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(54) **Title:** CONDUCTING A REACTION IN A MENISCUS MOVED OVER A SUBSTRATE

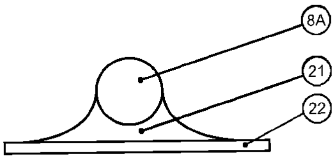

Fig. 4A

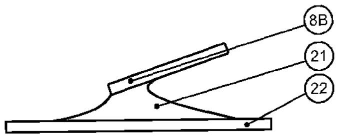

Fig. 4B

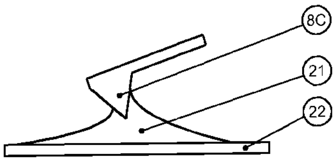

Fig. 4C

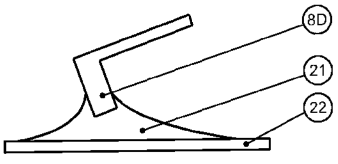

Fig. 4D

(57) **Abstract:** An apparatus that includes:a platform (12) for a substrate (22); a guiding element (8) that is movable with respect to the platform (12) and spreads a liquid over the substrate (22) to form a meniscus (21); an activating element (11, 14, 15, 16, 17) that changes physicochemical parameters of the liquid in the meniscus (21) and/or on the substrate covered by the liquid in the meniscus (21), wherein the activating element (11, 14, 15, 16, 17) is coupled with the guiding element (8); and wherein the guiding element is a rotationally asymmetrical solid (8B, 8C, 8D).

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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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CONDUCTING A REACTION IN A MENISCUS MOVED OVER A SUBSTRATE

DESCRIPTION

TECHNICAL FIELD

The present invention relates to an apparatus for acting on a liquid in a meniscus moved over a substrate and a method for conducting a reaction, in particular adapted to changing physicochemical parameters of a liquid in a meniscus and/or on a substrate covered by the liquid in the meniscus.

The present apparatus and method are particularly useful for producing, from organic or inorganic materials, structures with a controlled shape, thickness, and/or width on various types of substrates, including conductive and nonconductive substrates. For example, the present invention can be applicable to producing substrates with conductive paths, or to producing large-format devices of "plastic" electronics and solar cells, antireflective surfaces, superhydrophobic coatings, protein microarrays, or cell culture media.

BACKGROUND

One of the most common technologies used to form thin polymer films is a deposition from a solution by spin-coating (spin-casting). In this method, a polymer solution is applied on a substrate while the substrate is spinning or before it is rotated at a high speed (up to several thousand rotations per minute). A film of the polymer-solvent mixture is spread over the substrate due to the centrifugal force; this process also leads to rapid evaporation of the solvent. For a double system: a polymer and a solvent, the film thickness can be adjusted by changing the concentration of the polymer in the solution or the spinning velocity. The spin-coating method allows producing films with uniform thickness over the entire substrate area. With additional processing steps introduced before, during, or after the film deposition process, films with desirable structures can be produced. A disadvantage of this method is a limited size of substrates on which polymer films can be deposited.

Another method for producing thin polymer films is horizontal dipping (h-dipping), such as described in "Pattern replication in blends of semiconducting and insulating polymers casted by horizontal dipping" (J. Rysz et al., J. Polym. Sci. Part B Polym. Phys., 51 (2013), pp. 1419–1426).

Although the spin-coating method is commonly used in production facilities, the h-dipping method is more compatible with a roll-to-roll technology, which – as predicted by specialists in the field – will be commonly used in producing large-format devices of “plastic” electronics on flexible films. In this technology, a polymer solution is dosed between a substrate and a cylinder with a diameter of several mm, wherein the cylinder moves with respect to the substrate at a fixed height of several dozen micrometres. A thin layer of the solution is formed on the surface of the substrate downstream the cylinder. By changing the movement velocity and/or the distance of the cylinder with respect to the surface, a local change of the polymer film thickness is possible, which also relates to a change of its structure.

For molecular conductors, the electro-optical properties of the films of conjugated polymers strongly depend on their order. One of the polymer groups that is most commonly used in plastic electronics are polythiophenes with a main rigid chain and alkyl side groups. These polymers tend to crystallize in a film, while the electron level structure and charge carrier mobility strongly depend on the interactions between the chains in the crystallite. Higher order generally leads to a higher range of interaction between orbitals, which results in a higher conductivity or a shift of absorption spectra and light emission towards the infrared spectrum. Therefore, the crystallite orientation in a film plays an important role in controlling the electrooptical properties of those materials and thus on their application in plastic electronics.

For a blend of several polymers, in both methods of film deposition, phase separation of domains rich in various polymers and self-organization of these domains into “frozen” structures after solidification may occur during solvent evaporation. This way, from functional polymer solutions with different properties, composite films with domains constituting complementary structural components of electronic devices (e.g. semiconductor lamellae and FET gate dielectrics), photovoltaics (e.g. donor and acceptor materials creating a heterojunction), photonics (e.g. areas with different refractive index in antireflective coatings), and biotechnology (e.g. surface patterns of domains that group proteins in microarrays) can be produced in a simple and inexpensive way (as described, for example, in “Polymer blends spin-cast into films with complementary elements for electronics and biotechnology” (A. Budkowski et al., J. Appl. Polym. Sci., 125 (2012), pp. 4275–4284)).

For thin films, the phenomenon of polymer blend self-organization is considerably affected by the type of interaction with the substrate. Due to these interactions, domain structures produced by way of self-organization are controlled via the substrate surface properties. A modification of surface properties according to a particular template leads to forming area patterns with different structures in a film that is being produced. In a multi-step producing process, the substrate is first modified using, for example, lithography technologies (soft lithography, photolithography, or electron-beam lithography), and subsequently a polymer film is deposited onto such prepared substrate. Currently, the cheapest and most effective methods are soft lithography methods that use an elastic stamp to modify a specific area and transfer a pattern onto a surface. This leads to ordered polymer area patterns with a different structure and function (e.g. conducting and insulating), which is shown both for films formed by spin-coating (see “Polymer blends spin-cast into films with complementary elements for electronics and biotechnology” (A. Budkowski et al., J. Appl. Polym. Sci., 125 (2012), pp. 4275–4284)) and h-dipping (see “Pattern replication in blends of semiconducting and insulating polymers casted by horizontal dipping” (J. Rysz et al., J. Polym. Sci. Part B Polym. Phys., 51 (2013), pp. 1419–1426)).

The combination of soft lithography and polymer blend film deposition from a solution allows controlling areas, wherein the structure of the areas changes according to even very complicated patterns, e.g. films used as matrices of several dozen transistors (see for example “Solution based self-assembly of an array of polymeric thin-film transistors” (A. Salleo i A.C. Arias, Adv. Mater. 19 (2007), p. 3540)).

However, use of the soft lithography methods introduces another step that requires additional work (e.g. stamp preparation in accordance with a previously formed template), prolongs the entire process and increases the costs. Therefore, there is a need for simpler methods of producing polymer films with a predetermined spatial structure, e.g. already while depositing a polymer layer.

In the state of the art, an electric field applied perpendicularly to a film was also used for modifying the structure of a polymer film (see “Electrically induced structure formation and pattern transfer” (E. Schaeffer et al., Nature. 403 (2000), pp. 874–7)). In the described experiments, previously prepared films of one polymer were placed between capacitor plates, and then heated to a temperature above glass transition temperature or placed in solvent vapours. A strong electric field created forces that were able to overcome the surface tension and lead to instabilities in the liquid thin polymer film. Using electrodes with various shapes, it was possible to produce desirable polymer structures.

The above method was also used to form patterns of two polymers (see “Structure formation at the interface of liquid/ liquid bilayer in electric field” (Z. Lin et al., Macromolecules 35 (2002) 3971)). However, it required separate preparation of two polymer films, one deposited onto another.

Electric field was also used to modify a domain structure of polymer blend films produced by solvent evaporation (see "Electrohydrodynamic effect on phase separation morphology in polymer blend films" (T. Kikuchi et al., Langmuir 20 (2004), p. 1234)), including those produced by spin-coating of composite films of conductive polymer and insulating polymer (see "The effect of the electric-field on the phase separation of semiconductor-insulator composite film" (S. Wang et al., Chem. Commun. (Camb), 51 (2015), pp. 765–7)). Film morphology modification was achieved using an electric field that affected the phase separation process (see "Development of phase morphologies of poly(methyl methacrylate)-polystyrene-toluene mixtures in electric fields" (G. Venugopalvi S. Krause, Macromolecules 25 (1992), p. 4626)). In all those works, the electrodes were produced on the substrate or in the substrate. As a consequence, the electric field was parallel to the substrate, while the polymer film was only modified within a small area between the electrodes.

Conventional methods of pattern fabrication, such as lines and pads on printed circuit board (PCB), involve a complex procedure: designing a path structure, preparing a mask pattern, transferring it onto a PCB, path etching, PCB cleaning after etching. Thus, it is a time-, material-, and energy-consuming process. Therefore, new, cost-effective methods for forming surface structures are sought.

Printing methods using inkjet printers are increasingly more common. However, they require special inks, dedicated to a particular substrate and use.

Metallic paths can be obtained using materials of high conductivity (such as silver or gold) or organic materials. Such types of structures should be obtained in a controlled way, preferably from easily prepared solutions containing a deposited substance.

Another important type of modified surfaces are functional coatings in a form of self-assembled monolayers (SAM). They have significant importance in nanotechnology and nanofabrication methods. Such types of layers are usually obtained through deposition (e.g. grafting or the use of the characteristics of the relationship between a surface and molecules being applied) of photoreactive organic substances with the use of lithography technologies. It is important to obtain particular arrangement patterns of such a type of layers, as this translates into specific surface properties in subsequent steps. Therefore, the precise control of the arrangement, the size of an SAM layer, or local modifications of monomolecular layers is very important.

There are known methods for depositing gold metallic layers such as the one disclosed in US7641944. It includes preparing a solution containing gold ions and a reductant, immersing an object that is to be plated in the solution, irradiating the object with ultraviolet rays, and depositing gold on the object to form gold plating when the ultraviolet rays cause a photochemical reaction in the solution. The method does not provide for selectivity of the deposition of a metallic film.

A publication “Photochemical Deposition of Patterned Gold Thin Films” [Jpn. J. Appl. Phys., Vol. 45, No. 48 (2006)] discloses a method for creating gold paths through the reduction of auric ions to the metallic form. A drop of a solution containing $HAuCl_4$, Na_2SO_3 and ethylenediamine is applied onto a glass surface or a surface coated with ITO, or a PVC board, or a silicon wafer. In the subsequent step, a mask with a previously prepared pattern is applied and irradiated with ultraviolet rays using a high-pressure mercury lamp. This causes the reduction of auric ions according to the pattern of the mask.

Another publication, “Laser Photochemical Deposition of Gold from Trialkylphosphine Alkylgold(I) Complexes” (Chem. Mater. 1994, 6, 1712-1718), discloses deposition of paths of metallic gold from metal-organic precursors. The deposition is performed using laser photolysis (wavelength of 257 nm). However, structures obtained using that method demonstrate contamination with precursors and/or organic ligands, or photolysis by-products.

A publication “Photochemical Patterning of a Self-Assembled Monolayer of 7-Diazomethylcarbonyl-2,4,9-trithiaadmantane on Gold Films via Wolff Rearrangement” (Langmuir 2004, 20, 4933-4938) discloses use of selective irradiation of a surface coated with a photoreactive organic compound. The substrate surface is coated with a thin gold film, on which a compound containing sulphur atoms in its structure is adsorpted, creating an SAM. Then, a mask is applied to the prepared monolayer and irradiated using a UV lamp. This led to creating a pattern in the monomolecular film according to the mask. Such an approach requires preparing a mask every time.

There is a need for an apparatus and a method for forming paths that would allow producing polymer films with a predetermined spatial structure already during the film deposition process, without additional processing steps. For example, it would be advantageous to allow producing paths without a mask. Moreover, there is a need for fast production of uniform large-format films with a predetermined thickness (especially in a way compatible with the roll-to-roll technology) or paths with a predetermined thickness and a predetermined width using a small amount of chemical reagents. The present invention allows achieving at least some of the above needs.

SUMMARY OF THE INVENTION

In one aspect, the present invention relates to an apparatus comprising: a platform for a substrate; a guiding element that is movable with respect to the platform and configured to spread a liquid over the substrate to form a meniscus; an activating element that is configured to change physicochemical parameters of the liquid in the meniscus and/or on the substrate covered by the liquid in the meniscus, wherein the activating element is coupled with the guiding element; and wherein the guiding element is a rotationally asymmetrical solid.

