leads to a PS matrix with a thicker film. The mask thus obtained allows transferring patterns, by chemical etching, to an underlying substrate with high resolution, a large form factor and low roughness. Such wet etching is described, for example, in the publication entitled "Nanoscopic Templates from Oriented Block Copolymer Films", by T. Thurn–Albrecht, R. Steiner, J. DeRouchey, C. M. Stafford, E. Huang, M. Bal, M. Tuominen, C. J. Hawker, and T. P. Russell, *Advanced Materials*, vol. 12, no. 11, p. 787–791, 2000.

However, although we now know how to selectively remove the PMMA blocks from an irradiated PS–PMMA block copolymer to obtain a residual PS film usable as a nanolithography mask, the application has observed that this mask remains limited, since it does not permit creating several different and localized patterns to be transferred.

SUMMARY

The disclosure thus aims to remedy at least one of the disadvantages of the prior art. The disclosure especially aims to design nanolithography masks, said masks being based on PS–b–PMMA block copolymers, by selectively removing different blocks from the block copolymer so as to create different patterns on the same mask with high resolution, located in different places on the mask.

The solution proposed by the present disclosure responds to all these criteria and permits designing dedicated masks for block copolymers in which areas are locally defined to create different patterns.

In ~~an aspect~~the present disclosure, there is provided a manufacturing method for nanolithography masks from a PS–b–PMMA block copolymer film deposited on a surface to be etched, said copolymer film comprising PMMA nanodomains orientated perpendicularly to the surface to be etched, said process being characterized in that it comprises the following steps:

– partially irradiating said copolymer film to form a first irradiated area and a second non–irradiated area in said copolymer film, then

– treating the copolymer film in a developer solvent to selectively remove at least said PMMA nanodomains of said first irradiated area of said copolymer film.

In an aspect, there is provided a manufacturing method for nanolithography masks from a PS–b–PMMA block copolymer film deposited on a surface to be etched, said surface having been previously covered by a neutralizing layer, said copolymer film comprising PMMA nanodomains orientated perpendicularly to the surface to be etched, said method being characterized in that it comprises the following steps:

– partially irradiating (E1) said copolymer film to form irradiated areas and non–irradiated areas in said copolymer film, then

– treating (E2) said copolymer film in a developer solvent previously selected to selectively remove one or more nanodomains of said block copolymer film, said nanodomains being of different chemical composition, irradiated and/or non-irradiated, the selective removal consisting of removing at least said PMMA nanodomains of said irradiated areas of said copolymer film, said developer solvent being chosen among solvents or solvent mixtures having Hansen solubility parameters, calculated at 25°C, comprised within the following value ranges: $14.5 \leq \delta_D \leq 19.00$; $4.90 \leq \delta_P \leq 18.00$ and $5.10 \leq \delta_H \leq 15.26$.

In another ~~aspect~~embodiment, there is provided a developer solvent used in the manufacturing method of a nanolithography mask as defined above, said mask being created from a film of PS–b–PMMA block copolymer, said developer solvent being able to selectively remove at least the previously irradiated PMMA blocks, said solvent being characterized in that it is chosen from a group of solvents or solvent mixtures that includes at least one compound chosen from among alcohols, such as methanol, ethanol, isopropyl alcohol, butan–1–ol, octan–1–ol, (R, S)–octan–2–ol, 4–methyl–2–pentanol, or 2–ethylhexanol.

In another aspect, there is provided a developer solvent when used in the manufacturing method of a nanolithography mask as defined above, said mask being created from a film of PS–b–PMMA block copolymer, said developer solvent being able to selectively remove at least the previously irradiated PMMA blocks, said solvent being characterized in that it is selected depending on the nanodomains, of different chemical composition, irradiated and/or non irradiated, to be selectively removed of said copolymer film, and in that it is chosen among solvents or solvent mixtures having Hansen solubility parameters, calculated at 25°C, comprised within the following value ranges: $14.5 \leq \delta_D \leq 19.00$; $4.90 \leq \delta_P \leq 18.00$ and $5.10 \leq \delta_H \leq 15.26$.

In a further ~~aspect~~embodiment, there is provided a nanolithography mask obtained from a PS–b–PMMA block copolymer film deposited on a surface to be etched, said copolymer film comprising PMMA nanodomains orientated perpendicularly to the surface to be etched, said mask being characterized in that it comprises at least one previously irradiated residual polystyrene PS block, said at least one residual block being obtained after treatment in a developer solvent, such

as described as defined above, of said previously and partially irradiated copolymer film.

In another aspect, there is provided a nanolithography mask deposited on a surface to be etched from a PS–b–PMMA block copolymer film comprising PMMA nanodomains orientated perpendicularly to the surface to be etched, said mask being characterized in that it comprises different irradiated and non-irradiated areas into which one or more nanodomains, of different chemical composition, have been removed, by treatment in a developer solvent according to claim 13, letting appear different patterns into said mask.

In yet another embodimentaspect, a PS–b–PMMA block copolymer designed to be used in the method of manufacturing a nanolithography mask as defined above, characterized in that it has a molecular weight comprised between 5,000 $g.mol^{-1}$ and 1,000,000 $g.mol^{-1}$, and preferably comprised between 15,000 $g.mol^{-1}$ and 250,000 $g.mol^{-1}$.

