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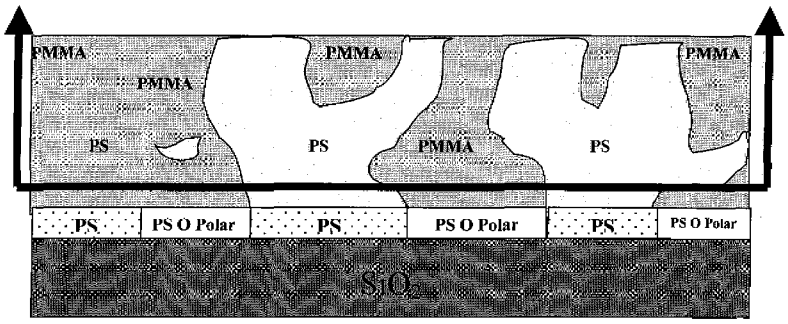
(54) **Title**: NANOFABRICATION METHOD

FIGURE 2B
Removal of top part of the film



(57) **Abstract**: The invention relates to a new nanofabrication method especially useful for patterns of two or more different sizes, shapes and/or heights. The method is especially useful for compositions containing block copolymers. The method involves coating the composition onto a multi-patterned substrate, with self-assembly of the polymer components to match the pattern, and the selective removal of the polymer components. A complementary technique is described where a polymer composition comprising domains of different chemical/physical properties can be used to create/change a structure after the application of a stimulus; where the polymeric composition is in bulk form, as a film, or as a coating on an unpatterned or patterned substrate. This structure can be dynamically controlled via the application of the stimulus. The invention is especially useful in the field of integrated circuits, and relates to a means of reducing transistor size and spacing. In addition, this invention can find applications in specialty coatings with antireflective, dirt resistance, controlled adhesion, and piezoelectric properties, and in photovoltaics, energy generation and sensor applications, among others.

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NANOFABRICATION METHOD

FIELD OF THE INVENTION

The invention relates to a new nanofabrication method especially useful for structures of two or more different sizes, and/or shapes and/or heights. The method involves coating onto a patterned substrate a composition (preferably a polymeric composition) having at least two different components, annealing the composition at a temperature above the glass transition temperature, Tg, or the melting temperature, Tm, during which self-assembly of the components to match the underlying pattern occurs, followed by the selective full and/or partial removal of the components. A complementary technique is additionally presented where a polymer composition of domains of different chemical/physical properties can be used to create a structure after the application of a stimulus; where the polymeric composition can be in bulk form, as a film, or as a coating on an unpatterned or patterned substrate. This structure can be dynamically controlled via the application of the stimulus. The invention is useful in the field of integrated circuits, and relates to a means of reducing transistor size and spacing. It is also useful in the area of specialty materials fabrication where a controlled morphology is desired. The method is especially applicable for block copolymer compositions.

BACKGROUND OF THE INVENTION

There is a continuing effort in the semiconductor industry to manufacture integrated circuits having higher device densities and smaller chip areas. This is driven by a desire to shrink the circuit dimensions so as to reduce manufacturing costs and improve circuit functionality.

The production of integrated circuits is most commonly done by lithography, where patterns of the device features are transferred to a resist layer on a semiconductor substrate, and portions of the resist layer are selectively removed based on the device feature patterns to produce gaps in the resist layer. The material under the resist layer may be selectively etched to produce gaps in the underlying material; only the layers under the resist layer gaps are etched, leaving the areas protected by the resist layer unaffected by the etching process. After the selective etching, a

material may be added to the etched gaps in the underlying material to create devices on the integrated circuit.

The known art describes several different lithographic methods for making patterned devices in integrated circuits. Photolithography involves the selective exposure, through a mask, of a light-sensitive polymer resist to create a pattern of gaps in the resist. The material under the patterned gaps may then be etched away to create devices. This method is costly and time consuming, and light diffraction around the edges of the mask limits the resolution – limiting the minimum size and spacing of features in the device.

Electron beam lithography uses a finely focused beam of electrons to create a pattern on the surface of a material. Due to the restrictions on electron beam systems, this method is generally limited to features above 30 nm and spacings above 50 nm. The method must be repeated for each individual device and there can be millions on a single integrated circuit. Ion beam and x-ray lithography have similar deficiencies.

Recently, block copolymer lithography has been proposed as a substitute for current lithographic techniques due to its many advantages, such as improved control on line edge roughness and critical dimensions.

US Patent 6,537,920 describes the use of block copolymer lithography for the formation of vertical resistors. The method involves placing a dielectric layer on a semiconductor substrate, depositing a copolymer layer over the dielectric layer, removing a portion of the a first block of the copolymer to form a void in the copolymer layer, then etching away the portion of the dielectric layer under the void to form an aperture. The block copolymer may consist of chemically different homopolymer blocks connected by covalent bonds at their chain ends. In the bulk, the similar blocks self-assemble to form nanometer-sized domains of like composition. Altering the total chain length, or the molecular weight of each block, creates a variety of potential bulk morphologies, such as lamellae, cylinders or spheres. Through selective removal of one type of block, a patterned array of structures is formed, which can be used as a patterned resist layer. Advantages of block copolymer lithography are the following: a) it can be integrated into already existing processes b) feature sizes can be smaller that 10 nm c) it achieves decreased line edge

roughness of structures. In addition, the method allows for concurrent device production with increased fabrication throughput.

Erik W. Edwards et al. in "Dimensions and Shapes of Block Copolymer Domains Assembled on Lithographically Defined Chemically patterned Substrates" *Macromolecules 2007, 40, 90-96* describe the directed assembly of block copolymers on lithographically defined chemically nanopatterned substrates, producing essentially defect-free patterns in the 5 – 50 nm range. The bulk lamellar period can be controlled by molecular weight and by using blends of diblock copolymers and homopolymers. Ricardo Ruiz et al. in "Density Multiplication and Improved Lithography by Directed Block Copolymer Assembly" describe a similar method. However, the current methods are still limited to symmetrical morphologies for long-range ordered structures, such as spheres, columns and lamellae.

The present invention overcomes the deficiencies of current block copolymer lithography processes by allowing for the fabrication of any possible structure, and more than one size, shape or height of structures in the same pattern. It also focuses on the short-range ordered structure in the area directly adjacent to the patterned substrate, rather than the longer range order of the prior art.

This invention can be used to replicate more than one type of structure of different size, shape or height within the same pattern by selecting the appropriate polymer composition, followed by annealing and selective removal of part of the components of the polymer composition. In addition, a complementary technique was invented where a polymer composition of domains of different chemical/physical properties can be used to create a structure after the application of a stimulus. The polymeric composition can be in bulk form, or as a film, or as a coating on an unpatterned or patterned substrate. This structure can be dynamically controlled via the application of the stimulus.

