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- (54) Title:** METHOD FOR REDUCING TIP-TO-TIP SPACING BETWEEN LINES

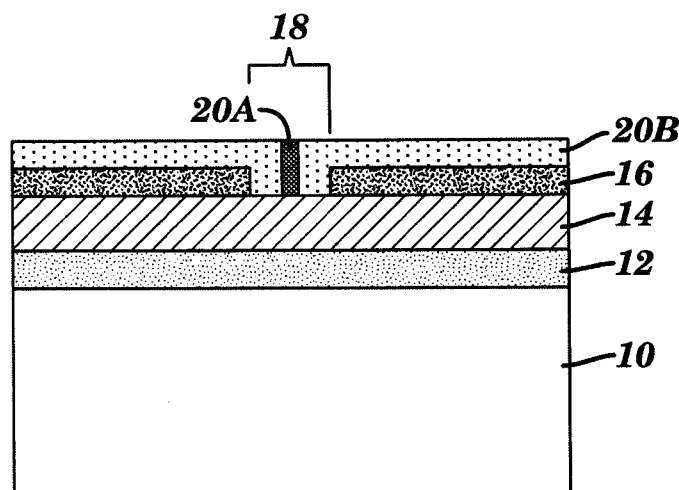


FIG. 10A

- (57) Abstract:** This invention provides a method for reducing tip-to-tip spacing between lines using a combination of photolithographic and copolymer self-assembling lithographic techniques. A mask layer is first formed over a substrate with a line structure. A trench opening of a width d is created in the mask layer. A layer of a self-assembling block copolymer is then applied over the mask layer. The block copolymer layer is annealed to form a single unit polymer block of a width or a diameter w which is smaller than d inside the trench opening. The single unit polymer block is selectively removed to form a single opening of a width or a diameter w inside the trench opening. An etch transfer process is performed using the single opening as a mask to form an opening in the line structure in the substrate.



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METHOD FOR REDUCING TIP-TO-TIP SPACING BETWEEN LINES

Technical Field

5 This invention relates to a photolithography process for semiconductor fabrication. More particularly, this invention is directed to a method for reducing tip-to-tip spacing between lines using a combination of photolithographic and copolymer self-assembling lithographic techniques.

10 Background of the Invention

Photolithography is commonly used to make miniaturized electronic components such as integrated circuits in semiconductor manufacturing. In a photolithography process, a layer of photoresist is deposited on a substrate, such as a silicon wafer. The substrate is baked to
15 remove any solvent remained in the photoresist layer. The photoresist is then selectively exposed through a photomask with a desired pattern to a source of actinic radiation. The radiation exposure causes a chemical reaction in the exposed areas of the photoresist and creates a latent image corresponding to the mask pattern in the photoresist layer. The photoresist is next developed in a developer solution to remove either the exposed portions
20 of the photoresist for a positive photoresist or the unexposed portions of the photoresist for a negative photoresist. The patterned photoresist can then be used as a mask for subsequent fabrication processes on the substrate, such as deposition, etching, or ion implantation processes.

25 Advances in semiconductor device performance have typically been accomplished through a decrease in semiconductor device dimensions. It is known that the tip-to-tip spacing between lines (e.g., PC lines) has a high impact on the unit cell density of the semiconductor device. Reducing the tip-to-tip distance between lines will greatly increase the unit cell density which in turn will lead to a shrinkage in the device dimension. However, due to the
30 line end shortening issue and the resolution limitation of photolithography, the currently available lithographic techniques can only achieve a tip-to-tip distance of not less than 100 nm.

It has been known that certain materials are capable of organizing into ordered structures without the need for human interference, which is referred to as the self-assembly of materials. Self-assembling copolymer lithographic techniques have been developed to form useful periodic patterns with dimensions in the range of 10 to 40 nm. Each self-assembling block copolymer system contains two or more different polymeric block components which are immiscible with one another. Under suitable conditions, these polymeric block components can separate into two or more different phases on a nanometer-scale and thereby form ordered nano-sized patterns. Such ordered patterns can be used for fabricating nano-scale structural units in semiconductor, optical and magnetic devices.

However, the complementary metal oxide semiconductor (CMOS) technology requires precise placement or registration of individual structural units to form metal lines and vias in the wiring level. The large, ordered array of repeating structural units formed by self-assembling block copolymers cannot be used in the CMOS technology, because of the lack of alignment or registration of the positions of individual structural units.

Summary of the Invention

The present invention provides a method for reducing tip-to-tip spacing between lines using a combination of photolithographic and copolymer self-assembling lithographic techniques.

In one aspect, the present invention relates to a method for reducing tip-to-tip spacing between lines involving the steps of providing a substrate and a line structure in the substrate; forming a mask layer over the substrate; performing a lithographic process over the mask layer to create a trench opening of a width d in the mask layer, wherein the trench opening is above the line structure in the substrate and perpendicular to the line structure; applying a layer of a block copolymer over the mask layer, wherein the block copolymer comprises at least first and second polymeric block components A and B respectively that are immiscible with each other; annealing the block copolymer layer to form a single unit polymer block of a width or a diameter w inside the trench opening, wherein $w < d$, and wherein the single unit polymer block comprises the polymeric block component B and is embedded in a polymeric matrix that comprises the first polymeric block component A;

selectively removing the second polymeric block component B to form a single opening of a width or a diameter w in the polymeric matrix inside the trench opening; and performing a first etch transfer process using the single opening as a mask to form an opening in the line structure in the substrate.

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In another aspect, the present invention relates to a method for reducing tip-to-tip spacing between lines involving the steps of providing a substrate and a line structure in the substrate; forming a first mask layer over the substrate; forming a second mask layer over said substrate, wherein the second mask layer is under said first mask layer; performing a lithographic process over the first mask layer to create a trench opening of a width d in the first mask layer, wherein the trench opening is above the line structure in the substrate and perpendicular to the line structure; applying a layer of a block copolymer over the first mask layer, wherein the block copolymer comprises at least first and second polymeric block components A and B respectively that are immiscible with each other; annealing the block copolymer layer to form a single unit polymer block of a width or a diameter w inside the trench opening, wherein $w < d$, and wherein the single unit polymer block comprises the polymeric block component B and is embedded in a polymeric matrix that comprises the first polymeric block component A; selectively removing the second polymeric block component B to form a single opening of a width or a diameter w in the polymeric matrix inside the trench opening; performing a second etch transfer process using the single opening as a mask to form an opening in the second mask layer; and performing a third etch transfer process using the opening in the second mask layer as a mask to form an opening in the line structure in the substrate.

25 The present invention may further involves the steps of forming an underlayer over the substrate before forming the mask layer or layers; and stripping any remaining block copolymer layer, mask layer or layers, and underlayer, after performing the etch transfer process or processes.

30 The block copolymer of the present invention, when placed and annealed on a planar surface, self-assembles into an ordered array of multiple unit polymer blocks embedded in the polymeric matrix, wherein each of the multiple unit polymer blocks has the width or

diameter w , and the multiple unit polymer blocks are spaced apart from each other in the ordered array by a distance s .

When $0.6(w + s) < d < 1.5(w + s)$, a single unit polymer block is formed inside and self-aligned to the trench opening. For example, when w ranges from about 10 nm to about 50 nm and s ranges from about 10 nm to about 60 nm, d may range from about 40 nm to about 160 nm.

The annealing of the block copolymer is preferably, but not necessarily, conducted at a temperature from about 130 °C to about 230 °C. The preferred annealing time is from about 40 minutes to about 80 minutes. The thickness of the block copolymer layer is preferably from about 15 nm to about 45 nm.

The block copolymer preferably comprises the first and second polymeric block components A and B at a weight ratio of from about 60:40 to about 40:60, and wherein the single unit polymer block comprises a lamella that stands perpendicular to the upper surface of said line structure.

Suitable block copolymers that can be used in the present invention include, but are not limited to: polystyrene-block-polymethylmethacrylate (PS-b-PMMA), polystyrene-block-polyisoprene (PS-b-PI), polystyrene-block-polybutadiene (PS-b-PBD), polystyrene-block-polyvinylpyridine (PS-b-PVP), polystyrene-block-polyethyleneoxide (PS-b-PEO), polystyrene-block-polyethylene (PS-b-PE), polystyrene-block-polyorganosilicate (PS-b-POS), polystyrene-block-polyferrocenyldimethylsilane (PS-b-PFS), polyethyleneoxide-block-polyisoprene (PEO-b-PI), polyethyleneoxide-block-polybutadiene (PEO-b-PBD), polyethyleneoxide-block-polymethylmethacrylate (PEO-b-PMMA), polyethyleneoxide-block-polyethylene (PEO-b-PEE), polybutadiene-block-polyvinylpyridine (PBD-b-PVP), and polyisoprene-block-polymethylmethacrylate (PI-b-PMMA).

Other aspects, features and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to preferred embodiments, as illustrated in the following figures:

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FIG. 1A shows a three-dimensional view of a pattern that is formed by a block copolymer with first and second polymeric block components A and B, while the pattern comprises an ordered array of lamellae composed of the polymeric block component B in a polymeric matrix composed of the polymeric block component A;

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FIG. 1B shows the top view of the pattern of FIG. 1A;

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FIG. 2A shows a three-dimensional view of a pattern that is formed by a block copolymer with first and second polymeric block components A and B, while the pattern comprises an ordered array of cylinders composed of the polymeric block component B in a polymeric matrix composed of the polymeric block component A;

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FIG. 2B shows the top view of the pattern of FIG. 4A;

FIG. 3 illustrates the dimensions of the ordered array of lamellae and the relative dimensions of a lithographic feature that can be used for precise placement of a single cylinder;

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FIG. 4 illustrates the dimensions of the ordered array of cylinders and the relative dimensions of a lithographic feature that can be used for precise placement of a single cylinder;

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FIGS. 5A-13B are cross-sectional and top views that illustrate exemplary processing steps for reducing tip-to-tip spacing between lines according to one embodiment of the present invention; and

FIGS. 14A-23B are cross-sectional and top views that illustrate exemplary processing steps for reducing tip-to-tip spacing between lines according to another embodiment of the present invention.

Detailed Description of the Preferred Embodiments

It is understood that when an element, such as a layer, region or substrate, is referred to as being “on” or “over” another element, it can be directly on the other element or intervening elements may also be present.

The present invention combines the conventional photolithography technology with the copolymer self-assembling lithographic techniques to reduce tip-to-tip spacing between lines.

