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(54) **Title**: HIGHLY ORDERED ARRAYS OF MICELLES OR NANOPARTICLES ON A SUBSTRATE SURFACE AND METHODS FOR PRODUCING THE SAME

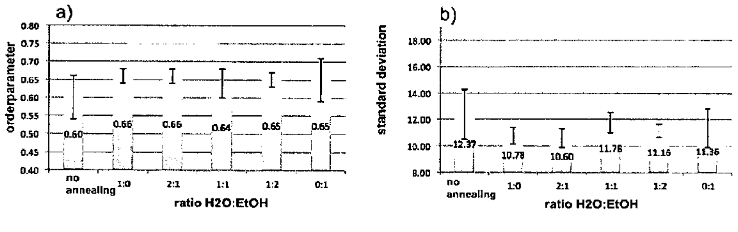

Fig. 2

(57) **Abstract**: The invention provides a method for increasing the order of an array of polymeric micelles or of nanoparticles on a substrate surface comprising: a) providing an ordered array of micelles or nanoparticles coated with a polymer shell on a substrate surface and b) annealing the array of micelles or nanoparticles by ultrasonication in a liquid medium which is selected from the group comprising H_2O, a polar organic solvent and a mixture of H_2O and a polar organic solvent. In a related aspect, the invention provides the highly ordered arrays of micelles or nanoparticles obtainable by the method of the invention.

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Highly ordered arrays of micelles or nanoparticles on a substrate surface and methods for producing the same

Background

In recent years substrate surfaces with periodic or quasi-periodic nanostructures have found widespread use in a broad range of different applications, e.g. in the fields of optics, electronics, spectroscopy, sensor technology, lithography etc.

Especially advantageous methods for generating such nanostructures involve the use of self-assembling techniques such as block copolymer micellar nanolithography (BCML) and similar methods. In comparison with "classic" lithographic processes, self-assembling techniques are relatively simple, inexpensive, very fast and are principally suitable to provide even rather extended or 3-dimensional surfaces with the desired nanostructures.

However, in contrast to conventional lithographic methods such self-assembling techniques are more prone to the generation of structural defects. It is possible to minimize the presence of such defects by selecting suitable process conditions but it is difficult to avoid such inherent defects completely. Moreover, the interparticle distances of such structures tend to vary to a certain extent. Both structural defects and variations of the interparticle distance are very undesirable for many applications. This limits the use of self-assembling techniques for structuring surfaces in spite of the above advantages.

It is known to heal structural defects of 3-dimensional crystals by thermal annealing processes. In the course of such annealing processes, the thermal energy applied to the crystalline system results in the generation of an excited state of the system which can be re-structured and re-ordered rather easily, leading to the elimination of structural defects. The corresponding increase of the crystal lattice order obtained by these processes is largely maintained when the crystalline system returns into the ground state.

Attempts have been made to improve the degree of order of self-assembled nanostructures on a substrate surface by annealing processes as well. For this purpose, processes based on either vapour annealing (Yoo et al., J. Mater. Chem. 2007, 17, 2969-2975) or solvent annealing (Cavicchi et al., Polymer, 46, 2005, 11635-11639) were developed. The method of vapour annealing involves exposing the nanostructured substrate for several hours to an atmosphere of a specific solvent, such as THF. This method is slow and requires a rather sophisticated equipment and the use of toxic solvents. In the method of solvent annealing a thin solvent film is applied onto the substrate and subsequently evaporated in a controlled manner in a suitable atmosphere such as nitrogen. This method is only applicable for some polymers and is also quite laborious due to the required controlled evaporation. Moreover, both methods are often not suitable to achieve a very high degree of order of the nanostructures.

Thus, an object of the present invention is to provide improved methods for producing highly ordered arrays of micelles or nanoparticles on a substrate which are fast, cost-efficient and simple to perform without the need of expensive equipment.

A further object is to provide large and very highly ordered arrays of micelles or nanoparticles on a substrate surface.

Said objects are achieved according to the present invention by providing novel methods for producing highly ordered arrays of micelles or nanoparticles on a substrate which involve an annealing step by ultrasonication in a polar liquid medium according to claim 1 and by providing the highly ordered array of micelles or nanoparticles according to claim 15. Further aspects and preferred embodiments of the invention are the subject of additional claims.

