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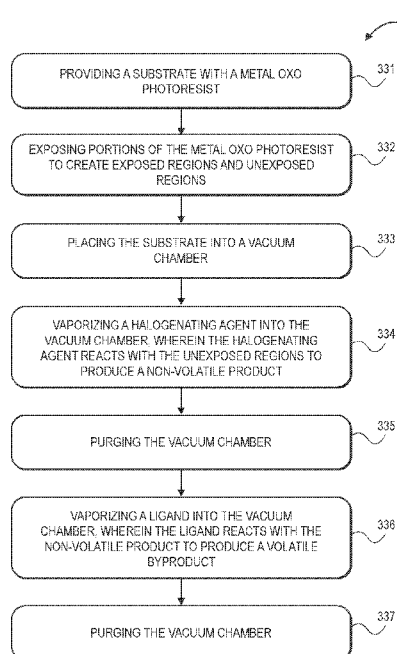


FIG. 3

(57) Abstract: Embodiments disclosed herein include methods of developing a metal oxo photoresist. In an embodiment, the method comprises providing a substrate with the metal oxo photoresist into a vacuum chamber, where the metal oxo photoresist comprises exposed regions and unexposed regions. In an embodiment, the unexposed regions comprise a higher carbon concentration than the exposed regions. The method may further comprise vaporizing a halogenating agent into the vacuum chamber, where the halogenating agent reacts with either the unexposed regions or the exposed regions to produce a volatile byproduct. In an embodiment, the method may further comprise purging the vacuum chamber.

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VAPOR PHASE THERMAL ETCH SOLUTIONS FOR METAL OXO PHOTORESISTS**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims priority to U.S. Non-provisional Application No. 17/348,589, filed on 15
5 June 2021, which claims the benefit of U.S. Provisional Application No. 63/047,157, filed on 01
July 2020, the entire contents of which are hereby incorporated by reference herein.

FIELD

Embodiments of the present disclosure pertain to the field of semiconductor processing and, in
10 particular, to methods of developing a metal oxo photoresist using vapor phase processes.

DESCRIPTION OF RELATED ART

Lithography has been used in the semiconductor industry for decades for creating 2D and 3D
patterns in microelectronic devices. The lithography process involves spin-on deposition of a
15 film (photoresist), irradiation of the film with a selected pattern by an energy source (exposure),
and removal (etch) of exposed (positive tone) or non-exposed (negative tone) region of the film
by dissolving in a solvent. A bake will be carried out to drive off remaining solvent.

The photoresist should be a radiation sensitive material and upon irradiation a chemical
transformation occurs in the exposed part of the film which enables a change in solubility
20 between exposed and non-exposed regions. Using this solubility change, either exposed or non-
exposed regions of the photoresist is removed (etched). Now the photoresist is developed and the
pattern can be transferred to the underlying thin film or substrate by etching. After the pattern is
transferred, the residual photoresist is removed and repeating this process many times can give
2D and 3D structures to be used in microelectronic devices.

Several properties are important in lithography processes. Such important properties include
25 sensitivity, resolution, lower line-edge roughness (LER), etch resistance, and ability to form
thinner layers. When the sensitivity is higher, the energy required to change the solubility of the
as-deposited film is lower. This enables higher efficiency in the lithographic process. Resolution
and LER determine how narrow features can be achieved by the lithographic process. Higher
30 etch resistant materials are required for pattern transferring to form deep structures. Higher etch
resistant materials also enable thinner films. Thinner films increase the efficiency of the
lithographic process.