Specifically, a mask layer is first formed over the substrate containing a line structure. A trench opening is then created in the mask layer by conventional lithography and etch techniques. Such a trench opening has a relatively large width d which is consistent with the resolutions of the conventional lithography technology. It is preferred that the trench opening is above the line structure in the substrate and perpendicular to the line structure. A thin layer of a self-assembling block copolymer is then applied over the mask layer. The block copolymer layer preferably has a thickness ranging from about 10 nm to about 50 nm, more preferably from about 15 nm to about 45 nm. The self-assembling block copolymer is annealed to form an ordered pattern. The width of the trench opening is carefully selected so that only a single unit polymer block can be formed inside the trench opening. The single unit polymer block is embedded in a polymeric matrix and has a width or diameter of w which is smaller than the width of the trench opening. The single unit polymer block can be selectively removed to form a single opening of a width or diameter of w in the polymeric matrix inside the trench opening. The single opening can then be used as a mask to form an opening in the line structure in the substrate.

There are many different types of block copolymers that can be used for practicing the present invention. As long as a block copolymer contains two or more different polymeric

block components that are not immiscible with one another, such two or more different polymeric block components are capable of separating into two or more different phases on a nanometer scale and thereby form patterns of isolated nano-sized structural units under suitable conditions.

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In a preferred, but not necessary, embodiment of the present invention, the block copolymer consists essentially of first and second polymeric block components A and B that are immiscible with each other. The block copolymer may contain any numbers of the polymeric block components A and B arranged in any manner. The block copolymer can have either a linear or a branched structure. Preferably, such a block polymer is a linear diblock copolymer having the formula of A-B.

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Specific examples of suitable block copolymers that can be used for forming the structural units of the present invention may include, but are not limited to: polystyrene-block-polymethylmethacrylate (PS-b-PMMA), polystyrene-block-polyisoprene (PS-b-PI), polystyrene-block-polybutadiene (PS-b-PBD), polystyrene-block-polyvinylpyridine (PS-b-PVP), polystyrene-block-polyethyleneoxide (PS-b-PEO), polystyrene-block-polyethylene (PS-b-PE), polystyrene-block-polyorganosilicate (PS-b-POS), polystyrene-block-polyferrocenyldimethylsilane (PS-b-PFS), polyethyleneoxide-block-polyisoprene (PEO-b-PI), polyethyleneoxide-block-polybutadiene (PEO-b-PBD), polyethyleneoxide-block-polymethylmethacrylate (PEO-b-PMMA), polyethyleneoxide-block-polyethylene (PEO-b-PEE), polybutadiene-block-polyvinylpyridine (PBD-b-PVP), and polyisoprene-block-polymethylmethacrylate (PI-b-PMMA).

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The specific structural units formed by the block copolymer are determined by the molecular weight ratio between the first and second polymeric block components A and B. For example, when the ratio of the molecular weight of the first polymeric block component A over the molecular weight of the second polymeric block component B is greater than about 80:20, the block copolymer will form an ordered array of spheres composed of the second polymeric block component B in a matrix composed of the first polymeric block component A. When the ratio of the molecular weight of the first polymeric block component A over the molecular weight of the second polymeric block component B is less than about 80:20

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but greater than about 60:40, the block copolymer will form an ordered array of cylinders composed of the second polymeric block component B in a matrix composed of the first polymeric block component A. When the ratio of the molecular weight of the first polymeric block component A over the molecular weight of the second polymeric block component B is less than about 60:40 but is greater than about 40:60, the block copolymer will form alternating lamellae composed of the first and second polymeric block components A and B. Therefore, the molecular weight ratio between the first and second polymeric block components A and B can be readily adjusted in the block copolymer of the present invention, in order to form desired structural units.

In one preferred embodiment of the present invention, the ratio of the molecular weight of the first polymeric block component A over the molecular weight of the second polymeric block component B ranges from about 60:40 to about 40:60, so that the block copolymer of the present invention will form an ordered array of lamellae composed of the second polymeric block component B in a matrix composed of the first polymeric block component A, as shown in FIGS. 1A and 1B. Preferably, the second polymeric block component B can be selectively removable relative to the first polymeric block component A, thereby resulting in either isolated and orderly arranged structural units composed of the un-removed component, or a continuous structural layer containing isolated and orderly arranged cavities left by the removable component B.

In a particularly preferred embodiment of the present invention, the block copolymer used for forming the self-assembled periodic patterns of the present invention is PS-b-PMMA with a PS:PMMA molecular weight ratio ranging from about 60:40 to about 40:60.

In another preferred embodiment of the present invention, the ratio of the molecular weight of the first polymeric block component A over the molecular weight of the second polymeric block component B ranges from about 80:20 to about 60:40, so that the block copolymer of the present invention will form an ordered array of cylinders composed of the second polymeric block component B in a matrix composed of the first polymeric block component A, as shown in FIGS. 2A and 2B. Preferably, the second polymeric block component B can be selectively removable relative to the first polymeric block component A, thereby resulting

in either isolated and orderly arranged structural units composed of the un-removed component, or a continuous structural layer containing isolated and orderly arranged cavities left by the removable component B.

5 In a particularly preferred embodiment of the present invention, the block copolymer used for forming the self-assembled periodic patterns of the present invention is PS-b-PMMA with a PS:PMMA molecular weight ratio ranging from about 80:20 to about 60:40.

10 In order to form the self-assembled periodic patterns, the block copolymer is first dissolved in a suitable solvent system to form a block copolymer solution, which is then applied onto a surface to form a thin block copolymer layer, followed by annealing of the thin block copolymer layer. The solvent system used for dissolving the block copolymer and forming the block copolymer solution may comprise any suitable solvent, including, but not limited to: toluene, propylene glycol monomethyl ether acetate (PGMEA), propylene glycol
15 monomethyl ether (PGME), and acetone. The block copolymer solution preferably contains the block copolymer at a concentration ranging from about 0.1 % to about 2 % by total weight of the solution. More preferably, the block copolymer solution contains the block copolymer at a concentration ranging from about 0.5 wt% to about 1.5 wt%. In a particularly preferred embodiment of the present invention, the block copolymer solution
20 comprises about 0.5 wt% to about 1.5 wt% PS-b-PMMA dissolved in toluene or PGMEA.

The block copolymer solution can be applied to the surface of a device structure by any suitable techniques, including, but not limited to: spin coating, spraying, ink coating, and dip coating. Preferably, the block copolymer solution is spin coated onto the surface of a
25 substrate to form a thin block copolymer layer.

The substrate is then annealed to effectuate micro-phase segregation of the different block components contained by the block copolymer. Annealing of the self-assembling block copolymer in the present invention can be achieved by various methods known in the art,
30 including, but not limited to: thermal annealing (either in a vacuum or in an inert atmosphere containing nitrogen or argon), ultra-violet annealing, laser annealing, solvent vapor-assisted annealing, or supercritical fluid-assisted annealing.

In a preferred embodiment of the present invention, a thermal annealing step is carried out to anneal the block copolymer layer at an elevated annealing temperature that is above the glass transition temperature (T_g) of the block copolymer, but below the decomposition or degradation temperature (T_d) of the block copolymer. Preferably, the thermal annealing step is carried out at an annealing temperature of about 100°C to about 250°C. More preferably, the annealing temperature is from about 130°C to about 230°C. The thermal annealing may last from about 30 minutes to about 10 hours, more preferably, from about 40 minutes to about 80 minutes.

The block copolymer, when applied and annealed on a planar surface, self-assembles into an ordered array of multiple structural units comprising said polymeric block component B embedded in a polymeric matrix comprising said first polymeric block component A. Each of said multiple structural units has a width or diameter w and is spaced apart from each other in the ordered array by a distance s (FIGS. 3 and 4).

In the present invention, the dimension of the trench opening in the mask layer is adjusted so that only a single unit polymer block can be formed and placed inside the trench opening from the self-assembling block copolymer. In order to achieve formation and placement of such a single structure unit inside the trench opening, it is preferred that the width of the trench opening d is more than $0.6(w + s)$, but less than $1.5(w + s)$. For example, when w ranges from about 10 nm to about 50 nm and s ranges from about 10 nm to about 60 nm, d may range from about 40 nm to about 160 nm.

FIGS. 5A-13B are cross-sectional and top views that illustrate exemplary processing steps for reducing tip-to-tip spacing between lines according to one embodiment of the present invention.

FIG. 5A shows the cross-sectional view of a substrate 10 with a line structure 12 on it. The cross-section site is across the line structure, as shown in FIG. 5B. The line structure is formed by any conventional lithography techniques. Preferably, the line structure is a gate line structure. The substrate in the present invention is suitably any substrate conventionally used in lithography processes. For example, the substrate can be silicon, silicon oxide,

aluminum-aluminum oxide, gallium arsenide, ceramic, quartz, copper or any combination thereof including multilayers.

A mask layer 16 is formed over the substrate 10, as shown in FIGS. 6A and 6B. The mask layer 16 may comprise any suitable organic or inorganic photosensitive materials that can be patterned by conventional lithography techniques. In a preferred embodiment, mask layer 16 is a photoresist. More preferably, mask layer 16 is a Si-containing photoresist. The mask layer may be applied by virtually any standard means including spin coating. The mask layer may be baked (PAB) to remove any solvent and improve the coherence of the mask layer. The preferred range of the PAB temperature is from about 70 °C to about 150 °C, more preferably from about 90 °C to about 130 °C. A typical bake time is from about 60 seconds to about 90 seconds. The preferred range of thickness of the mask layer is from about 20 nm to about 400 nm, more preferably from about 50 nm to about 300 nm.

Optionally, but not necessarily, an underlayer 14 may be applied over the substrate 10 with the line structure 12 before the mask layer 16 is formed, as shown in FIGS. 7A and 7B. The underlayer 14 is a planarizing layer used for leveling the topography of the substrate. Both organic and inorganic planarizing materials commonly used in photolithographic processes can be used in forming the underlayer 14. The thickness of the underlayer 14 is preferably from about 50 nm to about 300 nm.

Next, a lithographic process is performed over the mask layer 16 to create a trench opening 18 in the mask layer, and the upper surface of the underlayer 14 is exposed through the trench opening 18. The lithographic process involves conventional lithography and resist development steps. Specifically, the mask layer 16 is first exposed to a desired pattern of radiation (not shown). The exposed mask layer 16 is then developed in a conventional resist developer to form the trench opening 18 in the mask layer 16. The trench opening 18 has a width d that ranges from about 30 nm to about 200 nm, more preferably from about 40 nm to about 160 nm. It is preferred that the trench opening is above the line structure 12 in the substrate 10 and perpendicular to the line structure 12, as shown in FIGS. 8A and 8B.

