where R_1 is selected from the group consisting of C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 partially fluorinated alkyl, C_4-C_8 cycloalkyl moiety, C_4-C_8 cyclofluoroalkyl moiety, C_4-C_8 partially fluorinated cycloalkyl moiety, and C_2-C_8 hydroxyalkyl; R_2, R_3 and R_5 are independently selected from a group consisting of H, C_1-C_4 alkyl, CF_3 and F; R_4 is selected from the group consisting of H, C_1-C_8 alkyl, C_1-C_8 partially fluorinated alkyl and C_1-C_8 fluoroalkyl, n ranges from 1 to 5, R_6 is selected from the group consisting of H, F, C_1-C_8 alkyl and a C_1-C_8 fluoroalkyl and m ranges from 1 to 3.

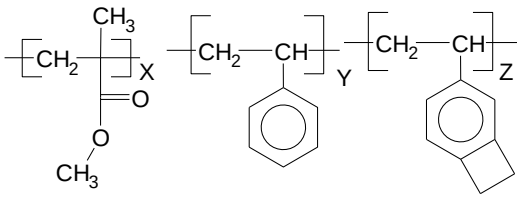
The present invention also relates to novel processes for forming patterns using directed self aligned lithography.

~~The present invention also relates to the use of a composition of the invention for forming a neutral layer for directed self assembly of block copolymers.~~

Detailed description of the invention

The present invention relates to novel neutral layer compositions~~, their use for forming a neutral layer for directed self assembly of block copolymers,~~ and novel self directed assembly processes for forming patterns with high resolution and good lithographic properties. The novel composition is capable of forming a neutral layer for use with self assembly of block copolymers. The neutral layer is an orientation control layer which allows the block copolymer coated above the neutral layer to align in the desirable direction relative to the substrate for obtaining high resolution lithography. The invention also relates to novel processes for use in directed self assembly of block copolymers, such as graphoepitaxy and chemoepitaxy, which use the neutral layer compositions. The invention leads to further improvement in resolution or CD uniformity of targeted features made by conventional lithographic techniques, such as UV lithography (450 nm to 10nm), immersion lithography, EUV or e-beam. The invention relates to neutral layer compositions comprising at least one random crosslinkable polymer. More than one polymer may be used in the present novel composition. The novel composition

C_4 alkyl; R_4 is selected from the group consisting of H and C_1-C_8 alkyl and n = 1; and R_6 is selected from the group consisting of H and C_1-C_8 alkyl and m = 1. In another embodiment R_2, R_3 and R_5 is hydrogen, R_1 is C_1-C_8 alkyl, and R_4 and R_6 is hydrogen. The neutral polymer may be represented by structure (4), where x, y and z are the mole% of the repeat units. In one embodiment the sum of x, y and z is 100%.



(4)

The novel random polymer can be prepared by a variety of ways by which alkene containing monomers can be polymerized randomly (such as nitroxide mediated polymerization, cationic, anionic condensation chain polymerization and the like) but generally they are prepared by radical polymerization such as the ones initiated by free radical initiators such as AIBN (azobisisobutyronitrile), benzoyl peroxide or other standard thermal radical initiators. These materials also do not need to form a comb like architecture by grafting on a substrate through an end group but can simply be spun on as a conventional polymer without covalent attachment to the substrate surface. The present polymer is ~~preferably~~ synthesized such that the concentration of the unit of structure 3 is greater than 10 mole%; unexpectedly, it has been found that having unit (3) greater than 10 mole% does not destroy neutrality toward the block copolymer and has the benefit of dramatically increasing the resistance of the neutral film to undesirable process damage, such as to solvents after post applied bake, which show no detectable film loss in organic solvents. It was generally thought previously that randomizing comonomers that form the block copolymer would give an acceptable neutral layer polymer; therefore any other comoneric units were kept to the minimum