Description of the invention

The method for increasing the order of an array of polymeric micelles or of nanoparticles on a substrate surface according to claim 1 comprises at least the following steps
a) providing an ordered array of micelles or nanoparticles coated with a polymer shell on a substrate surface and
b) annealing the array of micelles or nanoparticles by ultrasonication in a liquid medium which is selected from the group comprising H_2O, a polar organic solvent and a mixture of H_2O and a polar organic solvent.

In a more specific embodiment, the method according to the present invention comprises the following steps
a) providing an ordered array of polymeric micelles loaded with at least one metal salt on a substrate surface,
b) annealing the array of micelles or nanoparticles by ultrasonication in a liquid medium which is selected from the group comprising H_2O, a polar organic solvent and a mixture of H_2O and a polar organic solvent, and
c) converting the at least one metal salt in said micelles by an oxidation or reduction treatment into inorganic

nanoparticles and optionally partial or complete removal of the organic copolymer of the micelles by a plasma treatment.

The substrate surface to be coated may be any substrate capable to be coated with the polymeric micelles or nanoparticles coated with a polymer shell. Some non-limiting examples are glasses, Si, SiO_2, ZnO, TiO_2, Al_2O_3, C, InP, GaAs, GaP, GaInP, AlGaAs.

In a preferred embodiment of the method of the invention, the ordered array of micelles is a hexagonal array produced by a block copolymer micellar nanolithography (BCML) technique.

In the micellar nanolithography (see, e.g., EP 1 027 157) a micellar solution of a diblock-or multiblock copolymer is deposited onto a substrate, e.g., by immersion coating, and, given suitable conditions on the surface, forms an ordered film structure of chemically different polymer domains, depending, i.a., on the type, molecular weight and concentration of the block copolymer. For example, the distances of the individual polymer domains from each other are a function of the molecular weight and the concentration of the block polymer in the solution. The micelles in the solution can be charged with inorganic salts or acids that can be reduced to inorganic nanoparticles after the deposition with the polymer film.

Basically any micelle-forming block copolymer can be used as two-block or multi-block copolymer in this method that can be deposited as a film onto a substrate and that forms an ordered structure of different polymer domains. Suitable block copolymers are, for example, all block copolymers mentioned in the above-cited EP 1 027 157. In a more specific embodiment, the two-block- or multi-block copolymer is selected from the group of polystyrene (n)-b-poly (2-vinylpyridine (m), polystyrene (n)-b-poly (4-vinylpyridine (m), polystyrene (n)-b-poly (ethylene oxide) (m), in which n and m indicate the number of repetition units and are, independently of one another, integers in the range of 10-10,000, in particular 100-1000. The molecular weight (Mw) (dissolved block) is preferably selected >> Mw (poorly dissolved block).

Basically all inorganic metal compounds (e.g., metallic salts) that can be converted by oxidation or reduction into inorganic nanoparticles are suitable as inorganic compounds with which the micelles in the solution and the polymer domains in the deposited plastic film, respectively, can be charged. Suitable salts are, for example, all metallic salts mentioned in the above-cited EP 1 027 157. The metallic salts used in accordance with the invention preferably comprise at least one salt of the metals Au, Pt, Pd, Ag, In, Fe, Zr, Al, Co, Ni, Ga, Sn, Zn, Ti, Si or Ge. $HAuCl_4$ is especially preferred.

The nanoparticles coated with a polymer shell are preferably selected from the group comprising metals, such as Au, Ag, Pd, Pt, Cu, Ni and mixtures thereof, metal oxides such as Al_2O_3, Fe_2O_3, Cu_2O, TiO_2, SiO_2, Si or other semiconductors.

The polymer shell may comprise any polymer suitable for the desired purpose. Some specific, non-limiting examples are polymers selected from the group comprising polystyrene, polypyridine, polyolefines including polydienes, PMMA and other poly(meth)acrylates, and blends or copolymers thereof.

In a preferred embodiment, the shell-forming polymer has a terminal anchoring group with a high affinity to the surface of the nanoparticles. The term "anchoring group having a high affinity to the surface of the nanoparticles", as used herein, includes anchoring groups capable to form a covalent bond (or a bond with a strong covalent character) with molecules of the nanoparticles or functional groups thereon. Typically, the functional anchoring group is a thiol, amine, COOH, ester or phosphine group.

