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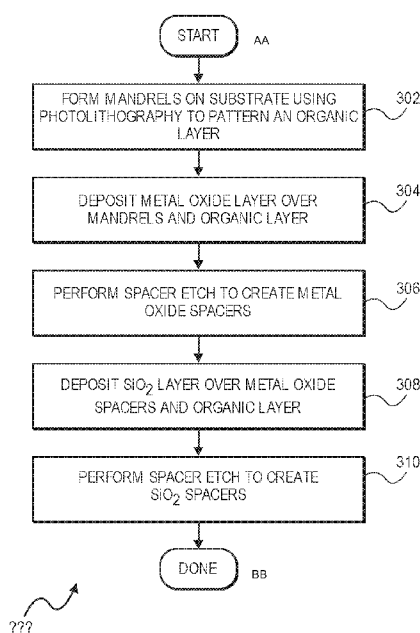


FIG. 3

(57) Abstract: An Atomic Layer Deposition (ALD) configured to deposit a metal oxide layer onto an organic photoresist on a substrate using a highly reactive organic metal precursor. By using a highly reactive metal precursor, the rate of growth of the metal oxide layer is very fast, creating a "seal" that effectively protects the organic photoresist from loss and degradation from subsequent exposure to oxygen species during subsequent ALD cycles. The ability to deposit metal oxide layers means metal oxide spacers can be used in multi-patterning, resulting in highly uniform, dense lines, and the elimination of photolithography-etch steps.

DEPOSITION TOOL AND METHOD FOR DEPOSITING METAL OXIDE FILMS ON ORGANIC MATERIALS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of U.S. Provisional
5 Application No. 62/690,210, filed June 26, 2018 and 16/052,286, filed August 1,
2018, which both are incorporated herein by reference for all purposes.

BACKGROUND

[0002] Atomic Layer Deposition (ALD) is a deposition method that has the
capability of controlling the thickness of thin films formed on semiconductor
10 substrates on the order of one atomic mono-layer.

[0003] Plasma Enhanced ALD (PEALD) is a further enhancement that enables
improved film properties at lower temperatures. PEALD uses chemical precursors,
similar to ALD, in an RF-induced plasma to create the necessary chemical reactions
to form the thin films in a highly controlled manner. PEALD offers many advantages,
15 including low temperature processing, excellent conformity and thickness control of
deposited layers and a capability of pre- and post-deposition in-situ treatments.

[0004] Multiple patterning is a technique to enhance feature density for integrated
circuits (ICs) beyond the limits of photolithography. Such multi-patterning techniques
include, for example, pitch splitting, sidewall image transfer, self-aligned contacts, via
20 patterning, layout splitting, self-aligned double or quadruple patterning, to name a
few. It is expected that multi-patterning will be necessary for 10 nm and 7 nm node
semiconductor processes and beyond.

[0005] Self Aligned Quadruple Patterning (SAQP) is essentially two cycles of
double patterning technique, often referred to as Self-Aligned Double Patterning
25 (SADP). Both SAQP and SAQP require a substrate with multiple layers formed
thereon. For instance, the layers on the substrate may include, from the bottom layer
up, a first carbon film referred to as an Ashable Hard Mask (AHM) or a Spin on
Carbon layer (SOC), a Silicon Oxide SiO₂ layer, a second carbon AHM/SOC layer,
and an Anti-Reflective Layer (ARL).

30 [0006] SAPD uses a photolithography step and additional etch steps to define
spacer-like features on a substrate. In the SADP process, the first step is to deposit a
resist material and then pattern, using photolithography, "mandrels" onto the top ARL

layer on the substrate. The mandrels typically have a pitch at or close to the limit of photolithography. The mandrels are next covered with a deposition layer such as Silicon Oxide (SiO_2). A "spacer etch" is subsequently performed, removing (a) the horizontal surfaces of the SiO_2 layer and (b) the photoresist. As a result, just the vertical surfaces of the SiO_2 remains on the ARL layer. These vertical surfaces define "spacers", which have a pitch finer than can be achieved with conventional photolithography.

[0007] SAQP is a continuation of the above-described double patterning process. With SAQP, the SiO_2 spacers are used as a mask in an etch step removing the underlying ARL and second AHM layers except under the masked regions. Thereafter, the SiO_2 spacers are removed, leaving second mandrels formed in the AHM layer. Another SiO_2 layer is then deposited followed by another "spacer etch", removing (a) the horizontal portions of the SiO_2 layer and (b) the second mandrels. The result is a structure having SiO_2 spacers formed on the underlying SiO_2 layer. With the SAQP process, the pitch of the second SiO_2 spacers are finer than the first spacers and significantly beyond limits of conventional lithography.

[0008] While multi-patterning offers significant benefits and helps extend the usefulness of conventional photolithography to next generation integrated circuitry, the various processes have their limitations. In particular, the multi-patterning requires numerous deposition, photolithography and etching steps to form the spacers. The finer the pitch of the spacers, the more photolithography-etch cycles are required. These additional steps significantly add to the cost and complexity of semiconductor fabrication. A more cost effective, simpler, solution for implementing certain multi-patterning processes, such as SADP and SAQP and beyond, is therefore needed.

SUMMARY

[0009] A system and method for depositing a metal oxide layer onto an organic photoresist on a substrate using an organic metal precursor is disclosed. In a non-exclusive embodiment, the system and method is implemented in an Atomic Layer Deposition (ALD) tool, wherein each ALD cycle includes (1) a first half-cycle using the organic metal precursor for depositing the metal oxide layer onto the organic photoresist layer on the substrate and (2) a second half-cycle that includes a plasma that contains an oxygen species that tends to degrade the organic photoresist. By using

a highly reactive precursor in the first half cycle, the metal oxide layer is deposited at a very fast rate, sufficient to seal and protect the organic photoresist from degradation and loss in the second half of subsequent ALD cycle(s). In a preferred but non-exclusive embodiment, the organic photoresist is effectively sealed with the metal oxide layer within three (3) ALD cycles or less.

