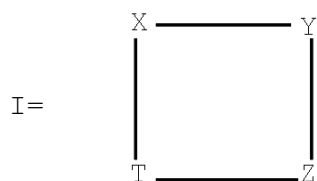


Process that enables the creation of nanometric structures  
by self-assembly of block copolymers

5 The invention relates to a process that enables the  
creation of nanometric structures by self-assembly of block  
copolymers, at least one of the blocks of which results  
from the polymerization of monomers comprising at least one  
cyclic entity corresponding to the formula I.

10



15

where X= Si (R<sub>1</sub>, R<sub>2</sub>) ; Ge (R<sub>1</sub>, R<sub>2</sub>)

Z= Si (R<sub>3</sub>, R<sub>4</sub>) ; Ge (R<sub>3</sub>, R<sub>4</sub>) ; O ; S ; C (R<sub>3</sub>, R<sub>4</sub>)

Y= O ; S ; C (R<sub>5</sub>, R<sub>6</sub>)

20 T= O ; S ; C (R<sub>7</sub>, R<sub>8</sub>)

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> are selected from hydrogen,  
linear, branched or cyclic alkyl groups, with or without  
heteroatoms, and aromatic groups with or without  
25 heteroatoms.

The invention also relates to the use of these materials in  
the fields of lithography (lithography masks), information  
storage but also the production of porous membranes or as  
30 catalyst support. The invention also relates to the block  
copolymer masks obtained according to the process of the  
invention.

The development of nanotechnologies has made it possible to constantly miniaturize products in the field of microelectronics and micro-electro-mechanical systems (MEMS) in particular. Today, conventional lithography techniques no longer make it possible to meet these constant needs for miniaturization, as they do not make it possible to produce structures with dimensions of less than 60 nm.

It has therefore been necessary to adapt the lithography techniques and create etching masks that make it possible to create increasingly small patterns with a high resolution. With the block copolymers it is possible to structure the arrangement of the constituent blocks of the copolymers, by phase segregation between the blocks thus forming nanodomains, on scales of less than 50 nm. Due to this ability to be nanostructured, the use of block copolymers in the fields of electronics or optoelectronics is now well known.

Among the masks studied for carrying out nanolithography, block copolymer films, in particular based on polystyrene-poly(methyl methacrylate), denoted hereinbelow as PS-b-PMMA, appear to be very promising solutions since they make it possible to create patterns with a high resolution. In order to be able to use such a block copolymer film as an etching mask, one block of the copolymer must be selectively removed in order to create a porous film of the residual block, the patterns of which may be subsequently transferred by etching to an underlying layer. Regarding the PS-b-PMMA film, the minority block, that is to say the PMMA (poly(methyl methacrylate)) is removed selectively in order to create a mask of residual PS (polystyrene).

In order to create such masks, the nanodomains must be oriented perpendicular to the surface of the underlying

layer. Such structuring of the domains requires particular conditions such as the preparation of the surface of the underlying layer, but also the composition of the block copolymer.

5 The ratios between the blocks make it possible to control the shape of the nanodomains and the molecular mass of each block makes it possible to control the dimension of the blocks. Another very important factor is the phase segregation factor, also referred to as the Flory-Huggins  
10 interaction parameter and denoted by " $\chi$ ". Specifically, this parameter makes it possible to control the size of the nanodomains. More particularly, it defines the tendency of the blocks of the block copolymer to separate into nanodomains. Thus, the product  $\chi N$  of the degree of  
15 polymerization,  $N$ , and of the Flory-Huggins parameter  $\chi$ , gives an indication as to the compatibility of two blocks and whether they may separate. For example, a diblock copolymer of symmetrical composition separates into microdomains if the product  $\chi N$  is greater than 10. If this  
20 product  $\chi N$  is less than 10, the blocks mix together and phase separation is not observed.

