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### METHOD OF PATTERNING A SEMICONDUCTOR STRUCTURE

#### **Abstract**

The disclosure provides a method of patterning a semiconductor structure. A first composite substrate including first spacers on a first substrate and a second composite substrate including second spacers on a second substrate are received. The second composite substrate is disposed on the first composite substrate, in which at least one of the first spacers is in direct contact with at least one of the second spacers. Spaces between the first spacers and the second spacers are filled with a directed self-assembly material, in which the directed self-assembly material includes first portions between the first spacers and the second substrate, second portions between the second spacers and the first substrate, and third portions being remaining portions. The second composite substrate, the first spacers, and the first portions and the second portions are removed. Oxide layers are filled between the third portions. The third portions are removed.

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## **Background/Summary**

#### **BACKGROUND**

Field of Invention

[0001] The present disclosure relates to a method of patterning a semiconductor structure. Description of Related Art

[0002] As the size of the semiconductor device becomes smaller and smaller, the method of fabricating the elements of the semiconductor device becomes challenging. For example, conventional photolithography is limited by the wavelength of the exposure light, so the space between the patterned structures may not be small enough as desired. Besides the challenge of obtaining smaller space between the patterned structures, another challenge includes failing to avoid obtaining the patterned structures without a wiggling shape. The wiggling shape of the patterned structures may cause drawbacks to the semiconductor device, such as structural defects, increasing resistance, etc., thus affecting the performance of the semiconductor device and the subsequent fabricating process. Therefore, it is necessary to develop a method of patterning the semiconductor structure that is satisfying in every aspect.

#### **SUMMARY**

[0003] The present disclosure provides a method of patterning a semiconductor structure. The method includes the following operations. A first composite substrate and a second composite substrate are received, in which the first composite substrate includes a first substrate and first spacers on the first substrate, and the second composite substrate includes a second substrate and second spacers on the second substrate. The second composite substrate is disposed on the first composite substrate, in which at least one of the first spacers is in direct contact with at least one of the second spacers. Spaces between the first spacers and the second spacers are filled with a directed self-assembly material, in which the directed self-assembly material includes first portions, second portions, and third portions, the first portions are between the first spacers and the second substrate, the second portions are between the second spacers and the first substrate, and the third portions are remaining portions of the directed self-assembly material. The second composite substrate, the first spacers, and the first portions and the second portions of the directed selfassembly material are removed. Oxide layers are filled between the third portions of the directed self-assembly material. The third portions of the directed self-assembly material are removed. [0004] In some embodiments, a central axis of the at least one of the first spacers that is in direct contact with the at least one of the second spacers is substantially aligned with a central axis of the at least one of the second spacers.

[0005] In some embodiments, projections of the third portions of the directed self-assembly material on the first substrate or the second substrate are complementary with projections of the first spacers and projections of the second spacers on the first substrate or the second substrate. [0006] In some embodiments, the third portions of the directed self-assembly material are substantially equally spaced.

[0007] In some embodiments, an arrangement of the first spacers on the first substrate is substantially identical to an arrangement of the second spacers on the second substrate. [0008] In some embodiments, the first composite substrate further includes a first anti-reflective coating layer between the first substrate and the first spacers; and the second composite substrate further includes a second anti-reflective coating layer between the second substrate and the second spacers.

[0009] In some embodiments, the first anti-reflective coating layer includes a first silicon-containing layer, and the second anti-reflective coating layer includes a second silicon-containing layer.

[0010] In some embodiments, the first spacers and the second spacers independently comprise an oxide.

[0011] In some embodiments, the directed self-assembly material includes a block copolymer.

[0012] In some embodiments, the method further includes applying a removable adhesive layer between the directed self-assembly material and the first substrate or between the directed self-assembly material and the second substrate.

[0013] In some embodiments, removing the first portions and the second portions of the directed self-assembly material includes using an etchant including C.sub.4F.sub.6, C.sub.4F.sub.8, or a combination thereof.