The annealing of nanostructures on a substrate surface according to the present invention is effected by means of ultrasonication in a liquid medium, preferably a polar liquid medium. More specifically, said liquid medium is selected from the group comprising H_2O, a polar organic solvent and a mixture of H_2O and a polar organic solvent.

Preferably, the liquid medium comprises or consists of a C_1-C_{10} alkanol, in particular methanol, ethanol, propanol and butanol, or a mixture of H_2O and a C_1-C_{10} alkanol, in particular methanol, ethanol, propanol and butanol.

In a more preferred embodiment, the solvent consists of ethanol or of a mixture of H_2O and ethanol in a ratio in the range from 2:1 to 0.01:1, preferably in a ratio of about 1:2.

Typically, the ultrasonication is effected at a frequency in the range of 20 kHz - 2 MHz, preferably from 30 kHz to 1 or 2 MHz or from 1 MHz to 2 MHz, and a power input in the range of 5 W/l to 50 W/l, preferably from 15 W/l to 30 W/l.

Contrary to annealing methods of the prior art, excellent results are obtained in a rather short time. Typically, the ultrasonication is effected for a time period in the range of from 10 to 500 s, preferably 30-200 s, such as 50-150 s.

The ultrasonication can be effected over a broad temperature range from 15°C to 70°C, more specifically 18-50°C or 18°C-40°C, but it is convenient and usually sufficient to use a temperature near room temperature, such as a temperature in the range from 20°C to 30°C, preferably from 20°C to 25°C.

In the method according to the present invention, said ultrasonication treatment typically results in at least 10 % increase of the order of the array of micelles or nanoparticles as indicated by a corresponding decrease of the standard deviation of the mean intermicelle or interparticle distance. If the array of micelles or nanoparticles initially provided has an especially low degree of order, the increase of order achieved by the method of the invention may be even higher.

It should be recognized that the method of the invention may also be applied advantageously to eliminate local structural defects of an extended array of micelles or nanoparticles which exhibits an overall relatively high degree of order.

Thus, even if the overall order of the array of micelles or nanoparticles is not increased considerably by the method of the invention, the elimination of local defects may still represent an essential improvement of the nanostructured substrate in order to qualify for a number of applications.

A closely related aspect of the present invention are the very highly ordered arrays of micelles or nanoparticles obtainable with the above methods.

Typically, such ordered arrays of micelles or nanoparticles, in particular inorganic nanoparticles, on a substrate surface have a mean distance of micelles or particles in the range from 25 nm to 250 nm and a standard deviation of the mean value of less than 10 %, preferably less than 5 %, such as 1-3 %.

The highly ordered arrays of micelles or nanoparticles obtainable by the methods of the present invention are of interest for a wide variety of applications, in particular in the fields of optics, electronics, spectroscopy, sensor technology, imaging technology, biochips, data storing and processing, lithography.

Thus, a further aspect of the invention relates to a device, in particular an optic device, spectroscopic device or sensor device, a mask, in particular a lithographic mask or photo mask, a biochip, a tool for a replication process, or a transistor, comprising said highly ordered arrays.

A further, closely related aspect of the invention relates to the use of these highly ordered arrays for manufacturing a device which is selected from the group comprising a mask, in particular a lithographic mask or photo mask, a biochip, a tool for a replication process, a sensor, an optical device or a transistor.

Brief Description of the Figures

Fig. 1 shows SEM micrographs of a substrate surface structured with gold nanoparticles (in order to show the order more clearly the individual particles have been masked with white circles): **(A)** before annealing; **B)** after annealing

Fig. 2 shows the results of an ultrasound annealing treatment of a micellar array with varying solvent ratios: **(A)** Increase of the degree of order of the micellar array; **(B)** Decrease of the standard deviation of the mean distance of the micellar array

Fig. 3 shows the results of an ultrasound annealing treatment of a micellar array with varying solvent ratios and subsequent plasma treatment to obtain a corresponding gold nanoparticle array; **(A)** Increase of the degree of order of the nanoparticle array ; **(B)** Decrease of the standard deviation of the mean distance of the nanoparticle array

Fig. 4 shows the results of an ultrasound annealing treatment of a micellar array with a solvent ratio ethanol:H_2O = 2:1 and varying duration of the annealing treatment: **(A)** Increase of the degree of order of the micellar array; **(B)** Decrease of the standard deviation of the mean distance of the micellar array

The present invention is illustrated in more detail in the following non-limiting examples.

