 Fig. 3 is showing a typical example of a WCA scan across a COP substrate 1 in the moving web direction treated by the plasma patterning process using a moving mask 7 with a line speed of mask and COP substrate of 1 m/min at a 20% duty cycle. Similar results were obtained using CO₂, and H₂ instead of O₂ as a mixing gas using a plasma treatment at 20% duty cycle.

10 It is clear from Fig.3 that it is possible to realize patterns with predefined structures of hydrophobic/hydrophilic areas (or vice versa) and sharp transitions between hydrophilic and hydrophobic area (or vice versa) on substrates by this invention which may be very useful in applications such as micro titer plates manufacturing, electrically conductive paths manufacturing and even transparent
15 conductive patterns manufacturing on substrates. In these applications, materials are deposited on the treated substrate, and adherence or reaction of the deposited material is defined by the hydrophobic/hydrophilic areas. In other applications, the treatment of the surface may further comprise etching the substrate 1, wherein the etching activity is determined by the treated/untreated areas of the substrate 1.

20 In order to quantitatively describe the sharp transition from hydrophilic to hydrophobic or vice versa we have defined a parameter which characterises how sudden the wettability transition η “happens”.

$$\eta = \left| \frac{WCA(x_2) - WCA(x_1)}{x_2 - x_1} \right| [^\circ/\mu\text{m}]$$

25 Where x_2 and x_1 represent the position of the droplets deposited at the border of the surface energy well. Difficulty is that the droplet cannot be deposited on the corner because the droplet will then move in to the surface energy well.

From Fig. 3 an $\eta = 8^\circ/\mu\text{m}$ can be derived, which indicates that sharp transitions between the hydrophilic to hydrophobic area (or vice versa) can be achieved smaller
30 than 10 micron. To obtain even more detailed information about the typical sharpness of the wettability transition more detailed analysis measurements were carried out with the micro contact angle equipment using 10 pl droplets taking intervals as small as 1

µm. Based on these measurements an $\eta = 50\%$ is observed, which indicates the transition between the hydrophilic to hydrophobic area (or vice versa) are very sharp and even smaller than 2 micron, e.g. smaller 0.2 micron.

Especially the invention can be used in the application of inkjet printing.

- 5 Although the inkjet printing nozzle may have a less accurate output the invented method allows to control the hydrophobic/hydrophilic surface parts very accurately in lateral scale. The liquid ink dispensed by the nozzle will automatically move to area of highest surface energy.

- 10 Materials which also may be used to coat the COP substrate are commercially available conductive inks containing for instance containing silver-particles. Also, gel-based inks based on transparent conductive material can be used. The sol-gel will adhere only to those areas of the substrate 1 which are hydrophilic. Subsequently, the transparent conductive sol gel can be cured by a temperature step or by UV curing. In this manner, a patterned transparent layout can be printed on a polymer surface, which
- 15 may be used for display applications, or photovoltaic cells.

The invented method can be used in other printing applications too like for instance offset printing.

CLAIMS

1. Method for treatment of a substrate surface (1) using an atmospheric pressure plasma, the method comprising:
 - 5 providing an atmospheric pressure plasma in a treatment space (5) between a first electrode (2) and a second electrode (3),
providing a substrate (1) and a mask web (7) in contact with the substrate (1), and
applying a plasma generating power to the first and second electrode (2, 3) for treatment of surface areas of the substrate (1) exposed by the mask web (7),
10 in which the substrate (1) and mask web (7) are moved synchronously through the treatment space (5).
2. Method according to claim 1, in which the mask web is electrically conductive.
- 15 3. Method according to claim 1 or 2, in which the substrate is a roll to roll substrate.
4. Method according to any one of claims 1-3, in which the mask web is a roll to roll mask web.
- 20 5. Method according to any one of claims 1-3, in which the mask web is a continuous mask web.
6. Method according to any one of claims 1-5, in which the mask web is held in contact with the web by a magnetic force.
- 25 7. Method according to any one of claims 1-6, in which the method further comprises depositing a material on the treated substrate.
8. Method according to claim 7, in which the material is an ink selected from the group consisting of a water based ink, a conductive ink, a gel based ink.
30
9. Plasma treatment apparatus for treatment of a surface of a substrate, comprising

a discharge electrode structure having a treatment space (5) and comprising a first electrode (2) and a second electrode (3), a power supply (11) connected to the first electrode (2) and the second electrode (3) for generating an atmospheric pressure plasma in the treatment space (5), and a transport installation for transporting the substrate through the treatment space (5),

in which the first electrode (2) is arranged to receive, in operation, the substrate (1) to be treated and a mask web (7) in contact with the substrate (1), in which the transport installation is arranged to move the substrate (1) and the mask web (7) synchronously through the treatment space.

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10. Plasma treatment apparatus according to claim 9, in which the transport installation comprises a roll to roll assembly (15, 16, 17) for the substrate.