[0014] In some embodiments, after removing the second composite substrate, the first spacers, and the first portions and the second portions of the directed self-assembly material, the third portions of the directed self-assembly material substantially remain intact on the first substrate.

[0015] In some embodiments, removing the third portions of the directed self-assembly material includes heating the third portions of the directed self-assembly material with a temperature from  $100^{\circ}$  C. to  $400^{\circ}$  C.

[0016] In some embodiments, an average space between the oxide layers is smaller than an average space between the first spacers.

[0017] In some embodiments, an angle between a top surface and a side surface of each one of the oxide layers is from 80° to 100°.

# **Description**

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The present disclosure can be more fully understood by reading the following detailed description of the embodiment, with reference made to the accompanying drawings as follows: [0019] FIG. **1** is a flow chart of a method of patterning a semiconductor structure according to some embodiments of the present disclosure;

[0020] FIGS. **2**, **3**, **4**, **5**A, **6**, **7**, **8**, **9**, and **10**A are schematics of the structures during the performance of using the method to pattern the semiconductor structure according to some embodiments of the present disclosure; and

[0021] FIGS. **5**B and **10**B are electron microscopic images of the structures relating to the structures of FIGS. **5**A and **10**A, respectively, according to some embodiments of the present disclosure.

#### **DETAILED DESCRIPTION**

[0022] To make the description of the present disclosure more detailed and complete, the following provides an illustrative description of the aspects of the implementation and the specific embodiments of the present disclosure. The disclosure is not to limit the implementation to only one form. The embodiments of the present disclosure may be combined or substituted with each other for a beneficial circumstance, and other embodiments may be appended without further explanation.

[0023] Spatially relative terms, such as above and below, etc., may be used in the present disclosure to describe the relation of one element or feature to another element or feature in the figures. The spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, the device may be oriented otherwise, e.g., 90 degrees or other orientations. Therefore, the spatially relative terms in the present disclosure can be interpreted correspondingly. In addition, in the present disclosure, unless otherwise stated, the same or similar reference numbers in different figures refer to the same or similar elements formed from the same or similar materials by the same or similar methods. [0024] The terms "about", "around", "approximately", "basically", "substantially", and so on used in the present disclosure include the stated values, characteristics, and the range of deviations from that values and characteristics that can be understood by one skilled in the art. For example, taking into account the errors of values and characteristics, the foregoing terms may include the values

within one or more standard deviations (e.g.,  $\pm 5\%$ ,  $\pm 10\%$ ,  $\pm 15\%$ ,  $\pm 20\%$ , or  $\pm 30\%$ ) of the stated value, or include the deviations from the practical operations of the stated characteristics (e.g., the "substantially parallel" may be close to parallel in practice rather than an ideally perfect parallel). In addition, the acceptable range of deviations may be selected according to the measurements or other properties, and not only one kind of deviation may be applicable to all values and characteristics.

[0025] The present disclosure provides a method of patterning a semiconductor structure, as shown in FIG. 1. The method 100 includes an operation 101 to an operation 106. The operation 101 includes receiving a first composite substrate and a second composite substrate, in which the first composite substrate includes a first substrate and first spacers on the first substrate, and the second composite substrate includes a second substrate and second spacers on the second substrate. The operation **102** includes disposing the second composite substrate on the first composite substrate, in which at least one of the first spacers is in direct contact with at least one of the second spacers. The operation **103** includes filling spaces between the first spacers and the second spacers with a directed self-assembly material, in which the directed self-assembly material includes first portions, second portions, and third portions, the first portions are between the first spacers and the second substrate, the second portions are between the second spacers and the first substrate, and the third portions are remaining portions of the directed self-assembly material. The operation **104** includes removing the second composite substrate, the first spacers, and the first portions and the second portions of the directed self-assembly material. The operation **105** includes filling oxide layers between the third portions of the directed self-assembly material. The operation **106** includes removing the third portions of the directed self-assembly material. The method **100** of the present disclosure is described in detail by the embodiments provided below.

