ABSTRACT:

The present invention relates to a process for reducing the structuring time of ordered films of a composition of block copolymers on a surface without increasing the level of defects, this being whatever the orientation (perpendicular to the substrate, parallel to the substrate, etc.); this composition having a product \(\chi_{\text{effective}} \times N\) (with \(\chi_{\text{effective}} = \text{chi effective Flory-Huggins parameter, and } N \text{ the total degree of polymerization}) \) of between 10.5 and 40.
Process for reducing the structuring time of ordered films of block copolymer

The present invention relates to a process for reducing the structuring time of ordered films of a composition of block copolymers on a surface without degradation of the other critical structuring parameters (structuring defects, period, thickness, critical dimension uniformity), this being whatever the orientation (perpendicular to the substrate, parallel to the substrate, etc.); this composition having a product $\chi_{\text{effective}}N$ (with $\chi_{\text{effective}} = \text{Flory-Huggins parameter between the blocks under consideration}$, and $N$ the total degree of polymerization of these blocks) of between 10.5 and 40, limits included, at the structuring temperature of the composition. $N$ can be linked to the molecular weight at the peak $M_p$ of a block copolymer measured by GPC ("Gel Permeation Chromatography") by the following relationship: $N = \frac{M_p}{m}$, where $m$ is the molar mass of the monomer and for several monomers: $m = \sum (f_i \cdot m_i)$, with $f_i = \text{mass fraction of the constituent "i" and } m_i \text{ its molar mass.}$

The invention also relates to the ordered films thus obtained that can be used in particular as masks in the lithography field and also to the masks obtained.

The use of block copolymers to generate lithography masks is now well known. While this technology is promising, it may only be accepted if the levels of defects resulting from the self-organization process are sufficiently low and compatible with the standards established by the ITRS (http://www.itrs.net/). As a result, it thus appears to be necessary to have available block copolymers, the structuring process of which generates the fewest possible
defects in a given time in order to facilitate the industrialization of these polymers in applications such as those of microelectronics. Compositions and processes for producing masks for lithography, for which the production time is as short as possible, are in particular sought. For a given block copolymer (type of monomers, number of blocks), it becomes difficult to structure and control the rapid orientation of the nanostructures when the molecular mass increases (X. Chevalier; C. Nicolet; C. Navarro, et al. "Blending approaches to enhance structural order in block-copolymer's self-assemblies", Proc. SPIE 9425, Advances in Patterning Materials and Processes XXXII, 94251N (March 20, 2015); doi: 10.1117/12.2085821).

For example, block copolymers (BCPs) consisting of blocks of a single monomer organizing themselves in ordered films with large periods are very difficult not only to rapidly structure, but also to orient perpendicular to the substrate, rapidly for relatively thick structured films. While the current trend is towards periods much lower than 20 nm, in particular through the use of copolymers which exhibit a high Flory-Huggins (\(\chi\)) parameter, the applicant has noted that the structuring of these copolymers is obtained for times which are sometimes too long on the industrial scale.

Thus, the applicant has noted that, within a range of the product \(X_{\text{effective}}^N\) at the structuring temperature of typically between 10.5 and 40, preferably between 15 and 30 and even more preferably between 17 and 25, the structuring in general, and in particular but non-exhaustively the structuring in which the orientation is perpendicular to a surface, of a composition comprising at least one block copolymer occurs more rapidly than when the product
\( \chi_{\text{effective}}N \) of the composition is greater than 40, for equivalent periods.

The term "structuring" refers to the process of establishing a self-organized phase, either in which the orientation of the structures is entirely homogeneous (for example perpendicular relative to the substrate, or parallel thereto), or which exhibits a mixture of orientations of the structures (perpendicular and parallel), and which has a degree of organization that can be quantified by any technique known to those skilled in the art. For example, but in a non-limiting manner, in the case of a perpendicular, hexagonal, cylindrical homogeneous phase, this order can be defined by a given amount of coordination number defects or, in a quasi-equivalent manner, a given "grain size" (the "grain" being a quasiperfect monocrystal in which the units exhibit similar periodic or quasiperiodic positional and translational order). In the case where the self-organized phase exhibits a mixture of orientations of its structures, the order may be defined according to amounts of orientation defects and a grain size; it is also considered that this mixed phase is a transient state tending towards a homogeneous phase.

The term "structuring time" refers to the time required for the structuring to reach a defined order state (for example a given amount of defects, or a given grain size), following a self-organization process defined by given conditions (for example thermal annealing performed at a given temperature, for a predetermined period of time).

In addition to the advantages described above, the process of the invention also makes it possible to advantageously reduce interface roughness defects. Indeed, for example but
non-exhaustively, in the case of lamellar morphology, a rough interface (denoted LER for "line edge roughness") can be observed when the structuring is not absolutely completed (which would require, for example, exceeding the time assigned for an industrial process, using annealing for a longer time) for the compositions not included in the invention. This roughness can also be observed if the desired film thicknesses are too large for given compositions, or else for example in the case of thermal annealing if the temperature required to establish the structuring is too high with respect to the heat stability of the composition. The invention makes it possible to overcome this problem given that the compositions described by the invention very rapidly complete their structuring, for large film thicknesses, with few or no defects, and for annealing temperatures that are lower than those required for block copolymers of equivalent dimensions not described by the invention.