11. Plasma treatment apparatus according to claim 9 or 10, in which the transport installation comprises an endless web assembly (18) for the mask web (7).

15

12. Plasma treatment apparatus according to any one of claims 9-11, in which the transport installation comprises a control unit for controlling the speed of the substrate and the speed of the mask web in the treatment space.

20

13. Plasma treatment apparatus according to any one of claims 9-12, in which the web mask comprises a paramagnetic material and the plasma treatment apparatus further comprises a magnetic layer (6) provided in the first electrode (2).

14. Plasma treatment apparatus according to any one of claims 9-13, in which the mask web (7) has a magnetic permeability of at least 1 Tm/A, e.g. equal to or larger than 5 Tm/A.

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15. Use of the method according to any one of claims 1-8 for providing a surface of a substrate (1) with a predefined pattern.

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16. Use of the method according to any one of claims 1-8 for providing a hydrophobic substrate (1) with a predefined hydrophilic pattern.

17. Use of the method according claim 17 for providing sharp defined transitions
5 between hydrophobic and hydrophilic areas of the substrate (1), in which a transition length is less than 10 microns, e.g. less than 2 micron, or even less than 0.2 micron.

18. Use of the method according to any one of claims 1-8 for etching a surface of a substrate (1) with a predefined pattern.

10

19. Use of the method according to any one of claims 1-8 for depositing material in a predefined pattern on a surface of a substrate (1).