[0026] In the embodiments as provided in FIGS. 2 to 4, before receiving the first composite substrate 200 and the second composite substrate 300 as shown in FIG. 5A, the method 100 may further include forming the first composite substrate 200 and the second composite substrate 300. It is noted that the first composite substrate 200 and the second composite substrate 300 may be identical for an easier implementation of the method 100, and for the simplicity of the present disclosure, the first composite substrate 200 and the second composite substrate 300 are drawn the same in the figures. However, the first composite substrate 200 and the second composite substrate 300 may be different for any suitable application.

[0027] Continue with the embodiments of forming the first composite substrate **200** and the second composite substrate 300. In FIG. 2, the first substrate 201 and the second substrate 301 are received. The first substrate **201** and the second substrate **301** may be semiconductor substrates and may include elemental semiconductor materials (e.g., carbon, monocrystalline silicon, polycrystalline silicon, amorphous silicon, germanium, tin, sulfur, selenium, tellurium, or the like), compound semiconductor materials (e.g., silicon carbide, boron nitride, aluminum nitride, gallium nitride, gallium phosphide, gallium arsenide, indium phosphide, indium arsenide, indium antimonide, zinc oxide, or the like), alloy semiconductor materials (e.g., SiGe, AlGaAs, InGaAs, InGaP, AlInAs, GaAsP, AlGaN, InGaN, AlGaInP, or the like), or combinations thereof. In some embodiments, the first substrate **201** and the second substrate **301** may further include an active component (e.g., a diode or a transistor, etc.), a passive component (e.g., a resistor, a capacitor, or an inductor, etc.), a conductive structure (e.g., a wire, etc.), or combinations thereof. In some embodiments, the first substrate **201** may include a first amorphous carbon layer **201**AC on the top, and the second substrate **301** may include a second amorphous carbon layer **301**AC on the top. In some embodiments, the method **100** may further include performing an ion implantation process to the first amorphous carbon layer **201**AC and the second amorphous carbon layer **301**AC to form the desired doping regions of the first substrate **201** and the second substrate **301**. In some embodiments, the doping agent used in the ion implantation process may be N type (e.g., including arsenic, phosphorus, or the like) or P type (e.g., including boron, gallium, or the like), depending on the design of the semiconductor structure.