concentration and typically around 2 mole%. The novel neutral layer can be highly crosslinked so that the solution of the block copolymer coated over it does not cause intermixing and yet unexpectedly remains neutral to the block copolymer. Unexpectedly, neutrality of the novel neutral layer is sustainable to common lithographic processing steps such as resist coating, resist soft bake, resist exposure, PEB, resist positive-tune and resist negative-tune developments, and resist stripping using organic solvents and TMAH developers. This in turn has the benefit of eliminating any solvent treatment step needed in many current neutral layers, which are normally needed to remove partially crosslinked surface material even after high post applied bake temperatures (such as 200°C). Generally, it was the belief that introducing higher than about 2 mole% of the crosslinking unit (3) would destroy neutrality toward the self assembly block copolymer. Unexpectedly the novel polymer of the present invention is capable of forming a highly process resistant film which can still maintain neutrality toward the self assembly block copolymer despite having greater than 10 mole% of the unit of structure (3). Additionally, unexpectedly the novel composition provides and maintains a crosslinked neutral layer with very good film uniformity across the substrate.

~~In one embodiment of the composition of the invention the polymer is capable of forming a crosslinked neutral layer relative to a block copolymer.~~

~~In a preferred embodiment the polymer is capable of forming a crosslinked neutral layer which is not soluble in an organic solvent for photoresist.~~

~~In a further preferred embodiment the polymer is capable of forming a crosslinked neutral layer which is not soluble in an aqueous alkaline developer.~~

~~In another embodiment of the composition of the invention the block copolymer comprises a block of monomeric units with high etch rate and a block of monomeric units with low etch rate in plasma comprising oxygen.~~

~~In a further embodiment of the composition of the invention the block copolymer comprises a block of monomeric units with high removal rate and a block of monomeric units with low removable rate in a solution.~~

~~In one embodiment~~ T~~t~~he neutral layer comprises units 1, 2 and 3, where unit 1 ranges from about 5 mole% to about 90 mole%; unit 2 ranges from about 5 mole% to about 90 mole% and unit 3 ranges from about 10 mole% to about 60 mole%. In another embodiment the neutral layer comprises units 1, 2 and 3, where unit 1 ranges from about 20 mole% to about 80 mole%; unit 2 ranges from about 20 mole% to about 80 mole% and unit 3 ranges from about 15 mole% to about 45 mole%. ~~In another embodiment the unit of structure (3) ranges from 10 mole% to 45 mole%.~~

Herein, alkyl refers to saturated hydrocarbon groups which can be linear or branched (e.g. methyl, ethyl, propyl, isopropyl, tert-butyl and the like), cycloalkyl refers to a hydrocarbon containing one saturated cycle (e.g. cyclohexyl, cyclopropyl, cyclopentyl and the like), fluoroalkyl refers to a linear or branched saturated alkyl group in which all the hydrogens have been replaced by fluorine, cyclofluoroalkyl refers to a cycloalkyl group in which all the hydrogens have been replaced by fluorine, partially fluorinated alkyl refers to a linear or branched saturated alkyl group in which part of the hydrogens have been replaced by fluorine, partially fluorinated cycloalkyl refers to a cycloalkyl group in which part of the hydrogens have been replaced by fluorine, hydroalkyl refers to an alkyl or cycloalkyl group which is substituted with a least one hydroxyl moiety (e.g. $–CH_2$-CH_2-OH, CH-CH(OH)-CH_3 and the like).

hardening conditions are determined by the type of photoresist used. As an example hardening can be a bake for 2 minutes at 200°C with or without a UV exposure. The block copolymer composition is used to form a coating and then treated to form self directed domains as described previously. Consequently, the domains of the block copolymer assembly (either spontaneously, through solvent treatment or thermally by annealing) are forced by the constraints of the topographical pattern overlying the critical neutral layer to align in such a way to multiply the spatial frequency of the fine topographical photoresist pattern, that is domains of high etch rate and etch resistant regions are formed perpendicular to the substrate surface. This multiplication of special frequency is the number of repeating sets of features along a given direction of the topographical pattern. Thus, the resulting pattern in the block copolymer assembly (the spatial frequency of the patterned block copolymer assembly) can be doubled, tripled, even quadrupled relative to the spatial frequency of the original fine topographical pattern. The segregation of the domains occurs such that a structure comprising repeating sets of domains is formed between the patterned photoresist topography with a spatial frequency for the domains (given by the number of repeating sets of domains in the given direction) of at least twice that of the spatial frequency for the topographical pattern.