SUMMARY OF THE INVENTION

The invention relates to a nanofabrication process for developing two or more patterns differing in size and/or shape and/or height, comprising the following steps:

a) forming a polymer composition comprising two or more different components, at least one component being a polymer;

b) coating said polymer composition onto a nano-patterned substrate, wherein said patterned substrate comprises two or more domains differing in size, shape, height and/or chemical/physical nature or other property difference;

c) annealing said coated polymer composition at a temperature above the Tg or Tm of at least one component, wherein said polymer composition self-assembles on said patterns;

d) selectively removing the unregistered polymer composition layer; and

e) selectively removing or partially removing one or more components in the registered layer.

In addition, a complementary technique is described where a polymer composition of domains of different chemical/physical properties can be used to create a structure after the application of a stimulus. The polymeric composition can be in bulk form, or as a film, or as a coating on an unpatterned or patterned substrate. This structure can be dynamically controlled via the application of the stimulus.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the creation of a pattern on a substrate as described in Example 1.

Figures 2A, 2B and 2C depict the nanofabrication method of Example 2.

Figures 3A and 3B depict the nanofabrication method described in Example 3.

Figures 4A and 4B depict the nanofabrication method described in Example 4.

Figures 5A and 5B depict the nanofabrication method described in Example 5.

Figures 6 A-E depict a nanofabrication method as described in Example 2 but showing a three dimensional perspective.

Figures 7 A-D depicts a variation of the nanofabrication method of Example 2 to create complex 3D structures.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention involves the replication of two or more structures differing in size, shape and/or height on a patterned substrate through the use of selective nanofabrication.

By "annealing" as used herein we define any type of process (mechanical, solvent, temperature assisted, etc.) that allows self-assembly/phase separation to take place.

By " registered" or "registration" as used herein we refer to the component(s) of the polymer composition in direct contact with the patterned substrate that replicate (or partially replicate or replicate with a degree of deviation) the pattern.

The "polymer composition" of the invention contains two or more different chemical components that are immiscible or semi-miscible with each other over a range of temperatures, so that they form separate domains. At least one of the components is a polymer. In one preferred embodiment, the polymer composition contains at least one block copolymer.

"Component(s)" as used herein means a chemical species that is chemically differentiated from and non-miscible (or partially miscible) over a range of temperatures with at least one other chemical species in the polymer composition. A component may be a homopolymer, a random copolymer, or one block of a block copolymer. A block copolymer would preferably have two polymer components (blocks) connected by a covalent bond and could have more than two polymer components (blocks). Other components may also be included in the polymer composition of the invention, including but not limited to inorganic or organic particles such as nanoparticles, nanotubes, polyhedral oligomeric silsesquioxane (POSS) particles, etc. Particles can be grafted onto polymers and can be treated to change the hydrophilic or hydrophobic nature of the particles.

"Block copolymer" as used herein means a polymer having two or more chemically differentiated polymer blocks. This could be a di-block, tri-block, star, comb, or other polymer with controlled architecture. Preferably the blocks have different chemical properties, such as the degree of hydrophilicity or hydrophobicity, and are non-miscible or partially miscible over a range of temperatures (i.e., the blocks form separate domains in the melt phase). Each of the individual polymer blocks may be a homopolymer or a random, gradient or statistical copolymer (i.e., a copolymer including two or more different monomers). The block copolymer can be formed by means known in the art, including but not limited to atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer polymerization (RAFT), nitroxide-mediated polymerization (NMP), boron-mediated polymerization, and catalytic chain transfer polymerization (CCT). Descriptions and comparisons of these types of polymerizations can be found in the ACS Symposium Series 768 entitled *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT*, edited by Krzystof Matyjaszewski, American Chemical Society, Washington, D.C., 2000.

Any type of component that fulfills the requirements of the patterned substrate may be used as part of the polymer composition. Parameters to be considered include molecular weight (end-to-end distance), Flory-Huggins (xN) parameters, composition, etch resistivities, and surface-component interactions. For any given pattern a variety of polymer compositions can be used to replicate the given pattern.

The molecular weight of the copolymer is preferably selected so that the end-to-end distance of the block is commensurate with the smallest feature of the pattern. Generally preferred molecular weights for each block of a block copolymer are from 200 to 1000,000 g/mol, preferably 2,000 to 100,000 g/mol. The chemistry of the blocks is preferably selected so the polymer components are non-miscible over a range of temperatures and therefore capable of self-assembly. The self-assembly at the patterned surface is based on a chemical difference, preferably in the hydrophilicity/hydrophobicity balance of each polymer component (block), or on some other property difference, so that the attraction to the pattern of one particular component (block) is preferred over the other component(s) in the block copolymer composition (the opposite holds true for repulsion between the pattern and the

components). The Flory Huggins parameter and chain asymmetry are chosen to result in the desired morphology.

A masterbatch polymer composition may be selected for replication of any pattern. This masterbatch could contain 1/3 block copolymer (A-B), 1/3 homopolymer A and 1/3 homopolymer B, or any combination of other components. The molecular weight of a polymer component is preferentially chosen in consideration of the smallest feature of the pattern to be fabricated. The components will be selected with respect to the necessary xN and the removal rate of any selective removal method, such as etch resistivities in a plasma. Other additives (to improve/control etch resistivity) and other homopolymers, copolymers or other components may be blended into the masterbatch to provide the appropriate polymer composition for a specific pattern. Unless otherwise noted, percentages are weight percentages, and molecular weights are weight average molecular weights.

The etch resistivities of the components are carefully selected to allow for differential removal of the components. For instance, in the simplest case of a single block copolymer, each block is selected to have the same or very similar etch resistivity to a particular plasma, to allow for removal of both blocks in the upper layers above the registered portion of the film. Once the upper layers have been removed, a second type of plasma is used to which the etch resistivity of the separate blocks is quite different, to allow preferential removal of only a single block that replicates the pattern on the substrate. Additives can selectively change the resistivities of one or more of the polymer components.

The process of the invention begins with a patterned substrate. A technique not using a patterned substrate for nanofabrication will be presented later. The pattern represents a difference in a physical or chemical property (such as the hydrophilicity/hydrophobicity balance) that favors one component over the other. The patterned substrate can be created with a variety of methods, as known in the art. In the present invention, patterns even smaller than 10 nm can be used.

A layer of the polymer composition is applied to the patterned substrate by known methods, such as brushing, rolling, spraying, inkjet application, or spin-coating. In one embodiment spin-coating is used as the preferred method of applying

the polymer composition to the patterned substrate. Once coated onto the patterned substrate the polymer composition is annealed at a temperature above the lowest value of T_g or T_m of at least one component in the polymer composition. During thermal annealing, the polymer components self-assemble to replicate (fully or partially or with a degree of deviation) the pattern on the substrate. Annealing time is selected to allow polymer self-assembly and is preferably in the range of 0.01 hours to 300 hours, and more preferably between 0.1 hours to 24 hours. No matter what the pattern on the substrate, by choosing the appropriate parameters (such as composition of the components, polymer-polymer interactions, polymer-particle interactions, surface interactions, end-to-end distance or molecular weight, and etch resistivities) one can obtain a registration, or better yet replication of this pattern in the vicinity of the substrate. The pattern of the substrate can be of any complexity and can be a combination of different geometries. Away from the substrate registration is not necessary.