Due to the constant needs for miniaturization, it is sought to increase this degree of phase separation, in order to produce nanolithography masks that make it possible to  
25 obtain very high resolutions, typically of less than 20 nm, and preferably of less than 10 nm.

In *Macromolecules*, 2008, 41, 9948, Y. Zhao et al. estimated the Flory-Huggins parameter for a PS-*b*-PMMA block copolymer. The Flory-Huggins parameter  $\chi$  obeys the  
30 following equation:  $\chi = a + b/T$ , where the values  $a$  and  $b$  are constant specific values dependent on the nature of the blocks of the copolymer and  $T$  is the temperature of the heat treatment applied to the block copolymer in order to

enable it to organise itself, that is to say in order to obtain a phase separation of the domains, an orientation of the domains and a reduction in the number of defects. More particularly, the values  $a$  and  $b$  respectively represent the  
5 entropic and enthalpic contributions. Thus, for a PS-*b*-PMMA block copolymer, the phase segregation factor obeys the following equation:  $\chi = 0.0282 + 4.46/T$ . Consequently, even though this block copolymer makes it possible to generate domain sizes of slightly less than 20 nm, it does not make  
10 it possible to go down much lower in terms of domain size, due to the low value of its Flory-Huggins interaction parameter  $\chi$ .

This low value of the Flory-Huggins interaction parameter therefore limits the advantage of block copolymers based on  
15 PS and PMMA for the production of structures having very high resolutions.

In order to get round this problem, M.D. Rodwogin et al., ACS Nano, 2010, 4, 725, demonstrated that it is possible to change the chemical nature of the two blocks of the block  
20 copolymer in order to very greatly increase the Flory-Huggins parameter  $\chi$  and to obtain a desired morphology with a very high resolution, that is to say the size of the nanodomains of which is less than 20 nm. These results have in particular been demonstrated for a PLA-*b*-PDMS-*b*-PLA  
25 (polylactic acid - polydimethylsiloxane - polylactic acid) triblock copolymer.

H. Takahashi et al., Macromolecules, 2012, 45, 6253, studied the influence of the Flory-Huggins interaction parameter  $\chi$  on the kinetics of the copolymer assembly and  
30 of reduction of defects in the copolymer. They have in particular demonstrated that when this parameter  $\chi$  becomes too large, there is generally a significant slowing down of the assembly kinetics, of the phase segregation kinetics

also leading to a slowing down of the kinetics of defect reduction at the moment of the organization of the domains. Another problem, reported by S. Ji et al., ACS Nano, **2012**, 6, 5440, is also faced when considering the organisation  
5 kinetics of block copolymers containing a plurality of blocks that are all chemically different from one another. Specifically, the kinetics of diffusion of the polymer chains, and hence also the kinetics of organization and defect reduction within the self-assembled structure, are  
10 dependent on the segregation parameters  $\chi$  between each of the various blocks. Moreover, these kinetics are also slowed down due to the multiblock nature of the copolymer, since the polymer chains then have fewer degrees of freedom for becoming organized with respect to a block copolymer  
15 comprising fewer blocks.

Patents US 8304493 and US 8450418 describe a process for modifying block copolymers, and also modified block copolymers. These modified block copolymers have a modified value of the Flory-Huggins interaction parameter  $\chi$ , such  
20 that the block copolymer has nanodomains of small sizes.

Due to the fact that PS-b-PMMA block copolymers already make it possible to achieve dimensions of the order of 20 nm, the Applicant has sought a solution for modifying this type of block copolymer in order to obtain a good  
25 compromise regarding the Flory-Huggins interaction parameter  $\chi$ , and the self-assembly speed and temperature.

Surprisingly, it has been discovered that a block copolymer, at least one of the blocks of which comprises entities (I), has the following advantages when it is  
30 deposited on a surface:

- Rapid self-assembly kinetics (between 1 and 20 minutes) for low molecular masses leading to domain sizes well below

10 nm, at low temperatures (between 333 K and 603 K, and preferably between 373 K and 603 K).