~~In one embodiment the invention provides a process for forming an image by graphoepitaxy comprising:~~

~~a) forming a coating of a neutral layer, preferably from the neutral layer composition of the invention or one of its specific embodiments, on a substrate;~~

~~b) heating the neutral layer to form a crosslinked neutral layer;~~

~~c) providing a coating of a photoresist layer over the crosslinked neutral layer;~~

~~d) forming a pattern in the photoresist;~~

~~e) applying a block copolymer comprising an etch resistant block and highly etchable block over the photoresist pattern and annealing until directed self assembly occurs; and,~~

~~f) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.~~

~~In a preferred embodiment the photoresist pattern is formed by imaging lithography selected from a group consisting of e-beam, broadband, 193 nm immersion lithography, 13.5 nm, 193nm, 248 nm, 365 nm and 436 nm. In a further preferred embodiment the photoresist is positive or negative.~~

In one embodiment, the present invention relates to a process for using a positive tone photoresist pattern for graphophoepitaxy. A neutral layer which is resistant to lithographic processes and maintain neutrality after crosslinking may be used. The process comprises forming a coating of the novel neutral layer composition on a substrate surface; baking the neutral layer to form a crosslinked and neutral layer; providing a coating of a positive acting photoresist layer over the neutral layer; forming a positive pattern in the photoresist; optionally, hardening the positive photoresist pattern by hardbaking, UV exposure or a combination of the two; applying a block copolymer comprising an etch resistant block and an etch labile block over the residual positive photoresist pattern and annealing the film stack until directed self assembly governed by the residual photoresist feature and neutral layer occurs, such that the domains form perpendicular to the substrate surface; and, etching the block copolymer so that the etch labile blocks are removed producing a line multiplication of the original residual pattern. The neutral layer is such that no damage occurs to the neutral layer during lithographic processing, as described previously.

In another embodiment, the present invention relates to a process for using a negative tone photoresist pattern for use in graphoepitaxy. A neutral layer which is resistant to lithographic processes and maintain neutrality after crosslinking may be used. The process comprises forming a coating of the novel neutral layer on a

substrate; baking the neutral layer to form a crosslinked and neutral layer; providing a coating of a negative acting photoresist layer over the neutral layer; forming a negative tone pattern in the photoresist; optionally, hardening the photoresist pattern by hardbaking, UV exposure or a combination of the two; applying a block copolymer comprising an etch resistant block and an etch labile block to the substrate containing the pattern and annealing the film stack until directed self assembly governed by the residual photoresist feature and the neutral layer occurs, such that the domains form perpendicular to the substrate surface; and, etching the block copolymer so that the etch labile block are removed producing a line multiplication of the original residual pattern. The neutral layer is such that no damage occurs to the neutral layer during lithographic processing, as described previously.

~~In a further embodiment the invention provides a process for forming an image by chemoepitaxy comprising:~~

~~a) forming a coating of a neutral layer, preferably from the neutral layer composition of the invention or one of its specific embodiments, on a substrate;~~

~~b) heating the neutral layer to form a crosslinked neutral layer;~~

~~c) providing a coating of a photoresist layer over the crosslinked neutral layer;~~

~~d) forming a pattern in the photoresist layer to remove the unexposed photoresist, thereby forming an uncovered crosslinked neutral layer region;~~

~~e) treating the uncovered crosslinked neutral layer region,~~

~~f) removing the photoresist,~~

g) applying a block copolymer comprising an etch resistant block and highly etchable block over the neutral layer and annealing until directed self assembly occurs; and,

h) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

In a preferred embodiment the photoresist pattern is formed by imaging lithography selected from a group consisting of e-beam, 193 nm immersion lithography, broadband, 13.5 nm, 193nm, 248 nm, 365 nm and 436 nm. Further, the photoresist is a negative or positive photoresist.