SUMMARY

- Embodiments disclosed herein include methods of developing a metal oxo photoresist. In an embodiment, the method comprises providing a substrate with the metal oxo photoresist into a vacuum chamber, where the metal oxo photoresist comprises exposed regions and unexposed regions. In an embodiment, the unexposed regions comprise a higher carbon concentration than the exposed regions. The method may further comprise vaporizing a halogenating agent into the vacuum chamber, where the halogenating agent reacts with either the unexposed regions or the exposed regions to produce a volatile byproduct. In an embodiment, the method may further comprise purging the vacuum chamber.
- 10 A method of developing a metal oxo photoresist may also comprise, providing a substrate with the metal oxo photoresist into a vacuum chamber, where the metal oxo photoresist comprises exposed regions and unexposed regions. In an embodiment, the unexposed regions comprise a higher carbon concentration than the exposed regions. The method may further comprise vaporizing a halogenating agent into the vacuum chamber, where the halogenating agent reacts with either the unexposed regions or the exposed regions to produce a non-volatile product. In an embodiment, the method may further comprise vaporizing a ligand into the vacuum chamber, where the ligand reacts with the non-volatile product to produce a volatile byproduct. In an embodiment, the method may further comprise purging the vacuum chamber.
- 15 A method of developing a metal oxo photoresist may also comprise, providing a substrate with the metal oxo photoresist into a vacuum chamber, where the metal oxo photoresist comprises exposed regions and unexposed regions. In an embodiment, the unexposed regions comprise a higher carbon concentration than the exposed regions. The method may further comprise vaporizing an organic acid into the vacuum chamber, where the organic acid reacts with either the unexposed regions or the exposed regions to produce a volatile byproduct. In an embodiment, the method may further comprise purging the vacuum chamber.
- 20
- 25

BRIEF DESCRIPTION OF THE DRAWINGS

- Figure 1 is a flowchart describing a process for developing a metal oxo photoresist using a vapor phase process with a halogenating agent, in accordance with an embodiment of the present disclosure.
- 30
- Figures 2A-2C are cross-sectional illustrations of a substrate and a photoresist depicting operations in the flowchart of Figure 1, in accordance with an embodiment of the present disclosure.

Figure 3 is a flowchart describing a process for developing a metal oxo photoresist using a vapor phase process with a halogenating agent and a protonated ligand, in accordance with an embodiment of the present disclosure.

Figures 4A-4C are cross-sectional illustrations of a substrate and a photoresist depicting

5 operations in the flowchart of Figure 3, in accordance with an embodiment of the present disclosure.

Figure 5 is a flowchart describing a process for developing a metal oxo photoresist using a vapor phase process with an organic acid, in accordance with an embodiment of the present disclosure.

Figure 6A and 6B are cross-sectional illustrations of a substrate and a photoresist depicting

10 operations in the flowchart of Figure 5, in accordance with an embodiment of the present disclosure.

Figure 7 is a cross-sectional illustration of a processing tool that may be used to implement portions of the process in Figure 1, Figure 3, or Figure 5, in accordance with an embodiment of the present disclosure.

15 Figure 8 illustrates a block diagram of an exemplary computer system, in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

Methods of developing a metal oxo photoresist using vapor phase processes are described herein.

20 In the following description, numerous specific details are set forth, such as thermal vapor phase processes and material regimes for developing photoresist, in order to provide a thorough understanding of embodiments of the present disclosure. It will be apparent to one skilled in the art that embodiments of the present disclosure may be practiced without these specific details. In other instances, well-known aspects, such as integrated circuit fabrication, are not described in
25 detail in order to not unnecessarily obscure embodiments of the present disclosure. Furthermore, it is to be understood that the various embodiments shown in the Figures are illustrative representations and are not necessarily drawn to scale.

To provide context, photoresist systems used in extreme ultraviolet (EUV) lithography suffer from low efficiency. That is, existing photoresist material systems for EUV lithography require
30 high dosages in order to provide the needed solubility switch that allows for developing the photoresist material. Organic-inorganic hybrid materials (e.g., metal oxo materials systems) have been proposed as a material system for EUV lithography due to the increased sensitivity to EUV radiation. Such material systems typically comprise a metal (e.g., Sn, Hf, Zr, etc.), oxygen, and carbon. Metal oxo based organic-inorganic hybrid materials have also been shown to provide
35 lower LER and higher resolution, which are required characteristics for forming narrow features.

In a metal oxo photoresist system, exposure to EUV radiation results in the removal of carbon. The difference in the carbon percentage between the exposed regions and the unexposed regions is used as the solubility switch during developing. Particularly, the unexposed regions with the higher carbon content are preferentially etched by the developer solution in a negative tone develop.

Metal oxo photoresist systems are currently developed using a wet chemistry. That is, after exposure, the unexposed regions of the photoresist are developed by organic solvents/base solution that is used with spin-dry process. A post-bake anneal may also be included. However, wet methods can be troublesome when dealing with high aspect ratio features due to the risk of pattern collapse (especially in line or pillar structures). Additionally, wet processes might not remove all of the material that is supposed to be removed and film materials/byproducts/solvents and the like may be trapped in small features.