Once the polymer composition has been applied and annealed to the patterned substrate, it is then removed in a two-step (or more) process involving mechanical cutting or etching (chemical or plasma). First, the unregistered components are removed by mechanical cutting or etching, leaving only the registered (or partially registered or registered with a degree of deviation) layers. Depending on the application one can choose to work (etch, cut) at any height of the registered (or partially registered or registered with a degree of deviation) layer. Secondly, the components in the registered layer are selectively removed by etching or other methods previously discussed.

As an example, if two polymer components exist, one component can be completely removed leaving the other component or majority of the other component to form the structure, which is an exact (or to some degree) replica of the pattern. In another example, if three or more components exist, each component can be removed to a different extent, giving rise to a three-dimensional structure of different heights.

Another example could be the use of a two-step etching technique to fabricate a pattern, as follows. As a first step one would use a plasma etching where the two blocks of the copolymer and the optional homopolymers have the same etch resistivity (in the non-registered area). When the registration layer is reached, one

switches to a different plasma where the etch resistivity is different for each polymer component. Thus, one component is removed and the structure is formed. The etch resistivity can be tuned by choosing the appropriate polymers or including additives or particles (organic or inorganic) that will modify the etch resistivity values.

While previous nanofabrication methods have focused on replication of symmetrical patterns, the present invention allows one to replicate complex patterns or combinations of patterns on one substrate by choosing the appropriate parameters. No other method takes advantage of this registration/replication close to the patterned surface. Any structure can be replicated if the appropriate block copolymer/homopolymer system is chosen. Preferably, the components of the composition, and their ratio, are determined depending on the pattern to be created (pattern size, shape, etc.).

The method of the invention can also be used to produce patterns of differing heights, and other three-dimensional patterns. After removing the first unregistered layer and before continuing to the second step of the selective removal of one or more of the polymeric components an additional step can be included. In this step, lithographic techniques can be used to create a pattern on top of the registered layer before a second coating of the same or a new polymer composition is applied. After self-assembly there is a layer of the original registered coating on the original pattern, a new registered layer on the patterned coating and an unregistered layer. The unregistered layer is now removed and upon selective etching of one or more components a three-dimensional structure encompassing the design of the two (or more) lithographically created patterns is formed. An example is presented in Figure 7.

In addition to this technique, a polymer composition of domains of different chemical/physical properties can be used to create a structure via the application of a stimulus. The polymeric composition can be in bulk form, or as a film, or as a coating on an unpatterned or patterned substrate. This structure can be dynamically controlled via the application of the stimulus. In the case of the non-patterned substrate a polymeric composition is applied on the substrate. After self-assembly a film/coating develops with domains of different physical or chemical properties. The property differences can be utilized to dynamically control the morphology of the film. A

stimulus can be applied to the film/coating to take advantage of the property difference. This stimulus can be a mechanical, thermal, humidity, acidity/basicity (pH), electrical, piezoelectric, solvent, or oxidation change. An example is presented in the following pages (Example 5). If the mechanical behavior of the domains is different (e.g., glassy and rubbery domains) the stimulus can be the application of a force/stress. When one applies a compression of the film parallel to the substrate the domains of lower modulus are deformed creating protrusions. If one applies an extension of the film parallel to the substrate these domains are deformed creating depressions. If the thermal expansion coefficients of the domains are different then the stimulus can be a temperature change. Changing the temperature can controllably and dynamically change the structure as described. This process can also be applied to a patterned substrate if a specific structure is of interest in addition to dynamic control of the pattern. The same processes would be used to generate the structures in the case where the polymer composition is a bulk or film.

It is clear that this invention has a wide range of applications and is not limited to a block copolymer lithography technique for the semiconductor industry. It can be advantageous in any application where the resulting product requires a controlled and/or dynamic morphology. In addition, while it has been described for the purposes of nanofabrication it also can be applied for microfabrication. The devices created by this invention can be utilized in applications such as specialty coatings with antireflective, dirt resistance, controlled adhesion, and piezoelectric properties, and in photovoltaics, energy generation and sensor applications, among others.

While the present invention has been described with respect to preferred embodiments, one of ordinary skill in the art will recognize that changes in form and details may be made without departing from the spirit and scope of the invention.

EXAMPLES

Example 1: Preparation of a patterned substrate

In this example we present one of the available techniques in literature that can be used to develop a chemically patterned substrate. A thin layer of polystyrene (PS) is deposited on a SiO_2 substrate by a method such as grafting/brush or spin-

coating. (a) A photoresist layer (polymethylmethacrylate (PMMA)) is applied. (b) Electron beam lithography is used to write the desired pattern. (c) The exposed photoresist is removed in the development step with a solvent and then the sample is exposed to O_2 plasma to create polar oxygen groups in the PS layer. (d) The remaining PMMA is removed with a solvent. The result is a patterned surface of domains of chemically different functionalities. The procedure is illustrated in Figure 1.

Example 2

Onto the patterned substrate (prepared as described in Example 1), a block copolymer film of polymethylmethacrylate (PMMA) and polystyrene (PS) is applied by spin-coating and then annealed under vacuum. The areas of the pattern that were exposed to oxygen plasma are wetted preferentially by the PMMA block. The rest of the patterned substrate is slightly preferential toward the PS block. While this is not a necessity, it is recommended to choose the molecular weight of the polymer such that the end-to-end distance of the block copolymer is commensurate with the smallest feature of the pattern. The block copolymer will self-assemble and replicate the pattern near the substrate. The thickness of the registered layer can range, depending on the system, from none of to the entire film thickness.

The unregistered part of the film will not self-assemble to replicate the pattern (see Figure 2A).

This unregistered layer is then removed in a plasma-etching step. Plasma is selected for which the two blocks have the same etch resistivity. A mixture of CF_4 and O_2 plasma is used for the first removal step. What remains is the layer where the block copolymer has replicated the pattern. Using O_2 plasma, the PMMA block is removed, creating the desired nanostructure to match the pattern on the substrate (Figures 2B and 2C). Figure 6 presents a three-dimensional presentation of the same example. Again, this reference is out of order.

Example 3

Onto the patterned substrate (of Example 1) a polymer composition of block copolymer (PMMA-PS), denoted "BC" in Figure 3, and homopolymers (PMMA and PS), denoted "H" in Figure 3, is spin-coated and annealed under vacuum. The homopolymer domains are illustrated as striped areas in Figure 3. The areas of the patterned substrate that were exposed to oxygen plasma are wetted preferentially by the PMMA block and the PMMA homopolymer. The other areas of the patterned substrate are wetted preferentially by the PS block and the PS homopolymer. While this is not a necessity, it is recommended to choose the molecular weight of the polymer such that the end-to-end distance of the block copolymer is commensurate with the smallest feature of the pattern. The block copolymer will self-assemble and replicate the pattern near the substrate. The homopolymer will be favorable to its chemically similar block, and will swell it. The thickness of the layer where the replication is possible will range, depending on the system, from anywhere from none of to the entire film thickness. The rest of the film will not self-assemble to replicate the pattern.