In a further embodiment the invention provides a process for forming an image by chemoepitaxy comprising:

a) forming a coating of a neutral layer, preferably from the neutral layer composition of the invention or one of its specific embodiments on a substrate;

b) heating the neutral layer to form a crosslinked neutral layer;

c) providing a coating of a photoresist layer over the crosslinked neutral layer;

d) forming a pattern in the photoresist layer;

e) applying a block copolymer comprising an etch resistant block and highly etchable block over the photoresist pattern and annealing until directed self assembly occurs; and,

f) etching the block copolymer with a plasma, thereby removing the highly etchable block of the copolymer and forming a pattern.

In a preferred embodiment the photoresist pattern is formed by imaging lithography selected from a group consisting of e-beam, broadband, 193 nm immersion lithography, 13.5 nm, 193 nm, 248 nm, 365 nm and 436 nm. Further, the photoresist is a negative or positive photoresist.

The film thickness was measured to be 17.8 nm after the soaking process, which indicates no detectable film loss.

Example 11

The neutral polymer blend (Formulation #18 described in Table 2) was deposited and baked at 255°C for 2 min to form a film of 16 nm. Over the neutral layer was coated a layer of photoresist AZ AX2110P (available from AZ Electronic Materials USA Corp., Somerville, NJ) and baked at 110 ^{o}C for 60 seconds so as to obtain a 120 nm film. This film stack was flood exposed with a 193nm Nikon 306D scanner at dose of 20mJ/cm^2 in a open-frame mode. A post exposure bake at 110C for 60 seconds was applied. The wafer was developed with AZ MIF300 (available from AZ Electronic Materials USA Corp., Somerville, NJ) for 30 seconds. The block copolymer solution of Block Copolymer formulation 1 was coated on the substrate and annealed at 255°C for 2 minutes (FT 29 nm). The wafer was analyzed in a CD SEM (~~critical dimension scanning electron microscopy,~~ Applied Materials Nano 3D) where it was seen that the block polymer was able to successfully form a self directed assembly over the neutral layer, which indicates perfect neutrality was maintained after the complete photoresist exposure process. Thus, no damage to the neutral layer from the exposure process was observed.

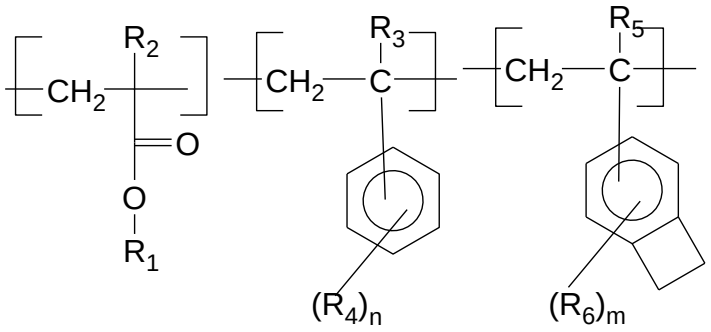
Example 12: Comparative Results

AIBN (0.4944 g , 0.003 mol), 4-vinylbenzocyclobutene (0.6543 g, 0.005 mol) , styrene (16.54 g 0.14 mol), methyl methacrylate (10.52 g, 0.105 mol) and 90 ml of 2-butanone were charged in a 250 ml flask equipped with a magnetic stirrer, water condenser and gas bubbler. After nitrogen gas was passed to purge for 30 minutes, the flask was immersed in a 80°C oil bath and stirred for 19 hrs. The reaction mixture was cooled to room temperature and the solution was poured slowly into methanol (2.5L) under stirring. The polymer obtained was isolated by filtering

Claims

1. A neutral layer composition capable upon heating of forming a crosslinked random copolymer neutral layer for directed self assembly of a block copolymer coated on top of the crosslinked neutral layer wherein the neutral layer composition comprises;~~block copolymers comprising at least one random copolymer having at least one unit of structure (1), at least one unit of structure (2) and at least one unit of structure (3)~~

(i) at least one random copolymer of structure (I) having at least one unit of structure (1), at least one unit of structure (2) and at least one unit of structure (3)



(I)