Summary of the invention:

The invention relates to a process which makes it possible to reduce the structuring time of ordered films of a composition comprising at least one block copolymer on a surface, and which comprises the following steps:

- mixing a composition comprising a block copolymer in a solvent, this composition exhibiting a product $x_{\text{effective}} N$ of between 10.5 and 40 at the structuring temperature;
- depositing this mixture on a surface, which is optionally pre-modified, whether it is organic or inorganic;
- curing the mixture deposited on the surface at a temperature between the highest $T_g$ (glass transition
temperature) of the block copolymer(s) and their decomposition temperature such that the composition can organize itself after evaporation of the solvent without degrading.

Detailed description:
As regards the composition used in the process in accordance with the invention, any block copolymer, or blend of block copolymers, may be used in the context of the invention, provided that the product $x_{\text{effective}}N$ of the composition comprising a block copolymer is between 10.5 and 40, preferably between 15 and 30, and even more preferably between 17 and 25 at the structuring temperature of this composition. According to a first preference, the composition comprises a triblock copolymer or a blend of triblock copolymers. According to a second preference, the composition comprises a diblock copolymer or a blend of diblock copolymers. Each block of the triblock or diblock copolymers of the composition may contain between 1 and 3 monomers, which will make it possible to finely adjust the $x_{\text{effective}}N$ between 10.5 and 40.

The copolymers used in the composition have a molecular weight at the peak measured by SEC (Size Exclusion Chromatography) of between 100 and 500,000 g/mol and a dispersity of between 1 and 2.5, limits included, and preferably of between 1.05 and 2, limits included.

The block copolymers can be synthesized by any technique known to those skilled in the art, among which may be mentioned polycondensation, ring opening polymerization or anionic, cationic or radical polymerization. When the copolymers are prepared by radical polymerization, the latter can be controlled by any known technique, such as NMP.
According to a preferred form of the invention, the block copolymers are prepared by nitroxide-mediated polymerization.

More particularly, the nitroxides resulting from the alkoxyamines derived from the stable free radical (1) are preferred.

\[
\begin{align*}
\text{R}_L & \quad | \\
-\text{C} & \quad \text{N} \quad 0^* \\
\end{align*}
\]

in which the radical R\textsubscript{L} exhibits a molar mass of greater than 15.0342 g/mol. The radical R\textsubscript{L} may be a halogen atom such as chlorine, bromine or iodine, a saturated or unsaturated, linear, branched or cyclic, hydrocarbon-based group, such as an alkyl or phenyl radical, or an ester group -COOR or an alkoxy group -OR or a phosphonate group -PO(OR)\textsubscript{2}, as long as it has a molar mass greater than 15.0342. The radical R\textsubscript{L}, which is monovalent, is said to be in the \(\beta\) position with respect to the nitrogen atom of the nitroxide radical. The remaining valencies of the carbon atom and of the nitrogen atom in the formula (1) can be bonded to various radicals, such as a hydrogen atom or a hydrocarbon radical, for
instance an alkyl, aryl or arylalkyl radical, comprising from 1 to 10 carbon atoms. It is not out of the question for the carbon atom and the nitrogen atom in the formula (1) to be connected to one another via a divalent radical, so as to form a ring. Preferably however, the remaining valencies of the carbon atom and of the nitrogen atom of the formula (1) are bonded to monovalent radicals. Preferably, the radical \( R_L \) exhibits a molar mass of greater than 30 g/mol. The radical \( R_L \) can, for example, have a molar mass of between 40 and 450 g/mol. By way of example, the radical \( R_L \) can be a radical comprising a phosphoryl group, it being possible for said radical \( R_L \) to be represented by the formula:

\[
\begin{array}{c}
  R^3 \\
  - P - R^4 \\
  \quad \text{O}
\end{array}
\]  

(2)

in which \( R^3 \) and \( R^4 \), which can be identical or different, can be chosen from alkyl, cycloalkyl, alkoxy, aryloxy, aryl, aralkyloxy, perfluoroalkyl or aralkyl radicals and can comprise from 1 to 20 carbon atoms. \( R^3 \) and/or \( R^4 \) can also be a halogen atom, such as a chlorine or bromine or fluorine or iodine atom. The radical \( R_L \) can also comprise at least one aromatic ring, such as for the phenyl radical or the naphthyl radical, it being possible for the latter to be substituted, for example with an alkyl radical comprising from 1 to 4 carbon atoms.

More particularly, the alkoxyamines derived from the following stable radicals are preferred:

- \( \text{N-} \text{(tert-butyl)-1-phenyl-2-methylpropyl nitroxide,} \)
- \(\text{N- (tert-butyl) -1- (2-naphthyl) -2-methylpropyl nitroxide,}\)
- \(\text{N- (tert-butyl) -1-diethylphosphono-2 ,2-dimethyl propyl nitroxide,}\)
- \(\text{N- (tert-butyl) -1-dibenzylphosphono-2, 2-dimethylpropyl nitroxide,}\)
- \(\text{N-phenyl-1-diethylphosphono-2 ,2-dimethylpropyl nitroxide,}\)
- \(\text{N-phenyl-1-diethylphosphono-1-methylethyl nitroxide,}\)
- \(\text{N-(1-phenyl-2-methylpropyl) -1-diethylphosphono-1- methylethyl nitroxide,}\)
- \(\text{4-oxo-2, 2,6, 6-tetramethyl-1-piperidinyloxy,}\)
- \(\text{2,4,6-tri (tert-butyl) phenoxy.}\)

The alkoxyamines used in controlled radical polymerization must allow good control of the linking of the monomers. Thus, they do not all allow good control of certain monomers. For example, the alkoxyamines derived from TEMPO make it possible to control only a limited number of monomers; the same is true for the alkoxyamines derived from 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO). On the other hand, other alkoxyamines derived from nitroxides corresponding to formula (1), particularly those derived from nitroxides corresponding to formula (2) and even more particularly those derived from \(\text{N- (tert-butyl) -1-diethylphosphono-2, 2-dimethyl propyl nitroxide,}\) make it possible to broaden the controlled radical polymerization of these monomers to a large number of monomers.