After the annealing step is completed the plasma-etching steps begin (see Figure 3A). Plasma is used for which the two blocks of the copolymer and the two homopolymers have the same etch resistivity, such as a blend of CF_4 and O_2 plasma. This plasma is used to remove the film that has not self-assembled to replicate the substrate pattern. Then O_2 plasma may be used to remove the PMMA block and PMMA homopolymer in the registered layer, thus creating the desired nanostructure (see Figure 3B).

Example 4

The patterned substrate is created in a process similar to the previous examples. In this example the process is modified to create three types of domains on the chemically patterned surface. A brush of PS is deposited on a SiO_2 substrate. A photoresist layer of PMMA is applied and electron beam lithography is used to write a pattern. The exposed photoresist is removed in the development step with a solvent and then the sample is exposed to O_2 plasma to create polar oxygen groups in the PS brush. A second lithography step is used to write a pattern on the remaining PMMA.

A second development step is performed and finally a chemically patterned surface of domains of (i) grafted PS, (ii) PS with polar oxygen groups and (iii) PMMA.

A blend of block copolymers (PMMA-PBA and PS-PBA where PBA stands for polybutylacrylate) is spin-coated to form a film on the patterned substrate, which is then annealed under vacuum. The PMMA domains are wetted preferentially by the PMMA block. The PS grafted domains are wetted preferentially by the PS block. The PS domain with oxygen polar groups will be mostly covered with the BA block. Of course the PMMA block will also be preferential to the areas with the polar oxygen groups. After annealing, the volume above each of the different types of the patterned domains will have a different total concentration for each of these.

After the annealing step has been completed the plasma-etching step is applied (Figure 4A). Plasma etching takes advantage of the fact that each component has a different etch resistivity. The plasma will remove completely the domains of higher PMMA concentration, it will remove partially the domains of higher BA concentration, and it will have a negligible effect on the domains of higher PS concentration. In this manner nanostructures of variable height are created (Figure 4 B).

Example 5

A film of a block copolymer (PMMA-PBA) is applied by spin coating on a patterned or non-patterned SiO_2 substrate and annealed under vacuum. The block copolymer is chosen such that the resulting morphology is lamellae or cylinders. The substrate is chosen such that it is wet equally by the PMMA and PBA blocks. In this manner, a film or coating is developed comprising glassy domains (PMMA) and rubbery domains (PBA) of lamellar or cylindrical morphology, which is self-assembled perpendicular to the substrate (see Figure 5A). If one compresses the film parallel to the substrate the rubbery domains are deformed, creating protrusions. If one stretches the film parallel to the substrate the rubbery domains are deformed, creating depressions. The same result could be obtained by applying a temperature change. Increasing the temperature would swell the PBA domains more than the PMMA domains due to the different thermal expansion coefficients of these polymer blocks (see Figure 5B).

This example, while relevant to block copolymer lithography for the semiconductor industry, it can also be utilized in applications such as specialty coatings with antireflective, dirt resistance, controlled adhesion, and piezoelectric properties, and in photovoltaics, energy generation and sensor applications, among others.

What is claimed is:

1. A nanofabrication process for forming two or more patterns differing in size and/or shape and/or height and/or chemical/physical nature comprising the following steps of:

a) forming a composition comprising two or more different components, at least one component being a polymer;
b) coating said polymer composition onto a patterned or unpatterned substrate, wherein said patterned substrate comprises two or more patterns differing in size, and/or shape and/or height and/or chemical/physical nature;
c) annealing said coated polymer composition, wherein said polymer composition self-assembles on said substrate;
d) removing the unregistered polymer composition layer; and
e) selectively removing or partially removing one or more components in the registered layer.

2. The process of claim 1, wherein said composition comprises one or more block copolymers.

3. The process of claim 1, wherein said block copolymer has polymer blocks that are immiscible or partially miscible over a range of temperatures such that they form separate domains.

4. The process of claim 1, wherein the polymer composition can be in the form of a masterbatch and/or a blend of block copolymers and homopolymers and/or a blend of polymers and/or a blend of organic or inorganic components.

5. The process of claim 1, wherein said removal of said polymer composition is accomplished by plasma etching, chemical etching, or mechanical means.

6. The process of claim 5, wherein the components of said unregistered layer have about equal etch resistivity to the plasma used for removal of said unregistered layer.

7. The process of claim 5, wherein one or more of the components of said registered layer have unequal etch resistivity at the plasma used for selective removal of said unregistered layer.

8. The process of claim 1, wherein said registered layer can be replicating, or partially replicating, or replicating with a degree of deviation the pattern.

9. A process where a stimulus is applied to a material, which is comprised of domains of different chemical/physical properties, to form a structure.

10. The process of claim 9, wherein said stimulus can be a mechanical, thermal, acidity/basicity (pH), electrical, piezoelectric, humidity, oxidation, or solvent change.

11. The process of claim 10, wherein said mechanical change can be a compression or extension for domains of different mechanical properties.

12. The process of claim 10, wherein said thermal change can be a temperature change for domains of different thermal expansion coefficients.