EXAMPLE 1

Preparation of highly ordered arrays of micelles on a substrate surface

Arrays of gold-salt loaded micelles on a glass substrate were prepared by micellar block copolymer nanolithography essentially according to published methods (e.g. EP 1 027 157).

As an initial step, a 5 mg/ml toluene solution of micelles of the diblock copolymer polystyrene-*block*-polyvinylpyridine (PS-b-P2VP; Mn(PS) 190.000; Mn (P2VP) 55.000; Mw/Mn = 1.10) loaded with $HAuCl_4$ was prepared and stored in a sealed glass vial.

This micellar solution was applied on a glass substrate (24 mm x 24 mm) by spin coating (6000 rpm, 1 min) in a spin coater (WS-400B, Laurell Technologies, North Wales, USA) and left drying.

The conditions were adjusted so that a sample with a mean micelle distance of 68-72 nm and a standard deviation of the mean distance value in range of 9-13 nm was obtained. If desired, it is possible to decrease the initial degree of order by adding ultra pure H_2O to the above polymer solution (e.g. 1 vol. %).

The resulting nanostructured sample was placed in a commercial sonifier (Sanorex, Bandelion electronic, Berlin) and immersed in a liquid medium consisting of a mixture of ethanol:H_2O in different ratios at room temperature and sonicated at a frequency of 35 kHz and a power input in the range of 5-50 W/l, preferably 15-30 W/l, for 120 s.

Fig. 2 shows the results of this ultrasound annealing treatment with different solvent ratios. These diagrams were obtained by image processing of corresponding SEM micrographs. The data are derived from 14 measuring points (7 different positions on 2 identically treated samples).

The degree of order as used herein is indicated by the "sixfold bond-orientational order parameter" ψ_6 as defined by D. Nelson and B. I. Halperin in *Physical Review* B 19.5 (1979), 2457-2484, for a hexagonal array.

$$\psi_6 = \left| \frac{1}{N_{bonds}} \sum_j \sum_k e^{i \cdot 6 \cdot \theta_{jk}} \right|$$

with N_{bonds} = number of connections between the central particle of a hexagon and its next neighbors; θ_{jk} = angle between a central particle and 2 next neighbors in juxtaposition, k = central particle and j = neighbor.

For an ideal structure exclusively consisting of perfect hexagons, the order parameter $\psi_6 = 1$.

A high order parameter corresponds to a low standard deviation of the interparticle distance, both values are largely inverse proportional to each other. Thus, for a more simple indication of the order of a nanostructured array, often the standard deviation of the interparticle or intermicelle distance is used herein.

As evident from Fig. 2, a marked increase of the degree of order of the micellar array and a corresponding decrease of the standard deviation of the mean distance of the micellar array is observed in each case. The influence of the specific solvent ratio is rather low.

In order to assess the influence of the duration of the annealing treatment, a micellar array was prepared as indicated above and ultrasonicated for different time periods with an ethanol: H_2O ratio of 2:1.

Fig. 4 shows that a rather short annealing time of about 35-55 s already provides excellent results with respect to the increased degree of order of the micellar array and a corresponding decrease of the standard deviation of the mean distance of the micellar array. Considerable longer annealing times resulted in rather marginal improvements.

EXAMPLE 2

Preparation of highly ordered arrays of nanoparticles on a substrate surface

A micellar array was prepared on a glass substrate and subjected to an ultrasound annealing treatment with varying solvent ratios analogous to Example 1.

The resulting micellar array was subjected to a plasma treatment essentially according to published methods (e.g. EP 1 027 157). Typically, the substrate was treated with W10 plasma (90 vol.% argon and 10 vol.% hydrogen) at a pressure of 0.4 mbar for 45 minutes and 150 W power input in a PlasmaSystem 100 (PVA TePla, Wettenberg, Germany) device.