[0028] Continue with the embodiments of forming the first composite substrate **200** and the second composite substrate **300**. In FIGS. **2** to **3**, a first hard mask layer **203** is formed on the first substrate **201**, and a second hard mask layer **303** is formed on the second substrate **301**. A first patterned photoresist layer **204** is formed on the first hard mask layer **203**, and a second patterned photoresist layer **304** is formed on the second hard mask layer **303**. The patterns of the first patterned photoresist layer **204** and the second patterned photoresist layer **304** are transferred to the first hard mask layer **203** and the second hard mask layer **303** to form the first patterned hard mask layer **203**' and the second patterned hard mask layer 303' by etching the portions of the first hard mask layer **203** and the second hard mask layer **303** that are exposed by the openings **2040** of the first patterned photoresist layer **204** and the openings **3040** of the second patterned photoresist layer **304**. The etching method may be any suitable method, for example, a plasma etching, and so on. [0029] For more details, the first patterned photoresist layer **204** and the second patterned photoresist layer **304** may be formed by any suitable photolithography method. In some embodiments, the first patterned photoresist layer 204 and the second patterned photoresist layer **304** may independently include a positive photoresist or a negative photoresist. In addition, the first hard mask layer **203** and the second hard mask layer **303** may have higher etch resistance than the first patterned photoresist layer **204** and the second patterned photoresist layer **304**, so the patterns transferred from the first patterned photoresist layer **204** and the second patterned photoresist layer **304** to the first hard mask layer **203** and the second hard mask layer **303** substantially remain identical in the first patterned hard mask layer **203**′ and the second patterned hard mask layer **303**′. For example, the width of the openings **2040** of the first patterned photoresist layer **204** is substantially the same as the width of the openings **203**'O of the first patterned hard mask layer **203**′, and the width of the openings **3040** of the second patterned photoresist layer **304** is substantially the same as the width of the openings **303**'O of the second patterned hard mask layer **303**′. In some embodiments, a preferable first hard mask layer **203** includes an oxide layer **2030**X disposed on a carbon layer 203C, and a preferable second hard mask layer 303 includes an oxide layer **303**OX disposed on a carbon layer **303**C, in which a thickness **203**CT of the carbon layer 203C is larger than a thickness 2030XT of the oxide layer 203OX, and a thickness 303CT of the carbon layer 303C is larger than a thickness 3030XT of the oxide layer 303OX. In some embodiments, preferable thickness ratios of the carbon layer 203C to the oxide layer 203OX and the carbon layer **303**C to the oxide layer **3030**X are independently from 1.7 to 5, for example, 1.7, 2.0, 2.5, 3, 3.5, 4.0, 4.5, or 5, in which 2.0 to 4.0 is more preferable. In some embodiments, a preferable thickness **203**CT of the carbon layer **203**C and a preferable thickness **303**CT of the carbon layer **303**C are independently from 50 nm to 70 nm (e.g., 50 nm, 55 nm, 60 nm, 65 nm, or 70 nm), and a preferable thickness **2030**XT of the oxide layer **203**OX and a preferable thickness **3030**XT of the oxide layer **3030**X are independently from 10 nm to 30 nm (e.g., 10 nm, 15 nm, 20 nm, 25 nm, or 30 nm). The oxide layer **203**OX and the oxide layer **303**OX may be etched completely in the formation of the first patterned hard mask layer 203' and the second patterned hard mask layer **303**′, so the formed first patterned hard mask layer **203**′ and second patterned hard mask layer 303' may substantially include the carbon layer 203C and the carbon layer 303C and exclude the oxide layer **2030**X and the oxide layer **303**OX.

[0030] Continue with the embodiments of forming the first composite substrate **200** and the second composite substrate **300**. In some embodiments, a first anti-reflective coating layer **202** and a second anti-reflective coating layer **302** may form on the first substrate **201** and the second substrate **301**, such that the first hard mask layer **203** is formed on the first anti-reflective coating layer **202** and the second hard mask layer **303** is formed on the second anti-reflective coating layer **302**. The first anti-reflective coating layer **202** and the second anti-reflective coating layer **302** reduce the reflective light during the photolithographic process of forming the first patterned photoresist layer **204** and the second patterned photoresist layer **304**, so the formed first patterned

photoresist layer 204 and second patterned photoresist layer 304 may have patterns closer to the desired patterns, which is beneficial for forming smaller patterns (e.g., forming the smaller widths of the openings **2040** and the openings **3040**). The first anti-reflective coating layer **202** and the second anti-reflective coating layer **302** in combination with the first spacers **205**′ and the second spacers **305**′ discussed later may provide surrounding environments for the directed self-assembly material **402** discussed later to self-assemble into at least two different regions (e.g., the first portions **402**A and the second portions **402**B of the present disclosure in one kind of region that is easier to be etched, and the third portions **402**C of the present disclosure in another kind of region that is more resistant to be etched). Specifically, different surrounding environments contribute different affinities to the directed self-assembly material 402 to form at least two different regions in the present disclosure, in which the at least two different regions of the present disclosure include at least two different alignments of the block copolymer that is present in the directed selfassembly material **402**. In the embodiments including the first anti-reflective coating layer **202** and the second anti-reflective coating layer **302**, the at least two different alignments of the block copolymer are much different to enhance the resolution of patterning the directed self-assembly material **402**. Details of patterning the directed self-assembly material **402** are provided in the following disclosure.