(1) (2) (3)

where R_1 is selected from the group consisting of a C_1-C_8 alkyl, C_1-C_8 fluoroalkyl, C_1-C_8 partially fluorinated alkyl moiety, C_4-C_8 cycloalkyl, C_4-C_8 cyclofluoroalkyl, C_4-C_8 partially fluorinated cycloalkyl, and a C_2-C_8 hydroxyalkyl; R_2, R_3 and R_5 are independently selected from a group consisting of H, C_1-C_4 alkyl, CF_3 and F; R_4 is selected from the group consisting of H, C_1-C_8 alkyl, C_1-C_8 partially fluorinated alkyl moiety and C_1-C_8 fluoroalkyl, n ranges from 1 to 5, R_6 is selected from the group consisting of H, F, C_1-C_8 alkyl and a C_1-C_8 fluoroalkyl and m ranges from 1 to 3~~.~~,and

wherein the neutral layer has unit 1 ranging from about 20 mole % to about 80 mole %; unit 2 ranging from about 20 mole % to about 80 mole % and unit 3 ranging from about 15 mole % to about 45 mole %, and

ii) a solvent.

2. The composition of claim 1, where the random copolymer~~polymer~~ is capable of forming a crosslinked neutral layer when coated and heated on a substrate ~~relative to a block copolymer~~.

3. The composition of claim 1~~ or 2~~, ~~where the polymer~~wherein the random copolymer is capable of forming a crosslinked neutral layer which when coated and heated on a subsrate is not soluble in an organic solvent for photoresist.

4. The composition ~~of any one~~ of claim~~s~~ 1 ~~to 3~~, ~~where the polymer~~wherein the random copolymer is capable of forming a crosslinked neutral layer which is not soluble in an aqueous alkaline developer when coated and heated on a substrate.

5. The composition of ~~any one of~~ claim~~s~~ 1~~ to 4~~, ~~where~~wherein the block copolymer to be self-assembled on the neutral layer random copolymer of structure (I) comprises at least two blocks ~~a block~~ of monomeric units with different~~high~~ etch rate~~s~~. ~~and a block of monomeric units with low etch rate in plasma comprising oxygen.~~

~~6. The composition of any one of claims 1 to 4, where the block copolymer comprises a block of monomeric units with high removal rate and a block of monomeric units with low removable rate in a solution.~~

~~7.~~6. The composition of ~~any one of~~ claim~~s~~ 1~~ to 6~~, where R_1 is selected from the group consisting of a C_1-C_8 alkyl; R_2, R_3 and R_5 are independently selected from the group consisting of H and C_1-C_4 alkyl; R_4 is selected from the group consisting of H, C_1-C_8 alkyl, and n = 1; and R_6 is selected from the group consisting of H, C_1-C_8 alkyl and m = 1.

~~8. The composition of any one of claims 1 to 7, where the unit of structure (3) ranges from 10 mole% to 45 mole%.~~

7. The composition of claim 1, wherein the composition comprises a blend of random copolymer of structure(I)

~~9.~~8. The composition of ~~any one of~~ claim~~s~~ 1~~ to 8~~, ~~where~~wherein the block copolymer to be self assembled on the neutral layer random copolymer of structure(I) is poly(styrene-b-methylmethacrylate).

~~10. The use of a composition according to any one of claims 1 to 9 for forming a neutral layer for directed self assembly of block copolymers.~~

~~11.~~9. A process for forming an image by graphoepitaxy comprising:

~~g)~~ a) forming a coating of a neutral layer from claim 1 on a substrate;

~~h)~~ b) heating the neutral layer to form a crosslinked neutral layer;

~~i)~~ c) providing a coating of a photoresist layer over the crosslinked neutral layer;

~~j)~~ d) forming a pattern in the photoresist;

~~k)~~ e) applying a block copolymer comprising an etch resistant block and highly etchable block over the photoresist pattern and annealing until directed self assembly occurs; and,

~~l)~~ f) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

~~12.~~10. The process of claim ~~11~~9 wherein the photoresist pattern is formed by imaging lithography selected from a group consisting of e-beam, broadband, 193 nm immersion lithography, 13.5 nm, 193nm, 248 nm, 365 nm and 436 nm.

~~13.~~11. The process of claim ~~9~~~~11 or 12~~, wherein the photoresist is positive or negative.

