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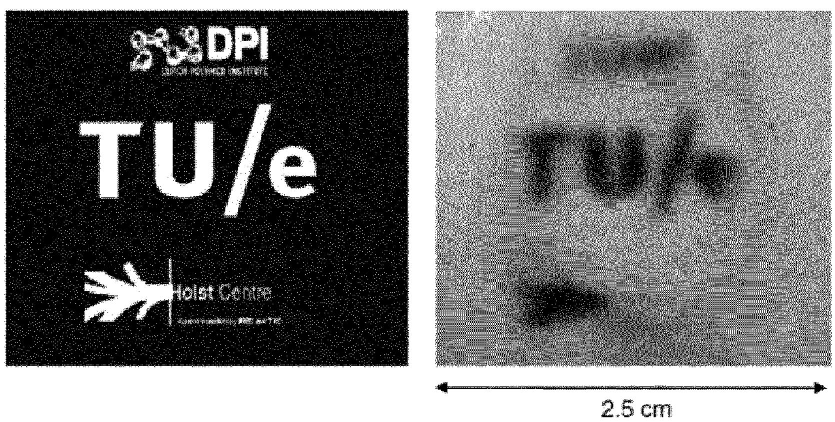

(a) (b)

Fig. 4

(57) Abstract: The invention relates to a method for controlling the deposition of a solute or dispersed particles in a liquid medium, comprising the steps of: a) providing a substrate provided with a layer of a liquid medium comprising the solute or the dispersed particles, b)modulating the surface temperature of the layer according to a heat pattern to induce movement of the solute or the dispersed particles and c) at least partially evaporating the liquid medium to deposit at least part of the solute or the dispersed particles during and/or after step b).

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Method for controlling deposition

The present invention relates to a method for controlling the deposition of a solute or particles dispersed in a liquid medium. The present invention also relates to an apparatus for use in such a method.

Upon drying of a solution, the solute is deposited and leaves a pattern formed by the solute or the particles. The same occurs with dispersed particles for a dispersion. Phenomena relating to drying of a liquid have been studied, particularly the movement of the liquid upon drying.

For generation of a pattern made by a solute, photosensitive polymers have been used, e.g. in the traditional photolithography. Moreover, chemical patterning can be applied to restrict deposition during a coating process to the more wettable regions. Further alternatives are selective deposition of material by means of printing such as inkjet- or screen printing, or masked deposition methods.

Another focus of interest lies in making the thickness of the liquid layer uniform. For this purpose, it is known to add homogenization surfactants to the liquid.

Controlling the evaporation of solvent of a liquid coating is known e.g. from Grigoriev, Physics of Fluids 14(6), p.1895 (2002). This publication deals with controlling of non-uniformities of thin volatile liquid films in the process of drying. The publication describes that the evaporative instability can be actively suppressed by an appropriate heating procedure. It is mentioned that thermal perturbations can be produced by irradiating the liquid film and/or the substrate with a spatially modulated source of visible, infrared, or microwave radiation. This publication does not deal with the deposition of a solute.

Movement of a fluid flow at small scales is known e.g. from US2005/0063875. US2005/0063875 discloses a method of producing a substantially uniform film on an object, the method comprising the steps of: disposing a fluid on the object at a given point; causing the fluid to flow away from the given point, wherein the flowing fluid defines a fluid front; and optically enhancing uniform flow at the fluid front. US2005/0063875 also discloses creating a thermal gradient in a given region of the object by irradiating the given region with electromagnetic radiation. This publication does not deal with the deposition of a solute.

It is an object of the present invention to provide a useful method for controlling the deposition of a solute from a solution or a dispersion.

According to the present invention, a method is provided for controlling the deposition of a solute or dispersed particles in a liquid medium. The method comprises the steps of:

a) providing a substrate provided with a layer of a liquid medium comprising the solute or the dispersed particles,

b) modulating the surface temperature of the layer according to a heat pattern to induce movement of the solute or the dispersed particles and

c) at least partially evaporating the liquid medium to deposit at least part of the solute or the dispersed particles during and/or after step b).

The invention is hereinafter described mainly referring to a solute. However, it is noted that the descriptions referring to a solute equally applies to dispersed particles. It is to be understood that descriptions relating to the dispersed particles are also made herein by the descriptions referring to the solute.

According to the method of the present invention, the surface temperature of the layer is modulated according to a heat pattern, i.e. certain areas of the layer are heated and other areas of the layer are not heated. The heated area may also be heated to varying degrees depending on the location. The temperature difference between the heated area and the less or non-heated area induces the movement of the liquid medium. The liquid medium carries the solute with it, changing the spatial distribution of the amount of the solute. The spatial distribution of the amount of the solute in the liquid medium can thus be controlled.

As the liquid medium evaporates, the solute deposits on the substrate. Hence, the spatial distribution of the solute to be deposited on the substrate is controlled. In the cases where a spatial inhomogeneity of the amount of the solute is induced, different amounts of solute are deposited at different locations depending on the heat pattern, generating a pattern formed by the higher amount of the solute distinguishable from the surrounding areas with a lower amount of deposited solute. In the cases where a spatial homogeneity of the amount of the solute is induced, the resulting layer of the deposited solute will be homogeneous. The resulting layer may be featureless and of uniform thickness and composition due to the homogeneity, unlike an inhomogeneous layer which can have areas with a higher amount of the solute which may be visible.

It is an advantage of the method of the present invention that the method provides a high degree of control over the evaporation of the liquid medium, and thus the deposition of the solute. The control is flexible and noninvasive. Further, the composition of the solution or the dispersion does not have to be altered in any way such as by adding surfactants.

Three mechanisms are known that induce movement of the solute by a temperature gradient.