Optionally, but not necessarily, the interior surfaces of the trench opening 18 are treated before the application of a layer of a block copolymer to adjust the surface affinities of a specific surface to the different block components of the block copolymer. Specifically, one or more surface layers are formed over the bottom surface and/or sidewall surfaces of the trench opening 18. These surface layers can provide the desired surface affinities for aligning the lamellar or cylindrical unit polymeric block formed by the block copolymer layer inside the trench opening 18.

If a surface has substantially the same surface affinity to both block components A and B of a block copolymer, such a surface is considered a neutral surface or a non-preferential surface, i.e., both block components A and B can wet such a surface. In contrast, if a surface has significantly different surface affinities for the block components A and B, such a surface is then considered a preferential surface, i.e., only one of block components A and B can wet such a surface, but the other cannot. For example, surfaces comprising one of silicon native oxides, silicon oxides, and silicon nitrides are preferentially wetted by PMMA block components, but not by PS block components. Therefore, such surfaces can be used as preferential surfaces for PS-b-PMMA block copolymers. On the other hand, a monolayer comprising a substantially homogenous mixture of PS and PMMA components, such as a random PS-r-PMMA copolymer layer, provides a neutral surface or a non-preferential surface for PS-b-PMMA block copolymers.

In order to form lamellar polymeric blocks that are aligned perpendicular to the bottom surface of the trench opening 18 from PS-b-PMMA, it is desired to deposit a neutral or non-preferential monolayer (e.g., a substantially homogenous mixture of PS and PMMA components) over the bottom surface of the trench opening 18, while the sidewall surfaces of the trench opening 18, which preferably comprise silicon nitrides or oxides, are either left untreated or are coated with a preferential wetting material (e.g., silicon native oxides, silicon oxides, and silicon nitrides). In this manner, the lamellar polymeric blocks formed from PS-b-PMMA will stand perpendicular to the bottom surface of the trench opening 18 and also perpendicular to the upper surface of said line structure

A thin layer of a self-assembling block copolymer 20 is applied over the mask layer 16, including the trench opening 18, as shown in FIGS. 9A and 9B. The block copolymer layer 20 preferably has a thickness that ranges from about 10 nm to about 50 nm, more preferably from about 15 nm to about 45 nm.

5 In a preferred embodiment, the block copolymer layer 20 is a diblock copolymer comprising a first and a second polymeric block components A and B with a molecular weight ratio ranging from about 60:40 to about 40:60. More preferably, the block copolymer layer 20 is a PS-b-PMMA block copolymer with a PS:PMMA molecular weight ratio ranging from
10 about 60:40 to about 40:60. Such a PS-b-PMMA block copolymer, when applied and annealed on a planar surface, self-assembles into an ordered array of PMMA lamellae in a PS matrix. However, because of the trench opening 18 of the width d in the mask layer 16, annealing of the block copolymer layer 20 results in only a single PMMA lamella 20A embedded in a PS matrix 20B inside the trench opening 18, as shown in FIGS. 10A and 10B.
15 The PMMA lamella 20A has a width w which is smaller than the width d and ranges from about 5 nm to about 60 nm, preferably from about 10 nm to about 50 nm.

Next, the single lamella 20A is selectively removed to form the single opening 22 of the width w , as shown in FIGS. 11A and 11B. For example, when the block copolymer layer 20
20 is a PS-b-PMMA block copolymer, the single lamella 20A can be selectively removed by immersing the entire structure as shown in FIGS. 10A and 10B in an acetic acid aqueous solution containing about 62% of acetic acid for a duration of about 1 minute.

The single opening 22 is then used as a mask in an etch transfer process to form an opening
25 24 in the line structure 12, exposing the upper surface of the substrate 10, as shown in FIGS. 12A and 12B. The etch transfer process may involve one or more dry or wet etch steps. It is possible that the entire or part of the block copolymer layer 20, the mask layer 16 and the underlayer 14 are removed during the etch transfer process.

30 Any remaining block copolymer layer 20, mask layer 16 and underlayer 14 after performing the etch process is stripped from the substrate, exposing the line structure 12 and the upper surface of the substrate 10 not covered by the line structure 12, as shown in FIGS. 13A and

13B. The opening 24 cuts the line structure 12 into two lines 12A and 12B. The tip-to-tip spacing between these two lines 12A and 12B is thus the width of the opening 24. Since the single opening 22 has a width w in the range from about 5 nm to about 60 nm, preferably from about 10 nm to about 50 nm, the width of the opening 24 is also in the similar range.

5 Such a small tip-to-tip spacing between these two lines 12A and 12B cannot be formed by the conventional lithography techniques.

FIGS. 14A-23B are cross-sectional and top views that illustrate exemplary processing steps for reducing tip-to-tip spacing between lines according to another embodiment of the present invention. This embodiment involves many steps that are the same as those in the previous embodiment, as illustrated in FIGS. 5A-13B.

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FIG. 14A shows the cross-sectional view of a substrate 10 with a line structure 12 on it. The cross-section site is across the line structure, as shown in FIG. 14B.

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A first mask layer 15 is formed over the substrate 10 and a second mask layer 17 is formed over the first mask layer 15, as shown in FIGS. 15A and 15B. The first mask layer 15 may comprise any suitable mask material, such as an oxide, nitride, or oxynitride, and it can be deposited by well known techniques such as chemical vapor deposition (CVD), plasma-assisted CVD, atomic layer deposition (ALD), evaporation, reactive sputtering, chemical solution deposition and other like deposition processes. Preferably, the first mask layer 15 comprises silicon nitride and is deposited by a CVD process.

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The second mask layer 17 may comprise any suitable organic or inorganic photosensitive materials that can be patterned by conventional lithography techniques. In a preferred embodiment, the second mask layer 17 is a photoresist. The second mask layer 17 may be applied by virtually any standard means including spin coating. The second mask layer 17 may be baked (PAB) to remove any solvent and improve the coherence of the mask layer. The preferred range of the PAB temperature is from about 70 °C to about 150 °C, more preferably from about 90 °C to about 130 °C. A typical bake time is from about 60 seconds to about 90 seconds. The preferred range of thickness of the second mask layer 17 is from about 20 nm to about 400 nm, more preferably from about 50 nm to about 300 nm.

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Optionally, but not necessarily, an underlayer 14 may be applied over the substrate 10 with the line structure 12 before the first mask layer 15 is formed, as shown in FIGS. 16A and 16B.

5 Next, a lithographic process is performed over the second mask layer 17 to create a trench opening 18 in the mask layer, and the upper surface of the first mask layer 15 is exposed through the trench opening 18. The lithographic process involves conventional lithography and resist development steps. The trench opening 18 has a width d that ranges from about 30 nm to about 200 nm, more preferably from about 40 nm to about 160 nm. It is preferred
10 that the trench opening is above the line structure 12 in the substrate 10 and perpendicular to the line structure 12, as shown in FIGS. 17A and 17B.

Optionally, but not necessarily, the interior surfaces of the trench opening 18 are treated before the application of a layer of a block copolymer to adjust the surface affinities of a
15 specific surface to the different block components of the block copolymer, as described in the previous embodiment.

A thin layer of a self-assembling block copolymer 20 is applied over the second mask layer 17, including the trench opening 18, as shown in FIGS. 18A and 18B. The block copolymer
20 layer 20 preferably has a thickness that ranges from about 10 nm to about 50 nm, more preferably from about 15 nm to about 45 nm.

In a preferred embodiment, the block copolymer layer 20 is a diblock copolymer comprising a first and a second polymeric block components A and B with a molecular weight ratio
25 ranging from about 60:40 to about 40:60. More preferably, the block copolymer layer 20 is a PS-*b*-PMMA block copolymer with a PS:PMMA molecular weight ratio ranging from about 60:40 to about 40:60. Because of the trench opening 18 of the width d in the second mask layer 17, annealing of the block copolymer layer 20 results in only a single PMMA lamella 20A embedded in a PS matrix 20B inside the trench opening 18, as shown in FIGS.
30 19A and 19B. The PMMA lamella 20A has a width w which is smaller than the width d and ranges from about 5 nm to about 60 nm, preferably from about 10 nm to about 50 nm.

The single lamella 20A is selectively removed to form the single opening 22 of the width w in the matrix 20B, as shown in FIGS. 20A and 20B.

5 The single opening 22 is then used as a mask in a first etch transfer process to form an opening 23 in the first mask layer 15, as shown in FIGS. 21A and 21B. The first etch transfer process may involve one or more dry or wet etch steps. It is possible that the entire or part of the block copolymer layer 20 and the second mask layer 17 are removed during the etch transfer process.

10 In a second etch transfer process, the opening 23 is used as a mask to form an opening 24 in the line structure 12, exposing the upper surface of the substrate 10, as shown in FIGS. 22A and 22B. The etch transfer process may involve one or more dry or wet etch steps. It is possible that the entire or part of the block copolymer layer 20, the second mask layer 17, the first mask layer 15 and the underlayer 14 are removed during the etch transfer process.

15 Any remaining block copolymer layer 20, the second mask layer 17, the first mask layer 15 and the underlayer 14 after performing the etch process is stripped from the substrate, exposing the line structure 12 and the upper surface of the substrate 10 not covered by the line structure 12, as shown in FIGS. 23A and 23B. As described in the previous
20 embodiment, the opening 24 cuts the line structure 12 into two lines 12A and 12B. The tip-to-tip spacing between these two lines 12A and 12B is thus the width of the opening 24 which ranges from about 5 nm to about 60 nm, preferably from about 10 nm to about 50 nm.

CLAIMS

1. A method for reducing tip-to-tip spacing between lines comprising the steps of:
providing a substrate and a line structure in said substrate;
5 forming a first mask layer over said substrate;
performing a lithographic process over said first mask layer to create a trench
opening of a width d in said first mask layer, wherein said trench opening is above said line
structure in said substrate and perpendicular to said line structure;
applying a layer of a block copolymer over said first mask layer, wherein said block
10 copolymer comprises at least first and second polymeric block components A and B
respectively that are immiscible with each other;
annealing said block copolymer layer to form a single unit polymer block of a width
or a diameter w inside said trench opening, wherein $w < d$, and wherein said single unit
polymer block comprises said polymeric block component B and is embedded in a
15 polymeric matrix that comprises said first polymeric block component A;
selectively removing said second polymeric block component B to form a single
opening of a width or a diameter w in said polymeric matrix inside said trench opening; and
performing a first etch transfer process using said single opening as a mask to form
an opening in said line structure in said substrate.
20
2. The method of claim 1, further comprising forming an underlayer over said substrate,
before forming said first mask layer.
3. The method of claim 2, further comprising stripping any remaining block copolymer
25 layer, first mask layer and underlayer, after performing said etch transfer process.
4. The method of any of claims 1 to 3, wherein said annealing is performed at a
temperature from about 130 °C to about 230 °C.
- 30 5. The method of any of claims 1 to 4, wherein said annealing is performed from about
40 minutes to about 80 minutes.