~~14.~~12. ~~A~~The process for forming an image by chemoepitaxy comprising:

~~i)~~ a) forming a coating of a neutral layer from claim 1 on a substrate;

~~j)~~ b) heating the neutral layer to form a crosslinked neutral layer;

~~k)~~ c) providing a coating of a photoresist layer over the crosslinked neutral layer;

~~l)~~ d) forming a pattern in the photoresist layer to remove the unexposed photoresist, thereby forming an uncovered crosslinked neutral layer region;

~~m)~~ e) treating the uncovered crosslinked neutral layer region,

~~n)~~ f) removing the photoresist,

~~o)~~ g) applying a block copolymer comprising an etch resistant block and highly etchable block over the neutral layer and annealing until directed self assembly occurs; and,

~~p)~~ h) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

~~15.~~13. The process of claim ~~14~~12 where the photoresist pattern is formed by imaging lithography selected from a group consisting of e-beam, 193 nm immersion lithography, broadband, 13.5 nm, 193nm, 248 nm, 365 nm and 436 nm.

~~16.~~14. The process of claim 12~~14 or 15~~, where the photoresist is a negative or positive photoresist.

~~17.~~15. A process for forming an image by chemoepitaxy comprising:

~~g)~~ a) forming a coating of a neutral layer from claim 1 on a substrate;

~~h)~~ b) heating the neutral layer to form a crosslinked neutral layer;

~~i)~~ c) providing a coating of a photoresist layer over the crosslinked neutral layer;

~~j)~~ d) forming a pattern in the photoresist layer;

~~k)~~ e) applying a block copolymer comprising an etch resistant block and highly etchable block over the photoresist pattern and annealing until directed self assembly occurs; and,

~~l)~~ f) etching the block copolymer with a plasma, thereby removing the highly etchable block of the copolymer and forming a pattern.

~~18.~~16. The process of claim 15~~17~~ where the photoresist pattern is formed by imaging lithography selected from a group consisting of e-beam, broadband, 193 nm immersion lithography, 13.5 nm, 193 nm, 248 nm, 365 nm and 436 nm.

~~19.~~17. The process of claim 15~~17 or 18~~, where the photoresist is a negative or positive photoresist.

~~20. The process according to any one of claims 11 to 19, where the coating of a neutral layer is formed from a neutral layer composition according to any one of claims 1 to 9.~~

18. The composition of claim 1 where the solvent is selected from the group consisting of ethyl cellosolve, methyl cellosolve, propylene glycol monomethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol dimethyl ether, propylene glycol n-propyl ether, diethylene glycol dimethyl ether; ethyl cellosolve acetate, methyl cellosolve acetate, propylene glycol monomethyl ether acetate; ethyl acetate, n-butyl acetate, amyl acetate; ethylene glycol diacetate, propylene glycol diacetate, methyl lactate, ethyl lactate, ethyl glycolate, ethyl-3-hydroxy propionate, methy pyruvate, ethyl pyruvate, ethyl 3-ethoxypropionate, methyl ethyl ketone, acetyl acetone, cyclopentanone, cyclohexanone, 2-heptanone, diacetone alcohol methyl ether, acetol, diacetone alcohol; 1,3 dioxalane diethoxypropane, butyrolactone, dimethylacetamide, dimethylformamide, anisole, and mixtures thereof.

19. The composition of claim 5 wherein the block of monomeric units comprising different etch rates is derived from monomers comprising oxygen and which do not contain refractory elements, and wherein the other block is derived from monomers rich in carbon or ones containing the refractory elements Si, Ge or Ti.

20. The composition of claim 5, wherein one of the blocks of monomeric units is selected; from the group consisting of methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth) acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, neopentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, hydroxyethyl (meth)acrylate and mixtures

thereof and the other block is selected from the group consisting of ethylene, propylene, 1-butene, 1, 3-butadiene, isoprene, dihydropyran, norbornene, maleic anhydride, styrene, 4-hydroxy styrene, 4-acetoxy styrene, 4-methylstyrene, alpha-methylstyrene and mixtures thereof.