[0031] For more details, in some embodiments, a preferable first anti-reflective coating layer **202** includes a first silicon-containing layer **202**S disposed on an oxide layer **2020**X, and a preferable second anti-reflective coating layer 302 includes a second silicon-containing layer 302S disposed on an oxide layer **3020**X, in which a thickness **2020**XT of the oxide layer **2020**X is larger than a thickness **202**ST of the first silicon-containing layer **202**S, and a thickness **3020**XT of the oxide layer **3020**X is larger than a thickness **302**ST of the second silicon-containing layer **302**S. In some embodiments, preferable thickness ratios of the oxide layer 2020X to the first silicon-containing layer **202**S and the oxide layer **3020**X to the second silicon-containing layer **302**S are independently from 1.5 to 5, for example, 1.5, 2.0, 2.5, 3, 3.5, 4.0, 4.5, or 5, in which 1.5 to 2.5 is more preferable. In some embodiments, a preferable thickness **2020**XT of the oxide layer **2020**X and a preferable thickness 3020XT of the oxide layer 3020X are independently from 15 nm to 25 nm (e.g., 15 nm, 20 nm, or 25 nm), and a preferable thickness 202ST of the first silicon-containing layer **202**S and a preferable thickness **302**ST of the second silicon-containing layer **302**S are independently from 5 nm to 15 nm (e.g., 5 nm, 10 nm, or 15 nm). In the embodiments including the first anti-reflective coating layer **202** and the second anti-reflective coating layer **302**, portions of the first silicon-containing layer **202**S of the first anti-reflective coating layer **202** are exposed by the openings **203**'O of the first patterned hard mask layer **203**', and portions of the second siliconcontaining layer **302**S of the second anti-reflective coating layer **302** are exposed by the openings **303**'O of the second patterned hard mask layer **303**'.

[0032] Continue with the embodiments of forming the first composite substrate 200 and the second composite substrate 300. In FIGS. 4 to 5A, a first spacer material 205 is deposited conformally on the first patterned hard mask layer 203' and in the openings 203'O of the first patterned hard mask layer 303', and a second spacer material 305 is deposited conformally on the second patterned hard mask layer 303' and in the openings 303'O of the second patterned hard mask layer 303'. In some embodiments, the deposition method may be any suitable method, for example, an atomic layer deposition (ALD), and so on. In some embodiments, the first spacer material 205 and the second spacer material 305 independently include oxide, for example, silicon oxide (e.g., silicon dioxide). The deposited first spacer material 205 and second spacer material 305 may be etched back by any suitable method to remain the portions on the sidewalls of the separated patterns of the first patterned hard mask layer 203' and the second patterned hard mask layer 303'. The remaining portions of the first spacer material 205 and the second spacer material 305 are referred to as the first spacers 205' and the second spacers 305', respectively. Next, the first patterned hard mask layer 203' and the second patterned hard mask layer 303' are removed to form the first composite

substrate **200** and the second composite substrate **300**. In some embodiments, the removing method may be any suitable method, for example, a wet etching process or a dry etching process. [0033] After forming the first composite substrate **200** and the second composite substrate **300**, the first composite substrate **200** and the second composite substrate **300** shown in FIG. **5**A are received in the operation **101**. In FIG. **5**A, the spaces between the first spacers **205**′ may include first larger spaces LS1 and first smaller spaces SS1, in which the first larger spaces LS1 are larger than the first smaller spaces SS1, and the spaces between the second spacers 305' may include second larger spaces LS2 and second smaller spaces SS2, in which the second larger spaces LS2 are larger than the second smaller spaces SS2. Specifically, the positions of the first larger spaces LS1 correspond to the positions of the openings 203'O of the first patterned hard mask layer 203', and the positions of the first smaller spaces SS1 correspond to the positions of the first patterned hard mask layer **203**′, so an average space (i.e., an average of the first larger spaces LS**1** and the first smaller spaces SS1) of the patterns of the first spacers **205**′ is smaller than an average space (i.e., the widths of the openings **203**'O) of the patterns of the first patterned hard mask layer **203**'. Similarly, the positions of the second larger spaces LS2 correspond to the positions of the openings **303**'O of the second patterned hard mask layer **303**', and the positions of the second smaller spaces SS2 corresponds to the positions of the second patterned hard mask layer 303′, so an average space (i.e., an average of the second larger spaces LS2 and the second smaller spaces SS2) of the patterns of the second spacers **305**′ is smaller than an average space (i.e., the widths of the openings **303**′O) of the patterns of the second patterned hard mask layer **303**′. Although the spaces of the patterns are reduced, the shapes of the patterns of the first spacers **205**′ and the second spacers **305**′ may not be satisfying. As shown in the electron microscopic image of FIG. 5B, the shapes of the first spacers **205**′ (and the second spacers **305**′) are wiggling, in which the surfaces of the first spacers **205**′ (and the second spacers **305**′) are significantly curved.