In the course of this process, the polymer shell of said micelles was removed and the gold salt contained therein was reduced to elemental gold, whereby a highly ordered array of gold nanoparticles was obtained.

Fig. 3 shows the results of the preceding ultrasound annealing treatment with different solvent ratios. These diagrams were obtained by image processing of corresponding SEM micrographs. The data are derived from 14 measuring points (7 different positions on 2 identically treated samples).

The plasma treatment results in a slightly lower degree of order as compared with the initial micellar array and a corresponding increase of the standard deviation of the mean interparticle distance to about 14.5 nm for the non-annealed sample.

A considerable increase of the degree of order of the nanoparticle array and a corresponding decrease of the standard deviation of the mean distance of the nanoparticle array was observed for each solvent ratio. In this case, however, a strong influence of the specific solvent ratio is evident. Best results were obtained with an ethanol:H_2O ratio of 2:1.

CLAIMS

1. A method for increasing the order of an array of polymeric micelles or of nanoparticles on a substrate surface comprising
   a) providing an ordered array of micelles or nanoparticles coated with a polymer shell on a substrate surface and
   b) annealing the array of micelles or nanoparticles by ultrasonication in a liquid medium which is selected from the group comprising H_2O, a polar organic solvent and a mixture of H_2O and a polar organic solvent.

2. The method according to claim 1 wherein the liquid medium comprises or consists of a C_1-C_{10} alkanol, in particular methanol, ethanol, propanol and butanol, or a mixture of H_2O and a C_1-C_{10} alkanol, in particular methanol, ethanol, propanol and butanol.

3. The method according to claim 2, wherein the solvent consists of ethanol or of a mixture of H_2O and ethanol in a ratio in the range from 2:1 to 0.01:1, preferably in a ratio of about 1:2.

4. The method according to any one of claims 1-3, wherein the ultrasonication is effected for a time period in the range of 10 to 500 s, preferably 30 to 200 s, such as 50 to 150 s.

5. The method according to any one of claims 1-4, wherein the ultrasonication is effected at a frequency in the range of 20 kHz to 2 MHz, preferably 30 kHz to 2 MHz,

and a power input in the range of 5 W/l to 50 W/l, preferably 15 W/l to 30 W/l.

6. The method according to any one of claims 1-5, wherein the ultrasonication is effected at a temperature in the range from 15°C to 70°C, preferably in the range of 20°C to 25°C.

7. The method according to any one of claims 1-6, wherein the ordered array of micelles is a hexagonal array produced by a block copolymer micellar nanolithography (BCML) technique.

8. The method according to any one of claims 1-7, wherein the substrate is selected from the group comprising glasses, Si, SiO_2, ZnO, TiO_2, Al_2O_3, C, InP, GaAs, GaP, GaInP, AlGaAs.

9. The method according to any one of claims 1-8, wherein the micelles are micelles of a two-block- or multi-block copolymer selected from the group of polystyrene (n)-b-poly (2-vinylpyridine (m), polystyrene (n)-b-poly (4-vinylpyridine (m), polystyrene (n)-b-poly (ethylene oxide) (m), in which n and m indicate the number of repetition units and are, independently of one another, integers in the range of 10-10,000, in particular 100-1000.

10. The method according to any one of claims 1-8, wherein the nanoparticles coated with a polymer shell are selected from the group comprising metals, such as Au, Ag, Pd, Pt, Cu, Ni and mixtures thereof, metal oxides such as Al_2O_3, Fe_2O_3, Cu_2O, TiO_2, SiO_2, Si or other semiconductors.

11. The method according to any one of claims 1-9, wherein the micelles are loaded with at least one metal salt.

12. The method according to claim 11, wherein the at least one metal salt is selected from the group comprising salts of Au, Ag, Pd, Pt, In, Fe, Zr, Al, Co, Ni, Ga, Sn, Zn, Ti, Si and Ge.

13. The method according to claim 11 or 12 comprising the following steps:
a) providing an ordered array of polymeric micelles loaded with at least one metal salt on a substrate surface,
b) annealing the array of micelles by ultrasonication in a liquid medium which is selected from the group comprising H_2O, a polar organic solvent and a mixture of H_2O and a polar organic solvent, and
c) converting the at least one metal salt in said micelles by an oxidation or reduction treatment into inorganic nanoparticles and optionally partial or complete removal of the organic copolymer of the micelles by a plasma treatment.

