- underlying block copolymer and non-crosslinked areas having a non-neutral affinity with respect to the underlying block copolymer;
- after the localized photo-crosslinking of the top coat layer, the stack is rinsed with the solvent which allowed the deposition of the prepolymer layer so as to remove the non-irradiated areas:
- another prepolymer material, which is not neutral with respect to the underlying block copolymer, is deposited in the areas which have not been irradiated beforehand and which are free of a top coat layer, and then said non-neutral prepolymer material is exposed to a stimulus so as to crosslink it in the predefined places;
- at the moment of the step of annealing the stack at the assembly temperature of the block copolymer, nanodomains are formed perpendicular to the interfaces in areas facing the areas of the neutral crosslinked top coat 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.

[0039] Finally, a subject of the disclosure is a polymeric stack deposited on a substrate and comprising at least two (co)polymer layers stacked one on the other, characterized in that the upper layer, known as the top coat, deposited on the first (co)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 surface protection for the aerospace or aeronautical or motor vehicle or wind turbine sector, paints, inks, the manufacture of membranes, the production of microelectronic, optoelectronic, or microfluidic components.

[0039a] In yet 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 to take 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, paints, inks, membranes, biocompatible implants, packaging materials, or optical components, such as optical filters, or microelectronic or optoelectronic or microfluidic components.

[0040] More particularly, this stack is intended for applications in the field of directed self-assembly nanolithography, the first (co)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 preferably have a neutral surface energy with respect to the blocks of the block copolymer.

[0041] 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 phnenomena,
- 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,

CLAIMS

1. A method for manufacturing a flat polymeric stack, said 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 in that an additional step consists in submitting said upper layer (30) to a stimulus, selected from plasma, ion bombardment, electrochemical process, chemical species, light radiation, 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 prepolymer composition (pre-TC) comprises a solvent, said solvent being selected so as to be entirely “orthogonal” to the polymeric system of the underlying layer.

3. The method according to Claim 1, wherein at least one of the chemical entities of the prepolymer composition has 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.

4. The method according to Claim 1, wherein said prepolymer composition (pre-TC) also comprises in its formulation:

- a chemical entity selected from an antioxidant, a weak acid or base, able to trap said chemical entity capable of initiating the crosslinking reaction, and/or
- one or more additives for improving the wetting and/or the adhesion, and/or the uniformity of the upper top coat (TC) layer (30) deposited on the underlying layer (20), and/or
- one or more additives for absorbing one or more ranges of light radiations of different wavelengths, or for modifying the electrical conductivity properties of the prepolymer (pre-TC).

5. The method according to Claim 1, wherein the first (co)polymer layer (20) comprise a block copolymer (BCP) and the top coat layer (30) have a neutral surface energy with respect to the blocks of the block copolymer.

6. The method according to Claim 1, wherein the first (co)polymer layer (20) comprise a block copolymer (BCP) able to nanostructure at an assembly temperature Tass, the assembly temperature Tass of the block copolymer 20 being lower than a temperature at which the top coat TC in its crosslinked form material behaves as a viscoelastic fluid, preferably lower than the glass transition temperature Tg of the top coat TC layer 30 in its crosslinked form.

7. The method according to Claim 1, wherein the prepolymer layer (30, pre-TC) comprise constituent monomer(s) and/or dimer(s) and/or oligomer(s) and/or polymer(s) selected from acrylate or diacrylate or triacrylate or multi-acrylate, methacrylate, or multi-methacrylate, or polyglycidyl or vinyl, fluoroacrylate or fluoromethacrylate, vinyl fluoride or fluorostyrene, alkyl acrylate or methacrylate, hydroxyalkyl acrylate or methacrylate, alkylsilyl acrylate or methacrylate derivatives, unsaturated esters/acids such as fumaric or maleic acids, vinyl carbamates and carbonates, allyl ethers, and thiol-ene systems.

8. The method according to Claim 1, wherein the first polymer layer (20) is a block copolymer (BCP) capable of nanostructuring at an assembly temperature, in that 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 in that, after the step of crosslinking the upper layer (30) to form a crosslinked top coat layer (TC), 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.

9. The method according to Claim 8, wherein the preliminary step of neutralizing the surface of the underlying substrate (10) consists in predrawing patterns on the surface of the substrate (10), 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.

10. The method according to Claim 8, wherein the first block copolymer (BCP) layer (20) is deposited to a thickness (e+E) at least equal to 1.5 times the minimum thickness (e) of the block copolymer.

11. The method according to Claim 2, wherein the solvent of the prepolymer layer (pre-TC) is selected from solvents or solvent mixtures, the Hansen solubility parameters of which 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$^{1/2}$.

12. The method according to Claim 11, wherein the solvent of the prepolymer layer (pre-TC) is selected from alcohols such as methanol, ethanol, isopropanol, 1-methoxy-2-propanol, ethyl lactate, diols such as ethylene glycol or propylene glycol, or from dimethyl sulfoxide (DMSO), dimethylformamide, dimethylacetamide, acetonitrile, gammabutyrolactone, water, or a mixture thereof.

13. The method according to Claim 1, wherein the composition of the prepolymer layer (pre-TC) comprises a multi-component mixture of monomers and/or dimers and/or oligomers and/or polymers each bearing functions ensuring crosslinking, and also different monomer units, the surface energies of which vary from one monomer unit to another.

14. The method according to Claim 1, wherein the composition of the prepolymer layer (pre-TC) also comprises plasticizers and/or wetting agents, added as additives.

15. The method according to Claim 1, wherein the composition of the prepolymer layer (pre-TC) also comprises rigid comonomers selected from derivatives including either one or more aromatic ring(s) in their structure, or monocyclic or polycyclic aliphatic structures, and having one or more chemical function(s) adapted to the crosslinking reaction targeted; and more particularly derivatives of norbornene, isobornyl acrylate or methacrylate, styrene, anthracene, adamantyl acrylate or methacrylate.

16. A method for manufacturing a nanolithography mask by directed assembly of block copolymers, said method comprising the steps according to Claim 5 and being characterized in that after the step of nanostructuring the block copolymer constituting the first layer (20), an additional step consists in removing the top coat layer (TC) 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 layer (30, TC), 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 suitable for use 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 layer (30, TC), the stack is subjected to light radiation and/or an electron beam localized 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 areas (pre-TC) having a non-neutral affinity with respect to the underlying block copolymer, and that after the localized photo-crossslinking of the top coat layer (30, TC), the stack is rinsed with the solvent which allowed the deposition of the prepolymer layer (pre-TC) so as to remove the non-irradiated areas, and another prepolymer material, which is not neutral with respect to the underlying block copolymer, is deposited in the areas which have not been irradiated beforehand and which are free of a top coat layer, and then said non-neutral prepolymer material is exposed to a stimulus so as to crosslink it at the predefined places.

19. The method for manufacturing a nanolithography mask according to Claim 16, wherein at the time 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 layer (TC), and nanodomains are formed parallel to the interfaces in areas of the block copolymer facing the areas free of a 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, paints, inks, membranes, biocompatible implants, packaging materials, or optical components, such as optical filters, or microelectronic or optoelectronic or microfluidic components.