In addition, the alkoxyamine opening temperature also influences the economic factor. The use of low temperatures will be preferred in order to minimize industrial difficulties. The alkoxyamines derived from nitroxides
corresponding to formula (1), particularly those derived from nitroxides corresponding to formula (2) and even more particularly those derived from N-(tert-butyl)-1-diethylphosphono-2,2-dimethyl propyl nitroxide, will therefore be preferred to those derived from TEMPO or 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO).

According to a second preferred form of the invention, the block copolymers are prepared by anionic polymerization.

When the polymerization is carried out in controlled radical fashion, the constituent monomers of the block copolymers will be chosen from vinyl, vinyldene, diene, olefinic, allyl or (meth) acrylic monomers. This monomer is more particularly chosen from vinilaromatic monomers, such as styrene or substituted styrenes, in particular α-methylstyrene, silylated styrenes, acrylic monomers, such as acrylic acid or its salts, alkyl, cycloalkyl or aryl acrylates, such as methyl, ethyl, butyl, ethylhexyl or phenyl acrylate, hydroxyalkyl acrylates, such as 2-hydroxyethyl acrylate, ether alkyl acrylates, such as 2-methoxyethyl acrylate, alkoxy- or aryloxypolyalkylene glycol acrylates, such as methoxypolyethylene glycol acrylates, ethoxypolyethylene glycol acrylates, methoxypolypropylene glycol acrylates, methoxypolyethylene glycol-polypropylene glycol acrylates or mixtures thereof, aminoalkyl acrylates, such as 2-(dimethylamino) ethyl acrylate (ADAME), fluoroacrylates, silylated acrylates, phosphorus-comprising acrylates, such as alkylene glycol acrylate phosphates, glycidyl acrylate or dicyclopentyloxyethyl acrylate, methacrylic monomers, such as methacrylic acid or its salts, alkyl, cycloalkyl, alkenyl or aryl methacrylates, such as methyl (MMA), lauryl, cyclohexyl, allyl, phenyl or naphthyl methacrylate,
hydroxyalkyl methacrylates, such as 2-hydroxyethyl methacrylate or 2-hydroxypropyl methacrylate, ether alkyl methacrylates, such as 2-ethoxyethyl methacrylate, alkoxy- or arylxopropyalkylene glycol methacrylates, such as methoxypropylene glycol methacrylates, ethoxy-polyethylene glycol methacrylates, methoxypolypropylene glycol methacrylates, methoxypolyethylene glycol-polypropylene glycol 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-methacryloxypropyltrimethylsilane, phosphorus-comprising methacrylates, such as alkylene glycol methacrylate phosphates, hydroxyethylimidazolidone methacrylate, hydroxyethylimidazolidinone methacrylate or 2-(2-oxo-1-imidazolidinyl) ethyl methacrylate, acrylonitrile, acrylamide or substituted acrylamides, 4-acryloylmorpholine, N-methylolacrylamide, methacrylamide or substituted methacrylamides, N-methylolmethacrylamide, methacrylamido-propyltrimethylammonium chloride (MAPTAC), glycidyl methacrylate, dicyclopentenyloxyethyl methacrylate, itaconic acid, maleic acid or its salts, maleic anhydride, alkyl or alkoxy- or arylxopropyalkylene glycol maleates or hemimaleates, vinylpyridine, vinylpyrrolidinone, (alkoxy)-poly (alkylene glycol) vinyl ethers or divinyl ethers, such as methoxypoly (ethylene glycol) vinyl ether or poly (ethylene glycol) divinyl ether, olefinic monomers, among which may be mentioned ethylene, butene, hexene and 1-octene, 1,1-diphenylethylene, diene monomers, including butadiene or isoprene, as well as fluoroolefinic monomers and vinylidene monomers, among which may be mentioned vinylidene fluoride, alone or as a mixture of at least two abovementioned monomers.
Indeed, while wishing to maintain a value of the product $X_{\text{effective}} N$ in the range of between 10.5 and 40, preferably between 15 and 30 and even more preferably between 17 and 25, it is sometimes necessary to use several monomers, typically 2 or 3, in one or more blocks when particular periods are targeted.

The term "period" is intended to mean the mean minimum distance separating two neighbouring domains having the same chemical composition, separated by a domain having a different chemical composition.

Typically, in the case of a diblock copolymer prepared by controlled or non-controlled radical polymerization, which is a preference in the context of the process that is the subject of the invention, it will be possible for example to consider a structure $A$-$b$- $(B$-$co$-$C)$ wherein the block $A$ consists of a single monomer $A$ and the block $B/C$ itself consists of two monomers $B$ and $C$, $C$ possibly being $A$. In the latter case, the structure of the diblock copolymer will be expressed $A$-$b$- $(B$-$co$-$A)$.