[0034] In the embodiments as provided in FIG. **6**, the second composite substrate **300** is disposed on the first composite substrate **200** in the operation **102**, for example, by turning the second composite substrate **300** upside down to face the first composite substrate **200**, such that at least one of the first spacers **205**′ is in direct contact with at least one of the second spacers **305**′. In some embodiments, some portions of the second spacers **305**′ may be in direct contact with the first spacers **205**′ and some portions of the first spacers **205**′ and the second spacers **305**′ may not be in direct contact with each other and separated from each other. In some embodiments, the central axis C1 of the at least one of the first spacers 205′ that is in direct contact with the at least one of the second spacers **305**′ is substantially aligned with the central axis C**2** of the at least one of the second spacers **305**′. In some embodiments, the arrangement of the first spacers **205**′ on the first substrate **201** is substantially identical to the arrangement of the second spacers **305**′ on the second substrate **301**. In the embodiments that the arrangement of the first spacers **205**′ is identical to the arrangement of the second spacers **305**′, the second spacers **305**′ shift from the first spacers **205**′ with a distance L that is equal to the width of a single one of the first smaller spaces SS1 plus the width of a single one of the first spacers **205**′. In some embodiments, the second composite substrate **300** may combine with the first composite substrate **200** by any suitable method, for example, a thermal binding process, bonding by reducing pressure between the second composite substrate **300** and the first composite substrate **200**, and so on. In some embodiments, a removable adhesive layer **401** may be formed on the second composite substrate **300** (e.g., on the second antireflective coating layer **302**) or on the first composite substrate **200** (e.g., on the first anti-reflective coating layer **202**) to provide adhesion between the second composite substrate **300** and the first composite substrate **200**. In some embodiments, the removable adhesive layer **401** may release the second composite substrate 300 from the first composite substrate 200 by any suitable method including mechanical peeling, laser lift-off, heating, applying pressure, and so on. In some embodiments, the removable adhesive layer **401** may be any suitable removable adhesive, for example, a silicone based adhesive, a fluorinated silicone based adhesive, an acrylic based

adhesive, or the like.

[0035] In the embodiments as provided in FIGS. 6 and 7, after the operation 102, the spaces (or the exposed regions) between the first spacers **205**' and the second spacers **305**' are filled with the directed self-assembly material **402** in the operation **103**. Since the first spacers **205**′ and the second spacers **305**′ are dislocated, the spaces between the first spacers **205**′ and the second spacers **305**′ may be surrounded by different combinations of the elements. In some embodiments, depending on the surrounding elements, the directed self-assembly material 402 may include at least two different regions that have obviously different etching resistances, in which one region is referred to as the first portions **402**A and the second portions **402**B in the present disclosure, and another region is referred to as the third portions **402**C in the present disclosure. Specifically, the first portions **402**A are between the first spacers **205**' and the second substrate **301**, the second portions **402**B are between the second spacers **305**′ and the first substrate **201**, and the third portions **402**C are remaining portions of the directed self-assembly material **402**. Since the affinities of the first portions **402**A and the second portions **402**B to their surrounding elements are much different from the affinity of the third portions **402**C to their surrounding elements, the directed self-assembly material **402** aligned differently in the first portions **402**A and the second portions **402**B compared with in the third portions **402**C. In some embodiments, the affinity of the third portions **402**C to their surrounding elements is larger than the affinities of the first portions **402**A and the second portions **402**B to their surrounding elements. In some embodiments, the directed self-assembly material **402** may include a block copolymer that includes at least two different blocks of polymerized monomers, for example, a block polymer of polystyrene and poly(methyl methacrylate), or the like. In some embodiments, the method 100 may further include heating the directed self-assembly material **402**, applying voltage on the directed self-assembly material **402**, or by any suitable method to further promote the alignment of the directed self-assembly material **402**.