[0010] In various non-exclusive embodiments, (a) the metal oxide layer is deposited at a rate of 1.0 Angstroms or more per ALD cycle, (b) the organic metal precursor is a metal organic for tin precursor, such as either an amino type precursor or a methoxy type precursor, (c) the organic photoresist is a carbon photoresist, a polymeric photoresist, a carbon Ashable Hard Mask film, or a carbon Anti Reflective Layer (ARL) and (d) the metal oxide layer is a tin oxide (SnO_2).

[0011] In yet other embodiments, the deposited metal oxide layer is used to form spacers on the substrate in a multi-patterning process flow. By using metal oxide spacers, a number of benefits are realized, including highly uniform spacers, resulting in highly dense feature patterns and smaller line widths and fewer required photolithography-etch steps. As a result, multi-patterning is significantly simplified, the cost and complexity of semiconductor fabrication is reduced, while accuracy and performance of the semiconductor devices is improved.

[0012] In yet other embodiments, the ALD tool is a Plasma Enhanced ALD tool (PEALD).

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The present application, and the advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawings in which:

[0014] FIG. 1 is a block diagram of an Atomic Deposition Layer (ALD) tool in accordance with a non-exclusive embodiment of the invention.

[0015] FIGS. 2A-2E are a series of semiconductor substrate cross sections showing the processing steps of a Self Aligned Quadruple Patterning (SAQP) process in accordance with a non-exclusive embodiment of the invention.

[0016] FIG. 3 is a flow diagram illustrating the process steps for implementing SAQP in accordance with a non-exclusive embodiment of the invention.

[0017] FIG. 4 is a block diagram of a system controller used for controlling an ALD tool in accordance with a non-exclusive embodiment of the invention.

[0018] In the drawings, like reference numerals are sometimes used to designate like structural elements. It should also be appreciated that the depictions in the figures are diagrammatic and not necessarily to scale.

DETAILED DESCRIPTION

[0019] The present application will now be described in detail with reference to a few non-exclusive embodiments thereof as illustrated in the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. It will be apparent, however, to one skilled in the art, that the present disclosure may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present disclosure.

[0020] Referring to Fig. 1, a block diagram of an Atomic Deposition Layer (ALD) tool 10 is illustrated. The tool 10 includes a processing chamber 12, a showerhead 14, a substrate holder 16 for positioning/holding a substrate 18, an optional RF source 20 and a system controller 22. During operation, reactant gas(es) or "precursors" are supplied into the process chamber 12 one at a time through the shower head 14. Within the shower head 14, the precursor is distributed via one or more plenums (not illustrated) into the chamber 12, in the general area above the surface of the substrate 18.

[0021] A two-part ALD cycle is used to form a film on the top surface of the substrate 18:

(1) In a first half of the ALD cycle, a first precursor is introduced via the showerhead 14 into the processing chamber 12. The first precursor reacts with the substrate 18, depositing a first layer of first particles on the surface. The processing chamber 12 is then purged.

(2) In the second half of the ALD cycle, a second precursor is introduced into the processing chamber. The second precursor also reacts with the substrate 18, forming a second layer of second particles on the surface.

[0022] The reaction of both the first and second precursors is self-limiting, meaning once a particular area of the surface of the substrate 18 is covered by a particle, additional particles do not accumulate in that same area. As a result, each reactant forms an atomic mono-layer on the surface of the substrate 18.

5 [0023] The above ALD cycle may be sequentially performed multiple times, creating alternating mono-layers of first and second particles. When a film of desired thickness is achieved, the ALD cycles are stopped and the process is complete.

[0024] In a non-exclusive embodiment, the ALD tool 10 is a Plasma Enhanced ALD or "PEALD" tool. With PEALD tools, an RF potential generated by the optional
10 RF generator 20, is applied to an electrode (not illustrated), either on the showerhead 14, the substrate holder 18 (also not shown), or possibly both the showerhead 14 and the substrate holder 18. Regardless of how applied, the RF potential generates a plasma 24 within the processing chamber 12.

[0025] During an ALD cycle in a PEALD tool, the first precursor is introduced
15 into the processing chamber 12 and the RF potential is applied. The resulting plasma 24 causes energized electrons to ionize or dissociate (i.e., "crack") from the first precursor, creating chemically reactive radicals. As these radicals react, the particles deposit and form the atomic mono-layer on the substrate 18. When the atomic mono-layer is complete, the processing chamber is purged. The second precursor is then
20 introduced into the processing chamber 12, a plasma is generated by the RF potential, and another mono-layer of second particles is formed on the surface of the substrate 18. The aforementioned two-part ALD cycle may be repeated multiple times until a film, formed from the alternating mono-layers of first and second particles, is of a desired thickness.

25 [0026] In various non-exclusive embodiments, the RF generator 20 may be a single RF generator or multiple RF generators capable of generating high, medium and/or low RF frequencies. For example, in the case of high frequencies, the RF generator 20 may generate frequencies ranging from 2-100 MHz and preferably 13.56 MHz or 27 MHz. When low frequencies are generated, the range is 50 KHz to 2
30 MHz, and preferably 350 to 600 KHz. In yet other embodiments, the RF source 20 may be inductively coupled or passively coupled to the RF generating electrode(s) provided on the showerhead 14 and/or the substrate holder 16 as previously noted.

[0027] With multi-patterning, the ability to deposit metal oxides is advantageous for several reasons. Such metal oxide films offer the benefits of (1) improved etch selectivity and (2) simplified multi-patterning processes, potentially reducing the required number of photoresist and etch steps.

5 [0028] However, the deposition of such thin metal films on organic carbon layers using conventional ALD precursors is problematic for several reasons. Conventional precursors used in the first half of the ALD cycle, such as Tetramethyltin, results in a very slow growth rate (e.g., in the order of 0.1 to 0.2 Angstroms) per ALD cycle. As a result, significant loss and degradation occurs to the organic carbon layers during the
10 second half of the ALD cycle due to exposure to oxygen species.