In considering the reactivity ratios $r_b$ and $r_c$ respectively of the monomers $B$ and $C$ ($C$ possibly being $A$), it will be possible to distinguish several configurations corresponding to particular advantages when the polymerization is carried out batchwise, that is to say that the monomers $B$ and $C$ are introduced entirely at the beginning of the polymerization of the $(B$-$co$-$C)$ block. These configurations are known from the literature, see for example the book by Gnanou and Fontanille, Organic and physical chemistry of polymers, Wiley, ISBN 978-0-471-72543-5. The composition diagram of page 298 of this book is reproduced in Figure 1.

According to a first preference, $r_b$ will be greater than 1 and $r_c$ less than 1. This will result in a block $(B$-$co$-$C)$,
the composition of which will be a gradient beginning with a composition rich in monomer B and low in monomer C and finishing with a composition rich in C and low in B.

According to a second preference, \( rb \) will be between 0.95 and 1.05 and \( rc \) will be between 0.95 and 1.05. This will result in a block (\( B\)-co-\( C \)), the composition of which will be random.

According to a third preference, \( rb \) will be less than 1 and \( rc \) less than 1. This will result in a block (\( B\)-co-\( C \)), the composition of which will have a marked tendency towards the alternating of the monomers B and C.

According to a fourth preference, \( rb \) will be less than 1 and \( rc \) greater than 1. This will result in a block (\( B\)-co-\( C \)), the composition of which will be a gradient beginning with a composition rich in monomer C and low in monomer B and finishing with a composition rich in B and low in C.

According to a fifth preference and depending on the type of monomers B and C used, to counteract the effects relating to the reactivity ratios, it will be possible to carry out a continuous injection of both or of one of the two monomers B and C. This makes it possible either to dispense with the composition drift related to the reactivity ratios or to force this composition drift.

According to a sixth preference, a combination of preferences one to four with the preference five may be used, that is to say that a portion of the block (\( B\)-co-\( C \)) may be prepared in a first step according to preference one to four, and another
portion may be prepared in a second step according to the same preference one to four or preference five.

According to a seventh preference, the synthesis of the (B-co-C) block will be carried out in two steps corresponding to two feedstocks of monomers B and C, optionally of equivalent composition, the second feedstock being added to the reaction mixture once the first feedstock has been converted or partially converted, the monomers not converted in the first step being removed before the introduction of the second feedstock, this being regardless of the values of rb and rc.

Preferably, A is a styrene compound, more particularly styrene, and B is a (meth)acrylic compound, more particularly methyl methacrylate. This preferred choice makes it possible to maintain the same chemical stability as a function of the temperature, compared with a PS-\(b\)-PMMA block copolymer and also enables the use of the same sublayers as for a PS-\(b\)-PMMA, these sublayers consisting of random styrene/methyl methacrylate copolymers.

When the polymerization is carried out by the anionic route, the monomers will be chosen, in a non-limiting manner, from the following monomers:

at least one vinyl, vinylidene, diene, olefinic, allyl or (meth)acrylic monomer. These monomers are more particularly chosen from vinlylaromatic monomers, such as styrene or substituted styrenes, in particular a-methylstyrene, acrylic monomers, such as 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 glycol acrylates, methoxypolypropylene glycol acrylates,
methoxypolyethylene glycol-polypropylene glycol acrylates or mixtures thereof, aminoalkyl acrylates, such as 2-(dimethylamino) ethyl acrylate (ADAME), fluoroacrylates, silylated acrylates, phosphorus-comprising acrylates, such as alkylene glycol acrylate phosphates, glycidyl acrylate or dicyclopentenyloxyethyl 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 methacrylate, alkoxy- or aryloxypolyalkylene glycol methacrylates, such as methoxypolyethylene glycol methacrylates, ethoxypolyethylene glycol methacrylates, methoxypolypropylene glycol methacrylates, methoxypolyethylene glycol-polypropylene glycol 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-methacryloyloxypropyltrimethylsilane, phosphorus-comprising methacrylates, such as alkylene glycol methacrylate phosphates, hydroxyethylimidazolidone methacrylate, hydroxyethylimidazolidinone methacrylate or 2-(2-oxo-1-imidazolidinyl) ethyl methacrylate, acrylonitrile, acrylamide or substituted acrylamides, 4-acryloylmorpholine, N-methylolacrylamide, methacrylamide or substituted methacrylamides, N-methylolmethacrylamide, methacrylamido-propyltrimethylammonium chloride (MAPTAC), glycidyl methacrylate, dicyclopentenyloxyethyl 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 methoxypoly (ethylene glycol) vinyl ether or poly (ethylene glycol) divinyl ether, olefinic monomers, among which may be mentioned ethylene, butene, hexene and 1-
octene, 1,1-diphenylethylene, diene monomers, including butadiene or isoprene, as well as fluoroolefinic monomers and vinlylidene monomers, among which may be mentioned vinlylidene fluoride, alone or as a mixture.

Indeed, while wishing to maintain a value of the product $X_{\text{effective}} \times N$ in the range of between 10.5 and 40, preferably between 15 and 30 and even more preferably between 17 and 25, it is sometimes necessary to use several monomers, typically two, in one or more blocks when particular periods are targeted.

The term "period" is intended to mean the mean minimum distance separating two neighbouring domains having the same chemical composition, separated by a domain having a different chemical composition.

Typically, in the case of a diblock copolymer which is a preference in the context of the process that is the subject of the invention, it will be possible for example to consider a structure A-b-(B-co-C) wherein the block A consists of a single monomer A and the block B-co-C itself consists of two monomers B and C, C possibly being A. In the latter case, the structure of the diblock copolymer will be expressed A-b-(B-co-A).