Thus, the fact of partially irradiating the copolymer film allows creating irradiated and non–irradiated areas that have different contrasts, in which the PS and PMMA blocks have different solubility properties. Partially irradiating the film and creating irradiated and non–irradiated areas allows selectively removing one or more irradiated and/or non–irradiated blocks from the film, depending on the developer solvent used. The selective removal of different copolymer blocks, depending on whether or not these blocks are irradiated, then creates different patterns located at different places on the same mask.

CLAIMS

1. A manufacturing method for nanolithography masks from a PS–b–PMMA block copolymer film ~~(20)~~ deposited on a surface ~~(10)~~ to be etched, said surface having been previously covered by a neutralizing layer, said copolymer film comprising PMMA nanodomains ~~(21)~~ orientated perpendicularly to the surface to be etched, said method being characterized in that it comprises the following steps:

– partially irradiating (E1) said copolymer film to form ~~a first~~ irradiated areas and ~~a second~~ non–irradiated areas in said copolymer film, then

– treating (E2) said copolymer film in a developer solvent previously selected to selectively remove one or more nanodomains of said block copolymer film, said nanodomains being of different chemical composition, irradiated and/or non-irradiated, the selective removal consisting of removing at least said PMMA nanodomains ~~(21)~~ of said ~~first~~ irradiated areas of said copolymer film, said developer solvent being chosen among solvents or solvent mixtures having Hansen solubility parameters, calculated at 25°C, comprised within the following value ranges: $14.5 \leq \delta_D \leq 19.00$; $4.90 \leq \delta_P \leq 18.00$ and $5.10 \leq \delta_H \leq 15.26$.

~~2. The method according to claim 1, characterized in that the developer solvent is chosen from a group of solvents or solvent mixtures that includes at least one compound chosen from among alcohols, such as methanol, ethanol, isopropyl alcohol, butan–1–ol, octan–1–ol, (R, S)–octan–2–ol, 4–methyl–2–pentanol, or 2–ethylhexanol.~~

~~3.~~**2.** The method according to claim 1, characterized in that when the treatment step also consists firstly of removing nanodomains of PMMA of irradiated areas and secondly of selectively and partially removing said PMMA nanodomains of said second non–irradiated areas of said copolymer film, so as to form holes whose diameter is less than the diameter of the holes left by removing the PMMA nanodomains of said ~~first~~ irradiated areas, ~~and in that~~ the developer solvent is chosen from a group (G1) of solvents or solvent mixtures that includes at least one compound chosen from among: acetic acid, acetonitrile or dimethylsulfoxide.

~~4. The method according to claim 1, characterized in that the developer solvent is chosen from among solvents or solvent mixtures having Hansen solubility parameters, calculated at 25°C, comprised within the following value ranges: $14.5 \leq \delta_D \leq 19.00$; $4.90 \leq \delta_P \leq 18.00$ and $5.10 \leq \delta_H \leq 15.26$.~~

~~5.~~**3.** The method according to one of claims 1 ~~or 4~~, characterized in that when the treatment step consists firstly of removing nanodomains of PMMA of irradiated areas and secondly of ~~in said developer solvent consists of also~~ removing said ~~second~~ non–irradiated areas of said copolymer film, ~~and in that~~ the developer solvent is chosen from a group (G4) of solvents or solvent mixtures that includes at least one compound chosen from among: ketones, such as acetone or pentan–2–one; amides such as N,N–dimethylformamide, N–methyl–2–pyrrolidone or N,N–dimethylacetamide; lactones such as γ–butyrolactone; or alcohols such as benzyl alcohol.

6.4. The method according to one of claims 1 to 53, characterized in that irradiation is carried out by UV radiation at a dose comprised between 300 $mJ.cm^{-2}$ and 1000 $mJ.cm^{-2}$.

7.5. The method according to claim 64, characterized in that irradiation by UV radiation is performed at a wavelength of 193 nm.

8.6. The method according to one of claims 1 to 53, characterized in that irradiation is carried out by electron beam at a dose comprised between 200 and 1000 $\mu C.cm^{-2}$.

9.7. The method according to one of claims 1 to 53, characterized in that irradiation is carried out by ion implantation at a dose comprised between 3 and 8 kev, and a dose comprised between 3.10^{12} and 2.10^{14} cm^{-2}.

10.8. The method according to claim 97, characterized in that when the implanted ions are hydrogen ions, the energy is preferably 3 kev and the dose is comprised between 1 and 2.10^{14} cm^{-2}; and when the implanted ions are oxygen ions, the energy is preferably 8 kev and the dose is comprised between 3.10^{12} and 10^{13} cm^{-2}.

11.9. The method according to one of claims 4 1 to 108, characterized in that when the radiation dose is close to the maximum value, said group of selected solvents extends to the following compounds (G5): ethyl acetate, dichloromethane, methyl ethyl ketone or propylene glycol monomethyl ether acetate.