[0036] For more details, the projections of the third portions **402**C on the first substrate **201** (or on the second substrate **301**) are complementary (or nor overlapped) with the projections of the first spacers **205**' and the projections of the second spacers **305**' on the first substrate **201** (or on the second substrate **301**). In the embodiments as provided in FIG. **7**, the third portions **402**C are substantially equally spaced.

[0037] In the embodiments as provided in FIG. **8**, the second composite substrate **300** (may also include the second anti-reflective coating layer **302** in some embodiments) is removed from the first composite substrate **200** in the operation **104**. The removing method may be any suitable method, for example, by the removable adhesive layer **401** in some embodiments. Next, the first spacers **205**′, the first portions **402**A, and the second portions **402**B may be removed together in the operation **104**, for example, by etching with C.sub.4F.sub.6, C.sub.4F.sub.8, or a combination of C.sub.4F.sub.6 and C.sub.4F.sub.8. Since the affinity of the third portions **402**C to the surrounding elements is larger than the affinities of the first portions **402**A and the second portions **402**B, the third portions **402**C substantially remain intact on the first substrate **201**.

[0038] In the embodiments as provided in FIGS. **9** and **10**A, after the operation **104**, oxide layers **206** are filled between the third portions **402**C in the operation **105**, and the third portions **402**C are removed to remain the oxide layers **206** in the operation **106**. In some embodiments, the oxide layers **206** may include any suitable deposition method, for example, a chemical vapor deposition. In some embodiments, removing the third portions **402**C of the directed self-assembly material **402** includes heating the third portions **402**C with a temperature from 100° C. to 400° C., for example, 100° C., 150° C., 200° C., 350° C., 350° C., or 400° C. After the operation **106**, an average space between each one of the oxide layers **206** is smaller than an average space between each one of the first spacers **205**′. Referring to FIG. **7**, the third portions **402**C of the directed self-assembly material

402 may form in the positions corresponding to the positions of both the first smaller spaces SS1 and the first larger spaces LS1 between the first spacers 205'. The third portions 402C of the directed self-assembly material 402 formed in the positions corresponding to the positions of the first larger spaces LS1 may be separated by the second portions 402B of the directed self-assembly material 402. Therefore, the third portions 402C of the directed self-assembly material 402 may be a mask for forming the oxide layers 206 with a smaller average space. In some embodiments, the average space between the oxide layers 206 is smaller than 50 nm. In some embodiments, the oxide layers 206 are equally spaced. In some embodiments, substantially all the edges of the oxide layers 206 are close to right angles (e.g., the angle  $\theta$  between the top surface and the side surface of each one of the oxide layers 206 is from 80° to 100° or more preferably from 85° to) 95° and the oxide layers 206 substantially have no wiggle shapes, as shown in the electron microscopic image of FIG. 10B, which are much better than those of the first spacers 205' shown in the electron microscopic image of FIG. 5B. After the operation 106, the patterns of the oxide layers 206 with smaller spaces and linear shapes may be transferred to the layers beneath the oxide layers 206 or may be used as a mask for any application in the subsequent processes.