6. The method of any of claims 1 to 5, wherein said layer of said block copolymer has a thickness from about 15 nm to about 45 nm.

7. The method of any of claims 1 to 6, wherein said block copolymer, when applied and annealed on a planar surface, self-assembles into an ordered array of multiple structural units comprising said polymeric block component B embedded in a polymeric matrix comprising said first polymeric block component A, wherein each of said multiple structural units has said width or diameter w , wherein said multiple structural units are spaced apart from each other in said ordered array by a distance s , and wherein $0.6(w + s) < d < 1.5(w + s)$.

8. The method of claim 7, wherein w ranges from about 10 nm to about 50 nm and s ranges from about 10 nm to about 60 nm, and wherein d ranges from about 40 nm to about 160 nm.

9. The method of any of claims 1 to 8, wherein said block copolymer comprises said first and second polymeric block components A and B, respectively, at a weight ratio of from about 60:40 to about 40:60, and wherein the single unit polymer block comprises a lamella that stands perpendicular to the upper surface of said line structure.

10. The method of any of claims 1 to 9, wherein said block copolymer is a diblock copolymer selected from the group consisting of polystyrene-block-polymethylmethacrylate (PS-b-PMMA), polystyrene-block-polyisoprene (PS-b-PI), polystyrene-block-polybutadiene (PS-b-PBD), polystyrene-block-polyvinylpyridine (PS-b-PVP), polystyrene-block-polyethyleneoxide (PS-b-PEO), polystyrene-block-polyethylene (PS-b-PE), polystyrene-block-polyorganosilicate (PS-b-POS), polystyrene-block-polyferrocenyldimethylsilane (PS-b-PFS), polyethyleneoxide-block-polyisoprene (PEO-b-PI), polyethyleneoxide-block-polybutadiene (PEO-b-PBD), polyethyleneoxide-block-polymethylmethacrylate (PEO-b-PMMA), polyethyleneoxide-block-polyethylene (PEO-b-PEE), polybutadiene-block-polyvinylpyridine (PBD-b-PVP), and polyisoprene-block-polymethylmethacrylate (PI-b-PMMA).

11. A method of any of claims 1, 4 to 10, wherein the method further comprises the steps of:

forming a second mask layer over said substrate, wherein the second mask layer is under said first mask layer; and

5 wherein said first etch transfer process comprises:

performing a second etch transfer process using said single opening as a mask to form an opening in said second mask layer; and

performing a third etch transfer process using said opening in said second mask layer as a mask to form an opening in said line structure in said substrate.

10

12. The method of claim 11, further comprising forming an underlayer over said substrate, before forming said second mask layer.

13. The method of claim 12, further comprising stripping any remaining block copolymer layer, first mask layer, second mask layer and underlayer, after performing said
15 third etch transfer process using said opening in said second mask layer as a mask to form said opening in said line structure in said substrate.

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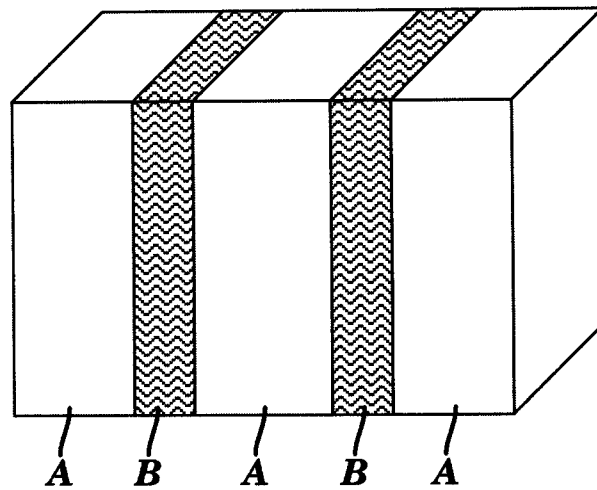


FIG. 1A
PRIOR ART

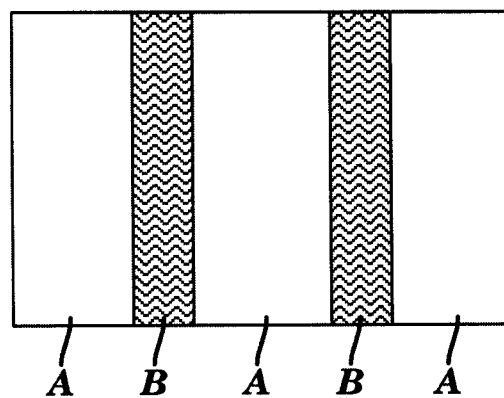


FIG. 1B
PRIOR ART

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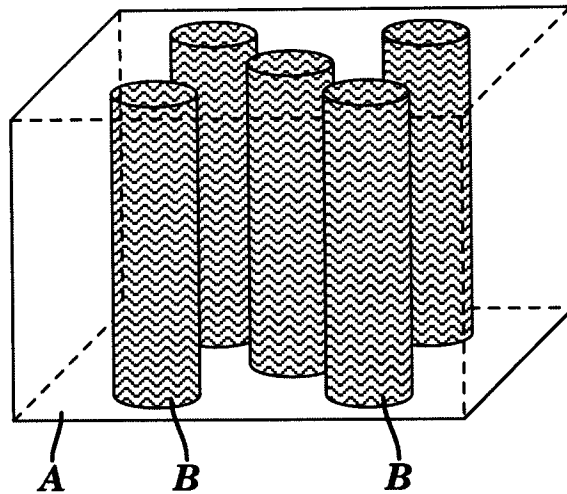


FIG. 2A
PRIOR ART

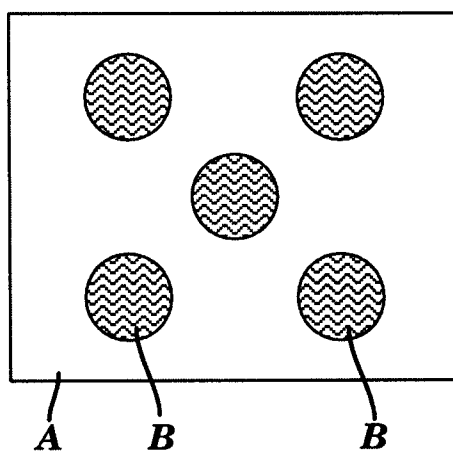


FIG. 2B
PRIOR ART

3/22

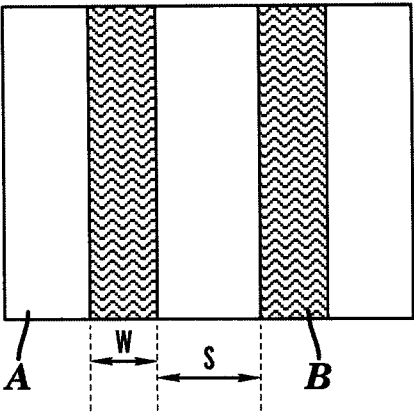


FIG. 3

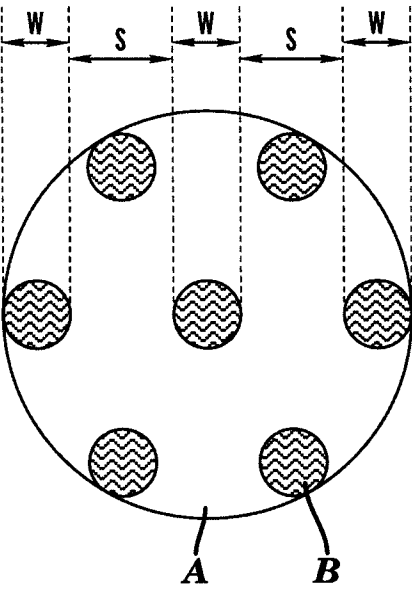


FIG. 4

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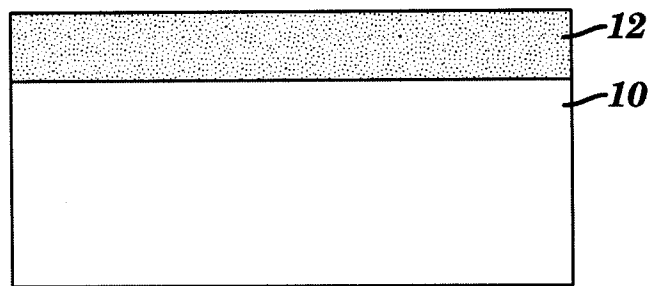


FIG. 5A

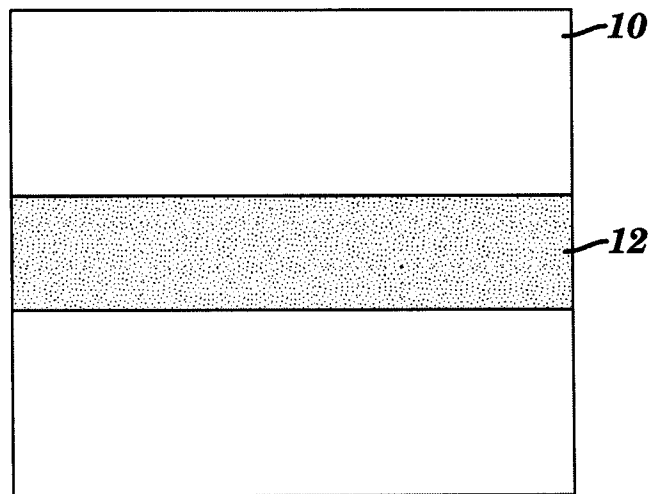


FIG. 5B

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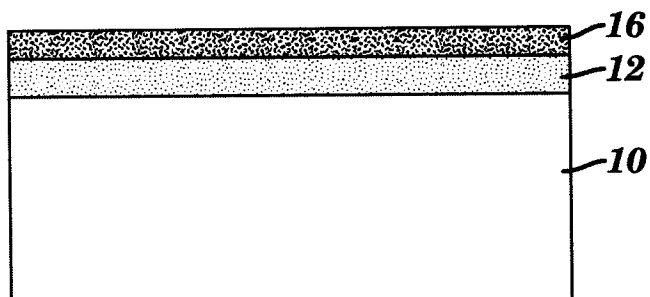