The activating element may be positioned inside the guiding element.

The activating element may be positioned outside the guiding element.

The activating element may comprise a light source configured to illuminate the meniscus during the formation of the path.

The activating element may comprise a direct voltage source connected between an electrode on a surface of the guiding element and the substrate.

The activating element may comprise a direct current source connected between the guiding element and the substrate.

The activating element may comprise a magnetic field source.

The activating element may comprise a heater configured to heat the guiding element.

The platform may be arranged horizontally.

The platform may be inclined.

The platform may be arranged vertically.

The apparatus may further comprise a system for adjusting the distance of the guiding element from the platform.

The system for adjusting the distance of the guiding element from the platform may be a micrometer positioner.

The apparatus may further comprise a system for controlling the distance and turn of the guiding element with respect to the substrate.

The system for controlling the distance and turn of the guiding element may comprise a laser, a detector and a slide mounted to the guiding element, wherein the laser is configured to emit a linear beam of light towards the slide, wherein the beam reflected from the slide falls onto the detector – video camera.

The platform may be mounted on a linear stage configured to move the substrate linearly with respect to the fixed guiding element.

The platform may comprise a system for adjusting inclination in at least one plane, preferably three planes.

The guiding element may be mounted to the platform comprising the system for adjusting inclination in at least two planes, preferably three planes.

The apparatus may be mounted on a platform standing on levelling feet, preferably three levelling feet.

The guiding element may be made of an insulating material, preferably glass or quartz glass.

The guiding element may be made of metal.

In another aspect, the present invention relates to an apparatus comprising: a platform for a substrate; a guiding element that is movable with respect to the platform and configured to spread a liquid on the substrate into a meniscus; and a direct current source connected between the guiding element and the substrate.

In yet another aspect, the present invention relates to an apparatus comprising: a platform for a substrate; a guiding element that is movable with respect to the platform and configured to spread a liquid over the substrate to form a meniscus; and an electric field source coupled with the guiding element.

In yet another aspect, the present invention relates to an a platform for a substrate; a guiding element that is movable with respect to the platform and configured to spread a liquid over the substrate to form a meniscus; and a heater configured to heat the guiding element.

The guiding element may be a cylinder.

The guiding element may be a rotationally asymmetrical solid.

In yet another aspect, the present invention relates to a method for changing physicochemical parameters of a liquid in a meniscus and/or on a substrate covered by the liquid in the meniscus, the method comprising the steps of: a) preparing the liquid to be spread over the substrate, b) applying the liquid to the substrate, c) forming the meniscus by dosing the liquid between the substrate and a guiding element, d) displacing the liquid by moving the guiding element with respect to the substrate, performed by the apparatus as described above.

The method may comprise inducing a photochemical reaction in the meniscus using a light source.

The method may comprise forming a polymer film using a direct current/votage source connected between the electrode on the surface of the guiding element and the substrate.

The method may comprise inducing an electroplating reaction in the meniscus using a direct current source connected between the guiding element and the substrate.

The method may comprise using a magnetic field source to act on the meniscus.

The method may comprise heating the surface of the guiding element.

An important advantage of the present invention is the possibility to form a path (metallic or organic) with a structure that is precisely determined at the application stage, with a small number of process steps. As opposed to methods known in the state of the art, the present method does not require any additional steps, such as for example preparing an irradiation mask in lithographic methods, which streamlines the manufacturing process and is cost-effective.

An additional advantage of the method according to the present invention is the possibility to form large-format polymer films on flexible substrates due to its compatibility with the roll-to-roll technology. In the case of single-component polymer films, activation of the electric field enforces respective organization of molecules or entire crystallites, which allows a local change of the polymer film properties. Furthermore, the method according to the present invention allows modifying the self-organization processes, so that predetermined polymer pattern areas are formed already during polymer film deposition. In turn, the use of structured electrodes and/or alternating field allows “printing” patterns, including paths, from semiconducting polymers.

The present invention significantly reduces material costs, because conducting a reaction in a meniscus does not require immersing the entire substrate in a solution, but only a small amount of the solution is applied between a guiding element and the substrate. For example, for a microscope slide having a width of 25 mm, the amount of the solution applied ranges from 50 to 200 μl depending on the guiding element distance from the substrate. By moving the meniscus over the substrate (using the guiding element and a linear stage) as well as by turning on and off the source of light, or changing the position of the light with respect to the guiding element that spreads the precursor solution, it is possible to activate a photochemical reaction locally (in precisely determined positions on the base surface) and, thus, to deposit a material on the substrate, for example to produce gold paths.

In one aspect of the invention, it is possible to deposit a metallic layer of silver or to modify the chemical properties of the substrate.

The method according to the invention allows creating functional patterns on the surface of the substrate with different performance characteristics. movement

Additionally, by controlling luminous intensity of the light and movement velocity, it is possible to modify the thickness of the layer produced.

BRIEF DESCRIPTION OF DRAWINGS

The present invention is shown by means of non-limiting example embodiments shown in a drawing, wherein:

Fig. 1 shows schematically an apparatus for conducting a photochemical reaction in a moving meniscus,

Fig. 2 shows schematically structural elements of the apparatus of Fig. 1, which allow controlling the guiding element distance from the sample surface, as well as the tilt of the guiding element with respect to the sample surface,

Figs. 3a, 3b, 3c show a schematic representation of different arrangements of the guiding element in the form of a cylinder with respect to the substrate.

Figs. 3d, 3e, 3f show respectively graphs representing the position of the laser spot as a function of the distance of a chuck with the cylinder from the sample surface.

Figs. 3g, 3h, 3i show respectively graphs representing the laser spot position difference as a function of the distance of the chuck with the cylinder from the sample surface,

Figs. 4A, 4B, 4C, 4D show various embodiments of the guiding elements,

Figs. 5A, 5B, 5C, 5D, 5E show various embodiments of the methods for conducting a reaction in the meniscus,

Fig. 6 shows a sample with a gold path formed thereon,

Fig. 7 shows a picture of a gold path taken with an optical microscope (4× magnification),

Fig. 8 shows a picture of a boundary of the gold path taken with an optical microscope (10× magnification),

Fig. 9 shows an image of Au_3^- ions obtained using ToF-SIMS method.

Fig. 10 shows differences between a refractive index n and an extinction coefficient k dependence on a light wave length for an RP3HT polymer film spread in a presence and in an absence of an electric field,

Figs. 11a – 11e show AFM images disclosing the impact of the electric field on phase separation in different polymer blends,

Fig. 12a shows a picture of the cylinder coated with electrodes, Figs. 12b, 12c show pictures of polymer films formed using a cylinder for different configurations of voltages applied to the electrodes coated on the cylinder,

Fig. 13a shows a picture taken with a fluorescence microscope and Figs. 13b, 13c, 13d show topographic images obtained with an AFM microscope presenting a difference in a structure of a polymer film formed using the method according to the present invention depending on voltage applied and Fig. 13e shows a picture taken with a fluorescence microscope presenting an increased boundary between various polymer film structures.

Fig. 14a shows a picture of another polymer film produced with the method according to the present invention using an alternating field and Fig. 14b shows a picture taken by a fluorescence microscope for this polymer film.

DETAILED DESCRIPTION

An apparatus for conducting a photochemical reaction in a moving meniscus allowing, among other things, producing paths with a set structure according to one example of this invention is shown schematically in Fig. 1.

The apparatus comprises a movement system 1, preferably a linear stage, that allows the movement of the substrate with respect to a guiding element 8, which causes the movement of the meniscus. The linear stage 1 allows choosing an appropriate velocity, as well as acceleration. The guiding element 8 is mounted in a chuck 5. In order to obtain a homogeneous layer over as large an area as possible, it is important to ensure the appropriate arrangement of the guiding element 8 with respect to the sample surface, and to level the entire system. In order to achieve that, a set of elements allowing the appropriate arrangement of particular components of the apparatus is used. A micrometer positioner 2 allows positioning the guiding element 8 to an appropriate distance from the sample, preferably with an accuracy of several µm. A first platform 12 allows correcting the sample slope, so that the guiding element 8 moves at a constant height along its entire length. A second platform 3 allows correcting the guiding element 8 tilt, so that it is parallel to the sample surface. The entire apparatus can be placed on a third platform 13 with three screws mounted that allow levelling of the entire apparatus.

In order to control the distance of the guiding element 8 from the sample surface, as well as to correct its tilt, the system for controlling the approach of an AFM probe to a sample surface, known, for example, from atomic force microscopy (AFM), can be used. In a standard system known in the state of the art, the laser spot is reflected from the surface of a cantilever on which the AFM probe is mounted and it is tracked by a four-segment photodetector. When the AFM probe comes in contact with the surface, the cantilever bends, which changes the position of the laser spot on the photodetector. In the distance adjustment system for controlling the guiding element 8 distance as used in this invention (as shown schematically in Fig. 2), an extended linear beam of light generated by the laser 9 (not a spot beam, as known in the AFM systems) is used, with the guiding element 8 that spreads the liquid solution over the substrate, not connected with the flexible bar, but with a rigid element, e.g. slide 7. The entire distance adjustment system for controlling the distance comprises the chuck 5, the guiding element 8, the ball end rod 6, the slide 7, the laser 9, the holder with video camera 4 — with the entire system mounted to the platform 3. The slide 7 with the guiding element 8 fixed to it is mounted in the chuck 5 using a ball end rod 6. Such installation allows not only the movement of the guiding element 8 and the slide 7 in the vertical direction (with respect to the apparatus), but also their turning, which is important when positioning the guiding element 8 in parallel to the sample surface so that its distance from the sample surface is the same along its entire length.

The operation of the distance adjustment system for controlling the guiding element 8 distance from the substrate involve detecting the extended linear beam coming from the laser 9 and reflected from the surface of the slide 7 on which the guiding element 8 is mounted. The laser beam is tracked by the detector 4 in the form of a camera mounted in a holder. If the guiding element 8 is parallel to the sample surface, then when it comes in contact with the surface, it touches the sample along its entire length and, as a result, with the chuck 5 further approaching the sample surface, the guiding element 8 moves upwards (without turning), which is observable in the detector 4 as a shift of the entire laser beam. If the guiding element 8 is not arranged in parallel to the surface, then when it is approaching the surface, one of its ends (right or left) comes in contact with the sample, which leads to the turning of the guiding element 8 and the slide 7. Consequently, the laser beam turns. When the chuck 5 with the guiding element 8 is further approaching the sample, at some point the other end of the guiding element 8 touches the sample surface (the guiding element 8 becomes aligned with the sample), which makes the entire element go upwards, as is the case with the parallel arrangement of the guiding element 8 with respect to the sample surface. An appropriate algorithm implemented in the controller of the distance adjustment system records the position of the entire reflected laser beam 9, as well as the position of the beam reflected from the right and the left end of the slide 7 with the guiding element 8 mounted. By tracking the changes in those three signals, it is possible to detect an incorrect position of the guiding element 8 with respect to the sample surface, as well as to set the appropriate guiding element 8 distance to the sample surface. Sample graphs are presented in Figs. 3a-3h, which presents examples where the left end (3a, 3d, 3g) or the right end (3c, 3f, 3i) of the guiding element 8 is positioned higher, as well as where the guiding element 8 is parallel (3b, 3e, 3h) to the sample surface.

By analysing the changes in the laser beam position in the camera 4 as a function of the distance, three main steps may be distinguished:

I) the guiding element 8 is above the sample surface,

II) one of the ends of the guiding element 8 touches the sample,

III) the other end of the guiding element 8 touches the sample and the entire guiding element 8 lies in parallel to the sample surface.