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Fig 1

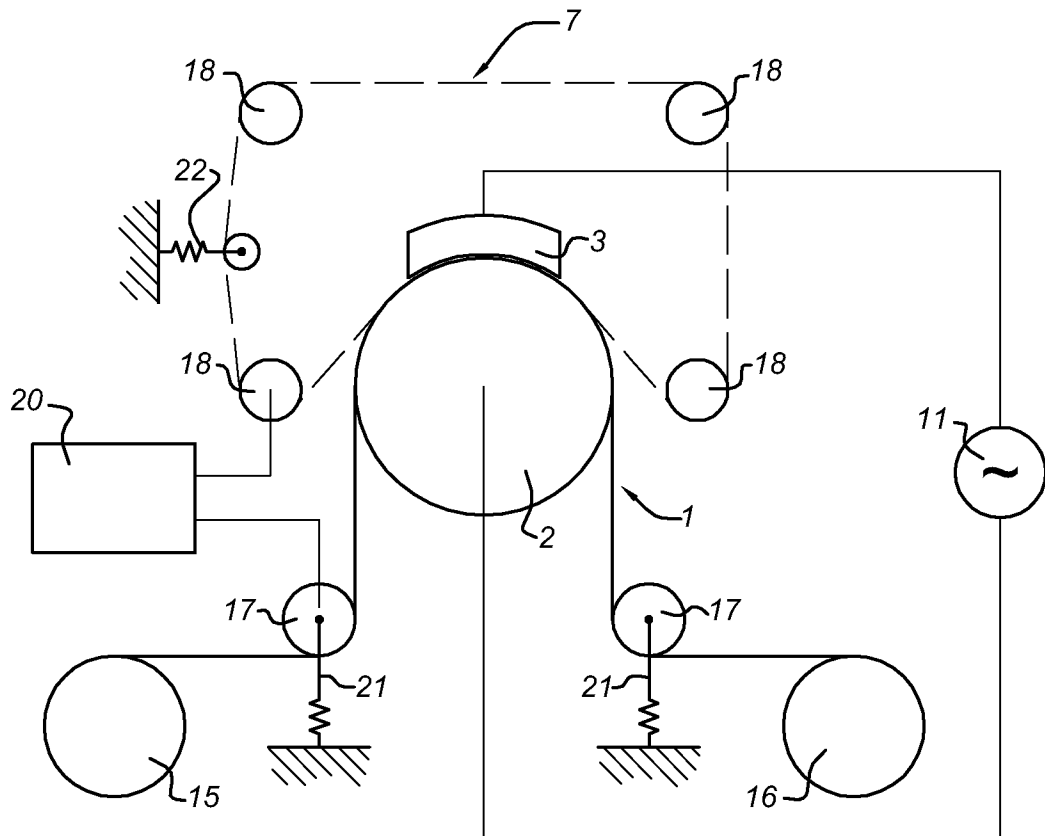


Fig 2

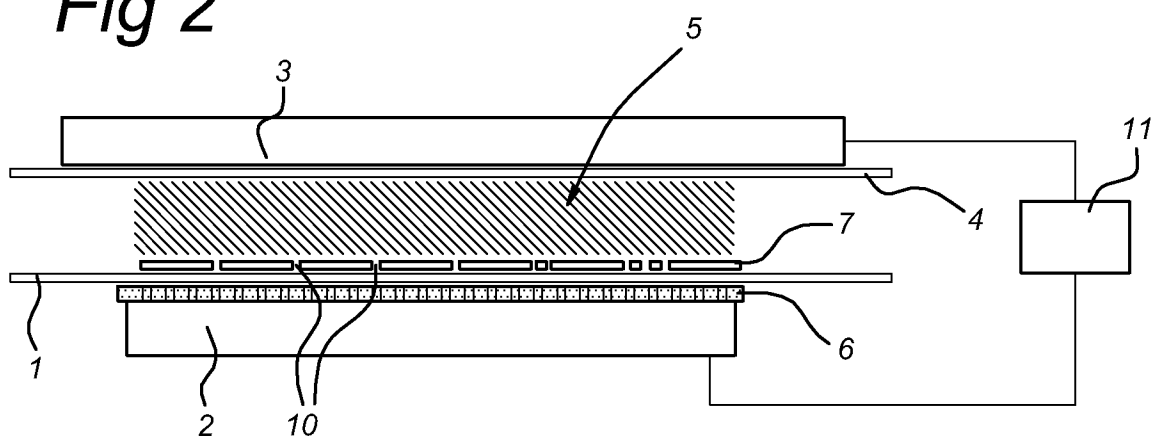
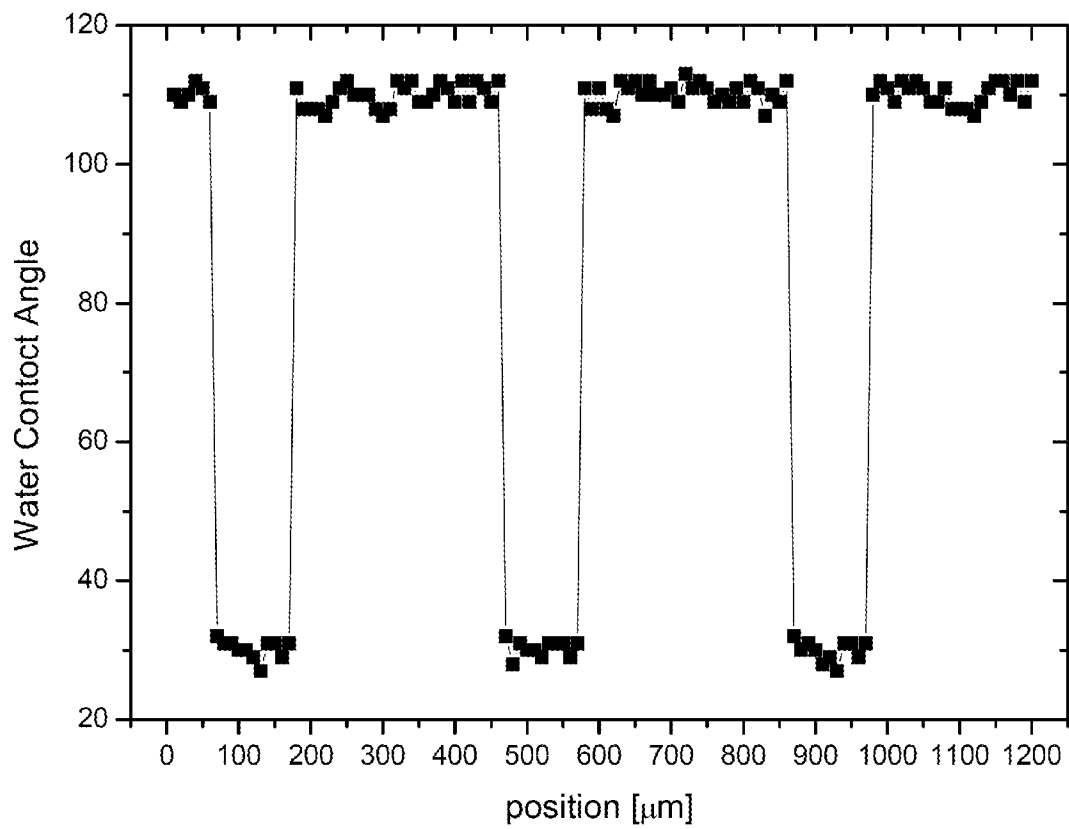


Fig 3

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER

INV. H01J37/32 C23C14/56 C23C14/04 H05H1/24

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)

H01J G03F C23C H05H

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/019381 A (SIGMA TECHNOLOGIES INTERNATIONAL [US]; MIKHAEL MICHAEL G [US]; YIALIZIS) 4 March 2004 (2004-03-04) cited in the application paragraph [0028] - paragraph [0029] paragraph [0033] - paragraph [0035] figures 5,6	1,3,4,7, 9-12,15, 19
Y	US 4 478 878 A (NEUWALD ANSELM [DE]) 23 October 1984 (1984-10-23) column 6, line 8 - column 7, line 26 figure 7	1,3,4,7, 9-12,15, 19
A	WO 2007/078556 A (3M INNOVATIVE PROPERTIES CO [US]) 12 July 2007 (2007-07-12) page 5, line 18 - page 9, line 9 figure 1A	1,9,15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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International application No
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