Upon local heating of a layer of a liquid medium, the heated area experiences an increase in the evaporation rate of the liquid medium. The decrease in the amount of the liquid medium induces the movement of the liquid medium comprising the solute towards the heated area. At the same time, the increase in the temperature decreases the surface tension and induces a flow in the liquid layer which moves the liquid medium away from the heated area, known as the thermocapillary flow mechanism. Further, the increase in the concentration of the solute can increase or decrease the surface tension, inducing a flow in the liquid layer which moves the liquid medium towards or away from the area with a higher concentration of the solute. The movement of the liquid medium is determined depending on the dominating mechanism.

The inventors have realized that parameters such as the type and quantity of the liquid medium and the solute as well as the type of the substrate and the heating means can be tuned to control which of these mechanisms become dominant, so that the movement of the solute and thus the spatial distribution of the deposition of the solute can be controlled.

By heating the layer according to a fixed heat pattern for a prolonged time, a spatial inhomogeneity in the amount of the solute can be induced. This generates a distinguishable layer thickness modulation between the heated area and the non-heated area upon deposition of the solute. In the cases where the solute accumulates in the heated area and the amount of the solute becomes higher in the heated area than in the non-heated area, a pattern made of deposited solute is made which corresponds to the heat pattern. The pattern made of deposited solute or dispersed particles, i.e. the pattern made of solute or dispersed particles in a larger amount than in the surrounding area, is hereinafter sometimes referred as a deposition pattern. In the cases where the solute moves away from the heated area and the amount of the solute becomes lower in the heated area than in the non-heated area, a deposition pattern is made by the non-heated area. Thus, the deposition pattern may be either the positive image of the heat pattern (the deposition pattern corresponds to the heat pattern) or the negative image of the heat pattern (the deposition pattern corresponds to the inverse of the heat pattern). The deposition pattern made in such a way is detectable by suitable means, but is preferably visible to the human eyes.

An analogous result is achieved among the heated areas which are heated to different degrees, i.e. a grayscale patterning is possible (e.g. by grayscale illumination). The amount of the deposited solute in the areas which are heated to a lower degree is between the amounts of the deposited solute in the highly heated area and the non-heated area.

It has been found that one of the factors which determine whether a positive image or a negative image is formed is the initial thickness of the layer of the liquid medium. In some systems, effects such as the solutocapillary effects are negligible and the initial thickness of the layer of the liquid medium determine the formation of the deposition pattern. An example of such a system is a solution of a polyfluorene light emitting polymer in mesitylene. Thus, it is possible in these systems to obtain either a positive image or a negative image by changing the initial thickness of the layer of the liquid medium.

In some cases, a spatial homogeneity of the amount of the solute to be deposited is induced. The resulting layer of the deposited solute will be homogeneous. This makes it even possible to obtain a uniform and featureless layer for the concentration where spots would be visible for inhomogeneous layer.

The heat pattern may be provided e.g. by bringing a wire to be heated in proximity of the substrate. Preferably, the wire pattern is provided on the side of the substrate opposite from the side on which the layer of the solution or deposition is provided. However, preferably, step b) involves irradiating the layer with an electromagnetic radiation according to an irradiation pattern. This provides a precise spatial control of the heating as well as a possibility for a quick temporal change in the heat pattern.

The duration of step b) largely depends on the type and the amount of the liquid medium, but typically is in the range of 1-120 minutes.

The electromagnetic radiation is typically a beam of light, which may be coherent light, such as a laser light. In other embodiments, the electromagnetic radiation is partially coherent or incoherent light.

The irradiation pattern may be provided by e.g. a photomask. The irradiation pattern is preferably controlled by means of a digital multi-mirror device (DMD). DMD allows an extremely precise temporal change in the irradiation pattern. DMD comprises individually controllable micromirrors, which either reflects the laser beam onto a corresponding position (pixel) in the substrate (ON state) or in a direction outside of the substrate (OFF state). Hence, the electromagnetic radiation is incident upon the DMD and a controlled portion of the electromagnetic radiation is irradiated onto the layer of the liquid medium on the substrate. Thus, an electromagnetic radiation according to an irradiation pattern allows the layer to be heated according to the heat pattern. The number of the micromirrors in the DMD is, among others, highly important for the resolution of the heat pattern. Some common DMD sizes are 800x600, 1024x768, 1280x720, and 1920x1080. The micromirrors may have different sizes, but generally smaller sizes give a higher resolution. In preferred embodiments, the micromirrors are of 10-20 µm size.

The micromirrors of the DMD can be switched between the ON state and the OFF state. In the simplest case, each of the micromirrors maintains its state until the end of the formation of the deposition pattern. In this case, there will only be the heated areas and the non-heated areas. The deposition pattern obtained will generally be clearly defined. In other cases, some of the micromirrors may be controlled to change their states during the formation of the deposition pattern. This allows grayscale patterning, i.e. the presence of highly heated area and low heated area and non-heated area. This results in a deposition pattern with a concentration gradient. The rate at which the micromirrors can be switched determines the temporal control of the heat pattern. In preferred embodiments, the individual micromirrors can be switched with a rate up to 16.3 kHz. Contemporary DMD chips can produce up to 1024 shades of gray (10 bits). Another way for obtaining a grayscale is to use dithering, by combining e.g. 3x3 pixels into one addressable unit. However, this reduces the effective resolution.

DMD usually comprises a window which seals and protects the DMD micromirrors. The range of wavelengths which the DMD can control depends on the wavelengths which the protective window transmits and the wavelengths the mirrors reflect. For example, a glass protective window may be used which cuts off the electromagnetic radiation at ~2.75 micron. The window can be tuned to transmit different wavelengths, e.g. by changing the material of the window. For example, a Ge window transmits the electromagnetic radiation at a higher wavelength. Suitable choice of the materials of the micromirrors of the DMD also allows the use of different wavelengths of the electromagnetic radiation.

Other ways to control the direction of an electromagnetic radiation such as laser light are also known to the skilled person and herein not described in detail.