- The presence of entities resulting from monomers of the family of (I) silicon or germanium carbide precursors after plasma treatment or treatment by pyrolysis that makes it possible to obtain hard masks during the mask etching step.

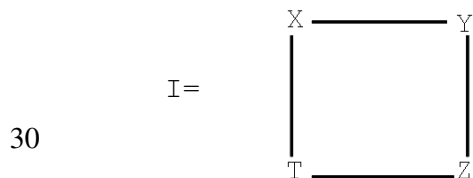
- The orientation of the domains during the self-assembly of such block copolymers does not require preparation of the support (no neutralization layer), the orientation of the domains being governed by the thickness of the block copolymer film deposited.

Thus, these materials show a very great advantage for applications in nanolithography for the production of etching masks of very small dimensions and that have a good etching contrast, and also the production of porous membranes or else as catalyst support.

20

Summary of the invention:

The invention relates to a nanostructured assembly process using a composition comprising a block copolymer, at least one of the blocks of which consists of at least one monomer corresponding to the following formula (I):



where  $X = \text{Si}(R_1, R_2); \text{Ge}(R_1, R_2)$

$Z = \text{Si}(\text{R}_3, \text{R}_4); \text{Ge}(\text{R}_3, \text{R}_4); \text{O}; \text{S}; \text{C}(\text{R}_3, \text{R}_4)$

$Y = \text{O}; \text{S}; \text{C}(\text{R}_5, \text{R}_6)$

$T = \text{O}; \text{S}; \text{C}(\text{R}_7, \text{R}_8)$

5 with  $\text{R}_1 = \text{R}_2$  and  $\text{R}_3 = \text{R}_4$  and  $\text{R}_5 = \text{R}_6$  and  $\text{R}_7 = \text{R}_8$  are selected from hydrogen, linear, branched or cyclic alkyl groups, with or without heteroatoms, and aromatic groups with or without heteroatoms and comprising the following steps:

- 10 - dissolving the block copolymer in a solvent,  
 - depositing this solution on a surface,  
 - annealing.

Detailed description:

15

The term "surface" is understood to mean a surface which can be flat or non-flat.

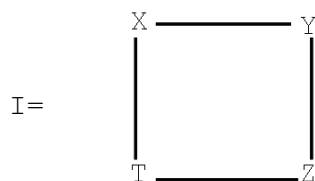
The term "annealing" is understood to mean a step of heating at a certain temperature that enables the  
 20 evaporation of the solvent, when it is present, and that allows the establishment of the desired nanostructuring in a given time (self-assembly).

The term "annealing" is also understood to mean the establishment of the nanostructuring of the block copolymer  
 25 film when said film is subjected to a controlled atmosphere of one or more solvent vapors, these vapors giving the polymer chains sufficient mobility to become organized by themselves on the surface. The term "annealing" is also understood to mean any combination of the abovementioned  
 30 two methods.

Any block copolymer, whatever its associated morphology, will be able to be used in the context of the invention,

whether diblock, linear or star-branched triblock or linear, comb-shaped or star-branched multiblock copolymers are involved, on condition that at least one of the constituent monomers of at least one of the blocks of the block copolymer has the structure (I). Preferably, diblock or triblock copolymers and more preferably diblock copolymers are involved.

The monomer entities used in the block copolymers of the invention are represented by the following formula (I):



where X= Si (R<sub>1</sub>, R<sub>2</sub>) ; Ge (R<sub>1</sub>, R<sub>2</sub>)

Z= Si (R<sub>3</sub>, R<sub>4</sub>) ; Ge (R<sub>3</sub>, R<sub>4</sub>) ; O ; S ; C (R<sub>3</sub>, R<sub>4</sub>) ;

Y= O ; S ; C (R<sub>5</sub>, R<sub>6</sub>)

T= O ; S ; C (R<sub>7</sub>, R<sub>8</sub>)

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> are selected from hydrogen, linear, branched or cyclic alkyl groups, with or without heteroatoms, and aromatic groups with or without heteroatoms and R<sub>1</sub>=R<sub>2</sub> and R<sub>3</sub> = R<sub>4</sub> and R<sub>5</sub> = R<sub>6</sub> and R<sub>7</sub> = R<sub>8</sub>.