[0029] With multi-patterning, sidewall uniformity of spacers is critically important. With conventional precursors used in ALD processes, however, the resulting sidewalls of spacers are substantially non-uniform due to losses and degradation incurred during the ALD cycle. The compromise of sidewall spacers
15 generally makes conventional precursors incompatible with patterning metal oxides films, such as tin oxide (SnO_2), in multi-patterning processes.

[0030] The Applicant has defined an ALD cycle that relies on one of several highly reactive precursors. By using a highly reactive precursor, the growth rate of metal oxides, even at lower temperatures commonly used with PEALD tools, occurs
20 much faster in the first half of the ALD cycle. As a result, the metal oxide effectively "seals" the underlying organic layer. The organic layer is thus substantially protected from significant loss/degradation due to exposure to oxygen species during the second half of the ALD cycle.

[0031] In a non-exclusive embodiment, the metal oxide layer is tin oxide (SnO_2)
25 deposited onto the organic photoresist during one or more ALD cycles. With tin oxide, the first half cycle uses a first precursor containing tin (Sn) and a second precursor containing an oxygen (O_2) species for the second half cycle. Each ALD cycle includes:

(1) a first half-cycle using a highly reactive organic metal precursor
30 containing tin for depositing the metal oxide layer onto the organic photoresist layer on the substrate; and

(2) a second half-cycle that includes an oxygen (O_2) species. A side effect of the oxygen species, however, is that it that degrades the organic photoresist.

[0032] With an organic metal precursor that is highly reactive, the deposited metal oxide layer effectively seals the organic photoresist within three (3) ALD cycles or less. For instance, if each first half cycle results in the metal oxide layer thickness of 1.0 Angstroms or more, then the organic photoresist will be effectively sealed from exposure from the oxygen species during the second half of the ALD cycles.

[0033] In non-exclusive embodiments, the organic metal precursor is a metal organic tin precursor, such as an amino 10 type precursor or a methoxy type precursor. Examples of amino 10 precursors include (a) Dimethylaminodimethyltin ($Me_2Sn(NMe_2)_2$), (b) Dimethylaminotrimethyltin ($Me_3Sn(MMe_2)$) or (c) Tetra kis dimethylamino tin ($Sn(Nme_2)_4$). d) Tetrakisdiethylamino tin ($Sn(Net_2)_4$). An example of a methoxy type precursor includes Dibutyl dimethoxy tin ($Bu_2Sn(OMe)_2$) or (b) amino tin and methoxy metal organic tin precursors

[0034] In yet other non-exclusive embodiments, the organic photoresist is a carbon photoresist, a polymeric photoresist, a carbon Hard Mask film and/or an Anti Reflective Layer (ARL).

[0035] By way of comparison, the Applicant has found that a conventional precursor resulted in a slow growth rate of the metal oxide layer in the order 0.1 to 0.2 Angstroms and a loss of the carbon layer in the range of more than 25 nanometers per ALD cycle. On the other hand, the use of one of the above-listed highly reactive precursors that accelerates growth in the order of 1.0-2.0 Angstroms per ALD cycle, losses were limited to less than 0.5 nanometers per ALD cycle. By limiting the losses to such a significant degree, the deposit of thin film oxides, such as tin oxide (SnO_2), becomes plausible in multi-patterning processes.

ALD Cycle Details

[0036] In a non-exclusive embodiment, process parameters for exemplary first and second half cycles of an ALD cycle for depositing a metal oxide layer, such as tin oxide (SnO_2) onto an organic photoresist, such as carbon, using an organic metal precursor are provided below.

[0037] The process parameters for first half cycle include (a) one of the above-listed organic metal precursors at a flow rate of 0.1 to 0.5 liters per minute, (b) a

temperature ranging from room or ambient temperature to 125° C, (c) an RF frequency of 13.5 MHz and a potential ranging from 50 to 1250 Watts, a chamber pressure ranging from 1.0 to 6.0 Torr, and a duration of 1.0 to 3.0 seconds.

[0038] The process parameters for second half cycle include (a) a plasma containing an oxygen species such as oxygen, nitrous oxide, carbon dioxide, ozone with flow rate of 0.1 to 2 liters per minute, (b) a temperature ranging from room or ambient temperature to 125° C, (c) an RF frequency of 13.5 MHz and a potential ranging from 50 to 1200 Watts, a chamber pressure ranging from 1.0 to 6.0 Torr, and a duration of 1.0 to 3.0 seconds. In yet other embodiments, Argon and helium can be included in the with the oxygen species in the second half of the cycle. The presence of Argon and helium aids in creating more uniform plasma in the chamber

Multi-Patterning Processes

[0039] The ability to deposit metal oxides over organic layers creates opportunities for significantly improving and simplifying multi-patterning by reducing (1) the number of layers involved and (2) the number of required lithography-etch cycles. These benefits are realized by introducing or creating spacers made from metal oxides, previously not plausible due non-uniformity issues as discussed above.

[0040] Referring to Figs 2A-2E, a series of cross-sections of a substrate showing the processing steps of a Self Aligned Quadruple Patterning (SAQP) sequence using metal oxide spacers is shown.

[0041] In Fig. 2A, the cross-section includes an organic Ashable Hard Mask (AHM) layer 40 and an organic Anti Reflective Layer (ARL) 42 formed on substrate 18. Mandrels 44, created by a photolithography step, are provided on the organic ARL layer 42. In certain embodiments, the mandrels 44 typically, although not necessarily, have a pitch equal or close to the limit of conventional lithography. In other embodiments, the mandrels 44 have a pitch that is larger than the limit. In yet other embodiments, the organic layers 42, 44 can be carbon and/or polymeric materials.

[0042] In Fig. 2B, a metal oxide layer 46 is formed over the mandrels 44 and the ARL layer 42. The metal oxide layer 46 is formed using three or less ALD cycles in the tool 10 as described above. In other words, a metal oxide layer having a thickness of at least 1.0 Angstroms is deposited per each half cycle. These layers serves to

effectively seal the underling organic mandrels 44 and ARL layer 42 from degradation and loss during the second half of each ALD cycle. In a non-exclusive embodiment, the metal oxide layer is tin oxide (SnO_2).