FIGURE 1

MAKING OF A PATTERNED SUBSTRATE

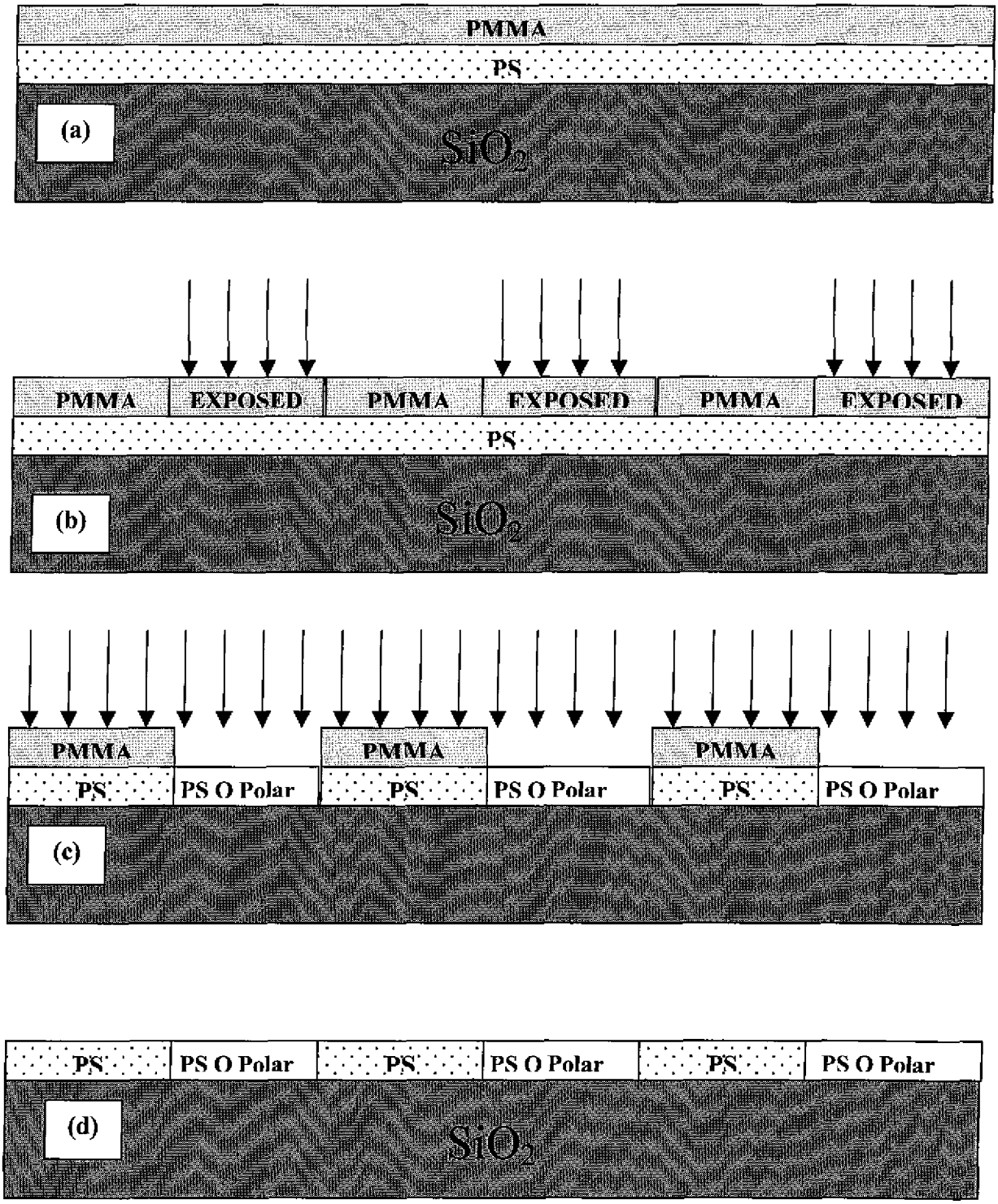


FIGURE 2A

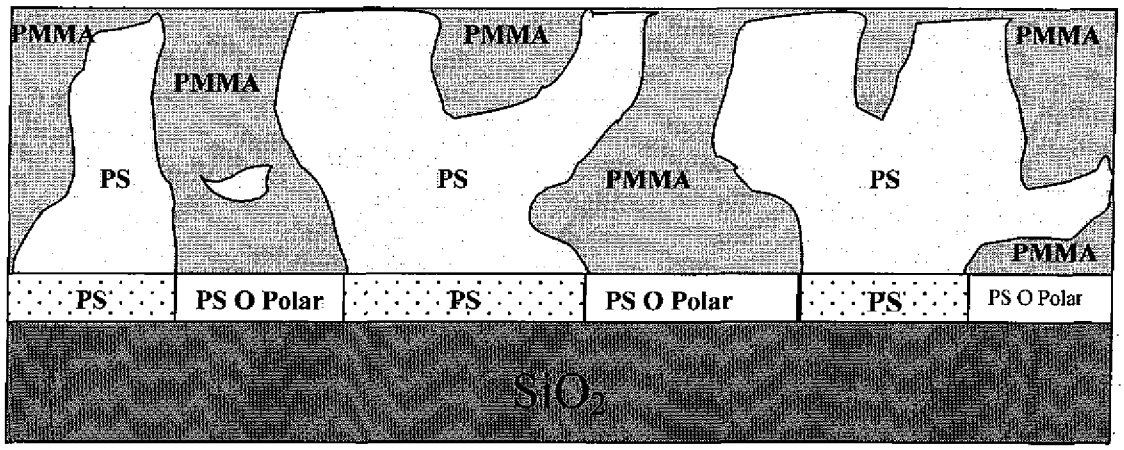


FIGURE 2B

Removal of top part of the film

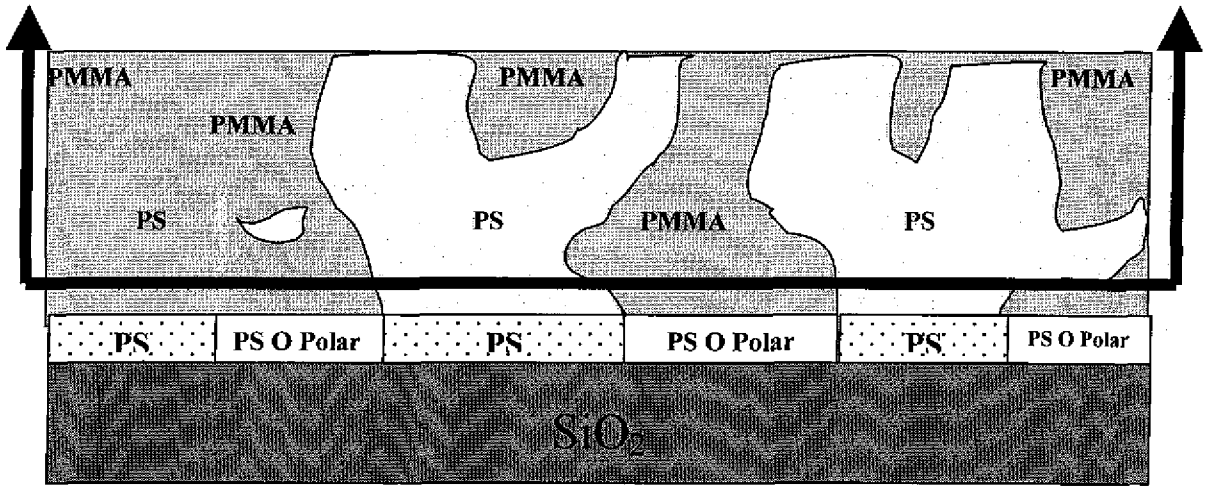


FIGURE 2C

Perfect Replication of patterned substrate

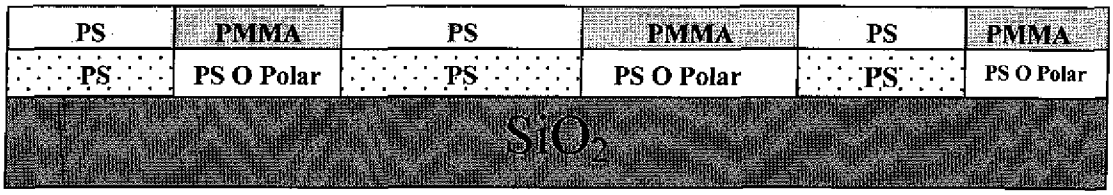


