[0043] Finally, a subject of the disclosure is a polymeric stack comprising at least two polymer layers stacked one on the other, characterized in that the upper layer, known as the top coat, deposited on the first polymer layer is obtained by in situ crosslinking in accordance with the method described above, said stack being intended to be used in applications selected from the production of coatings for the aerospace or aeronautical or motor vehicle or wind turbine sector, inks, paints, membranes, biocompatible implants, packaging materials, or optical components, such as optical filters, or microelectronic or optoelectronic or microfluidic components.

[0043a] In another aspect, there is provided a polymeric stack comprising at least two polymer layers (20, 30) stacked one on the other, wherein the upper layer (30), known as the top coat (TC), deposited on the first polymer layer (20) is in the form of a prepolymer composition, denoted pre-TC, comprising one or more monomer(s) and/or a dimer(s) and/or an oligomer(s) and/or a polymer(s) in solution, and the pre-TC is subjected to a heat treatment in order to cause a crosslinking reaction that takes place *in situ*, within the deposited pre-TC prepolymer layer, and generate a TC polymer of a high molecular mass by the crosslinking reaction of constituent molecular chains of the deposited prepolymer layer, and the first polymer layer (20) is deposited on a thickness (e+E) at least equal to 1.5 times the minimum thickness of the block copolymer, said stack being intended to be used in applications selected from the production of coatings for the aerospace or aeronautical or motor vehicle or wind turbine sector, inks, paints, membranes, biocompatible implants, packaging materials, or optical components, such as optical filters, or microelectronic or optoelectronic or microfluidic components.

[0044] More particularly, this stack is intended for applications in the field of directed self-assembly nanolithography, the first polymer layer is a block copolymer and the surfaces of the layer onto which the block copolymer is deposited and of the top coat layer have a neutral surface energy with respect to the blocks of the block copolymer.

[0045] Other features and advantages of the disclosure will become apparent upon reading the description given by way of illustrative and non-limiting example, with reference to the appended figures, which represent:

- Figures 1A to 1C, already described, diagrams viewed in the cross section of various polymer stacks and their evolution over time,
- Figure 2, already described, a diagram viewed in the cross section of a stack of polymers according to the invention, which does not undergo any dewetting or inter-diffusion phenomena,

- Figure 3, a diagram viewed in the cross section of a stack according to the invention dedicated to an application in directed self-assembly (DSA) nanolithography for the production of a nanolithography mask,
- Figure 4, the evolution of the residual thickness of PGFH copolymer crosslinked by heat treatment as a function of the thermal annealing,
- Figure 5, images obtained by scanning electron microscopy, of self-organized block copolymer samples, for different PGFH top coat compositions used, the top coat having been crosslinked by heat treatment,
- Figure 6, the evolution of the residual thickness of a PGFH copolymer, previously crosslinked by heat treatment, when it is subjected to a plasma, as a function of the plasma times,
- Figure 7, the main steps of an image processing to extract the areas of interest: a) raw CDSEM image (512x512 pixels, 13495nmx13495nm); b) contrasting image; c) thresholded image (the white areas correspond to the areas with dewetting); d) extraction of the outline and the corresponding area of each white area of the image c),

CLAIMS

1. A method for manufacturing a flat polymeric stack, method consisting in depositing on a substrate (10) a first layer (20) of non-crosslinked (co)polymer, and then a second layer (30) of (co)polymer, at least one of the (co)polymer layers initially being in a liquid or viscous state, said method being characterized in that, at the time of the deposition of the upper layer (30) on the first layer (20), the upper layer is in the form of a prepolymer composition (pre-TC), comprising one or more monomer(s) and/or dimer(s) and/or oligomer(s) and/or polymer(s) in solution, and wherein an additional step consists in submitting said upper layer (30) to a heat treatment, capable of causing a crosslinking reaction of the molecular chains within said prepolymer layer (30, pre-TC) and allowing the production of a crosslinked top coat (TC) layer.

2. The method according to Claim 1, wherein the heat treatment consists in heating the stack in a temperature range between 20 and 150°C, for a time preferably less than 15 minutes, more preferably less than 10 minutes and even more preferably less than 5 minutes.

3. The method according to Claim 1, wherein the prepolymer composition (pre-TC) is a composition formulated in a solvent, or used without solvent, and which comprises at least one monomer, dimer, oligomer or polymer chemical species, or any mixture of these various species, of totally or partly identical chemical nature, and each including at least one chemical function capable of ensuring the crosslinking reaction under the effect of a heat stimulus.

4. The method according to Claim 1, wherein the prepolymer composition (pre-TC) also comprises a heat-activatable catalyst, chosen from radical generators, or acid generators, or base generators.

5. The method according to Claim 1, wherein at least one of the chemical species of the prepolymer composition contains at least one fluorine and/or silicon and/or germanium atom, and/or an aliphatic carbon-based chain of at least two carbon atoms in its chemical formula.

6. The method according to Claim 1, wherein when the crosslinking is performed via a radical route, the prepolymer composition (pre-TC) also comprises a heat-activatable catalyst, chosen from derivatives of organic peroxide type, or alternatively derivatives including a chemical function of azo type such as azobisisobutyronitrile, or alternatively derivatives of alkyl halide type.

7. The method according to Claim 1, wherein the prepolymer composition comprises a mixture of monomer(s) and/or dimer(s) and/or oligomers(s) and/or polymer(s), preferably comprising epoxy/oxirane functions, and a catalyst for generating an acid and/or a coreagent for performing an addition reaction on the epoxy functions.

8. The method according to Claim 1, wherein the prepolymer composition comprises a mixture of one or more multifunctional acrylic monomer(s), of cyanoacrylate type, which are capable of spontaneously giving rise to a crosslinking reaction at ambient or moderate temperature, in the presence of ambient moisture.