5 [0043] In Fig. 2C, the substrate 18 is shown after a "spacer etch", which removes (a) the horizontal portions of the metal oxide layer 46 and (b) the mandrels 44. The resulting structure defines a plurality of metal oxide spacers 48. The metal oxide spacers 48 effectively act as second mandrels having a pitch that is significantly smaller than the mandrels 44.

10 [0044] In Fig. 2D, a Silicon Oxide (SiO_2) layer 50 is formed over the metal oxide spacers 48.

[0045] Finally, in Fig. 2E, a second spacer etch is performed, removing (a) the horizontal portions of the Silicon Oxide layer 50 and (b) the second mandrels (e.g., the metal oxide spacers 48). The resulting structure includes a plurality of Silicon Oxide spacers 52 on substrate 18 having a pitch that is significantly smaller than the metal oxide spacers 48.

15 [0046] By way of example, certain embodiments of the first mandrels 44 may have a pitch ranging from 32 to 128 nanometers, the metal oxide spacers 48 have a pitch ranging from 16 to 32 nanometers and the Silicon Oxide spacers 52 have a pitch ranging from 8 to 16 nanometers. The SAQP process described above thus results in lines and features having significantly smaller dimensions than possible with conventional precursors. It should be understood that these ranges merely exemplary and should not be construed as limiting. As semiconductor fabrication processes improve and feature sizes become smaller and smaller, these ranges will likely become smaller and smaller as well.

25 [0047] Using highly reactant precursors enables the formation of highly uniform metal oxide spacers, which offer a number of benefits. First, the uniformity of metal oxide spacers enables lines that are highly dense, resulting in very small feature sizes. Second, metal oxide spacers have a high modulus. Third, metal oxide spacers also reduce the number of photoresist-etch steps compared to conventional multi-patterning relying on conventional reactant precursors. By eliminating processing steps, the cost and complexity of multi-patterning, is reduced, while improving accuracy and performance.

30

[0048] In the above embodiments, tin oxide (SnO_2) is the only metal oxide mentioned. It should be understood, however, that other metal oxides may also be used, such as titanium dioxide, hafnium dioxide, zirconium dioxide, tantalum oxide, etc.

5 [0049] Referring to Fig. 3, a flow diagram 300 illustrating the process steps for implementing the SAQP sequence as described above is shown.

[0050] In step 302, mandrels 44 are formed on the substrate 18 using photolithography to pattern an organic layer, such as carbon or polymeric material.

[0051] In step 304, the metal oxide layer 46 is deposited over the mandrels 44 and
10 underlying organic layer. The metal oxide layer 46 is deposited using a highly reactive organic metal precursor, such as one of those listed above.

[0052] In step 306, a spacer etch is performed removing (a) the horizontal portions of the metal oxide layer 46 and (b) the mandrels 44. The result of the spacer etch is metal oxide spacers 48. The metal oxide spacers 48 effectively define second
15 mandrels that have a pitch finer than the first mandrels 44.

[0053] In step 308, a layer of Silicon Oxide (SiO_2) 50 is deposited over the substrate 18, including Silicon Oxide (SiO_2).

[0054] In step 410, a second spacer etch is performed, removing (a) the horizontal portions of the Silicon Oxide (SiO_2) 50 and (b) Silicon Oxide (SiO_2). The net result is
20 spacers 52 having a significantly smaller pitch than the mandrels 44.

System Controller

[0055] Referring to Fig. 4, a block diagram of the system controller 22 in accordance with a non-exclusive embodiment of the invention. The system controller 24 is used to control the overall operation of the ALD (or PEALD) tool 10 in general
25 and manage process conditions during deposition, post deposition, and/or other process operations.

[0056] The system controller 24 may have many physical forms ranging from an integrated circuit, a printed circuit board, a small handheld device, personal computer, server, a super computer, any of which may have one or multiple processors. The
30 computer system 24 further can include an electronic display device 404 (for displaying graphics, text, and other data), a non-transient main memory 406 (e.g., random access memory (RAM)), storage device 408 (e.g., hard disk drive), removable

storage device 410 (e.g., optical disk drive), user interface devices 412 (e.g., keyboards, touch screens, keypads, mice or other pointing devices, etc.), and a communication interface 414 (e.g., wireless network interface). The communication interface 414 allows software and data to be transferred between the system controller 24 and external devices via a link. The system controller 24 may also include a communications infrastructure 216 (e.g., a communications bus, cross-over bar, or network) to which the aforementioned devices/modules are connected.

[0057] The term “non-transient computer readable medium” is used generally to refer to media such as main memory, secondary memory, removable storage, and storage devices, such as hard disks, flash memory, disk drive memory, CD-ROM and other forms of persistent memory and shall not be construed to cover transitory subject matter, such as carrier waves or signals.

[0058] In certain embodiments, the system controller 24, running or executing system software or code, controls all or at least most of the activities of the tool 10, including such activities as controlling the timing of the processing operations, frequency and power of operations of the RF generator 20, pressure within the processing chamber 12, flow rates of reactants, concentrations and temperatures within the process chamber 12, timing of purging the processing chamber, etc.

[0059] Information transferred via communications interface 414 may be in the form of signals such as electronic, electromagnetic, optical, or other signals capable of being received by communications interface 414, via a communication link that carries signals and may be implemented using wire or cable, fiber optics, a phone line, a cellular phone link, a radio frequency link, and/or other communication channels. With such a communications interface, it is contemplated that the one or more processors 402 might receive information from a network, or might output information to the network. Furthermore, method embodiments may execute solely upon the processors or may execute over a network such as the Internet, in conjunction with remote processors that shares a portion of the processing.

[0060] It should be understood that the embodiments provided herein are merely exemplary and should not be construed as limiting in any regard. In general, the present application is intended to cover any a shower head having at least two set of holes defining two spiral patterns and two plenums for the two patterns respectfully.