It has been shown that if R<sub>1</sub>≠R<sub>2</sub> or R<sub>3</sub>≠R<sub>4</sub> or R<sub>5</sub>≠R<sub>6</sub> or R<sub>7</sub>≠R<sub>8</sub> the self-assembly does not take place for the low molecular masses compared with the copolymers of similar molecular mass but where R<sub>1</sub>= R<sub>2</sub> and R<sub>3</sub> = R<sub>4</sub> and R<sub>5</sub> = R<sub>6</sub> and R<sub>7</sub> = R<sub>8</sub>.

Preferably, X = Si (R<sub>1</sub>, R<sub>2</sub>) where R<sub>1</sub> and R<sub>2</sub> are linear alkyl groups, and preferably methyl groups, Y = C (R<sub>5</sub>, R<sub>6</sub>) where R<sub>5</sub> and R<sub>6</sub> are hydrogen atoms, Z = C (R<sub>3</sub>, R<sub>4</sub>) where R<sub>3</sub> and R<sub>4</sub> are

hydrogen atoms,  $T = C(R_7, R_8)$  where  $R_7$  and  $R_8$  are hydrogen atoms.

The blocks not comprising an entity (I) consist of the  
 5 following monomers: at least one vinyl, vinylidene, diene, olefinic, allyl or (meth)acrylic or cyclic monomer. These monomers are selected more particularly from vinylaromatic monomers, such as styrene or substituted styrenes, in particular  $\alpha$ -methylstyrene, acrylic monomers, such as  
 10 alkyl, cycloalkyl or aryl acrylates, such as methyl, ethyl, butyl, ethylhexyl or phenyl acrylate, ether alkyl acrylates, such as 2-methoxyethyl acrylate, alkoxy- or aryloxypolyalkylene glycol acrylates, such as methoxypolyethylene glycol acrylates, ethoxypolyethylene  
 15 glycol acrylates, methoxypolypropylene glycol acrylates, methoxypolyethylene glycol-polypropylene glycol acrylates or mixtures thereof, aminoalkyl acrylates, such as 2-(dimethylamino)ethyl acrylate (ADAME), fluoroacrylates, phosphorus-comprising acrylates, such as  
 20 alkylene glycol phosphate acrylates, glycidyl acrylate or dicyclopentenylloxyethyl acrylate, alkyl, cycloalkyl, alkenyl or aryl methacrylates, such as methyl (MMA), lauryl, cyclohexyl, allyl, phenyl or naphthyl methacrylate, ether alkyl methacrylates, such as 2-ethoxyethyl  
 25 methacrylate, alkoxy- or aryloxypolyalkylene glycol methacrylates, such as methoxypolyethylene glycol methacrylates, ethoxypolyethylene glycol methacrylates, methoxypolypropylene glycol methacrylates, methoxypolyethylene glycol-polypropylene glycol  
 30 methacrylates or mixtures thereof, aminoalkyl methacrylates, such as 2-(dimethylamino)ethyl methacrylate (MADAME), fluoromethacrylates, such as 2,2,2-trifluoroethyl methacrylate, silylated methacrylates, such as 3-

methacryloylpropyltrimethylsilane, phosphorus-comprising methacrylates, such as alkylene glycol phosphate methacrylates, hydroxyethylimidazolidone methacrylate, hydroxyethylimidazolidinone methacrylate or 2-(2-oxo-1-

5 imidazolidinyl)ethyl methacrylate, acrylonitrile, acrylamide or substituted acrylamides, 4-acryloylmorpholine, N-methylolacrylamide, methacrylamide or substituted methacrylamides, N-methylolmethacrylamide, methacrylamidopropyltrimethylammonium chloride (MAPTAC),