In step I, no changes in the laser beam position are observed in the camera 4 as the sample surface is being approached. When one of the ends of the guiding element 8 begins to touch the sample (step II), the guiding element 8 and the slide 7 begins to turn in the chuck 5 (Fig. 3a, 3c). Consequently, a laser beam position change is observed in the camera 4 (Fig. 3d, 3f). What is more, because of the turning of the guiding element 8, different positions of the laser beam reflected from the left end and the right end of the slide 7 with the guiding element 8 mounted are observed (Fig. 3g, 3i). When the other end of the guiding element 8 touches the sample (step III), another change in the laser beam position can be observed in camera 4 (Fig. 3d, 3f) and, at that moment, the entire guiding element 8 rests on the sample surface. If the chuck 5 with the guiding element 8 is further lowered, it starts to go upwards and the difference between the positions of the laser beam reflected from the left and from the right end of the slide 7 with the guiding element 8 mounted is constant (Fig. 3g, 3i). If the guiding element 8 is turned with respect to the sample surface, two “breakdowns” in the signal representing the laser beam position can be observed in the camera 4 as recorded as a function of the distance, as well as a clear spike in the difference between the positions of the laser beam reflected from the left and from the right end of the slide 7 with the guiding element 8 mounted can be seen. When the guiding element 8 is parallel to the substrate, both of its ends touch the sample surface at the same time (the guiding element 8 touches the sample along its entire length) without causing it to turn. It is observed as a single “bend” in the signal representing the laser beam position in the camera 4 recorded as a function of the distance (Fig. 3e), while there is no clear spike in the difference between the positions of the laser beam reflected from the left and from the right end of the slide 7 with the guiding element 8 (Fig. 3h). The presented distance adjustment system allows setting its distance from the sample surface with the accuracy of several micrometres; the distance adjustment system is also sufficiently sensitive to set the angle between the sample surface and the guiding element 8 (no parallelism of both surfaces) with the accuracy of 0.1°.

The guiding element 8 that spreads the liquid solution on the substrate is preferably made of glass. The guiding element 8 may be also made of other materials, depending on a type of the reaction conducted or on the liquid solution used on the substrate.

Into the above described apparatus for conducting a reaction in a meniscus a substrate is inserted, which is placed on a platform 12 equipped with a platform inclination adjustment system for adjusting an inclination in at least one plane, preferably in three planes, and embedded in a linear stage 1. Because the platform 13 stands on three levelling feet, it is possible to level the entire apparatus. Similarly, the platform 3 is equipped with a substrate inclination adjustment system for adjusting an inclination in at least two planes (preferably in three planes) and the chuck 5 for the slide 7 with the rod 6 and the guiding element 8 is fastened to it rigidly. After levelling, a liquid solution is applied between the substrate and the guiding element 8 to form a meniscus suspended between the guiding element 8 and the substrate, and, subsequently, by ensuring linear movement using the linear stage 1, the meniscus is moved. The thickness and homogeneity of the formed layer is changed by ensuring an appropriate distance and turning the guiding element 8 with respect to the substrate and by controlling the velocity and acceleration of the substrate linear movement, as well as the intensity of the medium that causes the reaction.

In the apparatus presented in Fig. 1, various types of guiding elements 8 shown schematically in Fig. 4A-4D can be used.

For example, the guiding element 8 can have a form of a cylinder 8A. The cylinder 8A is a solid of revolution, i.e. a solid that is rotationally symmetrical with respect to its axis.

Alternatively, the guiding element 8 can have a form of a flat plate 8B, a pyramid 8C, or a cuboid 8D. A common feature of the elements 8B, 8C, 8D is that they are rotationally asymmetrical solids, i.e. their surface is rotationally asymmetrical with respect to their axis, so that by adjusting their inclination angle with respect to the substrate 22, the shape of the formed meniscus 21 can be adjusted and, as a result, the reaction parameters can be affected. In particular, these guiding elements allow adjusting the shape of the formed meniscus 21, so that the formed meniscus at is asymmetric in a standstill, i.e. the shape of the meniscus at the front contact edge is different from its shape at the back contact edge.

In alternative embodiments of the apparatus, the guiding element 8 can be movable over a fixed base instead of the linear stage 1.

In yet other embodiments, instead of the linear stage 1, other substrate movement mechanisms can be used, for example a system of rollers for moving rigid substrates or systems that stretch flexible substrates.

In another embodiment, both the guiding element 8 and the substrate (on the linear stage or a different movement mechanism) can be movable at the same time.

In the presented embodiment, the platform 12 is supposed to be arranged horizontally (using the above-mentioned adjusting elements). However, alternative embodiments are also possible, wherein the platform 12 can be arranged at a specific angle or vertically.

In the apparatus presented in Fig. 1 various types of reactions can be conducted in the meniscus, depending on instrumentation installed.

For example, the apparatus for conducting a reaction can be equipped with a holder 10 for mounting a light source 11 (which is one embodiment of the activating element) for inducing a photochemical reaction, as shown in Fig. 1, 2, and 5A. If UV light is used for activating the photochemical reaction and it is directed at a 90° angle with respect to the substrate, a quartz guiding element can be used. For example, a deuterium lamp or a diode with a specific wavelength, such as 250 nm, can be used as the light source 11. Such a diode emits light within a limited range, which allows choosing a wavelength that is optimum for the photochemical reaction effectiveness. In another embodiment, a laser can be used as the light source 11. In addition, an element allowing precise positioning of the light source 11 with respect to the meniscus 21 shall be used. The system for conducting a reaction is shown schematically in Fig. 5A.

In another embodiment, the apparatus for conducting a reaction can be adapted to produce polymer films with patterns and can be equipped with a cylinder 8, the surface of which is coated with an electrode, for example a gold electrode. Using lithographic technologies or masks on surface of the cylinder 8, it is possible to form electrodes with a predetermined shape. Between the conductive sample 22 and the electrodes coated on the cylinder 8, a voltage differential is applied from a voltage source 14 (which is another embodiment of the activating element), which induces electric field directed perpendicularly to the substrate. In an alternative embodiment, a larger number of electrodes (e.g. two or three) isolated from each other can be coated on the cylinder 8, while the voltage differential can also be applied between the electrodes coated on the cylinder 8. By turning the voltage on and off and using appropriate voltage waveforms, the polymer film structure can be locally modified and given a desirable pattern. The voltage source 14 generates direct or alternating electric voltage having+, for example, square, sinusoidal, or triangular waveforms.

In another embodiment, between the guiding element 8 and the substrate 22, a source 15 of direct current can be connected – as another embodiment of the activating element – in order to conduct an electroplating reaction via the flow of current through the meniscus 21 between the guiding element 8 and the substrate 22, as shown schematically in Fig. 5C. For example, the reaction can be conducted for a current flow of between 1 mA/cm^2 and 100 mA/cm^2. In such a case, it is preferable to use a guiding element 8 coated with an appropriate material, e.g. a layer of metal applied in the electroplating process.

In another embodiment, the guiding element 8 can be coupled with, as another embodiment of the activating element, a magnetic field source 16, as shown in Fig. 5D. For example, it can be a coil located inside or outside the guiding element 8. The N-S direction is preferably adjustable to any orientation with respect to the substrate~~.~~ This type of the apparatus is particularly preferable for conducting reactions in mixtures of a polymer and magnetic nanoparticles – by correspondingly controlling (turning on and off) the magnetic field, the organization of magnetic nanoparticles in the polymer film can be controlled.

In another embodiment, the guiding element 8 can be coupled with a heater 17 of adjustable temperature (which is another embodiment of the activating element). The entire guiding element or only parts of it (especially in case of asymmetrical elements) can be heated. By adjusting the temperature, the course of reaction can be affected, especially in the case of reactions that require higher temperatures.

Furthermore, other embodiments are possible, which combine the elements shown in Figs. 5A-5E.

To sum up, the presented activating elements 11, 14, 15, 16, and 17 are used in general to change the physicochemical parameters of and/or to inducing a chemical reaction in the liquid in the meniscus 21 and/or on the substrate covered by the liquid in the meniscus.

Example 1 – producing a gold metallic path.

As a liquid solution on the substrate, a precursor solution was prepared, and it contained:

- 150 ml NaCl 2.5 M,
- 100 ml $HAuCl_4$ 50 mM,
- 180 ml Na_2SO_3 0.2 M.

As a substrate, a standard microscope glass slide coated with 3-mercaptopropyltrimethoxysilane (MPTES) was used. The apparatus for conducting a photochemical reaction in a meniscus was set up as follows:

- the glass cylinder placed 1.5 mm above the substrate;
- the velocity of the meniscus movement over the substrate 0.02 mm/s;
- the amount of the solution forming the meniscus between the cylinder and the substrate equal to 200 μl.
- the light falling onto the sample surface at an angle from 15° to 45° led out in an optical fibre cable from the deuterium lamp through the holders 10 and 11.

A slide coated with MPTMS was placed on the platform 12 and the precursor solution was dropped in between the substrate surface and the guiding element 8 in the form of a cylinder. The solution was spread between the substrate and the cylinder 8, creating a meniscus. Then, a photochemical reaction was initiated by irradiating a spot within the meniscus using the light from the optical fibre cable inserted through the holder 11. Continuing the irradiation, the meniscus was moved over the substrate. As affected by the light, gold was precipitated from the solution (Fig. 6) and was deposited on the substrate, which allowed forming a gold path with a length of 4 cm and a width of 1.5 mm (Fig. 7 and 9) — comparable to the width of the light spot irradiating the meniscus. A Time-of-Flight secondary ion mass spectrometer (ToF-SIMS) showed that the path visible in Fig. 6 and 7 is made of gold (Fig. 8). Optical microscope images show the internal structure of the path consisting of gold nanoparticle agglomerates precipitated from the solution under the influence of light (Fig. 8).

Example 2 – producing a uniform polymer film.

In order to confirm the applicability of the present method for producing polymer films with a predetermined spatial structure for achieving desired electro-optical properties of single-component polymer films, experiments have been conducted to show the impact of an electric field applied between the cylinder 8 and the substrate during spreading on the electro-optical properties of the said polymer films. The experiment used RP3HT conjugated polymer (regioregular poly(3-hexylthiophene-2,5-diyl) with a mean molecular weight M_n in the range from 54000 to 75000, as characterized by the manufacturer, solved in 15 mg/ml chlorobenzene. While spreading the solution, a voltage of 0 V and 30 V was supplied to the electrodes. The areas were examined using spectral ellipsometry providing information on the refraction index n and the extinction coefficient k. Graphs shown in Fig. 10 demonstrate that both the maximum of light refraction index n and the maximum of extinction coefficient k are shifted towards longer waves. This proves the change in the electron level structure in the areas formed in the presence of the electric field. Therefore, by applying an alternating electric field while spreading polymer films, single-component polymer films with patterns characterized by changed electro-optical properties can be produced.

Example 3 – producing composite films with a predetermined spatial structure using electric field applied during deposition of the film.

In order to demonstrate – for polymer blends – the possibility to produce polymer films with a predetermined spatial structure using an electric field applied during the film deposition, three commonly used polymer blends have been chosen. These polymers are two polythiophene-family semiconductors used in organic electronics and photovoltaics, featuring high charge mobility and market availability: regioregular poly(3-hexylthiophene-2,5-diyl) RP3HT and poli(3,3'''-didodecyl-2,2':5',2'':5'',2'''-quaterthiophene) PQT12. In the experiments conducted, they pair up with insulating polymers, such as poly(methyl methacrylate) PMMA or poly (ethylene glycol)-poly (ε-caprolactone) PEG-PCL, used previously in organic field-effect transistors (PMMA) or as a biocompatible polymer material (PEG-PCL). Tested polymer blends are RP3HT and PEG-PCL (Figs. 11a – 11c), RP3HT and PMMA (Fig. 11d), as well as PQT12 and PEG-PCL (Fig. 11e) systems. In prior art, the use of similar blends with strictly specified phase domain structure in the electrospinning of nanofibers – for the blend RP3HT/PCL ("Continuous production of uniform poly(3-hexylthiophene) (P3HT) nanofibers by electrospinning and their electrical properties" (S. Lee et al., J. Mater. Chem., 2009, 19, p. 743)), or in the produce of FET transistors on silicon substrates or flexible films – for the blend RP3HT/ PMMA ("Self-stratified semiconductor /dielectric polymer blends: vertical phase separation for facile fabrication of organic transistors" (X. Wang et al., J. Mater. Chem. C, 2013, 1, p. 3989)) and PQT12/ PMMA ("Solution based self-assembly of an array of polymeric thin-film transistors" (A. Salleo i A.C. Arias, Adv. Mater. 19 (2007), p. 3540)) was demonstrated.

The polymer blend solutions with concentration of 15 mg/ml were prepared in chlorobenzene. Mean molecular weight values of the polymers used as provided by the producers are: RP3HT – M_n in the range from 15000 to 45000 (Aldrich Chemical Co.), PMMA – M_n=61800 (PSS Polymer Standards Service GmbH), PEG-PCL – M_n~18000 (PCL ~13000, PEG ~5000) (Aldrich Chemical Co.). Films prepared using the RP3HT and PEG-

PCL polymer blend were spread with a velocity of 2 mm/s, while the RP3HT and PMMA blend and the PQT12 and PEG-PCL blend with a velocity of 1 mm/s.