[0039] The method of patterning the semiconductor structure of the present disclosure can form patterns with much smaller spaces. In addition, the quality of the patterns is improved, for example, by reducing the wiggling of the patterns and by increasing the similarity of each one of the patterns. Therefore, the improved patterns can apply to smaller semiconductor devices and have more applicability to different manufacturing processes.

[0040] The present disclosure is described in detail with some embodiments, but other embodiments may be applicable. Therefore, the description of the embodiments in the present disclosure should not be used to limit the scope and spirit of the appended claims.

[0041] For one skilled in the art, modifications and changes to the present disclosure may be made without departing from the scope and spirit of the present disclosure. The present disclosure is intended to cover the foregoing modifications and changes as long as such modifications and changes are within the scope and spirit of the appended claims.

## **Claims**

- 1. A method of patterning a semiconductor structure, comprising: receiving a first composite substrate and a second composite substrate, wherein the first composite substrate comprises a first substrate and first spacers on the first substrate, and the second composite substrate comprises a second substrate and second spacers on the second substrate; disposing the second composite substrate on the first composite substrate, wherein at least one of the first spacers is in direct contact with at least one of the second spacers; filling spaces between the first spacers and the second spacers with a directed self-assembly material, wherein the directed self-assembly material comprises first portions, second portions, and third portions, the first portions are between the first spacers and the second substrate, the second portions are between the second spacers and the first substrate, and the third portions are remaining portions of the directed self-assembly material; removing the second composite substrate, the first spacers, and the first portions and the second portions of the directed self-assembly material; filling oxide layers between the third portions of the directed self-assembly material; and removing the third portions of the directed self-assembly material
- **2**. The method of claim 1, wherein a central axis of the at least one of the first spacers that is in direct contact with the at least one of the second spacers is substantially aligned with a central axis of the at least one of the second spacers.
- **3.** The method of claim 1, wherein projections of the third portions of the directed self-assembly material on the first substrate or the second substrate are complementary with projections of the first spacers and projections of the second spacers on the first substrate or the second substrate.

- **4**. The method of claim 1, wherein the third portions of the directed self-assembly material are substantially equally spaced.
- **5.** The method of claim 1, wherein an arrangement of the first spacers on the first substrate is substantially identical to an arrangement of the second spacers on the second substrate.
- **6.** The method of claim 1, wherein: the first composite substrate further comprises a first anti-reflective coating layer between the first substrate and the first spacers; and the second composite substrate further comprises a second anti-reflective coating layer between the second substrate and the second spacers.
- **7**. The method of claim 6, wherein: the first anti-reflective coating layer comprises a first silicon-containing layer; and the second anti-reflective coating layer comprises a second silicon-containing layer.
- **8.** The method of claim 1, wherein the first spacers and the second spacers independently comprise an oxide.
- **9.** The method of claim 1, wherein the directed self-assembly material comprises a block copolymer.
- **10**. The method of claim 1, further comprising applying a removable adhesive layer between the directed self-assembly material and the first substrate or between the directed self-assembly material and the second spacers.
- **11**. The method of claim 1, wherein removing the first portions and the second portions of the directed self-assembly material comprises using an etchant comprising C.sub.4F.sub.6, C.sub.4F.sub.8, or a combination thereof.
- **12**. The method of claim 1, wherein after removing the second composite substrate, the first spacers, and the first portions and the second portions of the directed self-assembly material, the third portions of the directed self-assembly material substantially remain intact on the first substrate.
- **13**. The method of claim 1, wherein removing the third portions of the directed self-assembly material comprises heating the third portions of the directed self-assembly material with a temperature from  $100^{\circ}$  C. to  $400^{\circ}$  C.
- **14.** The method of claim 1, wherein an average space between the oxide layers is smaller than an average space between the first spacers.
- **15**. The method of claim 1, wherein an angle between a top surface and a side surface of each one of the oxide layers is from 80° to 100°.