The laser light may be UV light, visible light or infrared light. Preferably, the laser light is infrared light. For the purpose of the present application, infrared light is defined as a light having a wavelength of 0.7-300 µm. This has the advantage that many materials have an absorption peak in this range, allowing an efficient heating of the material. In some embodiments, the irradiation intensity may be up to 0.6 W/cm^2.

Upon irradiation, the absorption and heating may primarily occur in the liquid medium. In other cases, the heating occurs in the substrate or the solute. This depends on the absorption peak of each of the substrate, the liquid medium and the solute and the wavelength of the electromagnetic radiation. Preferably, the substrate, the liquid medium and/or the solute has an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation. This allows an efficient heating of the material. A movement of the liquid medium is induced by the temperature increase in the liquid medium which occurs directly by the absorption of the laser by the liquid medium, or indirectly by the temperature increase in the substrate or the solute which is then transferred to the liquid medium.

In some embodiments, the liquid medium is an organic solvent. In principle, there is no restriction on the type of the organic solvent which may be used in the present invention. For example, the liquid medium may be selected from the group consisting of: toluene, mesitylene, isopropanol, ethanol, acetone, chlorobenzene, decaline, tetraline, anisole, xylene, diisobutyl ketone and dimethylsulfoxide (DMSO). A suitable electromagnetic radiation for these organic solvents is an infrared laser light having a wavelength of e.g. 3-5 µm. The laser light is effectively absorbed by the organic solvent and the liquid medium is efficiently heated.

In some embodiments, the liquid medium is water. In these cases, an infrared laser light having a wavelength close to one of the absorption peaks of water, i.e. a wavelength around 1.47, 1.9, 2.87, 3.05, 4.65, 6.08 or 15 µm is preferably used. An advantage of the use of the water as the liquid medium is that it has absorption peaks over a wide range of wavelengths, which allows the use of a wide range of laser light. This is especially advantageous when usable laser source is limited by e.g. the restrictions on the means for controlling the direction of the laser such as the DMD.

In principle, there is no restriction on the type of the solute or the dispersed particles which may be used in the present invention. Preferred examples include poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), especially an aqueous dispersion of PEDOT:PSS is useful in the present invention. Another example of the solute is a light emitting polymer, which is suitable for application of the method according to the present invention in making an organic light emitting diode (OLED). Various types of light emitting polymers are available e.g. from Merck.

The substrate can be formed of any solid material which can be rigid or flexible which is suitable for use in combination with the solution or the dispersion. Exemplary suitable materials for substrate include various polymers and copolymers, such as polyethylene, polypropylene, polystyrenes, polyimides, polyesters, nylon and polycarbonates. Substrate can also be formed of inorganic materials such as glass, metal or silicon. Substrate can be formed from a single material or from a plurality of materials. Substrate can be formed from a single layer or a plurality of layers formed from different materials. In some embodiments, the substrate comprises an infrared absorbing glass or polymeric foil having an absorption peak between 0.7 and 11 µm. Examples of the polymeric foil include polyethylene, polypropylene, polystyrenes, polyimides, polyesters, nylon and polycarbonates. By matching the IR illumination wavelength with an absorption maximum of the substrate, the substrate is efficiently heated. This makes the method independent of the type of solvent or dispersant. This is particularly advantageous when the liquid medium absorbs the laser only to a small degree. A substrate according to particularly advantageous embodiments comprises a top layer on which the layer of the liquid medium is provided and a bottom layer under the top layer, wherein the bottom layer is made of an infrared absorbing glass. In this case, the top layer may advantageously be chosen without a limitation on its absorption properties and may be chosen based on other properties such as its hydrophobicity/hydrophilicity.

The main absorption of the electromagnetic radiation may even occur outside of the substrate or the layer of the liquid medium. The substrate may be contacted with a material having an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation during step b). This has a great advantage that the process may be applied irrespective of the type of the solute, the liquid medium and the substrate while ensuring an efficient heating.

The modulation of the surface temperature may also involve a feedback scheme. Step b) may involve b1) measuring the local thickness of the layer and/or the concentration of the solute or the dispersed particles and b2) adjusting the heat pattern based on the measured local thickness and/or the concentration of the solute or the dispersed particles.

A more precise result can be achieved by this feedback scheme. The measurement may be performed at or around the heated areas, at the non-heated areas, or over the whole area of the layer. For example, if certain portions of the areas intended to have a higher solute amount (areas to form deposition pattern) are measured to have a lower amount than the other portions of the deposition pattern, i.e. if the deposition pattern is inhomogeneous, the heat pattern can be adjusted to decrease the inhomogeneity. The measuring may be done at any point in time of the process after step a), and may also be done continuously. The local thickness of the layer and/or the concentration of the solute or the dispersed particles may be continuously monitored and the heat pattern may be continuously adjusted. This way, the fidelity of the desired pattern and the actual deposition pattern is improved.

The feedback scheme can also be used in a particularly advantageous manner whereby the homogeneity of the layer is increased. First, the layer is scanned to measure the local thickness of the layer and/or the concentration of the solute. Subsequently, the uniformity of the thickness of the layer and/or the concentration of the solute is determined and then the heat pattern is changed so as to increase the uniformity of the thickness of the layer and/or the concentration of the solute. This may be performed by calculating the average of the thickness of the layer and/or the concentration of the solute, determining areas which have a deviation from the average larger than a predetermined value and heating or stopping the heating (or increasing or decreasing the heating) for said regions. In this way, a so-called coffee stain effect can be avoided or reduced.