Accordingly, embodiments of the present disclosure provide a vapor phase thermal etching process to develop metal oxo photoresists. Particularly, vapor phase thermal etching processes provide the advantages of: 1) eliminating the generation of wet byproducts; 2) providing fewer defects and impurities; 3) lower waste streams due to dry chemistry being destroyed in an abatement system; 4) improvement of LER; and 5) less damage with dry thermal etch when compared to plasma damage in reactive ion etching (RIE). For example, at a pitch less than 30nm (e.g., line CD less than 14nm) and less than 15nm photoresist thickness, a plasma can potentially damage the photoresist mask which may result in poor LER/LWR or even a broken line pattern when the pattern is transferred to the underlayer.

Embodiments disclosed herein provide various vapor phase thermal etching processes that are executed after portions of a metal oxo photoresist are exposed with a suitable electromagnetic radiation source (e.g., an EUV source). In a first embodiment, the vapor phase thermal etching process includes vaporizing a halogenating agent into a vacuum chamber. The halogenating agent reacts with either the unexposed or exposed regions of the photoresist to produce a volatile byproduct that is removed from the vacuum chamber. In a second embodiment, the vapor phase thermal etching process includes vaporizing a halogenating agent into a vacuum chamber. The halogenating agent may react with either the unexposed or exposed regions of the photoresist to produce a non-volatile product. A ligand may then be vaporized into the chamber, and the ligand reacts with the non-volatile product to provide a volatile byproduct that can be removed from the vacuum chamber. In a third embodiment, the vapor phase thermal etching process includes vaporizing an organic acid into a vacuum chamber. The organic acid reacts with either the unexposed or exposed regions of the photoresist to produce a volatile byproduct that is removed from the vacuum chamber.

Referring now to Figure 1, a flowchart illustrating a process 120 for developing a metal oxo photoresist on a substrate surface is provided, in accordance with an embodiment of the present disclosure. Figures 2A-2C are cross-sectional illustrations of a substrate 261 and a metal oxo photoresist 262 after various operations in process 120.

5 In an embodiment, process 120 may begin with operation 121 which comprises providing a substrate with a metal oxo photoresist. Figure 2A is a cross-sectional illustration of a substrate 261 with a metal oxo photoresist 262 disposed over a surface of the substrate 261. In an embodiment, the substrate 261 may comprise any substrate material or materials typical of semiconductor manufacturing environments. For example, the substrate 261 may comprise a
10 semiconducting material. Substrate 261 may comprise semiconductor devices or portions of semiconductor devices. Examples of such semiconductor devices include, but are not limited to, memory devices or complimentary metal-oxide-semiconductor (CMOS) transistors fabricated in a silicon substrate and encased in a dielectric layer. The substrate 261 may also comprise a plurality of metal interconnects formed above the devices or transistors, and in surrounding
15 dielectric layers, and may be used to electrically couple the devices or transistors to form integrated circuits. In an embodiment, the substrate 261 may be a wafer.

In an embodiment, the metal oxo photoresist 262 (also referred to simply as “photoresist 262”), may be any metal oxo material system. Such material systems typically comprise a metal (e.g., Sn, Hf, Zr, etc.), oxygen, and carbon. In a particular embodiment, the photoresist 262, comprises
20 SnOC.

The photoresist 262 may be disposed over the surface of the substrate 261 using any suitable deposition process. In an embodiment, the photoresist is disposed on the surface of the substrate 261 with a wet chemistry using a spin-on process. In an alternative embodiment, the photoresist is disposed on the surface of the substrate 261 using a vapor phase process (i.e., a dry process). In
25 a vapor phase process, a metal precursor and an oxidant may be vaporized to a vacuum chamber, with the metal precursor and the oxidant reacting to deposit a metal oxo photoresist 262 on the surface of the substrate 261. Such dry processes may be characterized as a chemical vapor deposition (CVD) process, an atomic layer deposition (ALD) process, a plasma enhanced CVD (PE-CVD) process, or a plasma enhanced ALD (PE-ALD) process.