10 glycidyl methacrylate, dicyclopentenylloxyethyl methacrylate, maleic anhydride, alkyl or alkoxy- or aryloxypolyalkylene glycol maleates or hemimaleates, vinylpyridine, vinylpyrrolidinone, (alkoxy)poly(alkylene glycol) vinyl ethers or divinyl ethers, such as

15 methoxypoly(ethylene glycol) vinyl ether or poly(ethylene glycol) divinyl ether, olefinic monomers, among which may be mentioned ethylene, butene, hexene and 1-octene, diene monomers, including butadiene or isoprene, and also as fluoroolefinic monomers and vinylidene monomers, among

20 which may be mentioned vinylidene fluoride, cyclic monomers, among which may be mentioned lactones such as  $\epsilon$ -caprolactone, lactides, glycolides, cyclic carbonates such as trimethylene carbonate, siloxanes such as octamethylcyclotetrasiloxane, cyclic ethers such as

25 trioxane, cyclic amides such as  $\epsilon$ -caprolactam, cyclic acetals such as 1,3-dioxolane, phosphazenes such as hexachlorocyclotriphosphazene, N-carboxyanhydrides, phosphorus-comprising cyclic esters such as cyclophosphorinanes, cyclophospholanes or oxazolines,

30 where appropriate protected in order to be compatible with anionic polymerization processes, alone or as a mixture of at least two abovementioned monomers.

Preferably, the blocks not comprising an entity (I) comprise methyl methacrylate in weight proportions of greater than 50% and preferably greater than 80% and more preferably greater than 95%.

- 5 The block copolymers used in the invention are prepared by sequential anionic polymerization. Such a synthesis is well known to a person skilled in the art. A first block is prepared according to the protocol described by Yamaoka et coll., *Macromolecules*, 1995, 28, 7029-7031.
- 10 The following blocks are constructed in the same manner by sequentially adding the monomers in question, where appropriate preceded by a step of addition of 1,1-diphenylethylene or of any other molecule known to a person skilled in the art for controlling the reactivity of the
- 15 active center.

Once the block copolymer has been synthesized, it is dissolved in a suitable solvent then deposited on a surface according to techniques known to a person skilled in the

20 art such as for example the spin coating, doctor blade coating, knife coating system or slot die coating system technique, but any other technique may be used such as dry deposition, that is to say deposition without involving a predissolution. The films thus obtained have a thickness of

25 less than 100 nm.

Mention will be made, among the favored surfaces, of silicon, silicon having a native or thermal oxide layer, hydrogenated or halogenated silicon, germanium,

30 hydrogenated or halogenated germanium, platinum and platinum oxide, tungsten and oxides, gold, titanium nitrides and graphenes. Preferably, the surface is inorganic and more preferably silicon. More preferably

still, the surface is silicon having a native or thermal oxide layer.

It will be noted in the context of the present invention,  
5 even though it is not excluded, that it is not necessary to carry out a neutralization step (as is the case generally in the prior art) by the use of a suitably chosen statistical copolymer. This presents a considerable advantage since this neutralization step is disadvantageous  
10 (synthesis of the statistical copolymer of particular composition, deposition on the surface). The orientation of the block copolymer is defined by the thickness of the block copolymer film deposited. It is obtained in a relatively short time, of between 1 and 20 minutes limits  
15 included and preferably of between 1 and 5 minutes, and at temperatures between 333 K and 603 K and preferably between 373 K and 603 K and more preferably between 373 K and 403 K.

20 The process of the invention applies advantageously to the field of nanolithography using block copolymer masks or more generally to the field of surface nanostructuring for electronics.

25 The process of the invention also enables the manufacture of porous membranes or catalyst supports for which one of the domains of the block copolymer is degraded in order to obtain a porous structure.