FIG. 6A

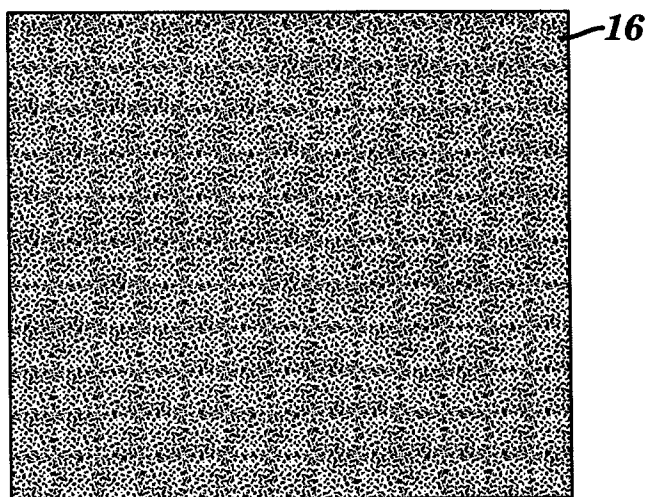


FIG. 6B

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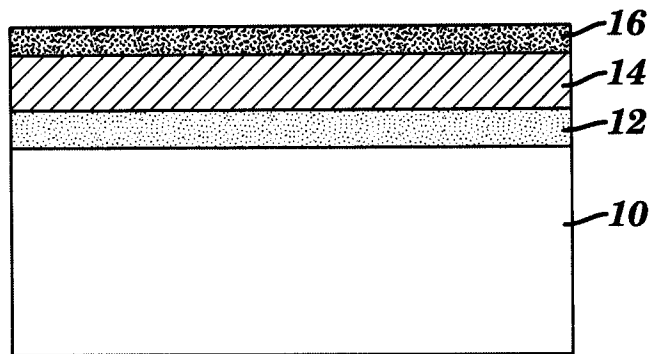