The substrates need not be stationary during the irradiation. This would greatly aid its incorporation into a roll-to-roll manufacturing line. The substrate may be moved during irradiation, and the irradiation pattern may be changed in a way synchronized to the movement of the substrate, so that the areas to be heated continue to be heated and the areas not to be heated remain non-heated. This is preferably achieved by the use of DMD. Because the DMD pattern can be adjusted in any conceivable way, the pattern could move on the DMD with the equivalent speed as the substrate roll. The net effect could be a projection pattern that is stationary relative to the moving substrate, if so desired. In particularly advantageous embodiments, the roller on which the substrate is applied is made of a material having an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation. Accordingly, the present invention provides a method for preparing a patterned device such as an OLED by a roll-to-roll process, comprising the steps of:

a) providing a substrate provided with a layer of a liquid medium comprising the solute or the dispersed particles on a roller,

b) modulating the surface temperature of the layer by irradiating the layer with an electromagnetic radiation according to an irradiation pattern to induce movement of the solute or the dispersed particles and

c) at least partially evaporating the liquid medium to deposit at least part of the solute or the dispersed particles during and/or after step b),

wherein the roller is made of a material having an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation.

According to a further aspect of the present invention, a patterned device comprising a substrate provided with a pattern made of a deposited solute or deposited particles, obtainable by the method according to the present invention. The patterned device may be an OLED or an organic photovoltaic device.

According to a further aspect of the present invention, an apparatus is provided for irradiating selected areas in a layer of a liquid medium comprising a solute or dispersed particles with an electromagnetic radiation, the apparatus comprising:

- a source for providing the electromagnetic radiation,
- a digital multi-mirror device (DMD) for directing the electromagnetic radiation to the layer according to an irradiation pattern and
- a measuring means operatively connected to the DMD for measuring the local thickness of the layer and/or the local concentration of the solute or the dispersed particles in the layer,

wherein the DMD adjusts the heat pattern according to the local thickness and/or the local concentration measured by the measuring means.

The apparatus may further comprise a coating means for applying the layer on a substrate. This allows a speedy process for obtaining a desired deposition pattern.

The apparatus may further comprise a means for moving the layer while the layer is irradiated with the infrared laser. The DMD may changes the irradiation pattern in such a way that the same areas are irradiated as the layer is moved. This is highly useful for use in roll-to-roll processing.

The apparatus may further comprise a means for cooling the DMD. This is advantageous for high irradiation powers.

According to a further aspect of the present invention, use of the apparatus according to the present invention is provided for the manufacture of the patterned device according to the present invention by roll-to-roll processing. In this aspect of the present invention, the apparatus according to the present invention is preferably used in a method for preparing a patterned device such as an OLED by a roll-to-roll process, comprising the steps of:

a) providing a substrate provided with a layer of a liquid medium comprising the solute or the dispersed particles on a roller,

b) modulating the surface temperature of the layer by irradiating the layer with an electromagnetic radiation according to an irradiation pattern to induce movement of the solute or the dispersed particles and

c) at least partially evaporating the liquid medium to deposit at least part of the solute or the dispersed particles during and/or after step b).

Preferably, the roller is made of a material having an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation. Preferably, the apparatus according to the present invention is preferably used for at least step b).

It is noted that the invention relates to all possible combinations of features described herein, particularly features recited in the claims.

Reference will now be made in greater detail to embodiments of the invention, examples of which are illustrated in the accompanying drawings in which:

Fig. 1 is a schematic drawing of an embodiment of a system for performing the method of the present invention;

Fig. 2(a) and (b) schematically show different mechanisms of the movement of the solution or the dispersion upon radiation;

Fig. 3 schematically shows the change in the irradiation pattern in a method where the substrate moves over time;

Fig. 4 (a) shows an example of an irradiation pattern used in the method of the present invention.

Fig. 4 (b) shows an example of a deposition pattern formed according to the irradiation pattern of Fig. 4(a).

Fig. 5 (a) shows a further example of an irradiation pattern used in the method of the present invention.

Fig. 5 (b) shows an example of a deposition pattern formed according to the irradiation pattern of Fig. 5(a).

Fig. 5 (c) shows a further example of a deposition pattern formed according to the irradiation pattern of Fig. 5(a).

Fig. 5 (d) shows a further example of a deposition pattern formed according to the irradiation pattern of Fig. 5(a).

Wherever possible, the same reference numerals will be used throughout the drawings and the description to refer to the same or like parts.

Fig. 1 schematically shows an embodiment of a system for performing the method of the present invention. An apparatus 100 for irradiating a sample 200 is shown. The apparatus comprises an IR laser source 10, a beam conditioning & homogenization optics 30 coupled to the IR laser souce 10 by an optical fiber 20, a DMD 40, a beam dump 50, a projection optics 60 and an imaging system 70. The IR laser from the IR laser source 10 is incident on the DMD 40. A portion of the laser is reflected to the beam dump 50 and a portion of the laser is reflected to the sample 200 via the projection optics 60. The sample 200 comprises a substrate on which a layer of a solution or a dispersion comprising a solute in a liquid medium (not shown). In this example, the portion of the laser directed to the sample 200 is incident on the imaging system 70 which shows the image of the layer of the liquid medium while the irradiation is performed. The imaging system 70 may be able to measure the local thickness of the layer and/or the local concentration of the solute in the layer.

Fig. 2(a) schematically shows the movement of the solution or the dispersion upon radiation in a relatively thin layer when thermocapillary flow dominates material redistribution. In this example, the temperature increase in the heated area induces the movement of the solution away from the heated area. The amount of the deposited solute is higher in the non-heated areas.

Fig. 2(b) shows the movement of the solution or the dispersion upon radiation in a relatively thick layer. In this example, the temperature increase in the heated area induces the movement of the solution towards the heated area. The amount of the deposited solute is higher in the heated areas.

Fig. 3 shows a substrate with a layer of a solution and a plurality of mirrors for directing a laser light. Each of the mirrors can be switched to direct (ON) or not direct (OFF) the light to the substrate. The substrate comprises first areas to be heated and second areas to be not heated. The method is highly suitable for a roll-to-roll process.