[0061] Although only a few embodiments have been described in detail, it should be appreciated that the present application may be implemented in many other forms without departing from the spirit or scope of the disclosure provided herein. For instance, the substrate can be a semiconductor wafer, a discrete semiconductor device,
5 a flat panel display, or any other type of work piece.

[0062] Therefore, the present embodiments should be considered illustrative and not restrictive and is not to be limited to the details given herein, but may be modified within the scope and equivalents of the appended claims.

CLAIMS

What is claimed is:

1. An Atomic Layer Deposition (ALD) tool configured to deposit a metal oxide layer onto an organic photoresist on a substrate using an organic metal precursor.
2. The ALD tool of claim 1, wherein the metal oxide layer is deposited onto the organic photoresist during one or more ALD cycles, wherein each ALD cycle includes:
 - a first half-cycle using the organic metal precursor for depositing the metal oxide layer onto the organic photoresist on the substrate; and
 - a second half-cycle that includes an oxygen species that degrades the organic photoresist.
3. The ALD tool of claim 2, wherein the organic metal precursor is sufficiently reactive to seal the organic photoresist with the deposited metal oxide layer within three (3) of the ALD cycles or less.
4. The ALD tool of claim 2, wherein the metal oxide layer is deposited at a rate of 1.0 Angstroms or more per ALD cycle.
5. The ALD tool of claim 1, wherein the organic metal precursor is a metal organic tin precursor.
6. The ALD tool of claim 1, wherein the organic metal precursor is an amino type precursor.
7. The ALD tool of claim 6, wherein the amino type precursor is selected from a group including:
 - (a) Dimethyl amino dimethyl tin ($\text{Me}_2\text{Sn}(\text{NMe}_2)_2$)
 - (b) Dimethylaminotrimethyltin ($\text{Me}_3\text{Sn}(\text{MMe}_2)$)
 - (c) Tetrakisdimethylamino tin ($\text{Sn}(\text{Nme}_2)_4$;
 - (d) Tetrakisdimethylamino tin ($\text{Sn}(\text{Net}_2)_4$); or
 - (e) other amino metal organic tin precursors.
8. The ALD tool of claim 1, wherein the organic metal precursor is a methoxy type precursor.
9. The ALD tool of claim 8, wherein the methoxy type precursor is selected from a group including:
 - (a) Dibutyl dimethoxy tin ($\text{Bu}_2\text{Sn}(\text{OMe})_2$); or

- (b) any methoxy or ethoxy tin precursor.
10. The ALD tool of claim 1, wherein the organic photoresist is a carbon photoresist.
11. The ALD tool of claim 1, wherein the organic photoresist is a polymeric photoresist.
12. The ALD tool of claim 1, wherein the organic photoresist is a carbon mask film.
13. The ALD tool of claim 1, wherein the organic photoresist is an Anti Reflective Layer (ARL).
14. The ALD tool of claim 1, wherein the metal oxide layer is a tin oxide (SnO_2) and the organic photoresist is a carbon photoresist.
15. The ALD tool of claim 1, wherein the metal oxide layer is a tin oxide (SnO_2) and the organic photoresist is a carbon Anti Reflective Layer (ARL).
16. The ALD tool of claim 2, further comprising:
a processing chamber; and
a substrate pedestal for supporting the substrate within the processing chamber,
wherein the one or more ALD cycles is/are performed within the processing chamber.
17. The ALD tool of claim 16, wherein the ALD tool is a Plasma Enhanced ALD tool (PEALD) comprising an RF source for generating a plasma in the processing chamber.
18. The ALD tool of claim 1, wherein the deposited metal oxide layer is used to form spacers on the substrate in a multi-patterning process flow.
19. A multi-patterning method performed on a substrate, the method comprising forming metal oxide spacers on an organic photoresist on the substrate using an organic metal precursor.
20. The multi-patterning method of claim 19, wherein forming the metal oxide spacers further comprises:
using photolithography to pattern the organic photoresist to define mandrels on the substrate;
depositing a layer of metal oxide over the mandrels on the substrate; and

forming the metal oxide spacers on the substrate by removing substantially horizontal surfaces of the layer of the metal oxide and the mandrels from the substrate.

21. The multi-patterning method of claim 20, further comprising:

5 forming a Silicon Oxide (SiO_2) layer over the metal oxide spacers on the substrate; and

forming SiO_2 spacers on the substrate by removing horizontal portions of the Silicon Oxide (SiO_2) layer and the metal oxide spacers.

22. The multi-patterning method of claim 21, wherein the metal oxide spacers
10 have a pitch that is smaller than the mandrels and the SiO_2 spacers have a pitch that is smaller than the metal oxide spacers.

23. The multi-patterning method of claim 20, wherein depositing the layer of metal oxide further comprises performing three or fewer Atomic Layer Deposition (ALD) cycles on the substrate, each ALD cycle resulting in a metal oxide film having
15 a thickness of 1.0 Angstroms or more.

24. The multi-patterning method of claim 23, wherein each ALD cycle further comprises:

depositing the metal oxide film, forming the metal oxide layer, during a first half-cycle; and

20 exposing the substrate to an oxygen species during a second half-cycle,

wherein the metal oxide film deposited during the first half-cycle aids in preventing the oxygen species degrading the mandrels during the second half-cycle.

25. The multi-patterning method of claim 21, wherein the organic metal precursor is a metal organic tin precursor.

25 26. The multi-patterning method of claim 25, wherein the organic metal precursor is an amino 10 type precursor.