30 In an embodiment, process 120 may continue with operation 122 which comprises exposing portions of the metal oxo photoresist to create exposed regions and unexposed regions. Figure 2B is a cross-sectional illustration depicting the exposure process. As shown, electromagnetic radiation 264 passes through a mask 263 to expose the exposed regions 262E. The unexposed regions 262U are blocked from the electromagnetic radiation by the mask 263. In an
35 embodiment, the electromagnetic radiation is EUV radiation. When EUV radiation is used, the

EUV radiation 264 may be reflected off the mask instead of passing through the mask. While EUV radiation specifically disclosed herein, it is to be appreciated that any suitable wavelength of electromagnetic radiation that can initiate a solubility switch in the metal oxo photoresist 262 may be used. For example, DUV radiation may be used in some embodiments.

- 5 In an embodiment, the solubility switch is provided by the loss of carbon. Particularly, the exposure to electromagnetic radiation results in the removal of carbon from the exposed regions 262E. The higher carbon content in the unexposed regions 262U renders the unexposed regions more susceptible to etching in the subsequent vapor phase development process.

In an embodiment, process 120 may continue with operation 123 which comprises placing the
10 substrate into a vacuum chamber. In an embodiment, the vacuum chamber may be any suitable chamber for providing sub-atmospheric pressure conditions. The vacuum chamber may also include heating/cooling features to provide thermal control of the vapor phase process. For example, a pedestal on which the substrate 261 is placed may be an actively heated and/or cooled pedestal. Additionally, walls of the vacuum chamber may be actively heated and/or cooled in
15 some embodiments.

Particularly, it is to be appreciated that embodiments disclosed herein do not require a plasma source in order to implement the vapor phase etching of the metal oxo photoresist. Accordingly, the construction of the vacuum chamber may be simplified compared to processes that include plasma based developing of the metal oxo photoresist. A more detailed description of a suitable
20 vacuum chamber is provided below with respect to Figure 7.

In an embodiment, process 120 may continue with operation 124 which comprises vaporizing a halogenating agent into the vacuum chamber. In an embodiment, the halogenating agent reacts with the unexposed regions 262U to produce a volatile byproduct. That is, the reaction between the halogenating agent and the unexposed regions 262U results in the removal of the unexposed
25 regions 262U from the substrate 261, as shown in Figure 2C. In other embodiments, the halogenating agent may react with the exposed regions 262E to produce a volatile byproduct. In an embodiment, the byproduct of the reaction is a volatile metal halide. Some metal halides have higher volatilities than others. For example SnCl_4 has a higher volatility than SnCl_2 , CoClL (where L is a ligand) has a higher volatility than CoCl_2 , and MoOCl_4 has a higher volatility than
30 MoCl_5 . Accordingly, the reaction may preferentially result in the formation of byproducts with higher volatilities. In an embodiment the byproducts may have the chemical formula MX_x or MO_yX_x , where M is a metal or semimetal, X is a halide, x is 1-6 and y is 1-5.

In an embodiment, the halogenating agent is a metal halide with a formula MX_a or MX_aL_b , where M is a metal or semimetal (e.g., Mo, W, Ta, Nb, Sn, V, Ti, or Si), X is a halide (e.g., Cl or

Br), L is a volatile ligand (e.g., alkyls, ethylenediamine, or Cp), a is 1-6 and b is 1-5. For example, the metal halide may comprise MoCl₅, TaCl₅, NbCl₅ or WCl₅.

In an additional embodiment, the halogenating agent is a metal oxy halide with a formula MO_aX_b or MO_aX_bL_c, where M is a metal or semimetal (e.g., Mo, W, Ta, Nb, Sn, V, Ti, or Si),

5 X is a halide (e.g., Cl or Br), L is a volatile ligand (e.g., alkyls ethylenediamine, or Cp), a is 1-5, b is 1-5, and c is 1-5. For example, the metal oxy halide may comprise MoOCl₄, MoO₂Cl₂, WOCl₄, or WO₂Cl₂.