Fig. 3(a) shows the state at time t1. At time t1, the mirror 1 and 3 are ON to heat the areas 1 and 3, respectively. The mirror 2 is OFF so as to not heat the area 2. The mirrors 4 to 6 are OFF.

In Fig. 3(b), the substrate has advanced to the right. Now the mirrors 2 and 4 are ON to heat the areas 1 and 3, respectively. The mirror 3 is OFF so as to not heat the area 2. The mirrors 1, 5 and 6 are OFF.

In Fig. 3(c), the substrate has advanced further to the right. Now the mirrors 3 and 5 are ON to heat the areas 1 and 3, respectively. The mirror 4 is OFF so as to not heat the area 2. The mirrors 1, 2 and 6 are OFF.

Fig. 4(a) shows an example of an irradiation pattern used in the method of the present invention. The white parts correspond to the areas to be irradiated.

Fig. 4(b) shows a deposition pattern formed according to the irradiation pattern of Fig. 4(a).

The deposition pattern of Fig. 4(b) has been made by the following experimental method.

Approximately 75 ml of an aqueous dispersion of PEDOT:PSS (Baytron P VPAI 4083) with a concentration of 1.2wt% was applied onto a hydrophilic region on a glass substrate by drop casting to form a layer of approximately 120 µm thickness. The layer was irradiated according to the irradiation pattern of Fig. 4(a) with spatially modulated infrared light using a DMD device and an infrared laser with a wavelength 1.47 micron and 17 W maximum source power. The irradiation was performed for approximately 15 minutes.

The irradiation was performed so that the areas in the liquid layer corresponding to the white parts in Fig. 4(a) (e.g. the letters TU/e) were irradiated. The darker areas in Fig. 4(b) are the areas with a higher amount of PEDOT:PSS particles which absorb more light. It is visible that the heated areas have accumulated more PEDOT:PSS particles, forming a positive pattern.

Fig. 5(a) shows a further example of an irradiation pattern used in the method of the present invention. The white parts correspond to the areas to be irradiated.

Fig. 5(b)-(d) show further deposition patterns formed according to the irradiation pattern of Fig. 5(a).

The deposition patterns of Fig. 5(b)-(d) have been made by the following experimental method.

Two solutions of a red and a blue light emitting polymer in mesitylene having a concentration of 1 wt% were prepared. Approximately 200 microliters of the solution were applied to approximately 5 cm x 5 cm large glass substrates by means of spin-coating to form layers of a thickness approximately between 10 and 30 microns. The layer was irradiated according to the irradiation pattern of Fig. 5(a) with spatially modulated infrared light using a DMD device and an infrared laser with a wavelength 1.47 micron and 17 W maximum sourcepower. The structured irradiation was performed for approximately 30 – 60 seconds.

Fig. 5(b) and 5(c) are results of DMD modulated evaporation experiments using two relatively thin films of blue light emitting polymer (LEP) solution in mesitylene. The illumination pattern was bright (hot) on the exterior of the letters DPI, i.e. the letters DPI were cooler than the surroundings. In the images, the blue light emitting polymer (LEP) layer was illuminated with UV/blue light of wavelength 405 nm and fluoresces/emits light of a longer wavelength. The intensity in the pictures is a measure of the local LEP film thickness. The brighter areas in Fig. 5(b) and (c) are the areas with a higher amount of the blue LEP. It is visible that the non-heated areas have accumulated more LEP, forming a negative pattern.

Fig. 5(b) shows two images of the same sample at the same spot. The right image was taken with an angle. The left image shows a dark region in the right half (around the letter “P”), but the right image does not show such a dark region. This means that the dark region in the right half of the left image is an illumination artifact and is not caused due to a strong non-uniformity in layer thickness.

For the experiment resulting in Fig. 5(b) the film thickness was smaller than in the experiment leading to Fig. 5(c) i.e.the pattern definition in this case was better for thinner films and correspondingly shorter drying times.

Fig. 5(d) is the result of DMD modulated evaporation experiments using a relatively thin film of red light emitting polymer (LEP) solution in mesitylene. The illumination pattern was bright (hot) on the exterior of the letters DPI, i.e. the letters DPI were cooler than the surroundings. In the image, the red light emitting polymer (LEP) layer is illuminated with UV/blue light of wavelength 405 nm and fluoresces/emits light of a longer wavelength. The intensity in the picture is a measure of the local LEP film thickness. The brighter areas in Fig. 5(d) are the areas with a higher amount of the red LEP. It is visible that the non-heated areas have accumulated more LEP, forming a negative pattern.

The red and blue LEP solutions have a different sign regarding d_gamma_d_c, i.e. surface tension gamma increases for one and decreases for the other upon an increase of concentration. These solutions therefore would react very differently if a solutocapillary mechanism were dominant and responsible for the observed accumulation. It can therefore be hypothesized that in these experiments the thermocapillary mechanism is dominant, which exhibits the same sign of d_gamma_d_T for both solutions. Hence, it is possible in the system of the LEP in mesitylene to obtain either a positive image or a negative image by changing the initial thickness of the layer of the liquid medium.