Preferably, A is a styrene compound, more particularly styrene, and B is a (meth)acrylic compound, more particularly methyl methacrylate. C is preferably a styrene derivative, and preferably styrene, an aryl (meth)acrylate or a vinylaryl derivative.

Preferably, and in order to incorporate the monomers into the (B-co-C) block as successfully as possible, the reactive species of the monomers B and C will exhibit a difference in pKa of less than or equal to 2.
This rule is described in Advance in Polymer Science, Vol. 153, Springer-Verlag 2000, p.79: The rule specifies that, for a given type of monomer, the initiator will have to have the same structure and the same reactivity as the propagating anionic species; in other words, the pKa of the conjugated acid of the anion that is propagating will have to correspond closely to the pKa of the conjugated acid of the species that is initiating. If the initiator is too reactive, side reactions between the initiator and the monomer may take place; if the initiator is not reactive enough, the initiating reaction will be slow and inefficient or may not take place.

The ordered film obtained with a composition comprising a block copolymer, this composition having a product between the effective Flory-Huggins parameter denoted $x_{\text{effective}}$ and the total degree of polymerization $N$, $x_{\text{effective}} \cdot N$, of between 10.5 and 40 will be able to contain additional compounds which are not block copolymers provided that this composition in the presence of these additional compounds has a product $x_{\text{effective}} \cdot N$, at the structuring temperature, typically between 10.5 and 40, preferably between 15 and 30 and even more preferably between 17 and 25. They can in particular be plasticizers, among which may be mentioned, without implied limitation, branched or linear phthalates, such as di (n-octyl), dibutyl, di (2-ethylhexyl), di (ethylhexyl), diisononyl, diisodecyl, benzyl butyl, diethyl, dicyclohexyl, dimethyl, di (linear undecyl) or di (linear tridecyl) phthalates, chlorinated paraffins, branched or linear trimellitates, in particular di (ethylhexyl) trimellitate, aliphatic esters or polymeric esters, epoxides, adipates, citrates, benzoates, fillers, among which may be mentioned inorganic fillers, such as carbon black, carbon or non-carbon nanotubes, ground or
unground fibres, (light, in particular UV, and heat) stabilizing agents, dyes, photosensitive inorganic or organic pigments, such as, for example, porphyrins, photoinitiators, that is to say compounds capable of generating radicals under irradiation, polymeric or non-polymeric ionic compounds, taken alone or as a mixture.

In terms of kinetic behaviour of the mixture during the structuring, this means that the composition used in the process which is the subject of the invention will allow faster structuring than a composition having a product $X_{\text{effective}} \cdot N$ greater than 40.

The values of $\chi$ can be calculated from the equations described in Brinke et al, Macromolecule, 1983, 16, 1827-1832.

The process of the invention allows an ordered film to be deposited on a surface such as silicon, the silicon exhibiting a native or thermal oxide layer, germanium, platinum, tungsten, gold, titanium nitrides, graphenes, BARC ("Bottom Anti-Reflective Coating") or any other organic or inorganic anti-reflective layer used in lithography. Sometimes, it may be necessary to prepare the surface. Among the known possibilities, a random copolymer, the monomers of which can be identical in all or part to those used in the composition of block copolymer and/or of the compound which it is desired to deposit, is deposited on the surface. In a pioneering article, Mansky et al. (Science, Vol. 275, pages 1458-1460, 1997) give a good description of this technology, now well known to those skilled in the art. In a manner entirely similar to that described by Mansky et al., the surface may be modified with any other polymer (for example, a homopolymer of the block copolymer described in the context
of this invention) or a copolymer that it will be judged appropriate to use.

The surfaces can be said to be "free" (flat and homogeneous surface, both from a topographical and from a chemical viewpoint) or can exhibit structures for guidance of the block copolymer "pattern", whether this guidance is of the chemical guidance type (known as "guidance by chemical epitaxy") or physical/topographical guidance type (known as "guidance by graphoepitaxy").

In order to manufacture the ordered film, a solution of the block copolymer composition is deposited on the surface and then the solvent is evaporated according to techniques known to those skilled in the art, such as, for example, the spin coating, doctor blade, knife system or slot die system technique, but any other technique can be used, such as dry deposition, that is to say deposition without involving a predissolution.

A heat treatment or treatment by solvent vapour, a combination of the two treatments, or any other treatment known to those skilled in the art which makes it possible for the block copolymer composition to become correctly organized while becoming nanostructured, and thus to establish the ordered film, is subsequently carried out. In the preferred context of the invention, the curing is carried out thermally, for times of less than 24 h, preferably less than 1 h, and even more preferentially less than 5 minutes, at temperatures below 400°C, preferably below 300°C and even more preferably below 270°C, but above the Tg of the copolymer(s) constituting the composition, this Tg being measured by differential scanning calorimetry (DSC).
The nanostructuring of a composition of the invention resulting in the ordered film can take the forms such as cylindrical (hexagonal symmetry (primitive hexagonal lattice symmetry "6 mm") according to the Hermann-Mauguin notation, or tetragonal symmetry (primitive tetragonal lattice symmetry "4 mm"), spherical (hexagonal symmetry (primitive hexagonal lattice symmetry "6 mm" or "6/mmm"), or tetragonal symmetry (primitive tetragonal lattice symmetry "4 mm"), or cubic symmetry (lattice symmetry "m3m")), lamellar or gyroidal. Preferably, the preferred forms taken by the nanostructurings are of hexagonal cylindrical or lamellar type.