12.10. The method according to one of claims 4 1 to 108, characterized in that when the mass fraction of polystyrene PS in the block copolymer is less than or equal to 50%, said group of selected solvents also extends to the following compounds (G3): ethyl L–lactate or propylene glycol monomethyl ether.

13.11. The method according to one of claims 4 1 to 108, characterized in that when the developer solvent temperature is above 25°C, said group of selected solvents extends to the following compounds (G1 and G3): acetic acid, acetonitrile, dimethylsulfoxide, ethyl L–lactate or propylene glycol monomethyl ether.

14.12. The method according to claim 64, characterized in that when the temperature of the developer solvent is below 20°C, the prior radiation dose is close to the minimum value.

~~15.~~13. A developer solvent when used in the manufacturing method of a nanolithography mask according to one of claims 1 to ~~14~~12, said mask being created from a film of PS–b–PMMA block copolymer, said developer solvent being able to selectively remove at least the previously irradiated PMMA blocks, said solvent being characterized in that it is selected depending on the nanodomains, of different chemical composition, irradiated and/or non irradiated, to be selectively removed of said copolymer film, and in that it is chosen among solvents or solvent mixtures having Hansen solubility parameters, calculated at 25°C, comprised within the following value ranges: $14.5 \leq \delta_D \leq 19.00$; $4.90 \leq \delta_P \leq 18.00$ and $5.10 \leq \delta_H \leq 15.26$~~is chosen from a group of solvents or solvent mixtures that includes at least one compound chosen from among alcohols, such as methanol, ethanol, isopropyl alcohol, butan–1–ol, octan–1–ol, (R, S)–octan–2–ol, 4–methyl–2–pentanol, or 2–ethylhexanol~~.

~~16. A solvent according to claim 15, characterized in that it is chosen from among solvents or solvent mixtures having Hansen solubility parameters, calculated at 25°C, comprised within the following value ranges: $14.5 \leq \delta_D \leq 19.00$; $4.90 \leq \delta_P \leq 18.00$ and $5.10 \leq \delta_H \leq 15.26$.~~

~~17.~~14. The developer solvent according to claim ~~16~~13, characterized in that it is chosen from a group (G4) of solvents or solvent mixtures that includes at least one compound chosen from among: ketones, such as acetone or pentan–2–one; amides such as N,N–dimethylformamide, N–methyl–2–pyrrolidone or N,N–dimethylacetamide; lactones such as γ–butyrolactone; or alcohols such as benzyl alcohol.

~~18.~~15. The solvent according to one of claims ~~16~~13 to ~~17~~14, characterized in that said group (G5) of selected solvents also comprises the following compounds: ethyl acetate, dichloromethane, methyl ethyl ketone, propylene glycol monomethyl ether acetate, acetic acid, acetonitrile, dimethylsulfoxide, ethyl L–lactate, or propylene glycol monomethyl ether.

~~19.~~16. The solvent according to claim ~~16~~13, characterized in that when the developer solvent is made up of a mixture of solvents, this mixture is chosen at least from among one of the following mixtures: a mixture of dimethyl sulfoxide and propylene glycol monomethyl ether; a mixture of ethanol and methyl ethyl ketone; a mixture of N,N–dimethylacetamide and 4–methyl–2–pentanol; a mixture of isopropyl alcohol and dichloromethane; a mixture of dimethylsulfoxide and methanol; a mixture of dimethylsulfoxide, methanol and N,N–dimethylformamide; a mixture of acetonitrile and γ–butyrolactone; a mixture of ethyl L–lactate and N,N–dimethylformamide; a mixture of dimethylsulfoxide and N,N–dimethylformamide; a mixture of ethanol and

acetone; a mixture of methyl isobutyl ketone and isopropyl alcohol or a mixture of ethanol and ethyl acetate.

~~20.~~17. A nanolithography mask ~~obtained~~ deposited on a surface to be etched from a PS–b–PMMA block copolymer film ~~deposited on a surface to be etched, said copolymer film~~ comprising PMMA nanodomains orientated perpendicularly to the surface to be etched, said mask being characterized in that it comprises different irradiated and non-irradiated areas into which one or more nanodomains, of different chemical composition, have been removed, by treatment in a developer solvent according to claim 13, letting appear different patterns into said mask.~~at least one previously irradiated residual polystyrene PS block, said at least one residual block being obtained after treatment in a developer solvent, such as described according to one of claims 15 to 19, of said previously and partially irradiated copolymer film.~~

~~21.~~18. A nanolithography mask according to claim 17,~~A PS–b–PMMA block copolymer designed to be used in the method of manufacturing a nanolithography mask according to one of claims 1 to 14,~~ characterized in that ~~it~~ the block copolymer has a molecular weight comprised between 5,000 g.mol^{-1} and 1,000,000 g.mol^{-1}, and preferably comprised between 15,000 g.mol^{-1} and 250,000 g.mol^{-1}.

~~22.~~19. A nanolithography mask according to claim 17,~~The copolymer according to claim 21,~~ characterized in that ~~the~~ the block copolymer comprises a mass fraction of polystyrene PS, which is comprised between 25 and 90%, and preferably between 40 and 80%.