CLAIMS

1. A method for controlling the deposition of a solute or dispersed particles in a liquid medium, comprising the steps of:
a) providing a substrate provided with a layer of a liquid medium comprising the solute or the dispersed particles,
b) modulating the surface temperature of the layer according to a heat pattern to induce movement of the solute or the dispersed particles and
c) at least partially evaporating the liquid medium to deposit at least part of the solute or the dispersed particles during and/or after step b).
2. The method according to claim 1, wherein step b) involves irradiating the layer with an electromagnetic radiation according to an irradiation pattern.
3. The method according to claim 2, wherein the electromagnetic radiation is an infrared laser light having a wavelength in the range of 0.7-300 µm.
4. The method according to claim 2 or 3, wherein the irradiation pattern is controlled by a digital multi-mirror device (DMD).
5. The method according to any of claims 2-4, wherein the substrate, the liquid medium and/or the solute or the dispersed particle has an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation.
6. The method according to any of claims 2-5, wherein the electromagnetic radiation is an infrared laser light having a wavelength of 2.5-11 µm and the liquid medium is an organic solvent selected from the group consisting of: toluene, mesitylene, isopropanol, ethanol, acetone, chlorobenzene, decaline, tetraline, anisole, xylene, diisobutyl ketone and dimethylsulfoxide.
7. The method according to any of claims 2-5, wherein the electromagnetic radiation is an infrared laser light having a wavelength of 0.7 to 15 µm, preferably around 1.47, 1.9, 2.87, 3.05, 4.65, 6.08 or 15 µm, and the liquid medium is water.
8. The method according to claim 7, wherein the liquid medium comprising the solute or the dispersed particles is an aqueous PEDOT:PSS dispersion.
9. The method according to any of the preceding claims, wherein step b) involves
b1) measuring the local thickness and/or the concentration of the solute or the dispersed particles and
b2) adjusting the heat pattern according to the measured local thickness and/or the concentration of the solute or the dispersed particles.
10. The method according to claim 9, wherein step b2) involves

b2)(i) determining the uniformity of the thickness of the layer and/or the concentration of the solute or the dispersed particles and

b2)(ii) changing the heating pattern so as to increase the uniformity of the thickness of the layer and/or the concentration of the solute or the dispersed particles.

11. The method according to any of the preceding claims, wherein the substrate is contacted with a material having an absorption peak substantially coinciding with the wavelength of the electromagnetic radiation during step b).
12. A patterned device comprising a substrate provided with a pattern made of a deposited solute or deposited particles obtainable by the method according to any one of claims 1-11.
13. An apparatus for irradiating selected areas in a layer of a liquid medium comprising a solute or dispersed particles with an infrared laser, the apparatus comprising:

- a source for providing the electromagnetic radiation,
- a digital multi-mirror device (DMD) for directing the electromagnetic radiation to the layer according to an irradiation pattern and
- a measuring means operatively connected to the DMD for measuring the local thickness of the layer and/or the local concentration of the solute or the dispersed particles in the layer,

wherein the DMD adjusts the heat pattern according to the local thickness and/or the local concentration measured by the measuring means.

14. The apparatus according to claim 13, further comprising a means for moving the layer while the layer is irradiated with the electromagnetic radiation and wherein the DMD changes the irradiation pattern in such a way that the same areas are irradiated as the layer is moved.
15. Use of the apparatus according to claim 13 or 14 for the manufacture of the patterned device according to claim 12 by roll-to-roll processing.