Atomic force microscopy (AFM) images presented in Fig. 11 reflect the phase structure of the polymer blend films with different composition weight ratio (given in parentheses), deposited without (0 V) and with an electric field (30 V). For the blend RP3HT and PEG-PCL (Figs. 11a, 11b), all the images, apart from Fig. 11a for 30 V, reflect a lateral domain structure, in which – with the higher weight content of RP3HT in the blend (ranging from 50 to 60% w/w) – the area occupied by higher domains rich in RP3HT becomes larger, while the lower domain area rich in the PEG-PCL insulator becomes smaller. This interpretation of the two domain types (higher and lower) has been confirmed by additional SIMS experiments. AFM images also show that in the case of 50:50 blends (RP3HT: PEG-PCL), films deposited without the electric field (Fig. 11a for 0 V) demonstrate a lamellar structure. Additional SIMS tests have confirmed the lamellar structure, with the semiconductor (RP3HT) lamella adjacent to the substrate and coated with a phase rich in the insulator (PEG-PCL). In prior art, composite films with a similar structure were used in FET transistors to form lamellae of an active semiconductor, coated – in the same deposition process – with a passivation lamella protecting an organic transistor against environmental impact (“Solution based self-assembly of an array of polymeric thin-film transistors” (A. Salleo i A.C. Arias, Adv. Mater. 19 (2007), p. 3540)). Self-stratified lamellae are formed during solvent evaporation from the deposited composite film as a result of the separation process of polymer phases directed by the film surfaces. It is known from the literature on the subject that even a slight change of the physicochemical properties of the substrate causes a modification of its interactions with the blend, leading to a different course of the processes of phase separation and film formation, allowing a substrate-controlled change from the lamellar structure to the lateral domain structure (“Polymer blends spin-cast into films with complementary elements for electronics and biotechnology” (A. Budkowski et al., J. Appl. Polym. Sci., 125 (2012), pp. 4275–4284)). Introduction of an electrical field in the conductive polymer solution modifies its deposition on the substrate and changes the substrate physicochemical properties (“Electric-field induced layer-by-layer assembly technique with single component for construction of conjugated polymer films” (S. Wang et al., RSC Adv., 2015, 5, p. 58499)). Analogous physicochemical changes of the film external surfaces, introduced in the apparatus according to the present invention by the electrical field at the start of the film formation process, i.e. only in the area under the spreading cylinder 8 with electrodes, modify both the remainder of the film formation process and the final structure of the polymer blend film (compare the images for 0 V and 30 V in Fig. 11a). Consequently, the structure may be changed from lamellar to lateral-domain by using an electrical field, just as by the substrate.

With a properly chosen polymer blend composition, a lamellar structure breakup entails fragmentation of the semiconductor into individual domains insulated in a continuous insulator phase – leading to electrical insulation (“Solution based self-assembly of an array of polymeric thin-film transistors” (A. Salleo i A.C. Arias, Adv. Mater. 19 (2007), p. 3540)). The spatial control of the process of lamellar and lateral separation achieved by using the substrate patterns allows producing polymer composite films from a solution in a single step, with the films serving as matrices for several dozen well-isolated transistors with zero crosstalk (“Solution based self-assembly of an array of polymeric thin-film transistors” (A. Salleo i A.C. Arias, Adv. Mater. 19 (2007), p. 3540)). The results illustrated using the images in Fig. 11a show that similar spatial control of the composite film structure can be achieved by using an electric field, turned on and off during the film deposition. Literature suggests that the structure change from lamellar to lateral-domain can also be produced by changing the composition weight ratio of a polymer blend (L. Qiu et al., “Versatile Use of Vertical-Phase-Separation-Induced Bilayer Structures in Organic Thin-Film Transistors”, Adv. Mater. 2008, 20, 1141). Also in the studied case (Fig. 5a and 5b), a change in the RP3HT:PEG-PCL composition from 50:50 to 55:45, at a zero field, leads to destruction of the lamellar structure in favour of the lateral-domain one, similar to turning the electric field on for the 50:50 blend. Further, a similar impact on the film morphology – by changing the composition (from 55:45 to 60:40) at a zero field or by turning the electric field on (for the 55:45 blend) – can be observed for films with lateral domain structure (Fig. 5b and 5c). In this case, the electric field (Fig. 11b) leads to the exchange of the matrix continuous phase (semiconductor instead of dielectric) and the isolated domain phase (dielectric instead of semiconductor), which – apart from morphological changes – causes changes of other film properties, such as lateral electrical conductivity. For the RP3HT: PEG-PCL blends with more asymmetric composition (60:40) and lateral structure of isolated domains in a continuous matrix, application of an electric field leads to the reduction of characteristic domain sizes. In turn, changing the domain sizes may lead to a modification of, for example, optical or thermal properties of the polymer blend films.

The above observations made for the RP3HT and PEG-PCL blend are confirmed in results produced for other polymer pairs. Thus, the above presumed impact of an electric field on the formation of extensive lateral domain structures at the cost of lamellar structures can also be argued for the 50:50 blend of RP3HT: PMMA (Fig. 11d). On the other hand, the impact of an electric field on decreasing the size of lateral isolated domains in a continuous matrix was also found for the 50:50 blend of PQT12: PEG-PCL systems (Fig. 11e).

Embodiment 4 – producing area patterns in polymer films (different shape of electrodes).

Using the apparatus for producing polymer films with a predetermined spatial structure described in the first embodiment, a possibility to form predetermined patterns of polymer areas with a different structure with the use of electrodes of different shapes coated on a cylinder 8 was demonstrated. To this end, using a properly prepared mask, three gold electrodes were coated on a glass cylinder 8, separated by gaps of about 1 mm. The shape of the electrodes is shown in Fig. 12a presenting a picture of the cylinder 8 with three visible electrode areas. Subsequently, a voltage of 20 V was applied to the outer electrodes, and a voltage of –20 V was applied to the middle electrode. Using this electrode, a film was spread (v = 2 mm/s) from the RP3HT and PEG-PCL (50:50) blend dissolved in chlorobenzene (Cp = 15 mg/ml), activating electric voltage on the two areas while spreading the polymer film. Pictures of the sample presented in Fig. 12b show three areas: two, where the electric field was applied between the grounded sample and the cylinder 8, and one, where no electric field was present. In the areas where the voltage differential was applied, continuous lines occurring at the electrode gaps were clearly visible. Fluorescence microscopy pictures (Fig. 13a and 13e) as well as AFM images (Fig. 13b - 13d) clearly present a different structure of the polymer film areas. The produced images of Fig. 13 show the domain structure in the area where the electric field was present while spreading the polymer film (as was the case for uniform electrodes) and suggest the lamellar structure in the area of the gaps on the electrodes – the same as for the area where polymer film spreading was performed with no electric field.

Subsequently, a polymer film was spread without applying voltage to the outer electrodes, i.e. using the cylinder 8 equipped with the electrode structure presented in Fig. 12a, the polymer film was spread, with voltage of –20 V applied to the middle electrode only. While spreading the polymer film, the electric field was introduced two times. The sample pictures (Fig. 12a) clearly show a modification of the polymer film in the area where the electrode with the electric field was used (–20 V).

Example 5 – producing patterns in polymer films (alternating fields)

In another embodiment of this invention, using the apparatus for producing polymer films with a predetermined spatial structure as described in the first embodiment, a possibility to form predetermined polymer patterns with the use of electrodes coated on a cylinder and an alternating field was demonstrated. To this end, using a mask, a 1.5 mm wide gold electrode was coated on a glass cylinder 8. Subsequently, an alternating electric field with a square waveform (amplitude ranging from 0 V to 20 V) and a frequency of 1 Hz was applied between the electrode and the conductive sample, and then a film of the RP3HT and PEG-PCL (50:50) blend dissolved in chlorobenzene was spread (Cp = 15 mg/ml). The picture of such a polymer film (Fig. 14a) shows different areas formed under the influence of the alternating electric field. The fluorescence microscopy picture (Fig. 14b) confirms the formation of alternate areas with visible domain and lamellar structure induced by the alternating electric field.

The above experiments demonstrate the possibility of using the method for forming polymer films with a predetermined spatial structure according to the present invention for forming pre-established polymer patterns by choosing appropriate polymers, solvent, and properly shaped electrodes or alternating electric field. This effect is reproducible, and patterns can be formed on large areas.

Further embodiments

While the invention has been described with respect to a limited number of examples, it will be appreciated that many variations, modifications and other applications of the invention may be made. Therefore, the claimed invention as recited in the claims that follow is not limited to the examples described herein.

CLAIMS

1. An apparatus comprising:

- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid over the substrate (22) to form a meniscus (21);
- an activating element (11, 14, 15, 16, 17) that is configured to change physicochemical parameters of the liquid in the meniscus (21) and/or on the substrate covered by the liquid in the meniscus (21), wherein the activating element (11, 14, 15, 16, 17) is coupled with the guiding element (8); and
- wherein the guiding element is a rotationally asymmetrical solid (8B, 8C, 8D).

2. The apparatus according to claim 1 wherein the activating element (16, 17) is positioned inside the guiding element (8).

3. The apparatus according to claim 1 wherein the activating element (11, 14, 15) is positioned outside the guiding element (8).

4. The apparatus according to any of the preceding claims wherein the activating element comprises a light source (11) configured to illuminate the meniscus during the formation of the path.

5. The apparatus according to any of the preceding claims wherein the activating element comprises a direct voltage source (14) connected between an electrode on a surface of the guiding element (8) and the substrate (22).

6. The apparatus according to any of the preceding claims wherein the activating element comprises a direct current source (15) connected between the guiding element (8) and the substrate (22).

7. The apparatus according to any of the preceding claims wherein the activating element comprises a magnetic field source (16).

8. The apparatus according to any of the preceding claims wherein the activating element comprises a heater (17) configured to heat the guiding element (8).

9. The apparatus according to any of the preceding claims wherein the platform (12) is arranged horizontally.

10. The apparatus according to any of claims from 1 to 8 wherein the platform (12) is inclined.

11. The apparatus according to any of claims from 1 to 8 wherein the platform (12) is arranged vertically.

12. The apparatus according to any of the preceding claims wherein it further comprises a system (2) for adjusting the distance of the guiding element (8) from the platform (12).

13. The apparatus according to claim 12 wherein the system for adjusting the distance of the guiding element (8) from the platform (12) is a micrometer positioner .

14. The apparatus according to any of the preceding claims wherein it further comprises a system for controlling the distance and turn of the guiding element (8) with respect to the substrate (22).

15. The apparatus according to claim 14 wherein the system for controlling the distance and turn of the guiding element (8) comprises a laser (9), a detector (4) and a slide (7) mounted to the guiding element (8), wherein the laser (9) is configured to emit a linear beam of light towards the slide (7), wherein the linear beam reflected from the slide (7) falls onto the detector (4).

16. The apparatus according to any of the preceding claims wherein the platform (12) is mounted on a linear stage (1) configured to move the substrate linearly with respect to the fixed guiding element (8).

17. The apparatus according to any of the preceding claims wherein the platform (12) comprises a system for adjusting inclination in at least one plane, preferably three planes.

18. The apparatus according to any of the preceding claims wherein the guiding element (8) is mounted to the platform (3) comprising the system for adjusting inclination in at least two planes, preferably three planes.

19. The apparatus according to any of the preceding claims wherein it is mounted on a platform (13) standing on levelling feet, preferably three levelling feet.

20. The apparatus according to any of the preceding claims wherein the guiding element (8) is made of an insulating material, preferably glass or quartz glass.

21. The apparatus according to any of claims from 1 to 19 wherein the guiding element (8) is made of metal.

22. An apparatus comprising:
- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid on the substrate (22) into a meniscus (21); and
- a direct current source (15) connected between the guiding element (8) and the substrate (22).

23. An apparatus comprising:
- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid over the substrate (22) to form a meniscus (21); and
- an electric field source (16) coupled with the guiding element (8).

24. The apparatus comprising:
- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid over the substrate (22) to form a meniscus (21); and
- a heater (17) configured to heat the guiding element (8).