30

Example 1:

Synthesis of poly(1,1-dimethylsilacyclobutane)-block-PMMA (PDMSB-b-PMMA).

1,1-Dimethylsilacyclobutane (DMSB) is a monomer of formula (I) where  $X=\text{Si}(\text{CH}_3)_2$ ,  $Y=Z=T=\text{CH}_2$ .

The polymerization is carried out anionically in a 50/50 (vol/vol) THF/heptane mixture at  $-50^\circ\text{C}$  by sequential addition of the two monomers with the secondary butyl lithium (sec-BuLi) initiator.

Typically, lithium chloride (85 mg), 20 ml of THF and 20 ml of heptane are introduced into a 250 ml flame-dried round-bottomed flask equipped with a magnetic stirrer. The solution is cooled to  $-50^\circ\text{C}$ . Next, 0.00015 mol of sec-BuLi is introduced, followed by an addition of 0.01 mol of 1,1-dimethylsilacyclobutane. The reaction mixture is stirred for 1 h and then 0.2 ml of 1,1-diphenylethylene is added. 30 minutes later, 0.01 mol of methyl methacrylate is added and the reaction mixture is kept stirring for 1 h. The reaction is completed by an addition of degassed methanol at  $-50^\circ\text{C}$ . Next, the reaction medium is concentrated by evaporation, followed by a precipitation in methanol. The product is then recovered by filtration and dried in an oven at  $35^\circ\text{C}$  overnight.

Examples 2-6.

These copolymers are prepared according to the protocol of example 1, while varying the amounts of the reactants. Comparative example 6 is prepared using 1-butyl-1-methyl silacyclobutane (BMSB).

The molecular masses and the dispersities, corresponding to the ratio of weight-average molecular mass ( $M_w$ ) to number-average molecular mass ( $M_n$ ), are obtained by SEC (size exclusion chromatography), using two Agilent 3  $\mu\text{m}$  ResiPore

columns in series, in a THF medium stabilized with BHT, at a flow rate of 1 ml/min, at 40°C, with samples at a concentration of 1 g/l, with prior calibration with graded samples of polystyrene using an Easical PS-2 prepared pack.

5 The results are given in table 1:

Table 1:

| Example         | M <sub>n</sub> SEC (g/mol) | sec BuLi (mole) | mole DMSB or BMSB | mole MMA | Polysilolethane/PMMA composition (wt%) | Dispersity Mw/Mn | Self-assembly temp (K) |
|-----------------|----------------------------|-----------------|-------------------|----------|----------------------------------------|------------------|------------------------|
| 1 (invention)   | 10850                      | 0.00015         | 0.01              | 0.01     | 43/57                                  | 1.15             | 453                    |
| 2 (invention)   | 16500                      | 0.00001         | 0.01              | 0.0043   | 74/26                                  | 1.10             | 453                    |
| 3 (invention)   | 5100                       | 0.00035         | 0.01              | 0.0043   | 77/23                                  | 1.05             | 373                    |
| 4 (invention)   | 5300                       | 0.00035         | 0.01              | 0.0043   | 79/21                                  | 1.06             | 373                    |
| 5 (invention)   | 6600                       | 0.00025         | 0.01              | 0.0043   | 74/26                                  | 1.08             | 453                    |
| 6 (comparative) | 7150                       | 0.00025         | 0.0067            | 0.01     | 63/37                                  | 1.10             | 453                    |

The films from examples 1 to 6 were prepared by spin coating from a 1.5 wt% solution in toluene and the thickness of the film was controlled by varying the spin coating speed (from 1500 to 3000 rpm). This thickness is typically less than 100 nm. The promotion of the self-assembly inherent to the phase segregation between the blocks of the copolymer was obtained by short annealings (5 min) on a hot plate at moderate temperature (between 373 K and 453 K).

The AFM images are given in figures 1 to 6 and correspond to the copolymers from examples 1 to 6. It is clearly seen that the block copolymers that are subject of the invention exhibit self-assembly, even for low molecular masses, whereas comparative example 6 does not exhibit self-assembly for a low molecular mass.