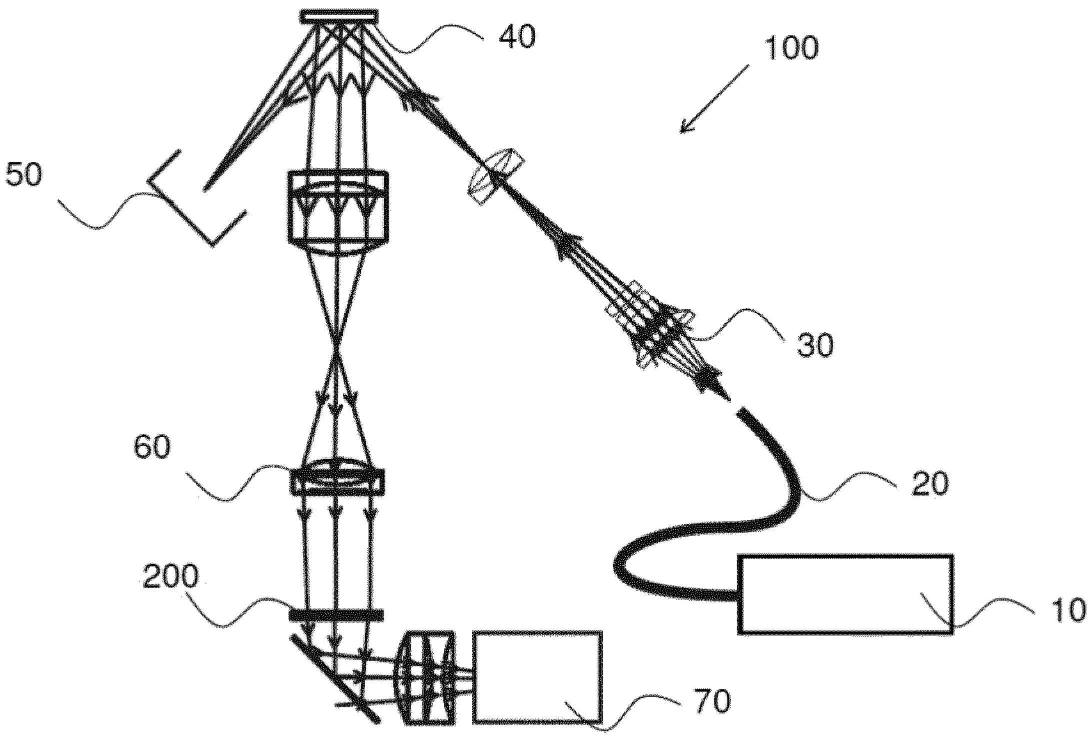


Fig. 1

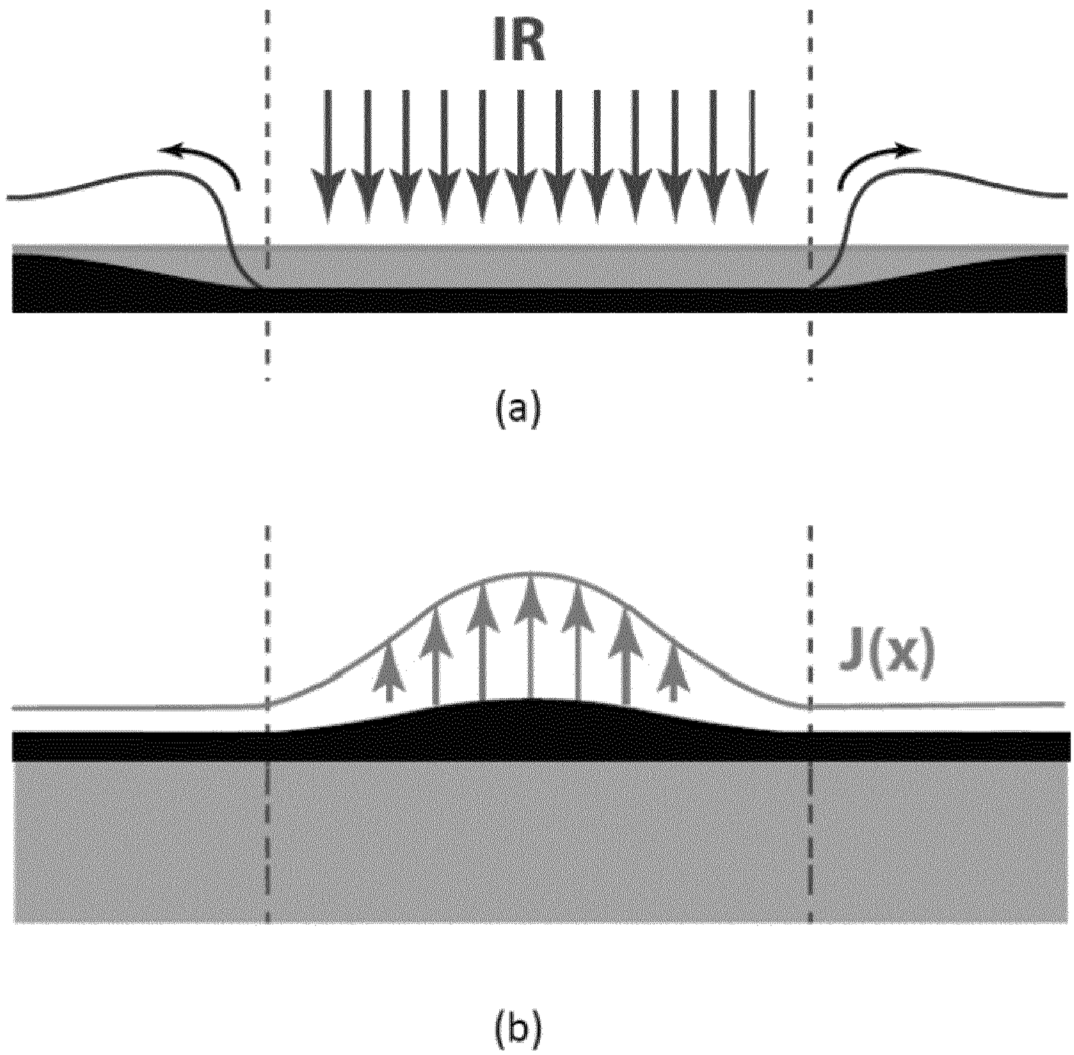


Fig. 2

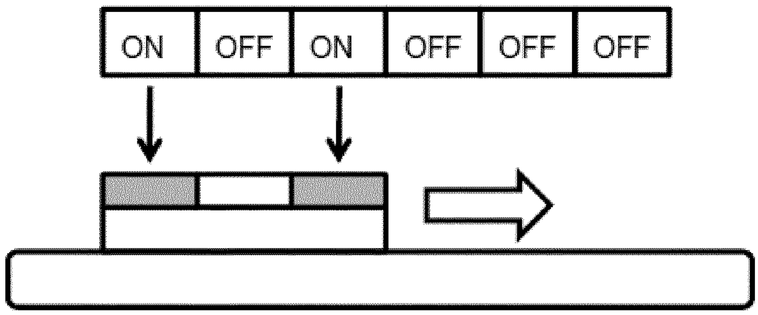


Fig. 3(a)

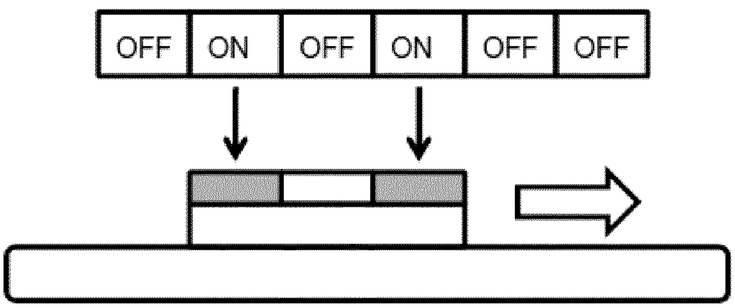


Fig. 3(b)