25. The apparatus according to any of claims from 22 to 24 wherein the guiding element (8) is a cylinder (8A).

26. The apparatus according to any of claims from 22 to 24 wherein the guiding element (8) is a rotationally asymmetrical solid (8B, 8C, 8D).

27. The apparatus according to any of claims from 22 to 26 further comprising at least one of the features according to claims from 9 to 21.

28. A method for changing physicochemical parameters of a liquid in a meniscus (21) and/or on a substrate covered by the liquid in the meniscus (21), the method comprising the steps of:

a) preparing the liquid to be spread over the substrate (22),

b) applying the liquid to the substrate (22),

c) forming the meniscus (21) by dosing the liquid between the substrate (22) and a guiding element (8),

d) displacing the liquid by moving the guiding element (8) with respect to the substrate (22), performed by the apparatus according to any of claims from 1 to 27.

29. The method according to claim 28, comprising inducing a photochemical reaction in the meniscus (21) using a light source (11).

30. The method according to any of claims from 28 to 29, comprising forming a polymer film using a direct current/voltage source (14) connected between the electrode on the surface of the guiding element (8) and the substrate (22).

31. The method according to any of claims from 28 to 30, comprising inducing an electroplating reaction in the meniscus (21) using a direct current source (15) connected between the guiding element (8) and the substrate (22).

32. The method according to any of claims from 28 to 31, comprising using a magnetic field source (16) to act on the meniscus (11).

33. The method according to any of claims from 28 to 32, comprising heating the surface of the guiding element (8).

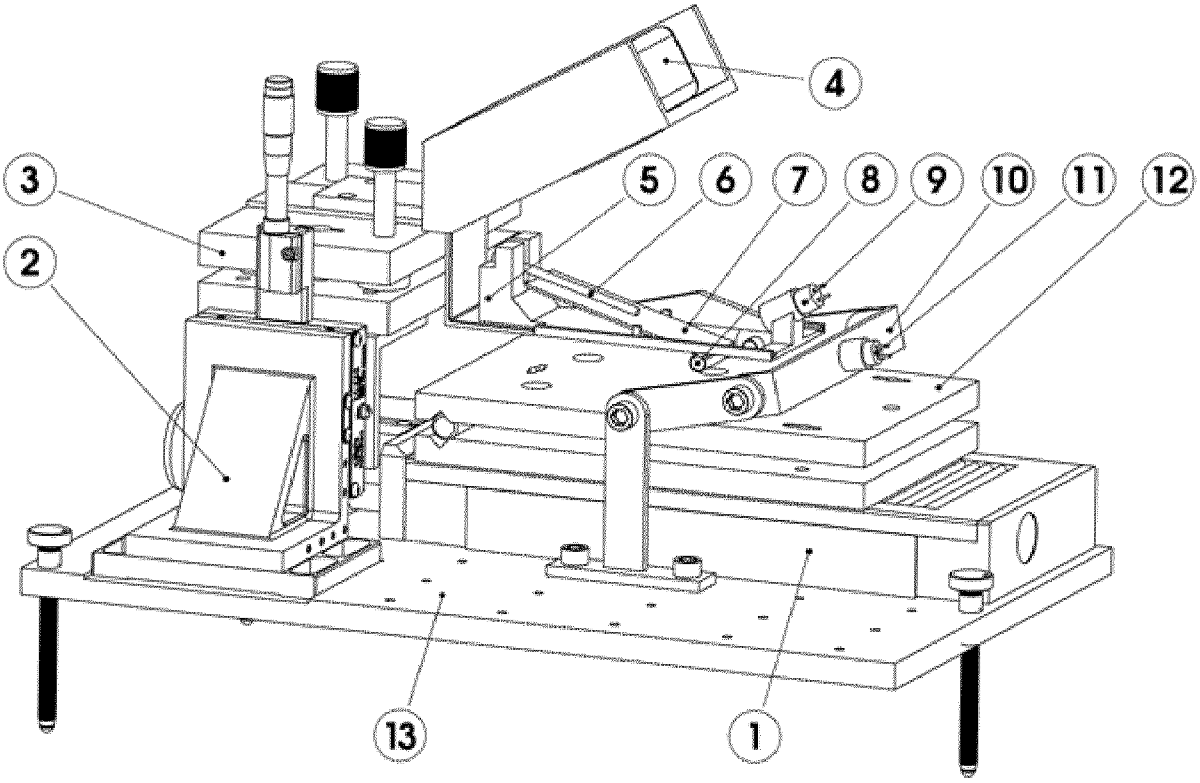


Fig. 1

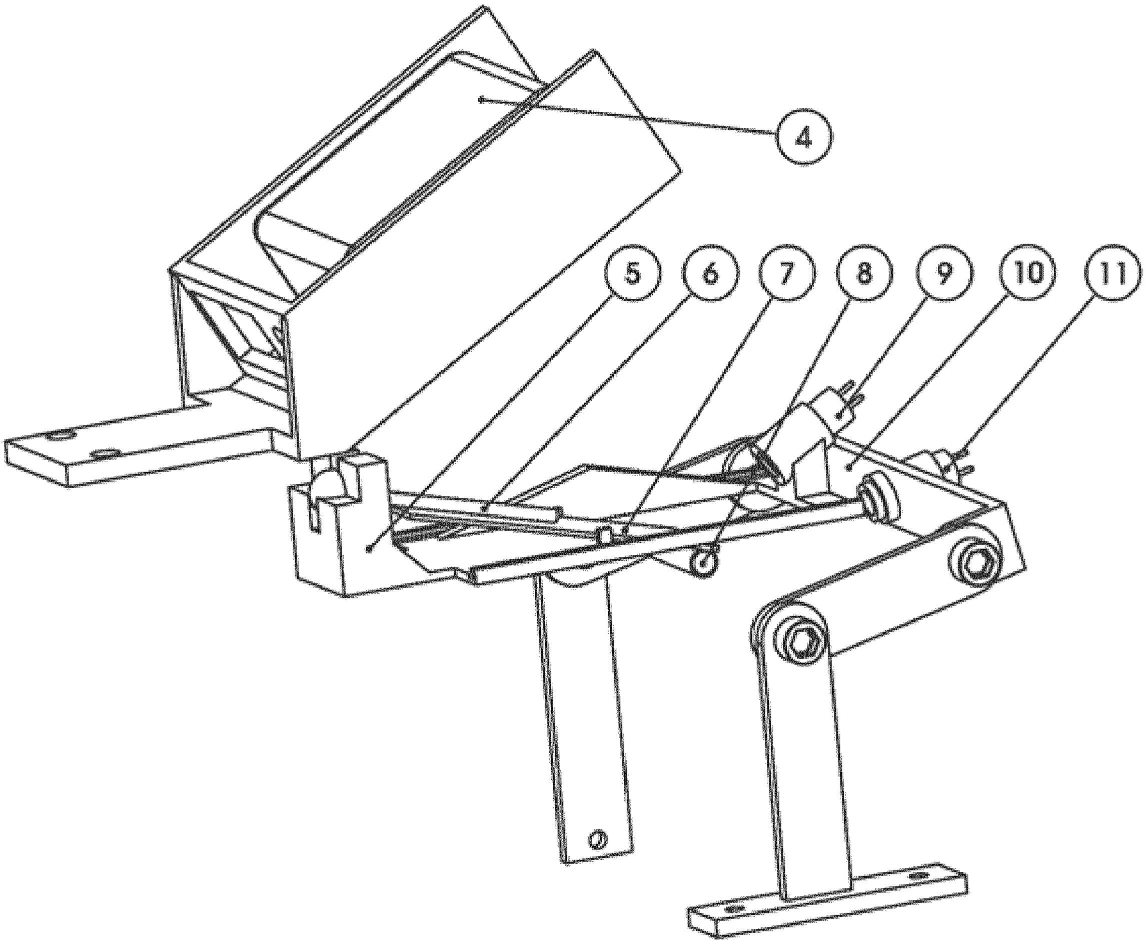


Fig. 2

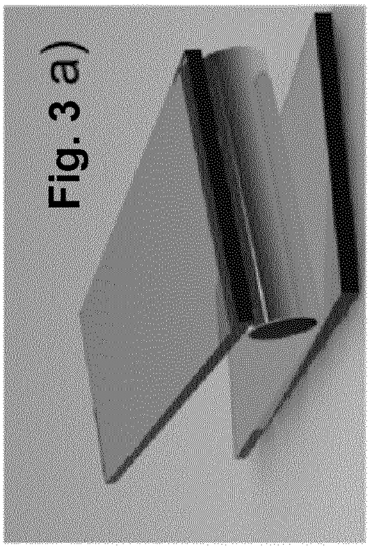


Fig. 3 a)

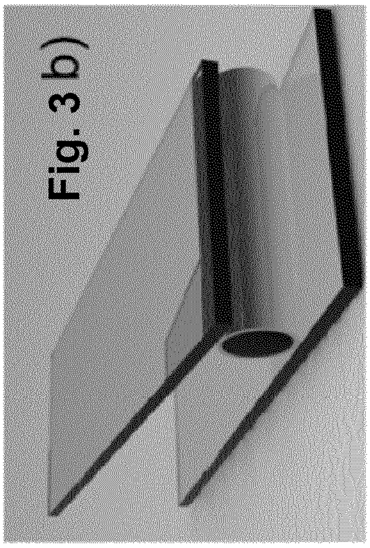


Fig. 3 b)

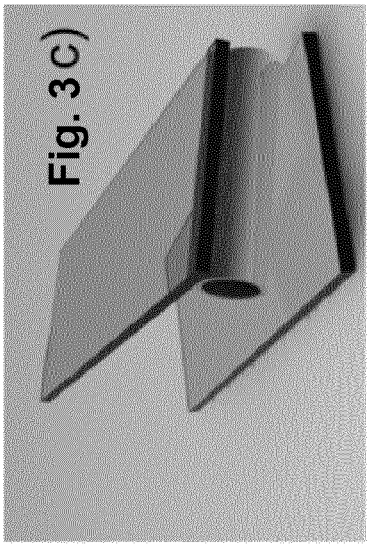


Fig. 3 c)

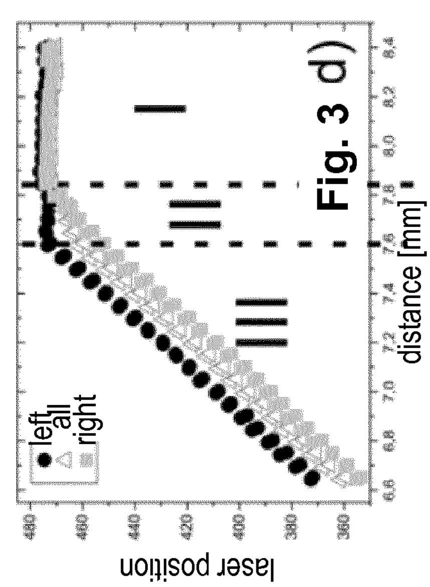


Fig. 3 d)

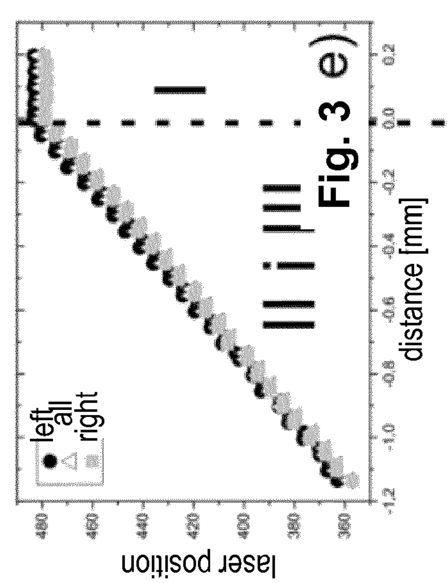


Fig. 3 e)

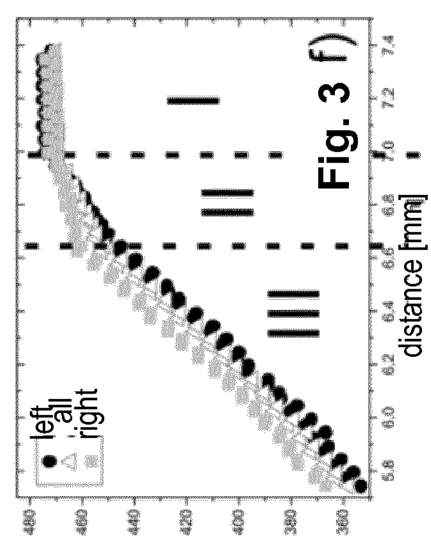


Fig. 3 f)