FIGURE 3A

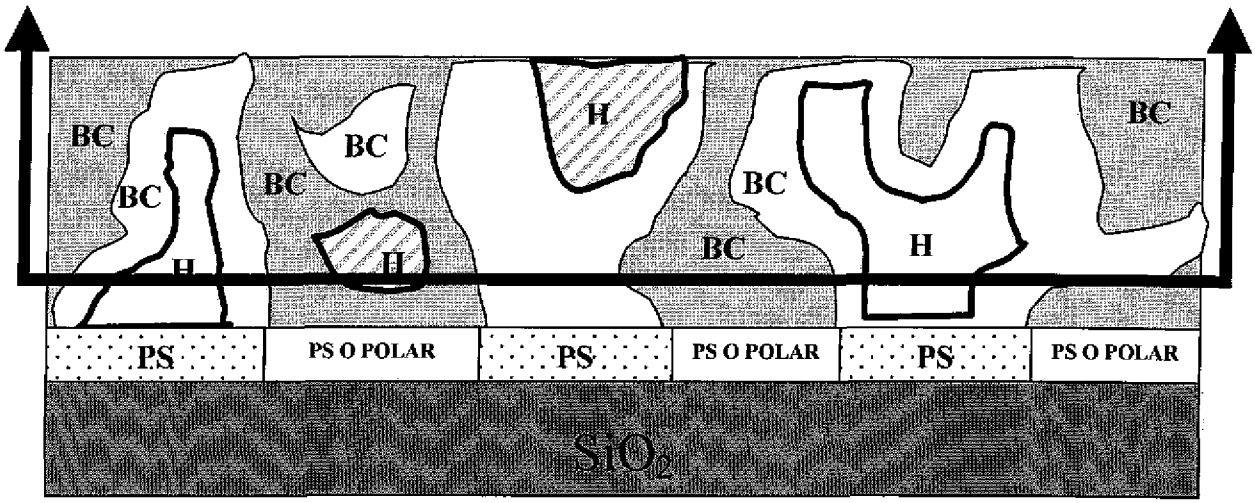


FIGURE 3B

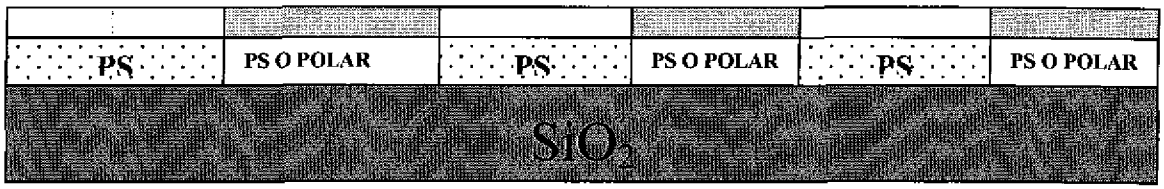


FIGURE 4A

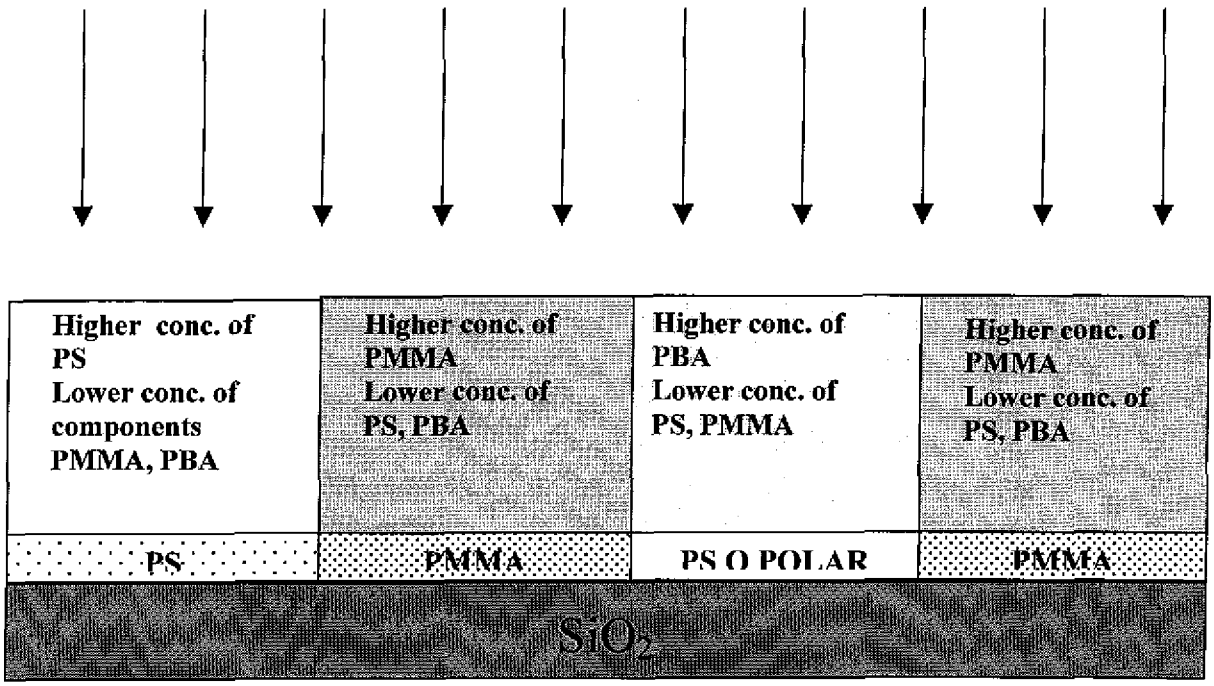


FIGURE 4B

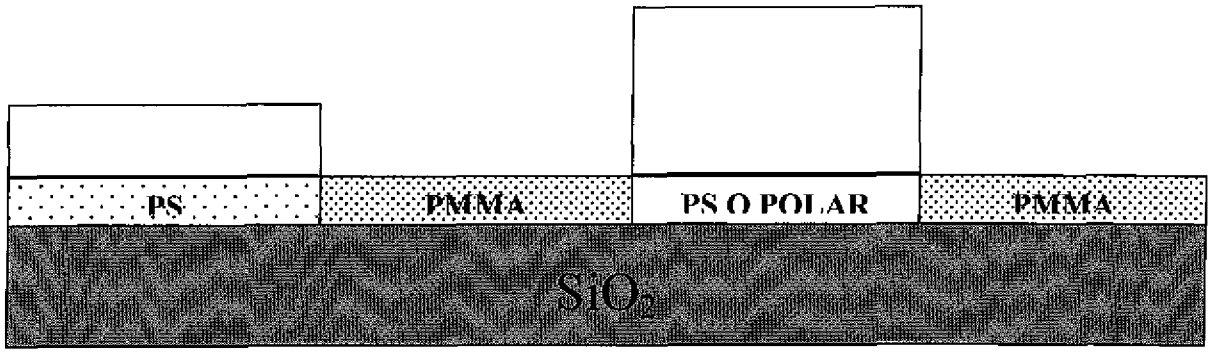


FIGURE 5A

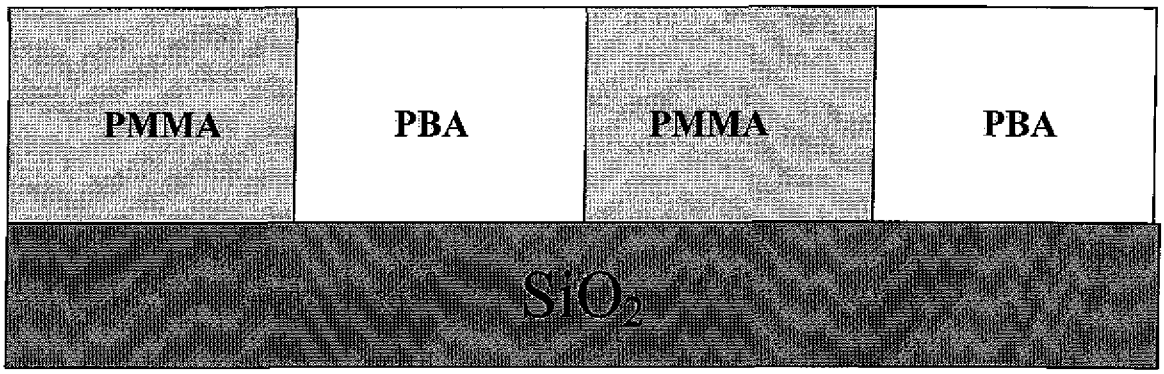
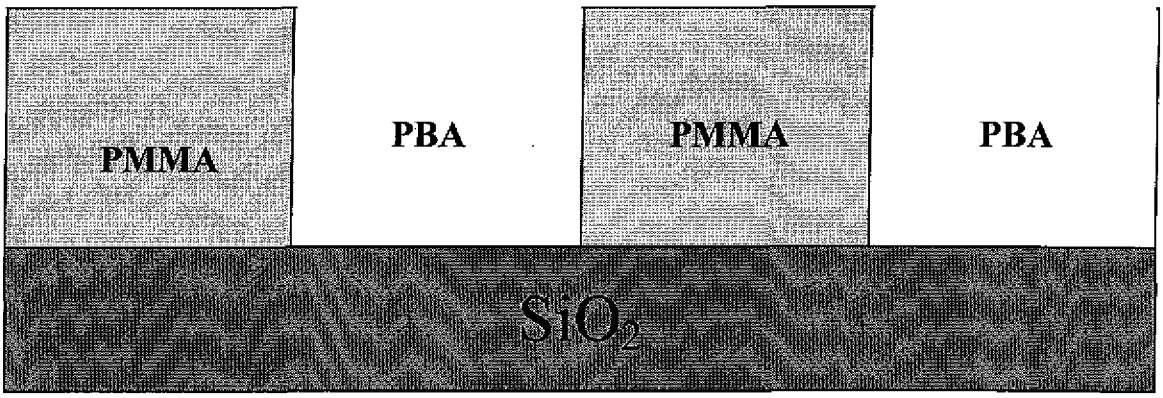