27. The multi-patterning method of claim 26, wherein the amino 10 type precursor is selected from a group including:

- (a) Dimethylaminodimethyltin ($\text{Me}_2\text{Sn}(\text{NMe}_2)_2$)
- 30 (b) Dimethylaminotrimethyltin ($\text{Me}_3\text{Sn}(\text{MMe}_2)$)
- (c) Tetrakis dimethylamino tin $\text{Sn}(\text{Nme}_2)_4$
- (d) Tetrakisdiethylamino tin ($\text{Sn}(\text{Net}_2)_4$); or

- (e) any metal organic amino tin precursor.
28. The multi-patterning method of claim 21, wherein the organic metal precursor is an methoxy type precursor.
29. The multi-patterning method of claim 28, wherein the methoxy type precursor
5 is selected from a group including:
- (a) Dibutyl dimethoxy tin ($\text{Bu}_2\text{Sn}(\text{OMe})_2$);
 - (b) any other methoxy or ethoxy tin precursor.
30. The multi-patterning method of claim 21, wherein the organic photoresist is one of the following:
- 10 (a) a carbon photoresist;
- (b) a polymeric photoresist;
- (c) a carbon mask film; or
- (d) a carbon Anti Reflective Layer (ARL).
31. The multi-patterning method of claim 19, wherein the metal oxide layer is a
15 tin oxide (SnO_2) and the organic photoresist is a carbon photoresist.
32. The multi-patterning method of claim 19, wherein the metal oxide layer is a tin oxide (SnO_2) and the photoresist is a carbon Anti Reflective Layer (ARL).
33. The multi-patterning method of claim 23, wherein each ALD cycle is performed at a temperature ranging from room to 125°C .
- 20 34. The multi-patterning method of claim 23, wherein depositing the metal oxide film during the first-half cycle further comprises introducing an organic metal precursor into a processing chamber at a flow rate ranging from 0.1 to 0.5 liters per minute.
35. The multi-patterning method of claim 34, further comprising ranging a
25 duration of the first half cycle from 1.0 to 3.0 seconds.
36. The ALD tool of claim 1, wherein the metal oxide layer is selected from the group including:
- (a) tin oxide;
 - (b) titanium dioxide;
 - 30 (c) hafnium dioxide;
 - (d) zirconium dioxide; or
 - (e) tantalum oxide.

37. A multi-patterning method of claim 19, wherein the metal oxide spacers comprise one of the following metal oxides:

- (a) tin oxide;
- (b) titanium dioxide;
- 5 (c) hafnium dioxide;
- (d) zirconium dioxide; or
- (e) tantalum oxide.