FIG. 7A

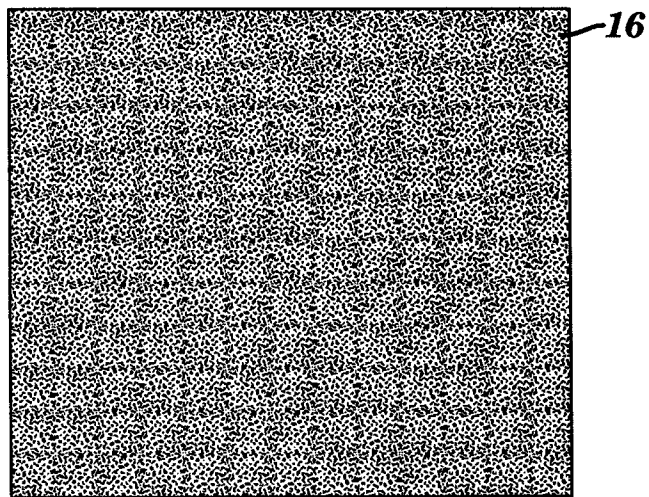


FIG. 7B

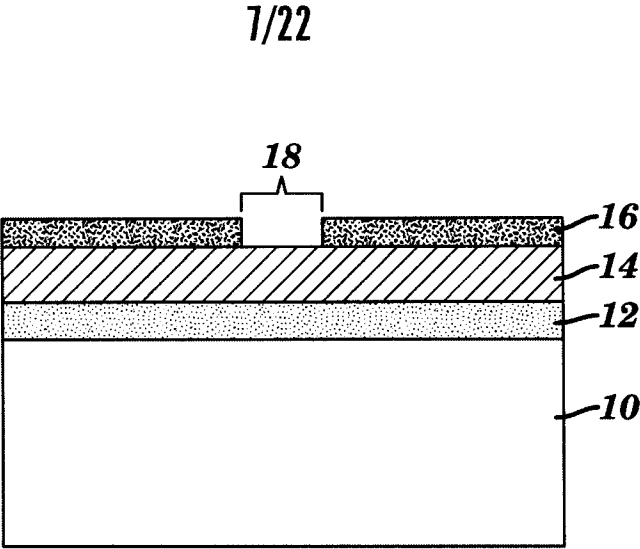


FIG. 8A

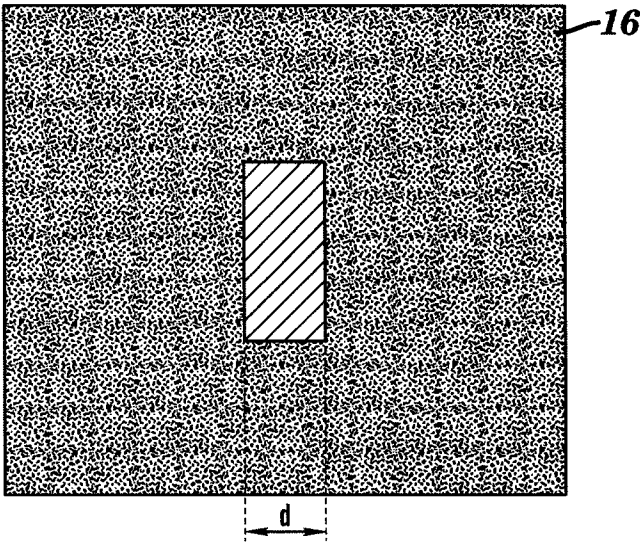


FIG. 8B

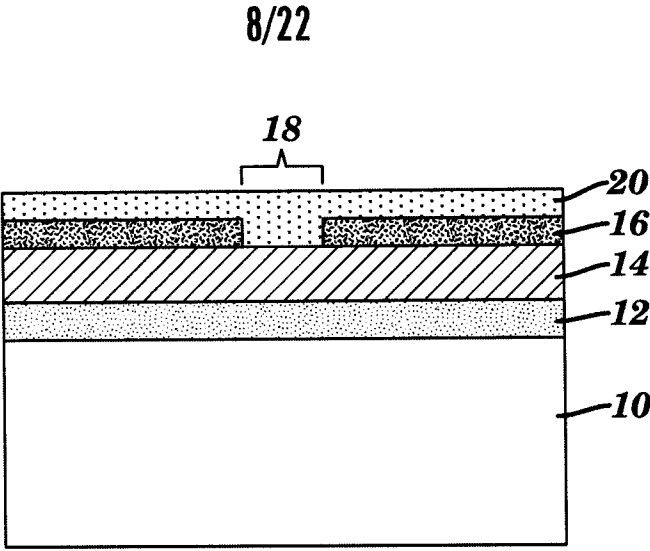


FIG. 9A

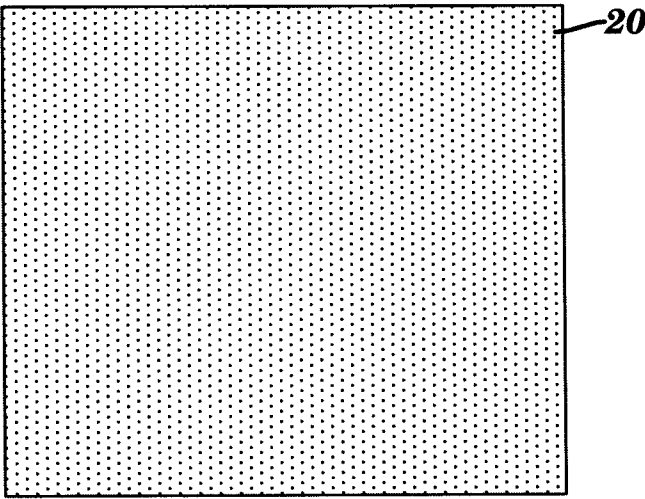


FIG. 9B

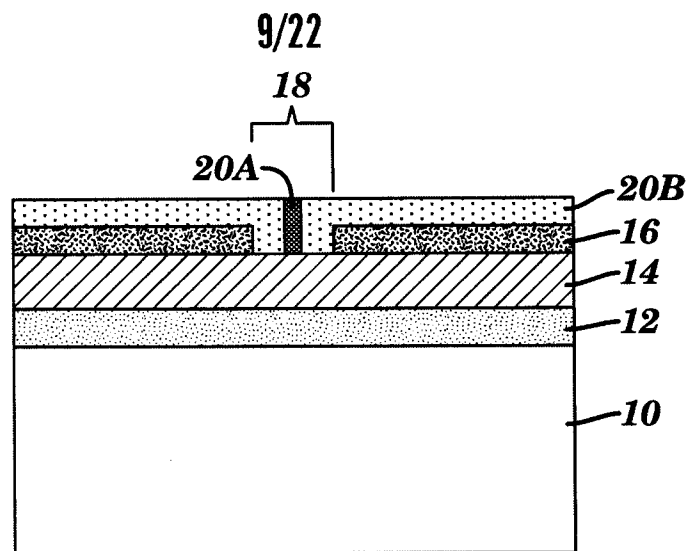


FIG. 10A

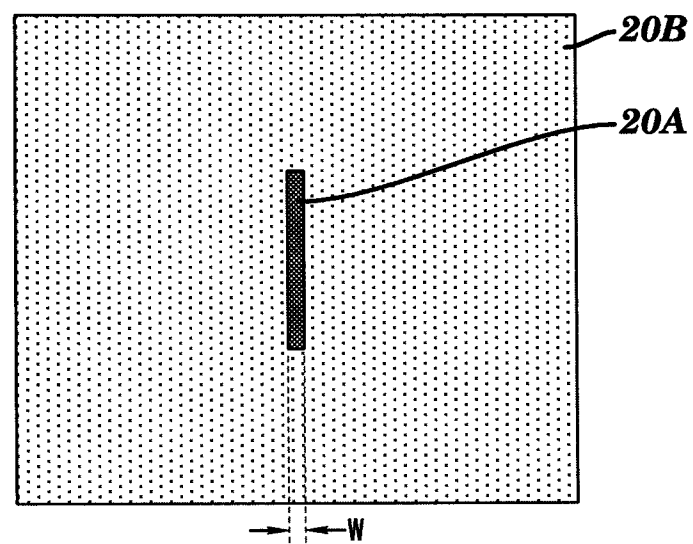


FIG. 10B

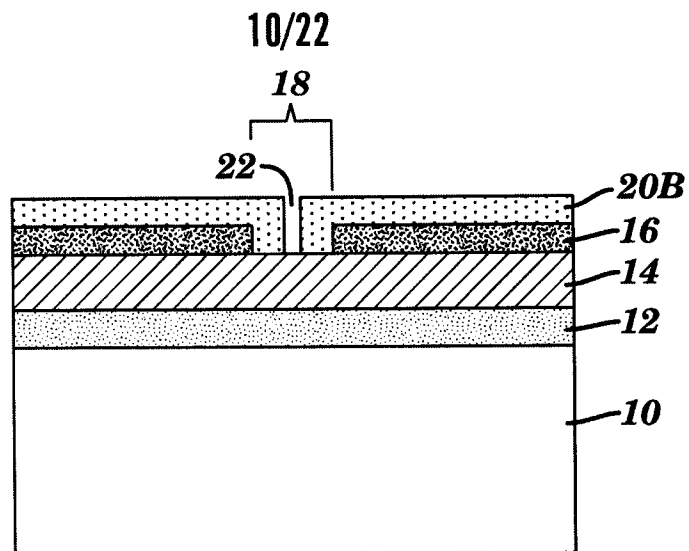


FIG. 11A

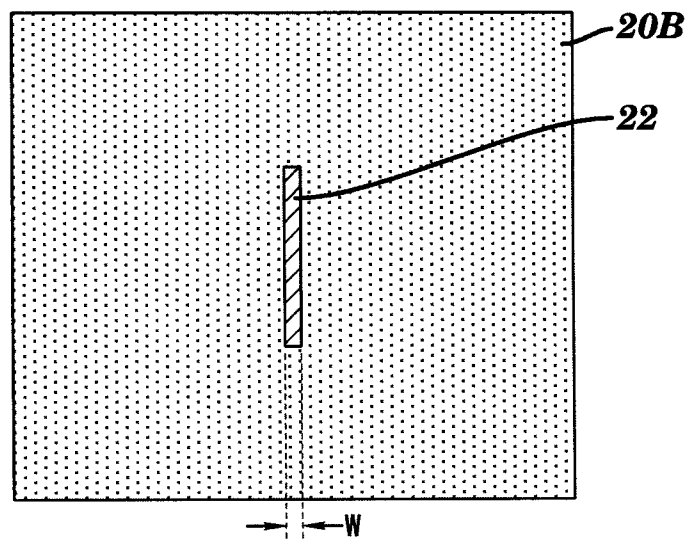


FIG. 11B

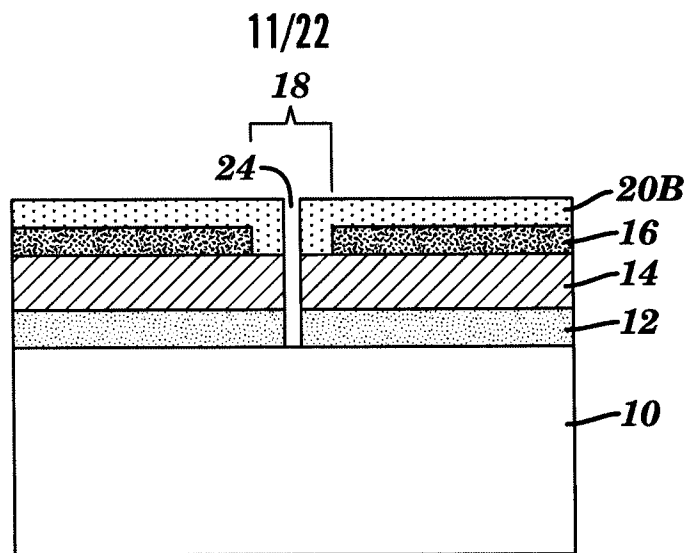


FIG. 12A

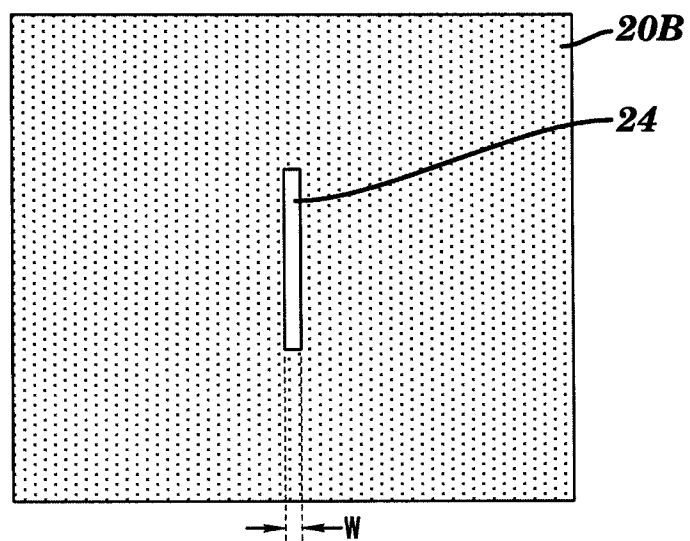


FIG. 12B

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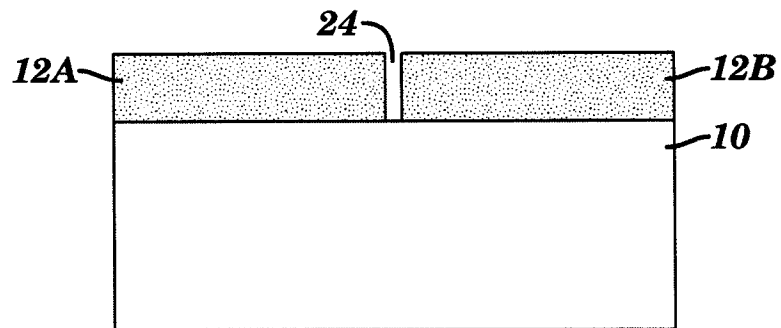


FIG. 13A

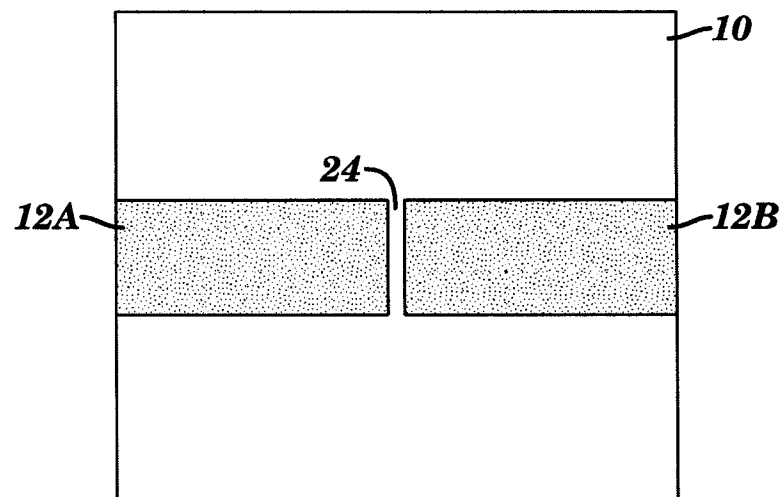


FIG. 13B

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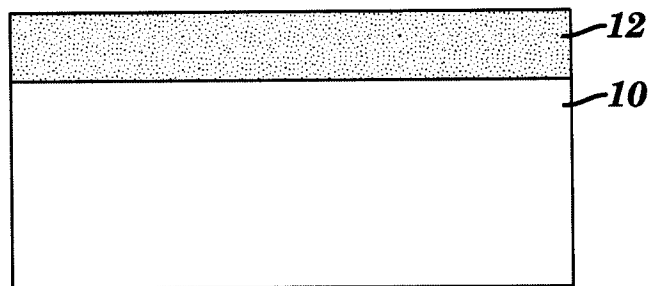


FIG. 14A

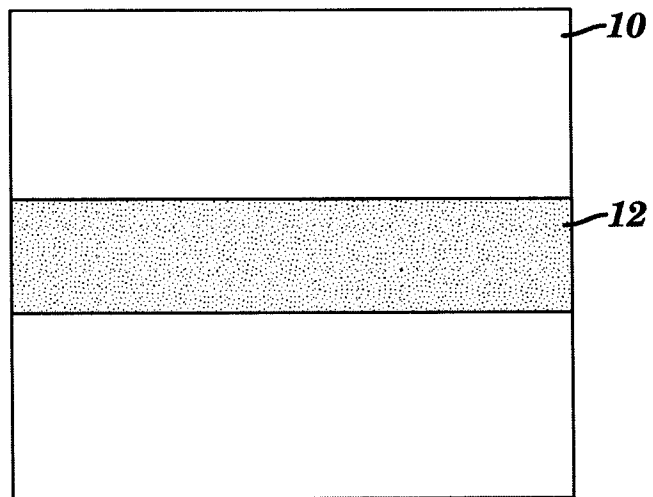


FIG. 14B

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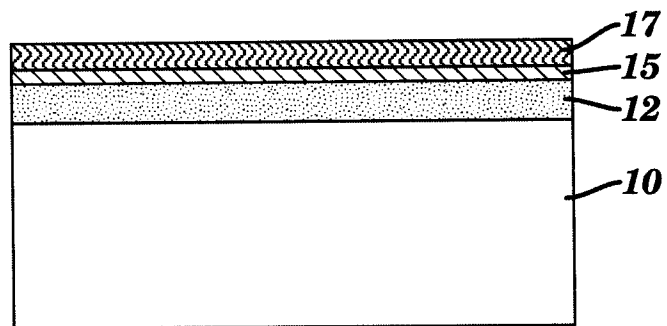


FIG. 15A

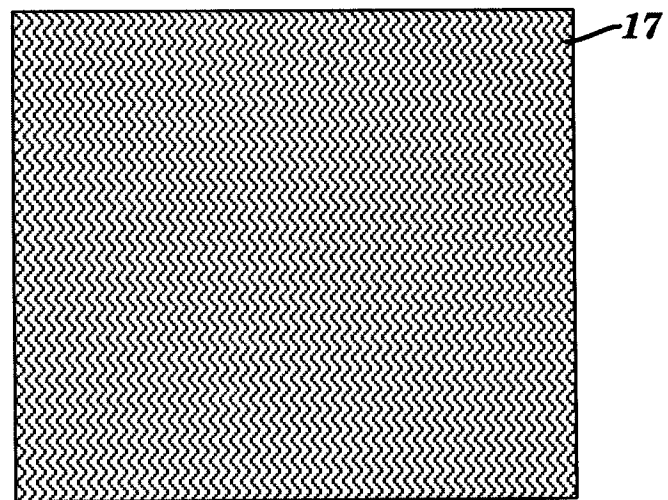


FIG. 15B

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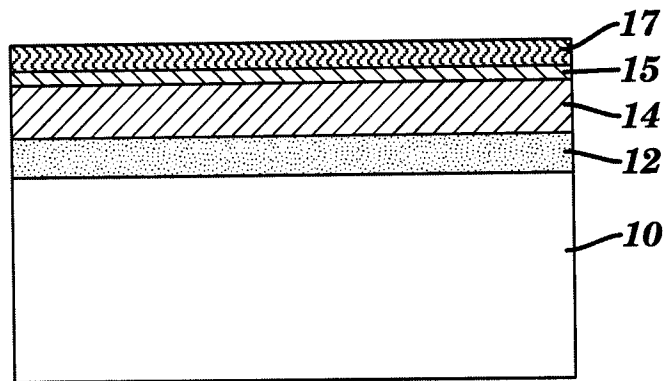