This nanostructuring may exhibit an orientation parallel or perpendicular to the substrate. Preferably, the orientation will be perpendicular to the substrate.

The invention also relates to the ordered films thus obtained that can be used in particular as masks in the lithography field and also to the masks obtained.

**Example n°1**

All the block copolymers were synthesized according to WO2015/011035.

**Determination of χ and χ_{eff} for Block copolymers (BCPs) involved in the study :**

- **PS-β-PMMA BCPs:**

  The χ parameter for PS-β-PMMA system was measured experimentally in Y. Zhao & al., *Macromolecules*, 2008, 41 (24), pp 9948-9951, its value is given by the equation (1):

  \[ \chi_{SM} = 0.0282 + (4.46/T) \]

  where « T » is the self assembly process temperature.
Thus at 225°C for instance, $\chi_{\text{eff}} \approx 0.03715$.

- PS-6-P (MMA-co-S) BCPs:

From G. ten Brinke et al., *Macromolecules*, 1983, 16, 1827-1832, for a diblock copolymer where only one of the block is constituted of two different comonomers, written as "A-b-(B-co-C)", the Flory-Huggins parameter of this system, written as "$\chi_{\text{eff}}$", can be determined by the formula (2):

$$\chi_{\text{eff}} = b^2 x_{BC} + b(x_d - x_{AC} x_{BC}) + x_{AC}$$

where:

- $\langle a \rangle$, $\langle b \rangle$, $\langle c \rangle$, are the volumic fraction corresponding to each monomer in the block copolymer (for instance, $\langle b \rangle$ is the volumic fraction of "B" monomer)
- $\langle x_{AB} \rangle$, $\langle x_{AC} \rangle$, $\langle x_{BC} \rangle$ are the respective Flory-Huggins interaction parameter between each relative monomers in the block copolymer (i.e. $\chi_{AB}$ represent the interaction between the monomers A and B)

In the particular case where monomer "C" is the same than the one denoted "A" in the BCP formula, then (2) is simplified in:

$$\chi_{\text{eff}} = b^2 x_{AB}$$

Since the relation (4) $b = (1 - c)$ is true, then equation (3) turns also to:

$$\chi_{\text{eff}} = (1 - c)^2 \chi_{AB}$$

Thus in this particular case the $\chi_{\text{eff}}$ parameter is a function of only the volumic fraction of the added co-monomer "C" in the modified block, in the notation "A-b-(B-co-C)" as compared to the simplest "A-b-B" one, and the initial $\chi$ parameter between monomers "A" and "B".

By analogy to the system of interest noted "PS-b-P (MMA-co-S)", the relation (5) becomes:
(6) \( \chi_{\text{eff}} = (1 - S)^2 \chi_{\text{SM}} \)

Where «s» is the volumic fraction of styrene monomer introduced in the initial PMMA block, and \( \chi_{\text{SM}} \) is the classical Flory-Huggins interaction parameter between styrene and methylmethacrylate blocks.

By progressively varying the styrenic fraction in the MMA block, and combining the relations (1) and (6), the \( \chi_{\text{eff}} \) parameter is known for each value of the self-assembly temperature. The following table (Table 1) gathers these as-calculated values of \( \chi_{\text{eff}} \) for each point of interest in the styrene fraction versus self-assembly temperature matrix.

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Volumic fraction of styrene in the (MMA-co-S) block
Table 1: Value of $\chi_{\text{eff}}$ for the BCP "PS-b-P (MMA-co-S)" system, calculated for specific values of styrene volumic fraction and self-assembly temperature.

From the Table 1, the variation of the $\chi_{\text{eff}}$ parameter as a function of the styrene volumic fraction and for a specific temperature can be plotted on a graph as in figure 2, for a better understanding and representation and witch represents values of $\chi_{\text{eff}}$ for a "PS-b-P (MMA-co-S)" system extracted from Table 1 for a particular temperature (225°C) across the whole possible range of styrene volumic fraction.

Example n° 2

Extraction and calculus of $\chi N$ or $\chi_{\text{eff}} N$ values for synthesized BCPs in the context of the invention:

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<th>BCP architecture</th>
<th>BCP reference n°</th>
<th>Period (h)</th>
<th>$M_p$ (kg/mol)</th>
<th>$%$ PS</th>
<th>$%$ PMMA</th>
<th>$%$ in (MMA-co-S) (%)</th>
<th>$N$ (°)</th>
<th>$\chi_{\text{eff}}$ (°)</th>
<th>$\chi_{\text{eff}}N$ value</th>
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<td>A</td>
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<td>136</td>
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<td>898</td>
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<td>(220°C)</td>
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</table>
Table 2: Molecular characteristics of BCPs used in the examples (a) determined from SEM experiment; (b) determined by SEC using standard PS; (c) determined by $^1$H NMR; (d) determined from Mp; (e) extracted from Table 1).

For more clarity, BCPs "C" and "D" are synthesized within the invention, whereas BCPs "A" and "B" are references BCPs presenting respectively the same dimensions (see column "period") than "C" and "D" but synthesized out of the scope of the invention (standard PS-fc-PMMA BCPs taken for the direct comparison with modified ones).

This example illustrate how the invention can be used to tailor an "initial" $\chi$N product of given BCPs (i.e. the ones of references BCPs "A" and "B") toward a range of more appropriated values selected as regard to the associated dimension (period) of the system.