14. The method according to any one of claims 1-13, wherein the ultrasonication treatment results in at least 10 % increase of the order of the array of micelles or nanoparticles as indicated by a corresponding decrease of the standard deviation of the mean intermicelle or interparticle distance.

15. An ordered array of micelles or inorganic nanoparticles on a substrate surface having a mean distance of micelles or particles in the range from 25 nm to 250 nm

and a standard deviation of the mean value of less than 10 %, preferably less than 5 %, such as 1-3 %.

16. Use of the ordered array of micelles or nanoparticles according to claim 15 in the fields of optics, electronics, spectroscopy, sensor technology, imaging technology, biochips, data storing and processing, lithography.

17. The use according to claim 16 for manufacturing a device which is selected from the group comprising a mask, in particular a lithographic mask or photo mask, a biochip, a tool for a replication process, a sensor, an optical device or a transistor.

18. A device comprising the ordered array of micelles or inorganic nanoparticles according to claim 15.

19. The device according to claim 18 which is a mask, in particular a lithographic mask or photo mask, a biochip, a tool for a replication process, a sensor, an optical device or a transistor.

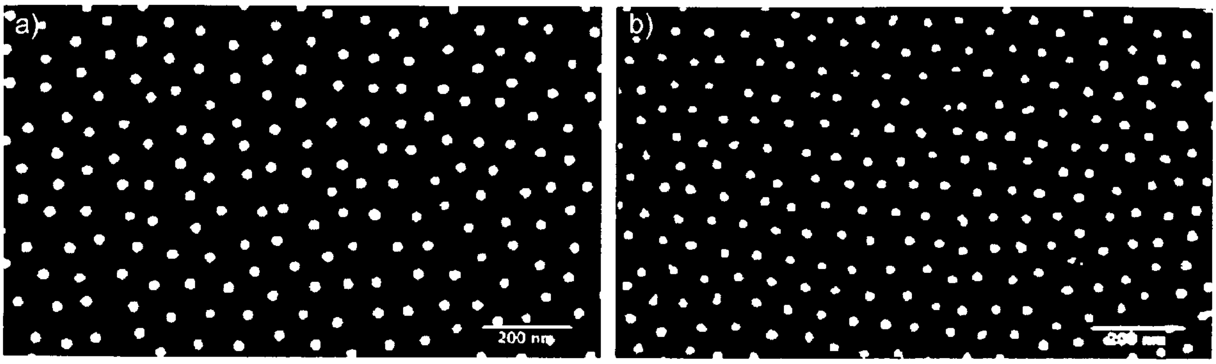

Fig. 1

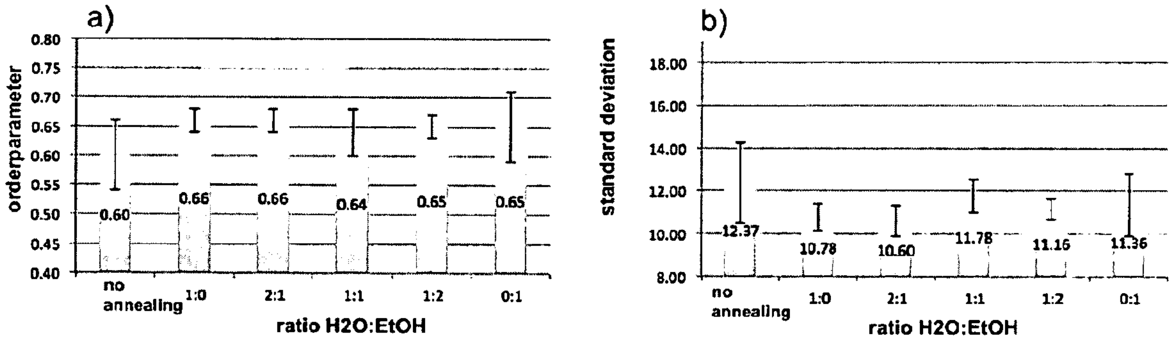

Fig. 2

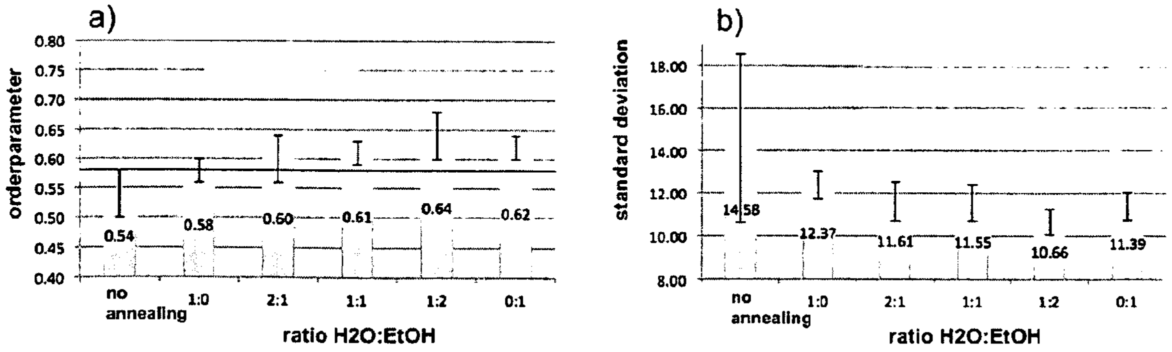

Fig. 3

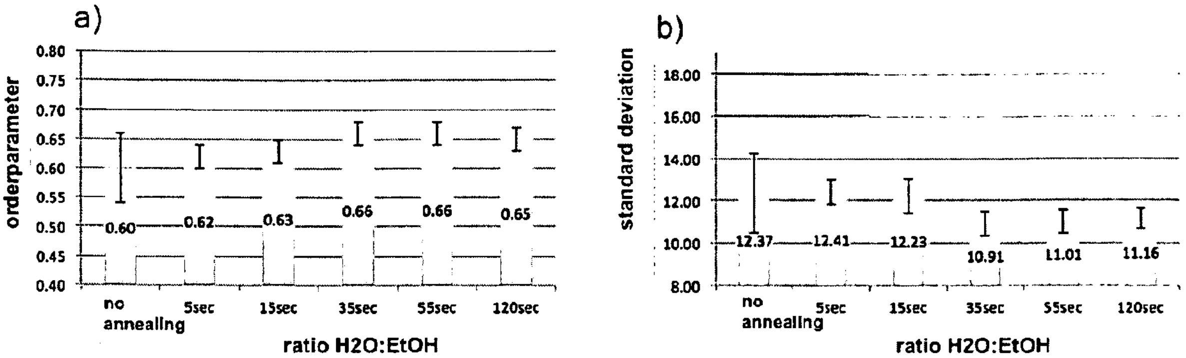
a)
orderparameter