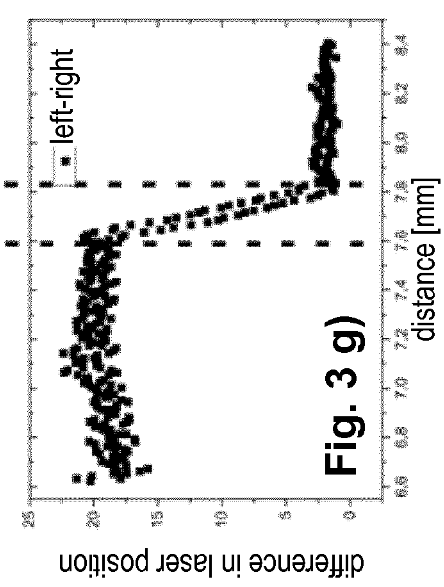


Fig. 3 g)

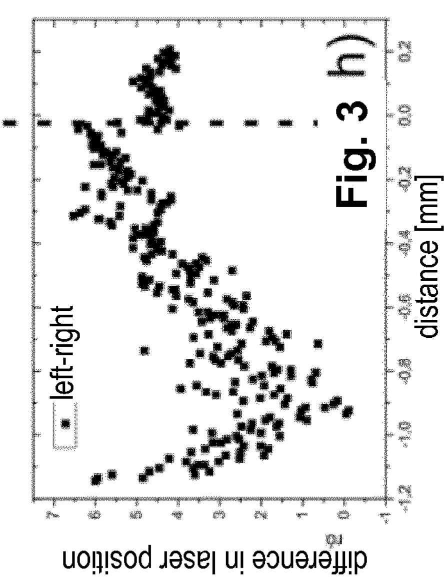


Fig. 3 h)

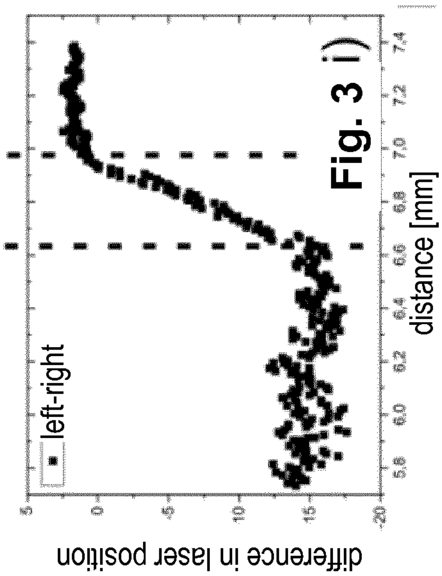


Fig. 3 i)