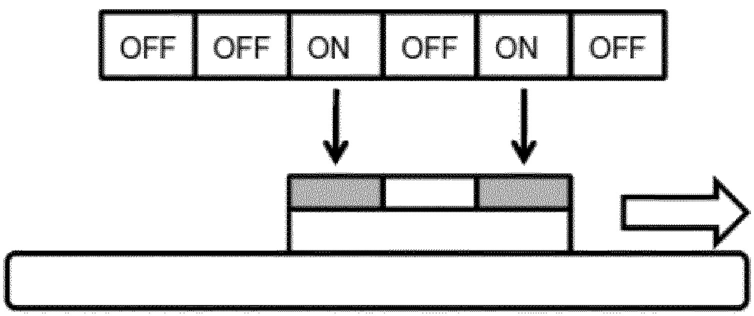
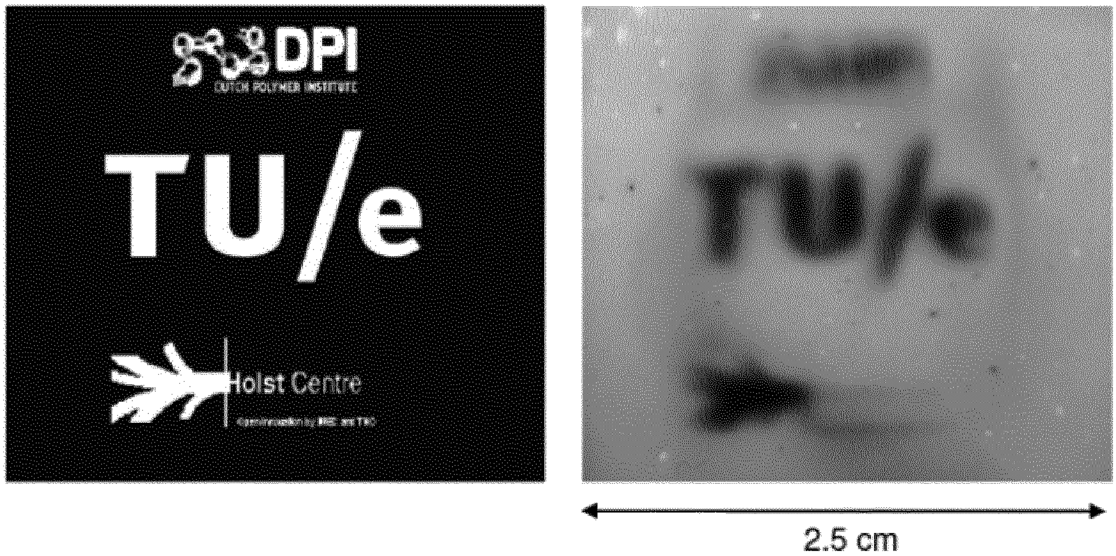


Fig. 3(c)



(a) (b)

Fig. 4

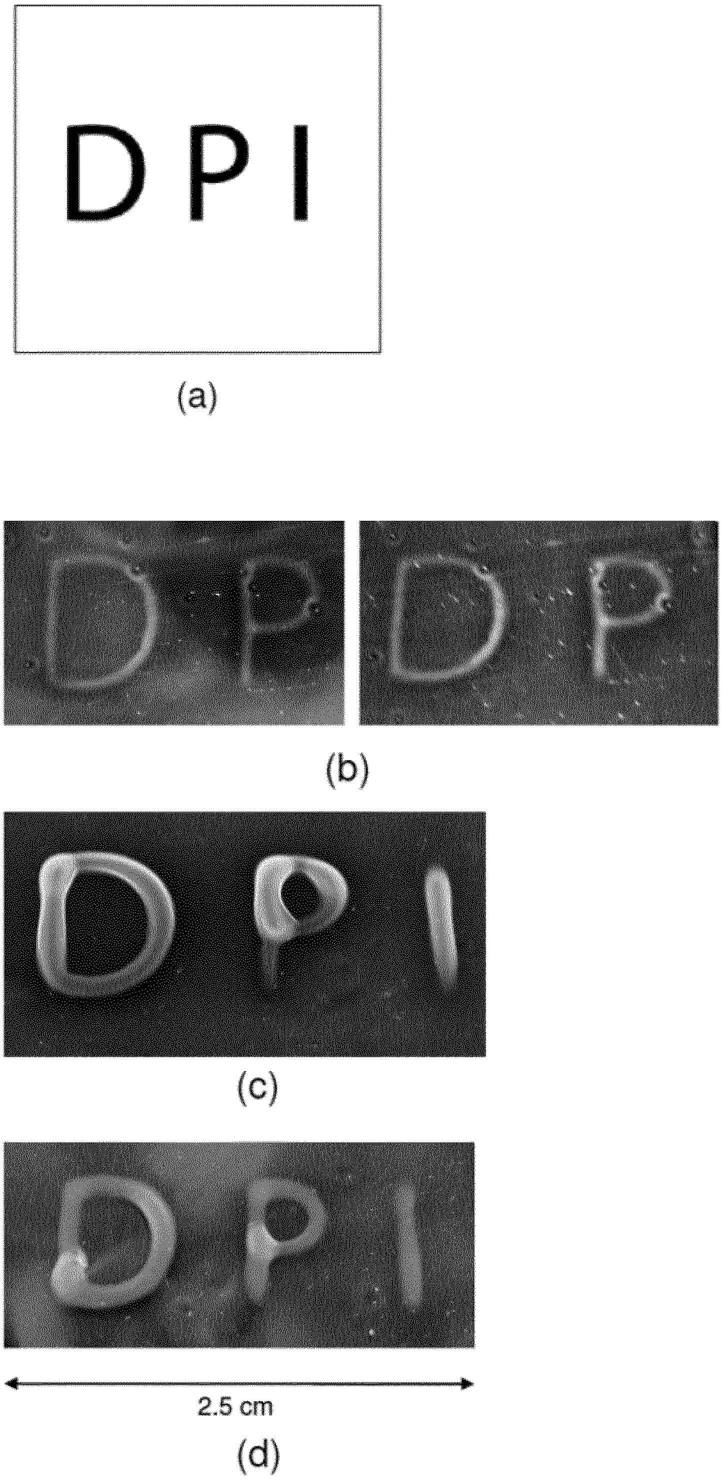


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/058030

A. CLASSIFICATION OF SUBJECT MATTER
INV. H05K3/00 G03F7/20 H01L51/00
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)
G03F H05K H01L

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

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Y	claim 1 paragraph [0041] paragraphs [0039], [0044], [0046] -----	5-8,11
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Y	paragraphs [0027], [0029], [0041], [0046] -----	4
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	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 June 2012	05/07/2012

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/058030

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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