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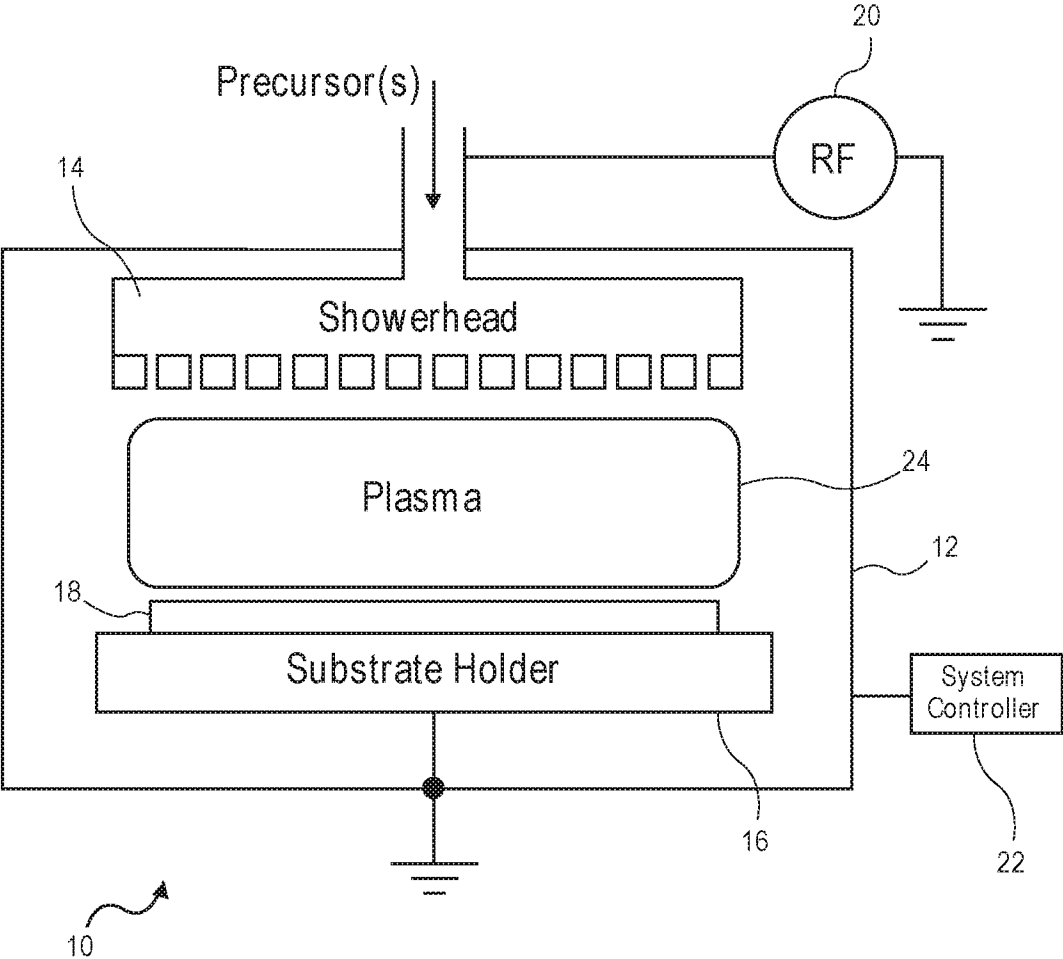
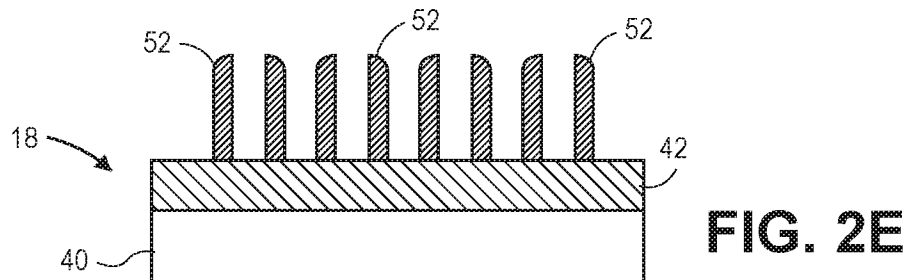
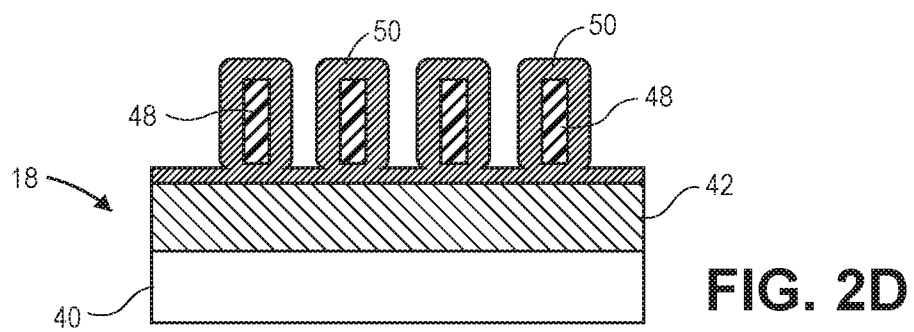
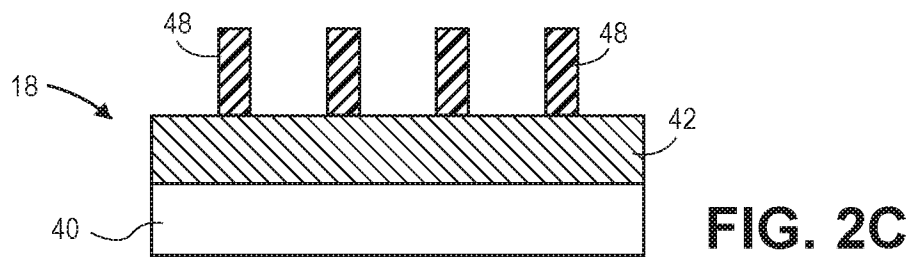
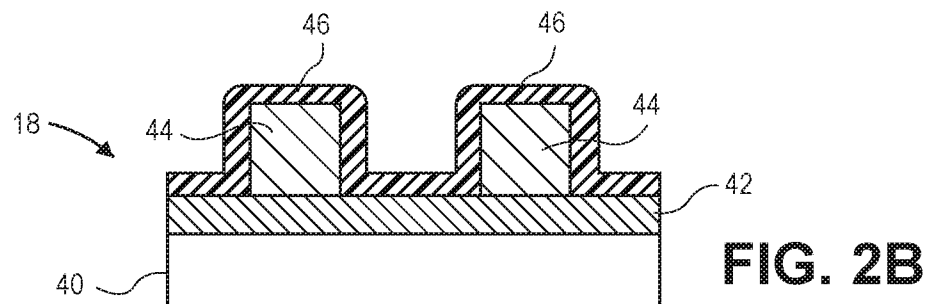
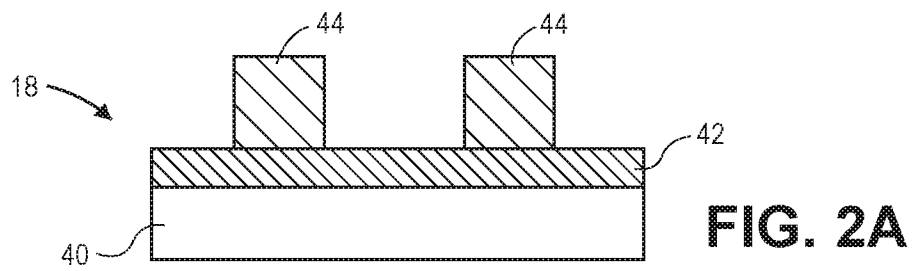
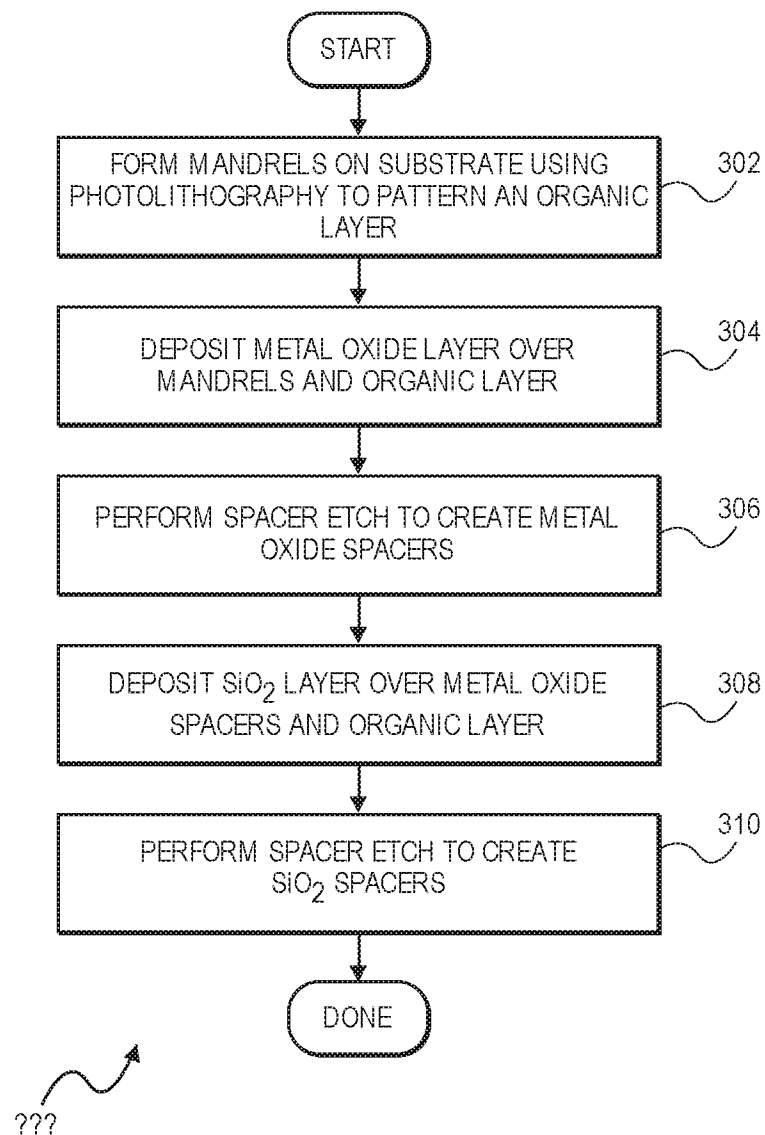
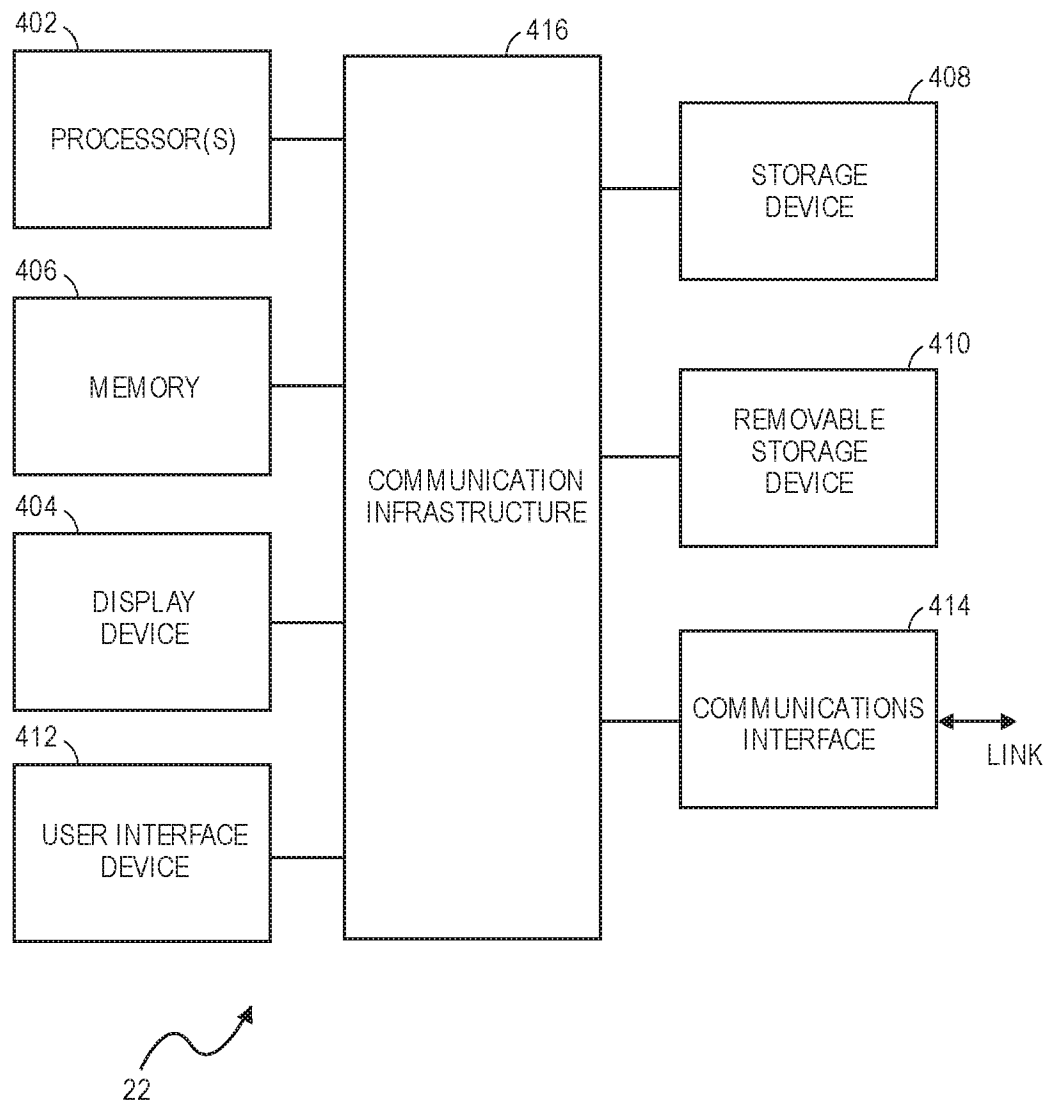