Example n°3

Realization of typical BCP thin film:

Underlayer powder of appropriate composition and constitution is dissolved in a good solvent, for instance propylene glycol monomethylether acetate (PGMEA), in order to get a 2% by mass solution. The solution is then coated to dryness on a cleaned substrate (i.e. silicon) with an appropriate technique (spin coating, blade coating ... known in the state of the art) in order to get a film thickness of around 50nm to 70nm. The substrate is then baked under an appropriate couple of temperature and time (i.e. 200°C during 75 seconds, or 220°C during 10 minutes) in order to ensure the chemical grafting of the underlayer material onto the substrate; the non-grafted material is then washed away from the substrate by a rinse-step in a good solvent, and the functionalized the substrate is blown-dried under a
nitrogen (or another inert gas) stream. In the next step, the BCP solution (typically 1% or 2% by mass in PGMEA) is coated on the as-prepared substrate by spin coating (or any other technique known in the state of the art) in order to get a dry film of desired thickness (typically few tens of nanometer). The BCP film is then baked under an appropriate set of temperature and time conditions (for instance 220°C during 5 minutes, or any of the other temperatures reported in the Table 2, or by using any other technique or combination of techniques known in the state of the art) in order to promote the self-assembly of the BCP. Optionally, the as-prepared substrate can be immersed in glacial acetic acid during few minutes, then rinsed with deionized water, and then submitted to a mild oxygen plasma during few seconds, in order to enhance the contrast of the nanometric features for SEM characterizations.

One can notice that in the following experiments and examples, the underlayer material is selected so as to be "neutral" for the studied block copolymer (i.e. so that it is able to balance the interfacial interaction between the substrate and the different blocks of the BCP material, to get a non-preferential substrate as regard to the different blocks chemistries) in order to get a perpendicular orientation of the BCP features.

In the following examples, the BCP films are characterized through SEM-imaging experiments with a CD-SEM (Critical Dimensions Scanning Electron Microscope) tool "H-9300" from Hitachi. Pictures are taken at constant magnification (appropriated for the dedicated experiment: for instance defectivity experiments are performed at magn. *100 000 to get enough statistics, whereas critical dimensions (CD) ones are performed at magn. *200 000 or magn. *300 000 to get a
better precision in the dimensions) in order to allow a
careful comparison of the different BCP materials.

**Example n°4**

The figure 3 and figure 4 gather the raw CD-SEM results
obtained for the comparison of different BCPs systems of
interest, under various self-assembly conditions.

Figure 3 : Example of raw CDSEM pictures obtained for BCP
systems of ~52nm period, for various film thicknesses and
the best self-assembly process temperature for each BCP
(250°C for PS-b-PMMA, 220°C for PS-b-P (MMA-co-S ),
respectively).

The figure 3 is dedicated to the comparison of the PS-b-PMMA
and PS-b-P (MMA-co-S) systems of 52nm period. The film
thickness are targeted to be either the same (i.e. 70nm) and
different for the two systems, and the self-assembly
temperature is chosen to be best known one for each BCP (i.e.
the couple bake temperature/bake time is chosen so as to get
the maximum of perpendicular cylinders for each BCP system).

Figure 4 : Example of raw CDSEM pictures obtained for BCP
systems of ~44nm period, for various film thicknesses and a
self-assembly temperature of 220°C.

The figure 4 is dedicated to the comparison of the PS-b-PMMA
and PS-b-P (MMA-co-S) systems of 44nm period. The comparison
is performed for the same film thicknesses (i.e. 35 and 70nm)
or different ones, and for the same self-assembly process
(self-assembly bake temperature 220°C during 5minutes) for
a direct comparison of the two systems.
The various SEM images acquired for each BCPs under the various experimental conditions were treated with appropriate softwares already well described in the existing literature (see for instance X. Chevalier & al., Proc. SPIE 9049, Alternative Lithographic Technologies VI, 90490T (March 27, 2014); doi:10.1117/12.2046329), in order to extract their corresponding coordination defect-level of interest in the frame of the present invention. The extraction process for each picture is depicted in the figure 5 as a reminder.

Figure 5 : Example of a SEM picture treatment to extract its defectivity level : the raw SEM image (left) is first binarized (middle) and then treated so as to detect each cylinder and its direct environment. Cylinders presenting more or less than six neighbors are counted as a defect, whereas those having exactly 6 neighbors are counted as good ones.

The CD-SEM pictures treatment results are gathered in the Table 3 below, with the corresponding associated experimental processing parameter. Each defect-level value is determined through the treatment of 10 different picture for the associated conditions, randomly chosen on the sample.
Table 3: Experimental parameters followed for the self-assembly of each BCP depicted in the figure 3 and figure 4, and their respective defectivity measurement associated (each value of defect percentage is a mean obtained from the treatment of 10 different CDSEM pictures).

The various results gathered in the Table 3, figure 6 and figure 7, allow the careful comparison of the different BCP systems in the frame of the invention:

- The figure 6 compares defectivity results obtained for the systems having ~52nm period; the film thicknesses taken at ~70nm for the two systems clearly indicate that the self-assembly quality is much better thanks to a lower defect level in the case of the system "PS-b-P (MMA-co-S)", relevant for the invention, as compared to the "PS-b-PMMA" one. This is valid even if the self-assembly conditions (i.e. bake temperature) are not strictly the same.
The figure 6 is a Graphical representation of the defectivity measurements corresponding to BCPs "A" and "C" of 52nm period reported in the Table 3. It illustrates the better quality for the self-assembly of PS-b-P (MMA-co-S) system as compared to the one of PS-fc-PMMA, even for very thick films.