FIGURE 5B



Increasing temperature results in a larger decrease of the density of the PBA block than PMMA. Due to confinement from the surrounding glassy PMMA domains, hills are formed.

FIGURE 6A

Patterned substrate

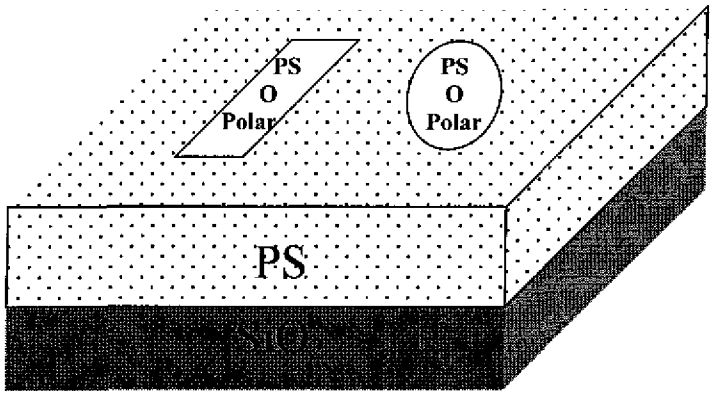
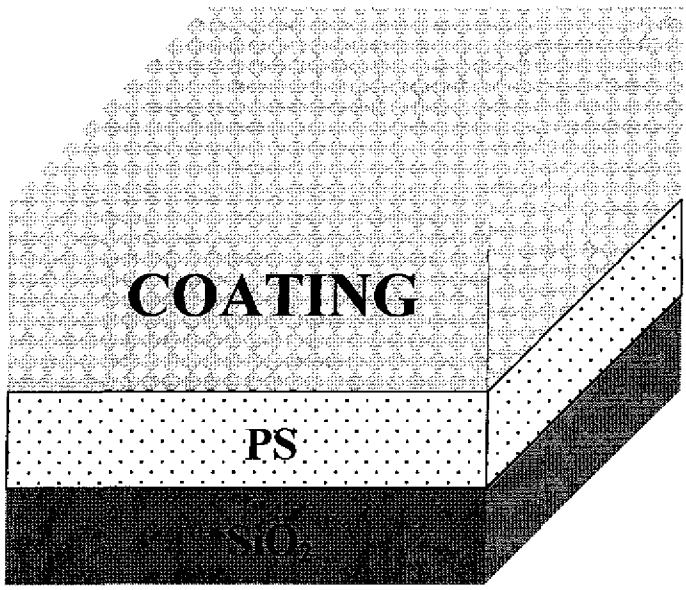