FIG. 16A

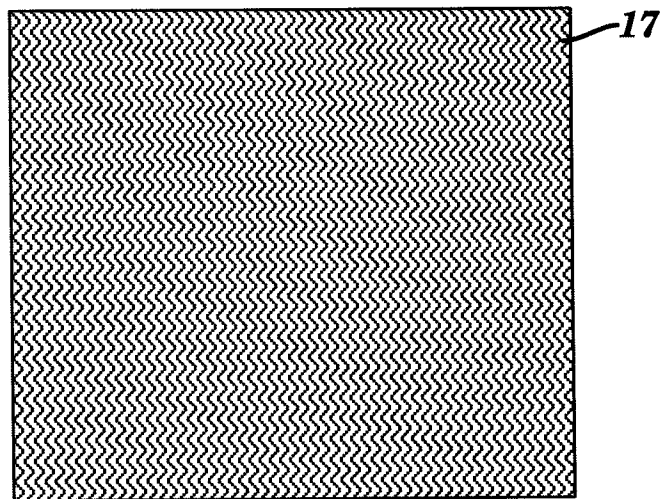


FIG. 16B

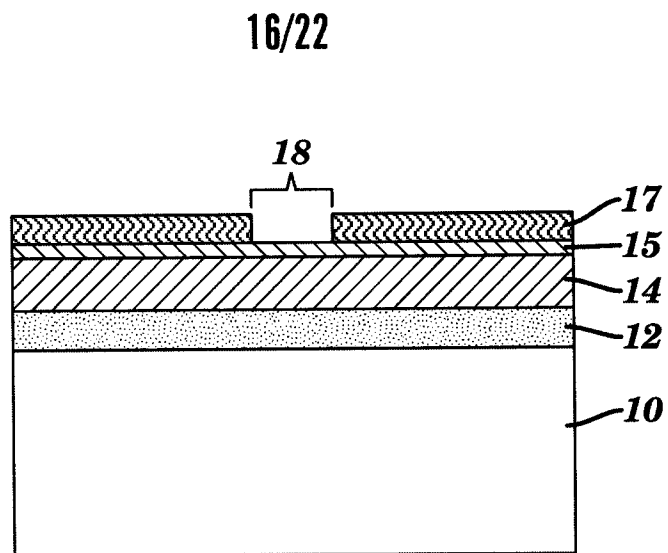


FIG. 17A

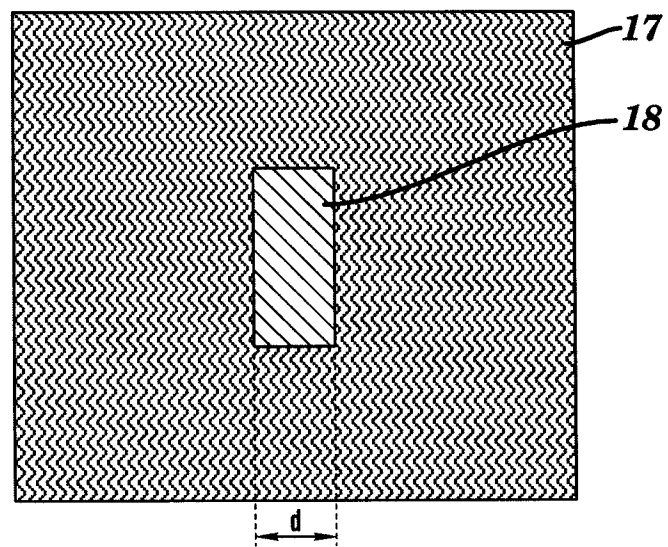


FIG. 17B

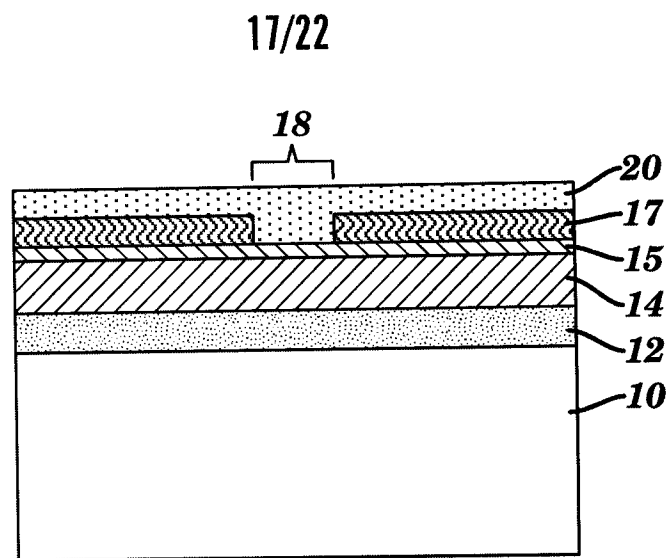


FIG. 18A

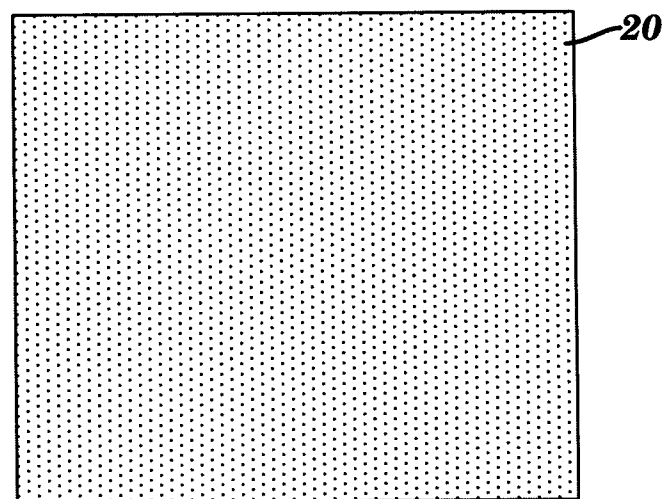


FIG. 18B

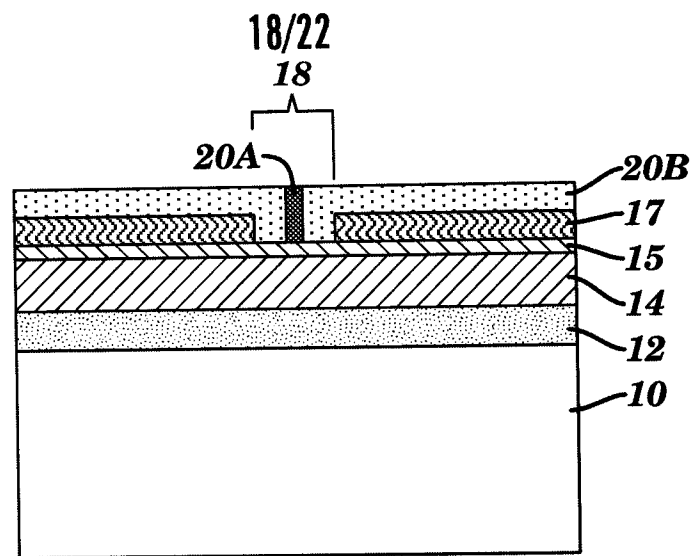


FIG. 19A

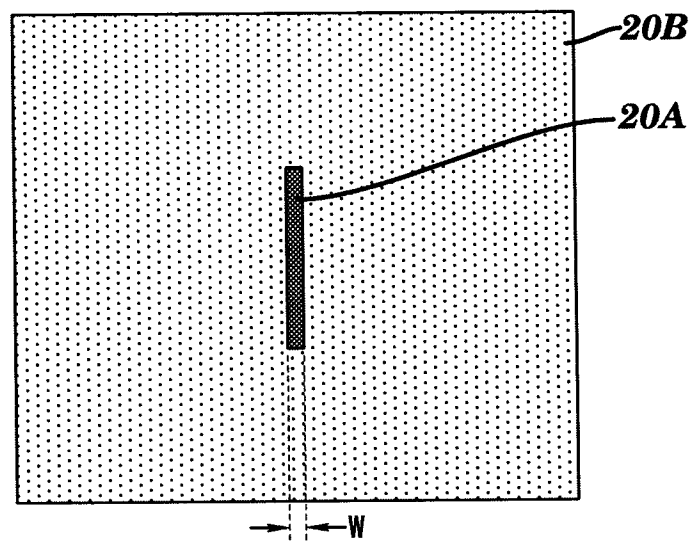


FIG. 19B

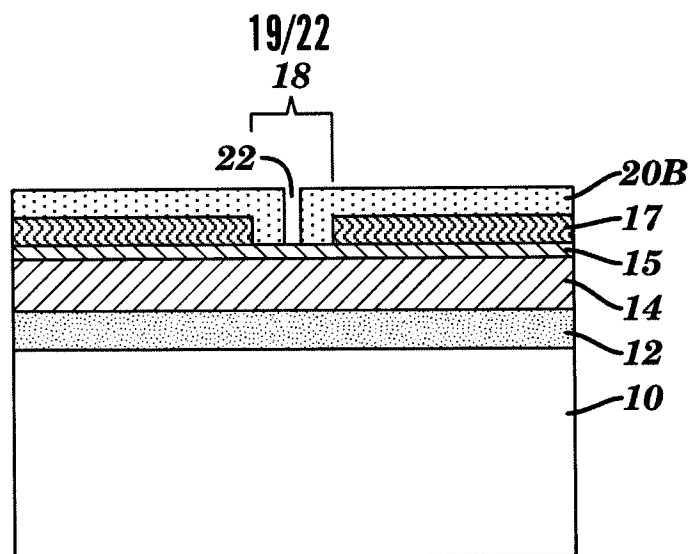


FIG. 20A

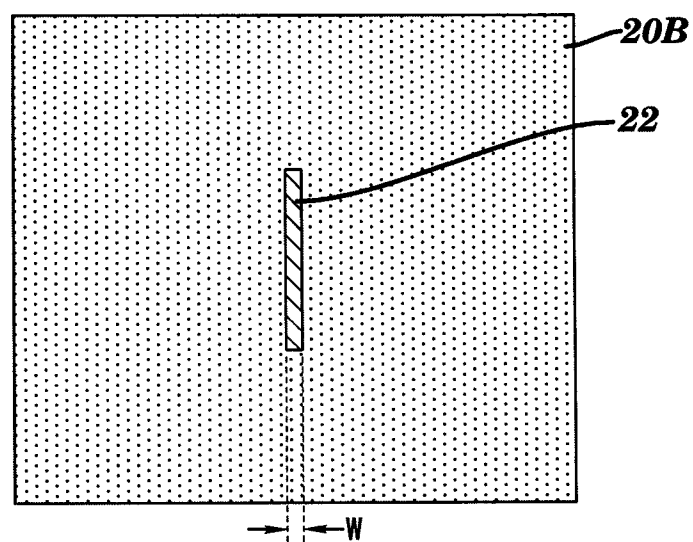


FIG. 20B

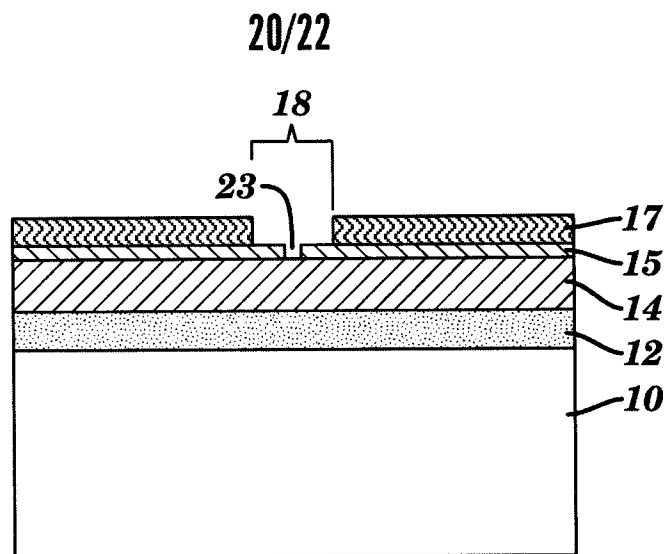


FIG. 21A

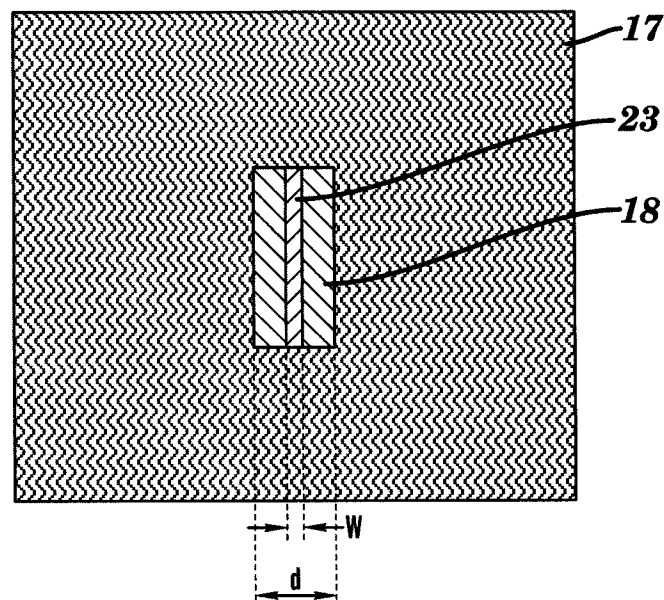


FIG. 21B

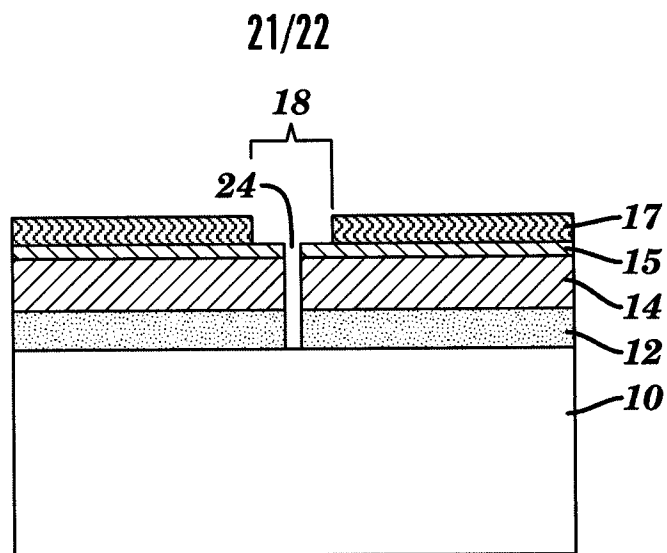


FIG. 22A

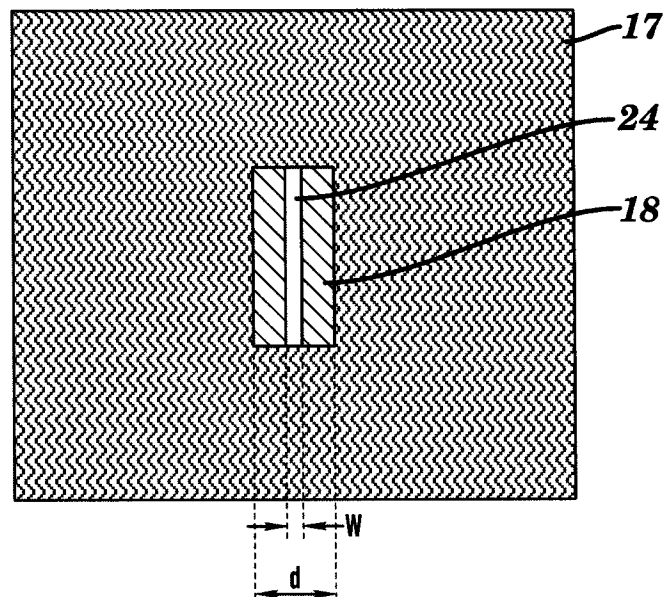


FIG. 22B

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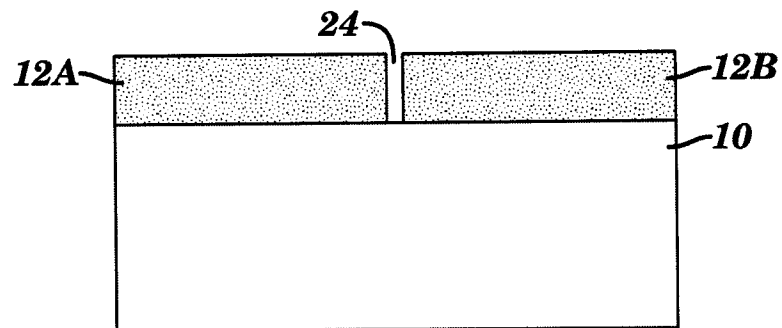


FIG. 23A

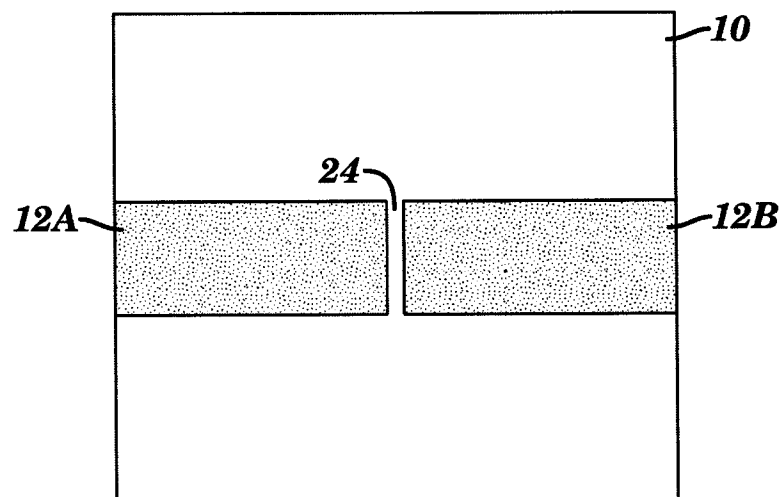


FIG. 23B

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/065847

A. CLASSIFICATION OF SUBJECT MATTER

INV. G03F7/40 G03F7/00 B81C1/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G03F B81C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/099845 A1 (YANG HAINING [US] ET AL) 1 May 2008 (2008-05-01) paragraphs [0036], [0043], [0068], [0073] - [0076]; claims 13-20; figures 1-5 -----	1-13
X	US 2005/208752 A1 (COLBURN MATTHEW E [US] ET AL) 22 September 2005 (2005-09-22) claims 1,4,5,13,16,17; figure 3 -----	1-13
X	WO 2006/112887 A2 (WISCONSIN ALUMNI RES FOUND [US]; NEALEY PAUL F [US]; KIM SANGOUK [KR];) 26 October 2006 (2006-10-26)	1-10
Y	page 9, lines 18-26; claims 1,27; figures 3,4,17 page 18, lines 6-19 ----- -/--	11-13