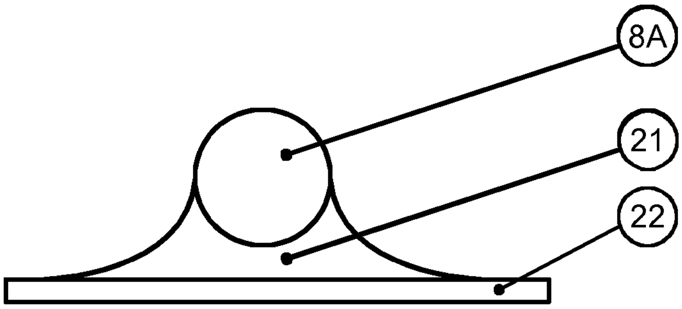


Fig. 4A

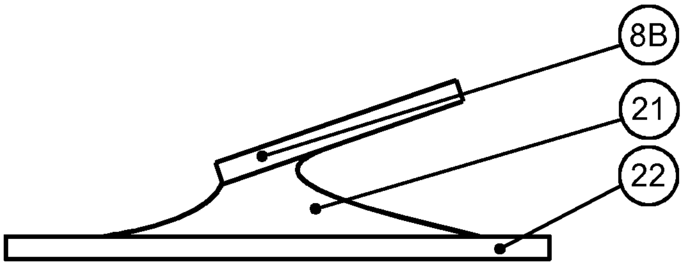


Fig. 4B

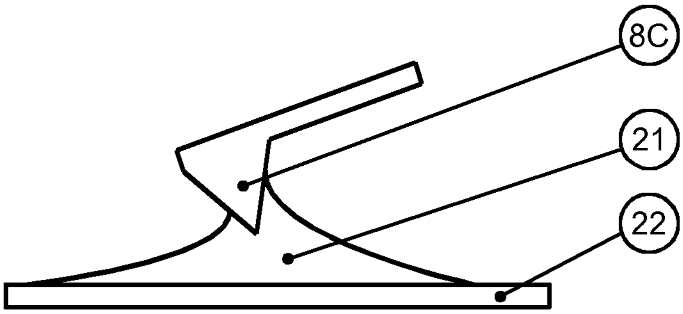


Fig. 4C

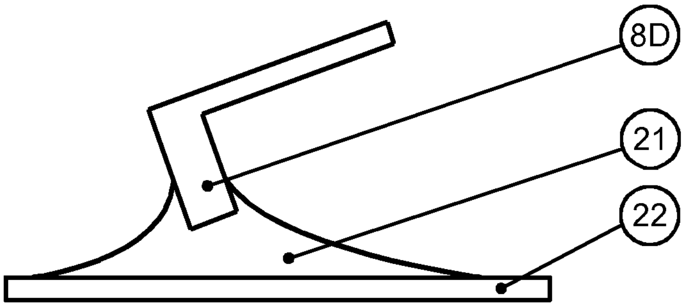


Fig. 4D

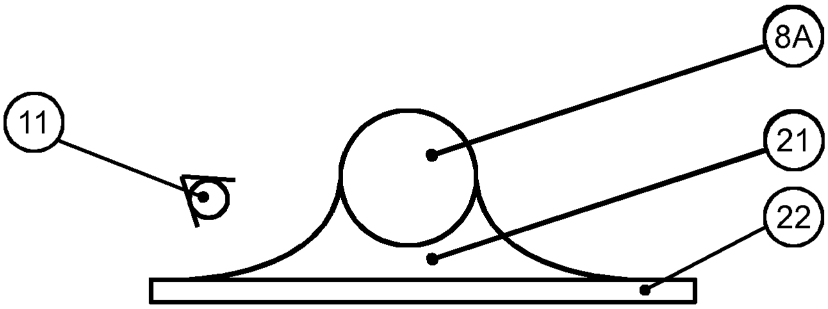


Fig. 5A

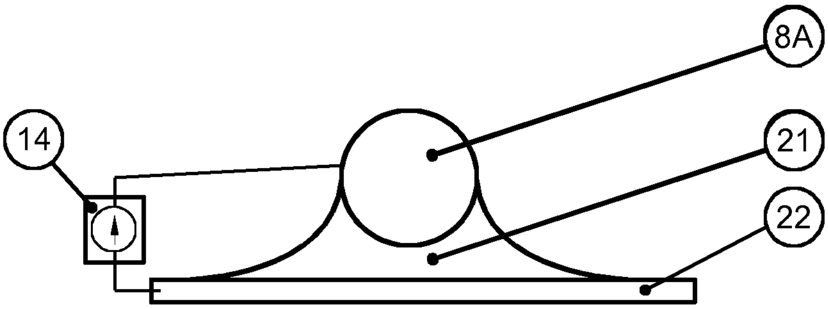


Fig. 5B

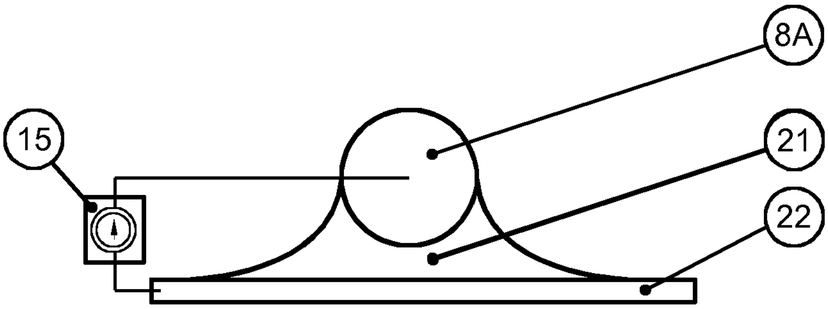


Fig. 5C

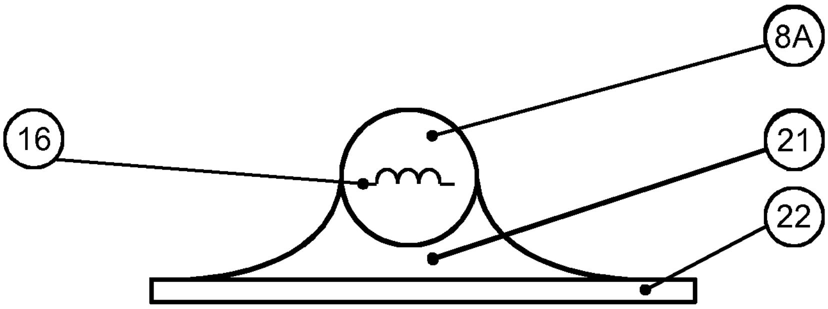


Fig. 5D

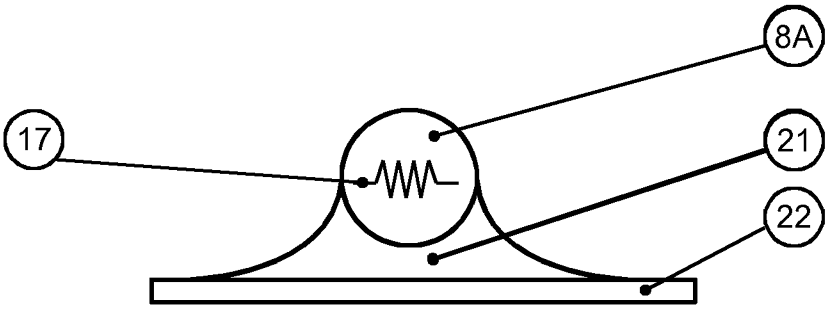


Fig. 5E

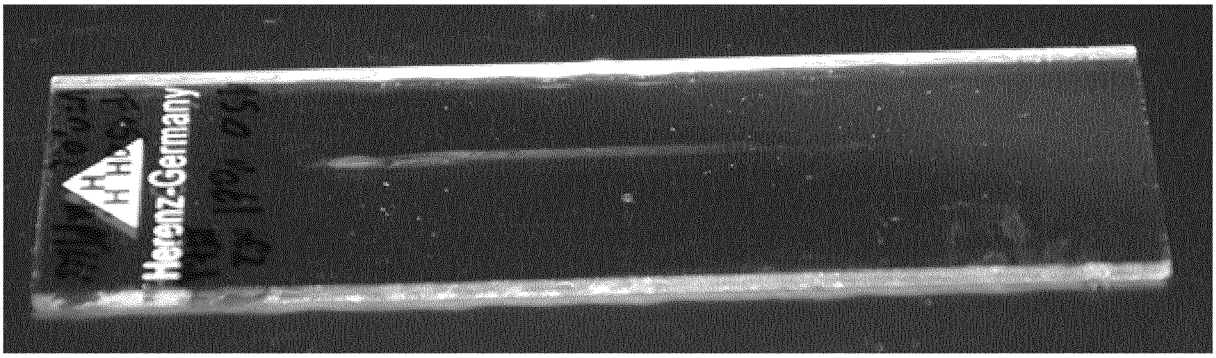


Fig. 6

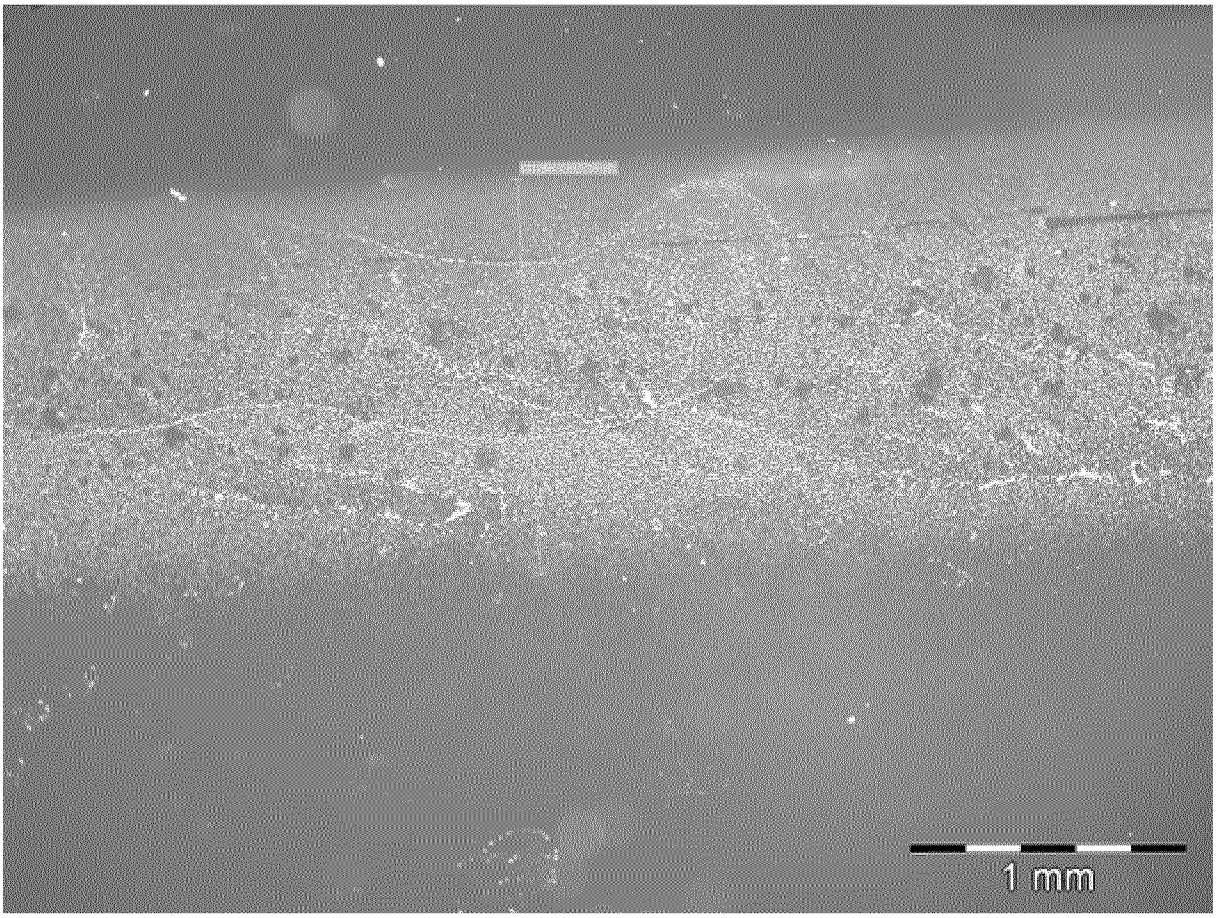


Fig. 7

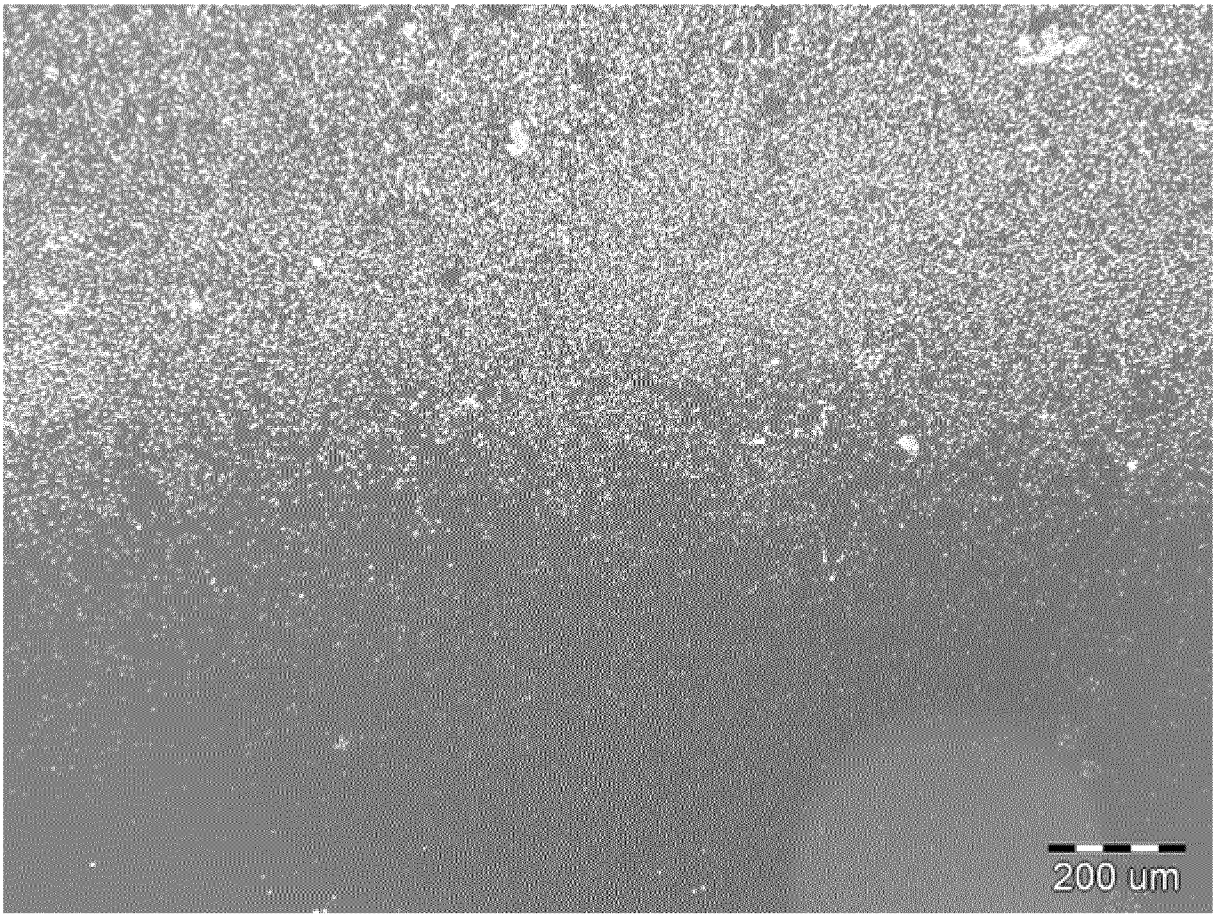


Fig. 8

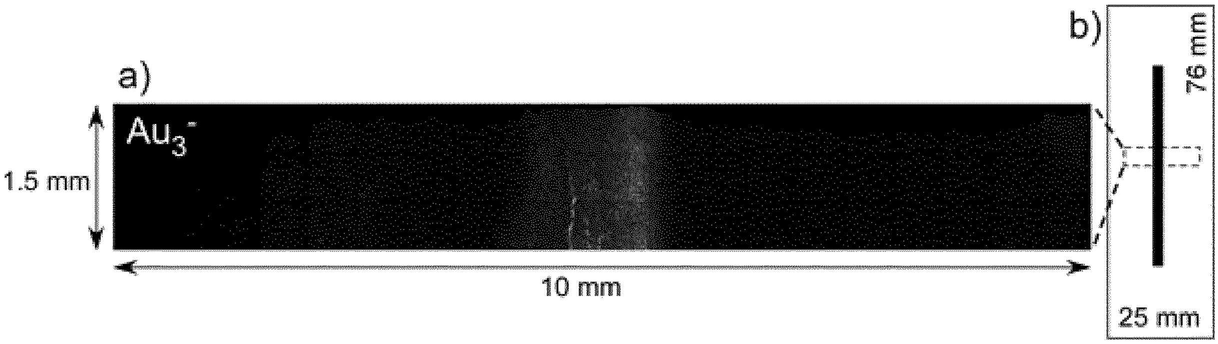
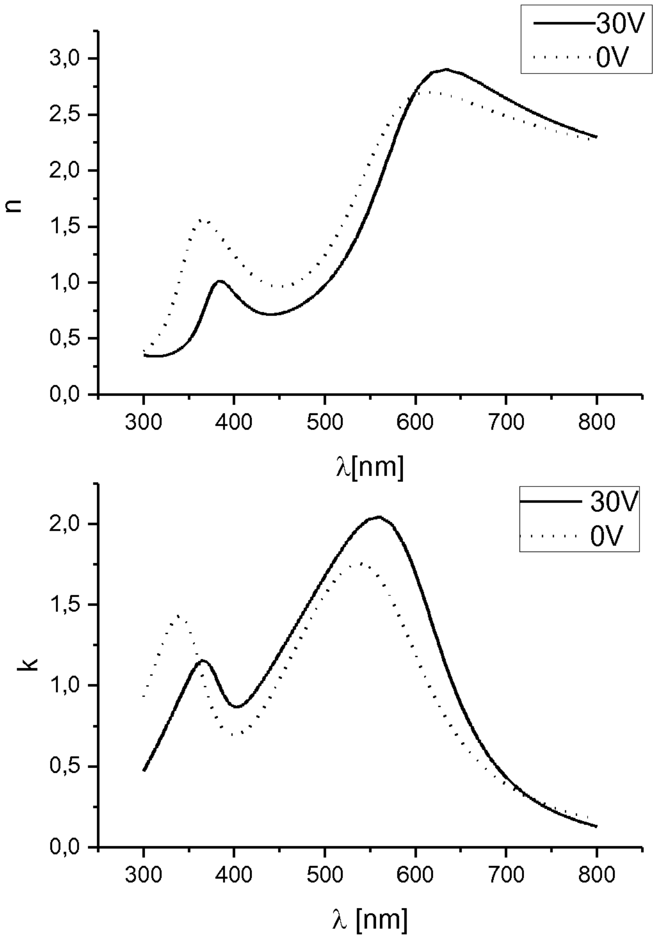


Fig. 9


30V
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2,0
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n
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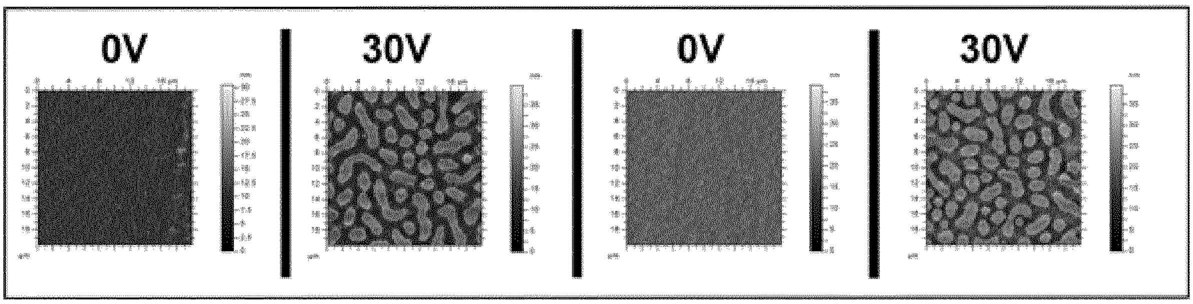
600
700
800
λ[nm]
30V
0V
2,0
1,5
1,0
0,5
0,0
k
300
400
500
600
700
800
λ [nm]

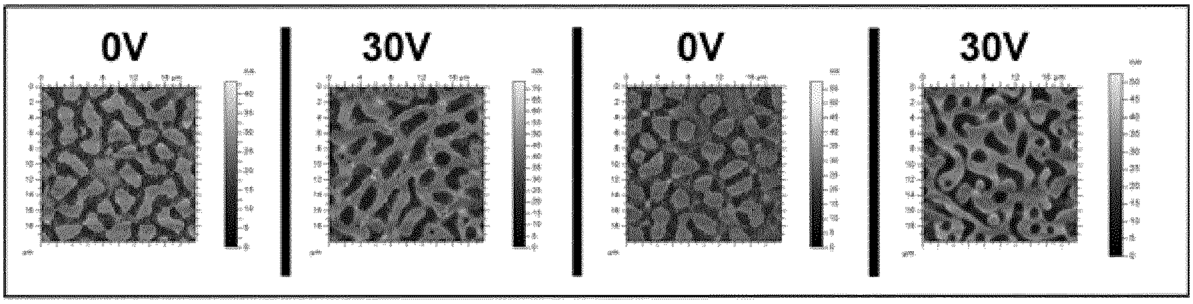
Fig. 10

Fig. 11

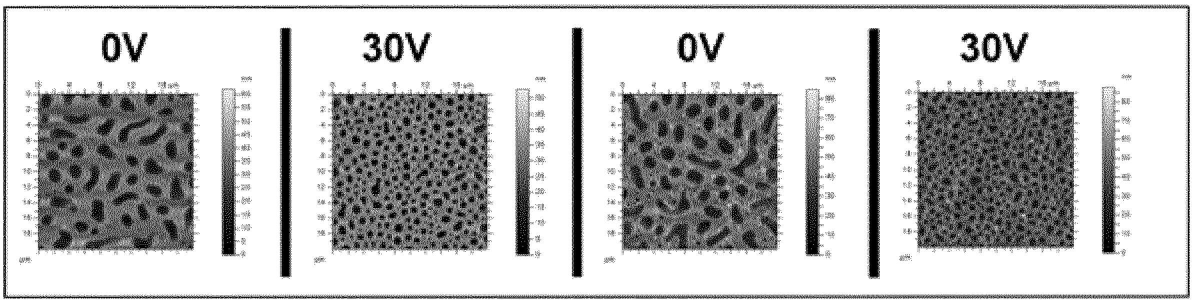
a) RP3HT+PEG-PCL (50:50)