The figure 7 compares the defectivity results obtained for BCPs having a ~44nm period; in this case, the two different systems can be directly compared through the same film thicknesses (35 and 70nm) and self-assembly conditions (bake temperature at 220°C during 5 minutes) experimentally used. In this case again, the measurement indicates a much better self-assembly quality for the "PS-b-P (MMA-co-S)" system relevant for the invention through a lower defectivity value as compared to the PS-fc-PMMA system.

The Figure 7 is a Graphical representation of the defectivity measurements corresponding to BCPs "B" and "D" of 44nm period reported in the Table 3, for the same self-assembly parameters (self-assembly bake at 220°C during 5 minutes). It illustrates the better quality for the self-assembly of PS-b-P (MMA-co-S) system as compared to the one of PS-fc-PMMA, for the same film thicknesses of thicker films.

Even if the conditions are not identical ones, the figures 6 and 7 both indicate lower defectivity values the systems in the frame of the invention, independently of the film thickness used (i.e. all the defectivity values are lower
for the "PS-b-P (MMA-co-S)" system than for the PS-fc-PMMA one, whatever the film thickness is).

In the particular cases where films thicknesses are identical (for the respective periods, 52nm and 44nm), the graphs and Table 3 indicate a lower defectivity values for the BCP under the frame of the invention (not only for these specific thicknesses as written above, but the following example does consider only the same thicknesses for the demonstration) .

For a particular film thickness, it is well stated now (see for instance W. Li & al., Macromolecules , 2010, 43, 1644-1650.) that the correlation length ("E") (equivalent to the defect concentration) follows a power law as function of self-assembly time ("t") as: $E \propto t^{(1/3)}$. Thus, it means that at constant film thickness, if a system presents a higher defect concentration than another one [of same dimension, of course], it will need more annealing time so as to reach the same defect level than this former system. In other words, the system with a lower defect level presents a better self-assembly kinetic, or, for a given defect level, is able to reach this defect level for a shorter self-assembly annealing time. Therefore, as the two systems of type PS-b-P (MMA-co-S) relevant for the invention do present lower defect levels for the same self-assembly time than classical PS-b-PMMA ones, these systems of interest are able to reduce the self-assembly time initially required for a PS-b-PMMA to reach a specific defect value.

These two different graphs (figure 6 and figure 7) clearly highlight that the BCPs under the frame of the invention (i.e. "PS-b-P (MMA-co-S)" like systems) allow to generate thicker films with lower defect levels, and for shorter self-assembly annealing time, than those achievable with classical systems like PS-b-PMMA one.
When the figure 6 and figure 7 are combined with the $\chi^*N$ or $\chi_{eff}^*N$ value for the corresponding BCP reported in the Table 2, it clearly highlights the meaningfulness of the control the $\chi^*N$ value for electronic applications, through the architecture and modification of the BCP under the frame of the present invention, i.e. a form « $A-b-(B-co-C)$ » or « $A-b-(B-co-A)$ » (like in the PS-$b$-P (MMA-co-S) example) for the BCP instead of the classical "A-b-B" one. In other words, the control of $\chi^*N$ or $\chi_{eff}^*N$ value through the architecture modification (like in the PS-fc-P (MMA-co-S)) allows to self-assemble the nano-features under shorter bake times than those reported for the non-modified systems.
Claims

1. Process which makes it possible to reduce the structuring time of ordered films of a composition comprising a di-block copolymer on a surface, comprising the following steps:

- mixing a composition comprising a di-block copolymer in a solvent, in which the diblock copolymer has a structure A-b-(B-co-C) wherein the block A consists of a single monomer A, the block B-co-C itself consisting of two monomers B and C, C possibly being A, this composition exhibiting a product \( \text{X} \text{effective} \times N \) of between 10.5 and 40 at the structuring temperature once the solvent has been evaporated off,
- depositing this mixture on a surface,
- curing the mixture deposited on the surface at a temperature between the highest \( T_g \) of the block copolymer(s) and their decomposition temperature such that the composition can organize itself after evaporation of the solvent.

2. Process according to Claim 1, in which A and C are styrene, and B is methyl methacrylate.

3. Process according to Claim 1, in which the block copolymer is synthesized anionically.

4. Process according to Claim 1, in which the block copolymer is prepared by controlled radical polymerization.

5. Process according to Claim 4, in which the block copolymer is prepared by nitroxide-mediated radical polymerization.
6 Process according to Claim 5, in which the block copolymer is prepared by N-tert-butyl-l-diethylphosphono-2,2-dimethylpropyl nitrooxide-mediated radical polymerization.

7 Process according to one of Claims 1 to 6, in which the orientation of the ordered film is perpendicular to the surface.

8 Ordered film obtained according to the process of one of Claims 1 to 7, which can be used in particular as masks in the lithography field.

9 Mask obtained from an ordered film according to Claim 8.
Figure 1:

Composition variation of FB inside block (B-co-C)
As a function of comonomer proportion B (fB)

Figure 2:

Volume fraction of styrene in the (MMA-co-S) block

\( \gamma_{\text{eff. value}} \) vs. Volume fraction
Figure 3

Block copolymer film thickness

70nm

35nm

25nm

PS-b-PMMA

Block copolymer film thickness

70nm

50nm

PS-b-P(MMA-co-S)
Figure 6

Figure 7
A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G03F B82Y C09D C08L

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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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search: 6 March 2017

Date of mailing of the international search report: 15/03/2017

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) 340-3018

Authorized officer: Eggers, Kari

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