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.60
0.62
0.63
0.66
0.66
0.65
no annealing
5sec
15sec
35sec
55sec
120sec
ratio H2O:EtOH
b)
standard deviation
18.00
16.00
14.00
12.00
10.00
8.00
12.37
12.41
12.23
10.91
11.01
11.16
no annealing
5sec
15sec
35sec
55sec
120sec
ratio H2O:EtOH

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/002090

A. CLASSIFICATION OF SUBJECT MATTER
INV. B81C1/00 B82Y40/00 C09D7/00
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)
C23C B81C B82Y

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 2 260 995 A1 (MAX PLANCK GESELLSCHAFT [DE]) 15 December 2010 (2010-12-15)	1,4-19
A	abstract column 3, paragraph 11 - column 7, paragraph 41 column 9, paragraph 52 column 10, paragraph 57 - column 11, paragraph 59 column 11, paragraph 62 - column 12, paragraph 64 column 13, paragraphs 71,72 ----- -/--	2,3

☒ 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 16 January 2013	Date of mailing of the international search report 24/01/2013
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 Ekoué, Adamah

1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/002090

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ROMAN GLASS ET AL: "Block copolymer micelle nanolithography on non-conductive substrates; Block copolymer micelle nanolithography on non-conductive substrates", NEW JOURNAL OF PHYSICS, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 6, no. 1, 1 August 2004 (2004-08-01), pages 101-101, XP020080459, ISSN: 1367-2630, DOI: 10.1088/1367-2630/6/1/101	1,4-19
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