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 April 2010

Date of mailing of the international search report

27/04/2010

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer

Thiele, Norbert

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/065847

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 1599, column 2, lines 1-54 -----	11-13
X	US 2008/311347 A1 (MILLWARD DAN B [US] ET AL) 18 December 2008 (2008-12-18)	1-10
Y	paragraphs [0041] - [0049]; claims 1,15,16,19; figures 13-15 -----	11-13
X	US 2008/164558 A1 (YANG HAINING [US] ET AL) 10 July 2008 (2008-07-10) paragraphs [0010], [0011], [0039], [0040]; claims 1,5,6,8-13; figures 9-11,13 -----	1-13
X	WO 2008/097736 A2 (MICRON TECHNOLOGY INC [US]; MILLWARD DAN B [US]) 14 August 2008 (2008-08-14)	1-10
Y	paragraph [0009]; claims 1-8,14 -----	11-13
Y	SANG-MIN PARK ET AL: "Directed Assembly of Lamellae-Forming Block Copolymers by Using Chemically and Topographically Patterned Substrates" ADVANCED MATERIALS, WILEY VCH VERLAG, DE LNKD- DOI:10.1002/ADMA.200601421, vol. 19, no. 4, 26 January 2007 (2007-01-26), pages 607-611, XP007905662 ISSN: 0935-9648 [retrieved on 2007-01-26] figures 1-3 -----	1-13
X,P	WO 2009/094282 A1 (IBM [US]; DALTON TIMOTHY [US]; DORIS BRUCE B [US]; KIM HO-CHEOL [US];) 30 July 2009 (2009-07-30) paragraph [0068]; claims 1-8,12 -----	1-13
Y,P	WO 2009/102551 A2 (MICRON TECHNOLOGY INC [US]; MILLWARD DAN B [US]; STUEN KARL [US]) 20 August 2009 (2009-08-20) claims 1-26; figures 12-14 -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/065847

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