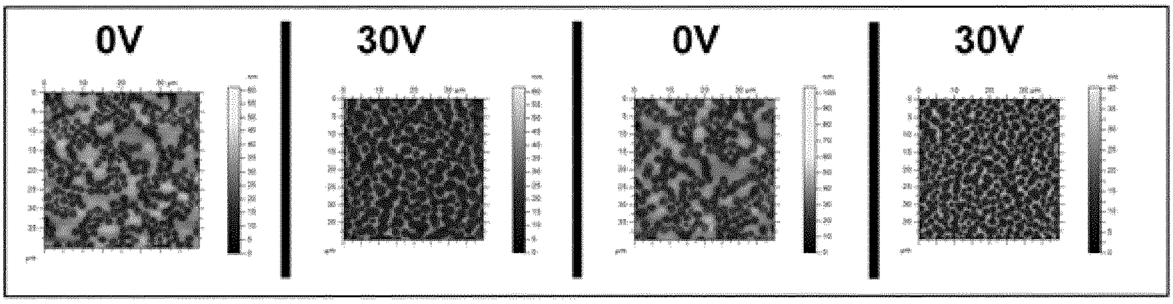
b) RP3HT+PEG-PCL (55:45)



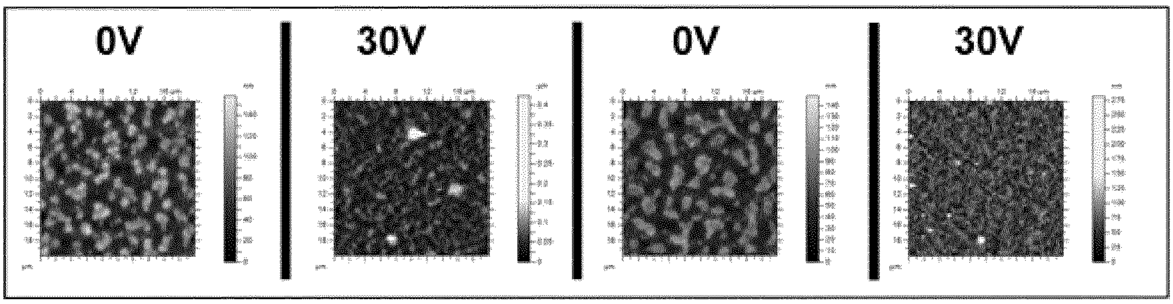
c) RP3HT+PEG-PCL (60:40)



d) RP3HT+PMMA (50:50)



e) PQT12+PEG-PCL (50:50)



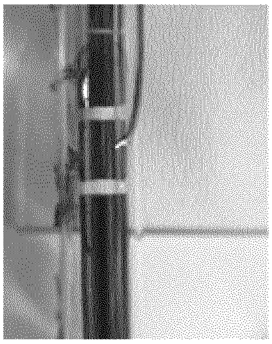


Fig. 12a

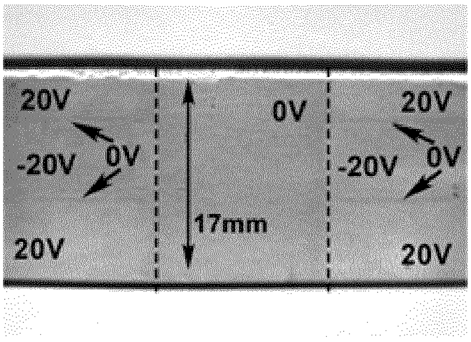


Fig. 12b

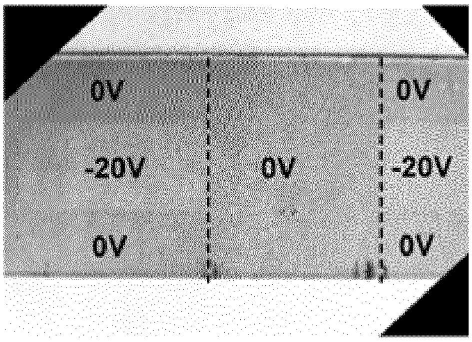


Fig. 12c

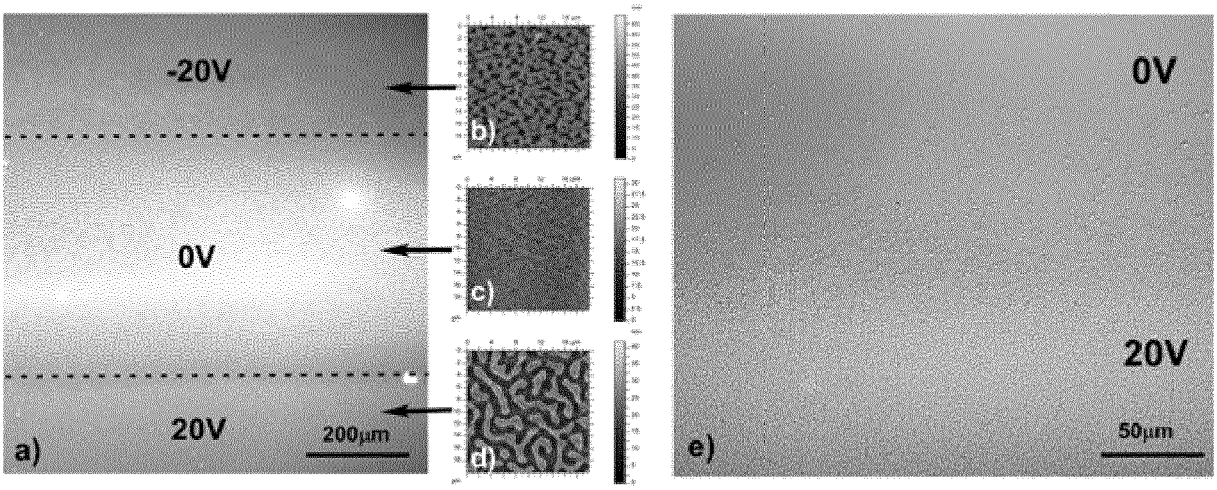


Fig. 13

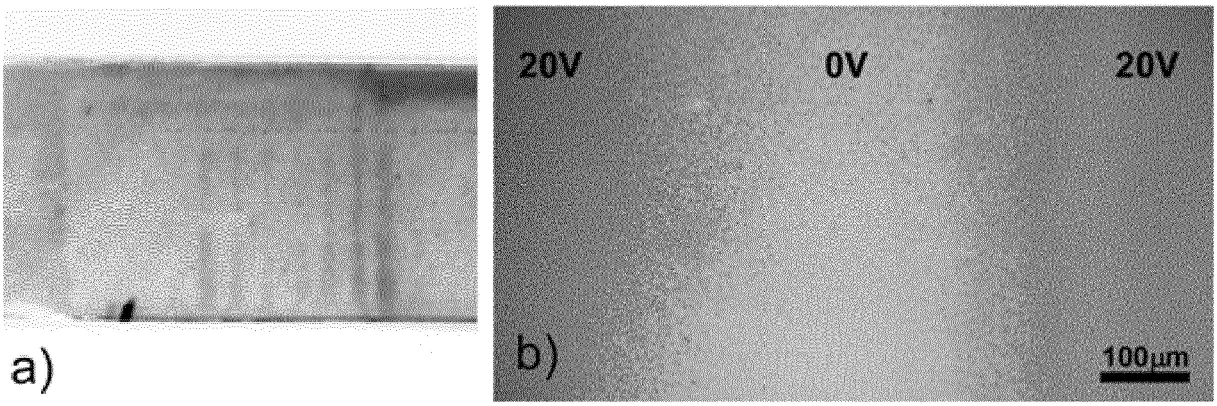


Fig. 14

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/055935

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C18/14 C25D5/04 B05D1/28 C25D17/12 C23C18/02
C25D5/00
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)
C25D C23D B05D C23C

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 397 230 A1 (UNIV OSAKA [JP]) 21 December 2011 (2011-12-21) paragraphs [0010] - [0014] paragraphs [0022] - [0024] paragraphs [0037] - [0041] paragraphs [0043] - [0049] paragraphs [0092] - [0103] paragraphs [0119] - [0122] paragraphs [0159] - [0162] figures 1-2 -----	1-8,26, 28-33

-/--

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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 21 June 2019	Date of mailing of the international search report 26/08/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Crottaz, Olivier

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 741 075 A2 (FEI CO [US]) 11 June 2014 (2014-06-11) paragraphs [0029] - [0030] paragraph [0055] paragraph [0069] paragraphs [0060] - [0063] figures 1-2,19-20 -----	1-3,5-8, 26,28, 30-33
X	US 2013/142566 A1 (YU MIN-FENG [US]) 6 June 2013 (2013-06-06) paragraphs [0010] - [0012] paragraph [0015] paragraph [0023] paragraph [0024] paragraph [0028] paragraphs [0100] - [0110] figures 1,2,3a -----	1-3,5-8, 26,28, 30-33
A	US 2009/000364 A1 (YU MIN-FENG [US]) 1 January 2009 (2009-01-01) paragraphs [0010] - [0016] paragraphs [0065] - [0071] -----	1-8,26, 28-33

1

International application No.
PCT/EP2019/055935

INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8, 26(completely); 28-33(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8, 26(completely); 28-33(partially)

An apparatus comprising:
- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid over the substrate (22) to form a meniscus (21);
- an activating element (11, 14, 15, 16, 17) that is configured to change physicochemical parameters of the liquid in the meniscus (21) and/or on the substrate covered by the liquid in the meniscus (21), wherein the activating element (11, 14, 15, 16, 17) is coupled with the guiding element (8); and- wherein the guiding element is a rotationally asymmetrical solid (8B, 8C, 8D);

where the activating element is further characterized by the features of claims 2-8;
or a method for changing physicochemical parameters of a liquid in a meniscus (21) performed by said apparatus.

---

2. claims: 9-21, 27

An apparatus comprising:
- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid over the substrate (22) to form a meniscus (21);
- an activating element (11, 14, 15, 16, 17) that is configured to change physicochemical parameters of the liquid in the meniscus (21) and/or on the substrate covered by the liquid in the meniscus (21), wherein the activating element (11, 14, 15, 16, 17) is coupled with the guiding element (8); and- wherein the guiding element is a rotationally asymmetrical solid (8B, 8C, 8D);

where the platform or positioning of the guiding element is is further characterized by the features of claims 9-21;
or a method for changing physicochemical parameters of a liquid in a meniscus (21) performed by said apparatus.

---

3. claims: 22-25(completely); 28-33(partially)

An apparatus comprising:
- a platform (12) for a substrate (22);
- a guiding element (8) that is movable with respect to the platform (12) and configured to spread a liquid on the substrate (22) into a meniscus (21); and
- a direct current source (15) or an electric field source or a heater connected between the guiding element (8) and the substrate (22)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/055935

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 2397230	A1	21-12-2011	EP 2397230	A1	21-12-2011
			JP 5322245	B2	23-10-2013
			JP WO2010092836	A1	16-08-2012
			KR 20110115162	A	20-10-2011
			US 2011315052	A1	29-12-2011
			WO 2010092836	A1	19-08-2010
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			EP 2741075	A2	11-06-2014
			JP 6411022	B2	24-10-2018
			JP 2014128871	A	10-07-2014
			US 2014151335	A1	05-06-2014
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			US 2012000770	A1	05-01-2012