FIG. 1



**FIG. 3**

**FIG. 4**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/035638**A. CLASSIFICATION OF SUBJECT MATTER****C23C 16/455(2006.01)i, C23C 16/04(2006.01)i, C23C 16/40(2006.01)i, C23C 16/458(2006.01)i, C23C 16/505(2006.01)i, H01L 21/02(2006.01)i**

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)

C23C 16/455; G02B 6/124; G03F 7/00; H01L 21/02; H01L 21/033; H01L 21/311; C23C 16/04; C23C 16/40; C23C 16/458; C23C 16/505

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: organic photoresist, atomic layer deposition, metal oxide, metal precursor, cycle, lithography, multi-patterning

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016-0293418 A1 (NOVELLUS SYSTEMS, INC.) 06 October 2016 See paragraphs [0005], [0029]-[0030], [0034]-[0040], [0050]-[0051], [0062]-[0063], [0073], [0077]-[0078], [0104], claims 6, 14 and figures 1-4, 9.	1-37
A	US 2007-0238299 A1 (NIROOMAND et al.) 11 October 2007 See paragraphs [0039], [0047]-[0057], claim 1, and figures 2A-8A.	1-37
A	US 2015-0287612 A1 (APPLIED MATERIALS, INC.) 08 October 2015 See paragraphs [0015]-[0020], [0027], claim 1, and figures 2-3E.	1-37
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A	KR 10-2017-0141673 A (BOARD OF REGENTS, THE UNIVERSITY OF TEXAS SYSTEM) 26 December 2017 See paragraphs [0027]-[0046] and claims 1-4.	1-37



Further documents are listed in the continuation of Box C.



See patent family annex.

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