FIGURE 6B

Coating polymer composition



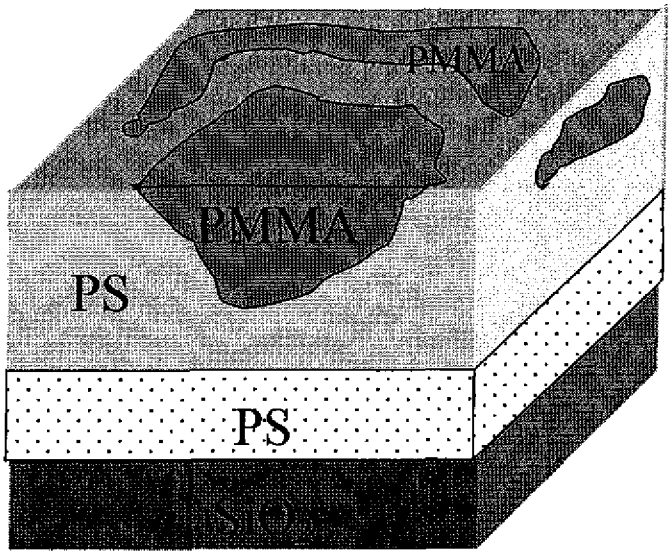


FIGURE 6C
Self-assembly of coating

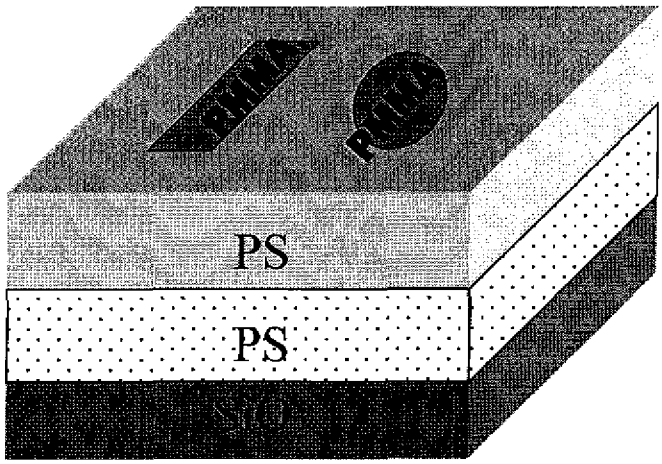


FIGURE 6D
Removal of unregistered top layer with etching

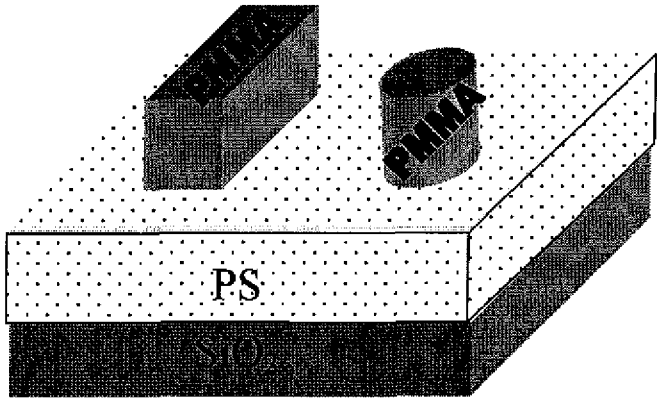
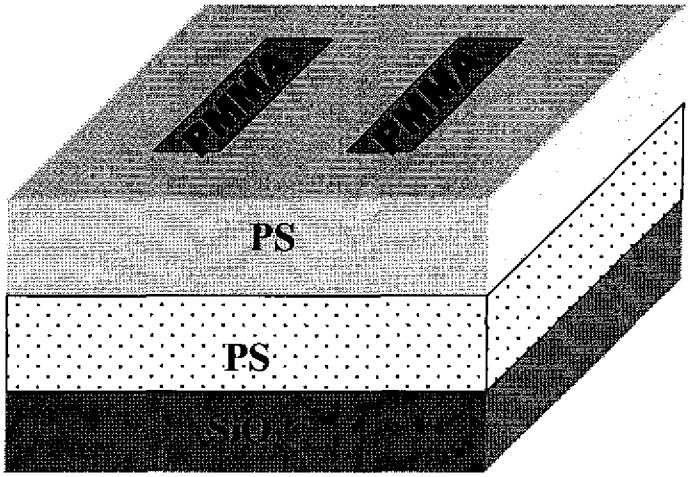


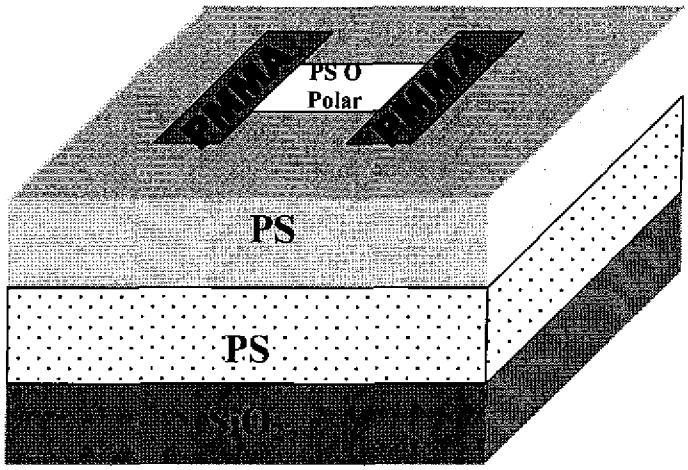
FIGURE 6E
Selective removal of registered bottom layer

FIGURE 7A



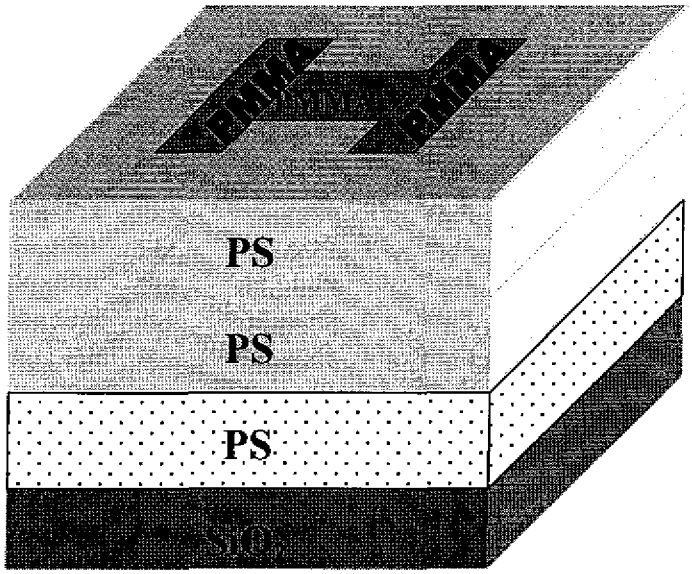
Starting configuration is the result from the removal of the unregistered top layer. If continuing from this step as before two identical structures would remain.

FIGURE 7B



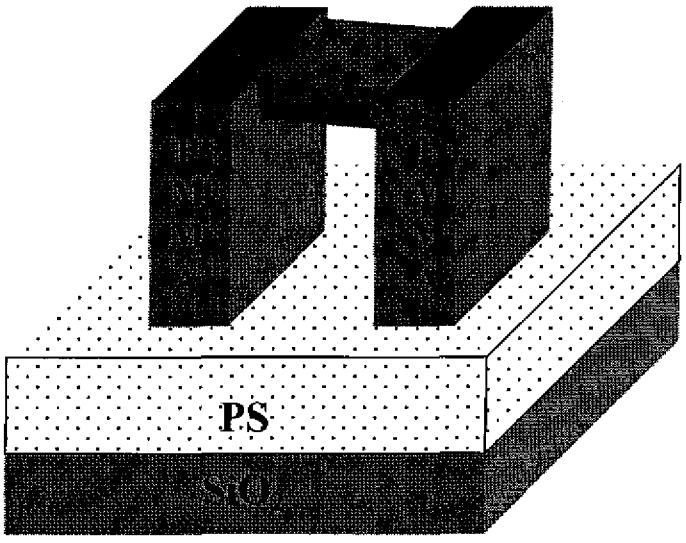
A new pattern is created on the registered layer of the previous step

FIGURE 7C



Self-assembly takes place and removal of new unregistered layer

FIGURE 7D



Selective removal of the registered layer