9. The method according to Claim 1, wherein the crosslinking temperature of the layer of prepolymer composition(pre-TC) is below the glass transition temperature Tg of the first polymer layer (20) and wherein the highest glass transition temperature Tg of the first polymer layer (20) is greater than 25°C.

10. The method according to Claim 1, wherein the prepolymer composition (pre-TC) also comprises a solvent chosen from solvents or solvent mixtures whose Hansen solubility parameters are such that $\delta_p \geq 10$ MPa$^{1/2}$ and/or $\delta_h \geq 10$ MPa$^{1/2}$, and with $\delta_d < 25$ MPa$^{1/2}$.

11. The method according to Claim 1, wherein the first polymer layer is a block copolymer (BCP) capable of nanostructuring at an assembly temperature, and wherein prior to the step of depositing the first layer (20) of block copolymer, the method comprises a step of neutralizing the surface of the underlying substrate (10) and wherein, after the step of crosslinking the upper layer (30) to form a crosslinked top coat layer, the method comprises a step of nanostructuring the block copolymer constituting the first layer (20) by subjecting the stack obtained to an assembly temperature, said assembly temperature being lower than a temperature at which the top coat (TC) material behaves like a viscoelastic fluid, said temperature being higher than the glass transition temperature of said top coat material and, preferably, said assembly temperature being lower than the glass transition temperature of the top coat (TC) layer (30) in its crosslinked form

12. The method according to Claim 11, wherein the preliminary step of neutralizing the surface of the underlying substrate (10) consists in predrawing patterns on the surface of the substrate, said patterns being predrawn by a lithography step or a sequence of lithography steps of any nature prior to the step of depositing the first layer (20) of block copolymer (BCP), said patterns being intended to guide the organization of said block copolymer (BCP) by a technique known as chemical epitaxy or graphoepitaxy, or a

combination of these two techniques, in order to obtain a neutralized or pseudo-neutralized surface.

13. The method according to Claim 11, wherein the block copolymer comprises silicon in one of its blocks.

14. The method according to Claim 11, wherein when the prepolymer composition comprises a mixture of one or more multifunctional acrylic monomer(s), of cyanoacrylate type, the crosslinking temperature of the layer of prepolymer composition (pre-TC) is below the highest glass transition temperature Tg of the block copolymer (BCP) layer (20) and the block copolymer has at least one block for which at least 40% of the composition has a glass transition temperature of greater than 25°C.

15. The method according to Claim 11, wherein the first block copolymer (BCP) layer (20) is deposited on a thickness (e+E) at least equal to 1.5 times the minimum thickness of the block copolymer.

16. A method for manufacturing a nanolithography mask by directed assembly of block copolymers, said method comprising the steps according to Claim 11, and wherein after the step of nanostructuring the block copolymer constituting the first layer (20), an additional step consists in removing the top coat (TC) layer in order to leave a film of nanostructured block copolymer of a minimum thickness (e), and then at least one of the blocks (21, 22) of said block copolymer, oriented perpendicular to the interfaces, is removed in order to form a porous film suitable for use as a nanolithography mask.

17. The method for manufacturing a nanolithography mask according to Claim 16, wherein when the block copolymer is deposited to a thickness greater than the minimum thickness (e), an overthickness (E) of said block copolymer is removed simultaneously with or successively to the removal of the top coat (TC) layer (30), so as to leave a film of nanostructured block copolymer of a minimum thickness (e), and then at least one of the blocks of said block copolymer, oriented perpendicular to the interfaces, is removed so as to form a porous film that is capable of serving as a nanolithography mask.

18. The method for manufacturing a nanolithography mask according to Claim 16, wherein, at the time of the step of crosslinking the top coat (TC) layer (30), the stack is subjected to localized heat treatment, on some areas of the top coat layer, so as to create crosslinked top coat (TC) areas having a neutral affinity with respect to the underlying block

copolymer and non-crosslinked (pre-TC) areas having a non-neutral affinity with respect to the underlying block copolymer.

19. The method for manufacturing a nanolithography mask according to Claim 16, wherein another prepolymer material, which is not neutral with respect to the underlying block copolymer, is deposited in the areas which have not been heat-treated beforehand and which are free of a top coat layer, then said non-neutral prepolymer material is subjected to a localized heat treatment so as to crosslink it in the predefined places, and wherein, at the moment of the step of annealing the stack at the assembly temperature (Tass) of the block copolymer (BCP), nanodomains (20, 21, 41, 42) are formed perpendicular to the interfaces in areas facing the areas of the neutral crosslinked top coat (TC) layer, and nanodomains are formed parallel to the interfaces in areas of the block copolymer facing the areas free of crosslinked neutral top coat layer.

20. A polymeric stack comprising at least two polymer layers (20, 30) stacked one on the other, wherein the upper layer (30), known as the top coat (TC), deposited on the first polymer layer (20) is in the form of a prepolymer composition, denoted pre-TC, comprising one or more monomer(s) and/or a dimer(s) and/or an oligomer(s) and/or a polymer(s) in solution, and the pre-TC is subjected to a heat treatment in order to cause a crosslinking reaction that takes place *in situ*, within the deposited pre-TC prepolymer layer, and generate a TC polymer of a high molecular mass by the crosslinking reaction of constituent molecular chains of the deposited prepolymer layer, and the first polymer layer (20) is deposited on a thickness (e+E) at least equal to 1.5 times the minimum thickness of the block copolymer, said stack being intended to be used in applications selected from the production of coatings for the aerospace or aeronautical or motor vehicle or wind turbine sector, inks, paints, membranes, biocompatible implants, packaging materials, or optical components, such as optical filters, or microelectronic or optoelectronic or microfluidic components.