Figure 1 shows the thin-film self-assembly of the block copolymer from example 1 having lamellae oriented perpendicular to the substrate. Scale 100 nm.

Figure 2 shows the thin-film self-assembly of the block copolymer from example 2 having cylinders oriented parallel to the substrate. Scale 100 nm.

Figure 3 shows the thin-film self-assembly of the block copolymer from example 3 having cylinders oriented parallel to the substrate. Scale 100 nm.

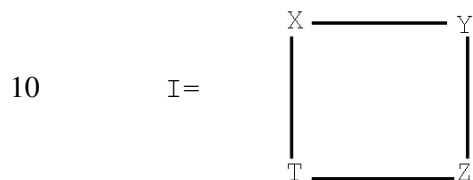
Figure 4 shows the thin-film self-assembly of the block  
5 copolymer from example 4 having cylinders oriented parallel to the substrate. Scale 100 nm.

Figure 5 shows the thin-film self-assembly of the block copolymer from example 5 having cylinders oriented perpendicular to the substrate. Scale 100 nm.

10 Figure 6 shows the absence of self-assembly of the copolymer from example 6 as a thin film, the lines are the guides that are used for the promotion of self-assembly in graphoepitaxy. Scale 100 nm.

## Claims

1 A nanostructured assembly process using a composition  
 5 comprising a block copolymer, at least one of the blocks of  
 which consists of at least one monomer corresponding to the  
 following formula (I):



where  $X = \text{Si}(R_1, R_2); \text{Ge}(R_1, R_2)$

15  $Z = \text{Si}(R_3, R_4); \text{Ge}(R_3, R_4); \text{O}; \text{S}; \text{C}(R_3, R_4)$

$Y = \text{O}; \text{S}; \text{C}(R_5, R_6)$

$T = \text{O}; \text{S}; \text{C}(R_7, R_8)$

with  $R_1 = R_2$  and  $R_3 = R_4$  and  $R_5 = R_6$  and  $R_7 = R_8$  are selected  
 20 from hydrogen, linear, branched or cyclic alkyl groups,  
 with or without heteroatoms, and aromatic groups with or  
 without heteroatoms and comprising the following steps:

- dissolving the block copolymer in a solvent,
- 25 - depositing this solution on a surface,
- annealing.

2 The process as claimed in claim 1, wherein the block  
 copolymer is a diblock copolymer.

30

3 The process as claimed in claim 1, wherein  $X = \text{Si}(R_1, R_2)$ ,  
 $Z = \text{C}(R_3, R_4)$ ,  $Y = \text{C}(R_5, R_6)$ ,  $T = \text{C}(R_7, R_8)$ .

4 The process as claimed in claim 3, wherein  $R_1=R_2=CH_3$ ,  
5  $R_3=R_4=R_5=R_6=R_7=R_8=H$ .

5 The process as claimed in claim 1, wherein the block or  
5 blocks not comprising an entity (I) comprise methyl  
methacrylate in weight proportions of greater than 50%.

6 The process as claimed in claim 1, wherein the  
orientation of the block copolymer is carried out during a  
10 time of between 1 and 20 minutes, limits included.

7 The process as claimed in claim 1, wherein the  
orientation of the block copolymer is carried out at a  
temperature of between 333 K and 603 K.

15

8 The process as claimed in claim 1, wherein the annealing  
is carried out under a controlled atmosphere comprising  
solvent vapors, or a solvent atmosphere/temperature  
combination.

20

9 The process as claimed in claim 1, wherein the  
nanostructured assembly has a thickness of less than 100  
nm.

25 10 The use of the process as claimed in one of claims 1 to  
9, in the field of lithography, or more generally in the  
field of surface nanostructuring for electronics.

11 A block copolymer mask obtained as claimed in the  
30 process of one of claims 1 to 9.