In yet another additional embodiment, the halogenating agent may be an organic halogenating agent. For example, the halogenating agent may comprise thionyl chloride (SOCl₂),

10 methanesulfonyl chloride (CH₃SO₂Cl), trichloromethanesulfonyl chloride (CCl₃SO₂Cl), 4-toluenesulfonyl chloride (tosyl chloride), oxalyl chloride (ClCOCOCl), *tert*-butyl hypochlorite ((CH₃)₃COCl), N-chlorophthalimide, 1,3-dichloro-5,5-dimethylhydantoin, trimethylsilyl chloride, HCl, Cl₂, PCl₅, BCl₃, HBr, Br₂, CCl₃Br, CBr₄, 1,2-dibromo-1,1,2,2-tetrachloroethane (Cl₂CBrCBrCl₂), BBr₃, PBr₃, *N*-bromosuccinimide, *N*-bromoacetamide, 2-bromo-2-cyano-*N,N*-
15 dimethylacetamide, 1,3-dibromo-5,5-dimethylhydantoin, 2,4,4,6-tetrabromo- 2,5-cyclohexadienone, or trimethylsilyl bromide.

In yet another embodiment, the halogenating agent may comprise one or more of SOBr₂ (thionyl bromide), SO₂Cl₂ (sulfuryl chloride), and SO₂Br₂ (sulfuryl bromide).

In an embodiment, the halogenating agent may be diluted with an inert gas. For example, inert
20 gases such as Ar, N₂, or He may be used to dilute the halogenating agent. Generally, it has been shown that the etch selectivity of the unexposed regions of the photoresist 262U relative to the exposed regions of the photoresist 262E increases with increases in pressure. In an embodiment, the pressure may be between approximately 1 torr and approximately 100 torr. In a particular embodiment, the pressure may be between approximately 3 torr and approximately 10 torr.

25 In an embodiment, the substrate 261 may have a controlled temperature during operation 124. For example, the temperature may vary between approximately 0°C and approximately 500°C. In a particular embodiment, the temperature may vary between approximately 50°C and approximately 200°C. Generally, it has been shown that increased substrate temperatures provide an increase in the etch selectivity of the unexposed regions of the photoresist 262U relative to the
30 exposed regions of the photoresist 262E.

In an embodiment process 120 may continue with operation 125 which comprises purging the vacuum chamber. Purging the vacuum chamber removes the byproducts from the reaction in operation 124 from the vacuum chamber. In an embodiment, operation 124 may be implemented as a soak followed by a single purge in operation 125. In alternative embodiments, operations
35 124 and 125 may define a cycle comprising a pulse of the halogenating agent followed by a

purge. In such embodiments, a plurality of cycles may be repeated in order to clear the unexposed regions of the photoresist 262U.

Referring now to Figure 3, a flowchart describing a process 330 for patterning a metal oxo photoresist is shown, in accordance with an embodiment of the present disclosure. Figures 4A-4C are corresponding cross-sectional illustrations depicting various processing operations in process 330. In an embodiment, process 330 may be beneficial when the halogenating agent is not able to fully convert the unexposed regions of the photoresist into a volatile byproduct. Particularly, process 330 further comprises vaporizing a protonated ligand into the vacuum chamber to convert unexposed regions of the photoresist into a volatile byproduct.

10 In an embodiment, process 330 may begin with operation 331, which comprises providing a substrate with a metal oxo photoresist. In an embodiment, the substrate and metal oxo photoresist may be substantially similar to the substrate and metal oxo photoresist described above with respect to operation 121 of process 120.

In an embodiment, process 330 may continue with operation 332, which comprises exposing portions of the metal oxo photoresist to create exposed regions and unexposed regions. In an embodiment, the exposure process of operation 332 may be substantially similar to the exposure process of operation 122 of process 120. Figure 4A provides a cross-sectional illustration of the substrate 461 and exposed regions of the photoresist 462E and unexposed regions of the photoresist 462U.

20 In an embodiment, process 330 may continue with operation 333, which comprises placing the substrate into a vacuum chamber. The vacuum chamber used in process 330 may be substantially similar to the vacuum chamber used in process 120.

In an embodiment, process 330 may continue with operation 334, which comprises vaporizing a halogenating agent into the vacuum chamber. In an embodiment, the halogenating agent may react with the unexposed regions of the photoresist 462U to provide a non-volatile product 462U'. That is, in some embodiments, the halogenating agent, by itself, is not able to fully convert the unexposed regions of the photoresist 462U into a volatile product that is removable from the vacuum chamber. In other embodiments, the halogenating agent may react with the exposed regions 462E to produce a non-volatile product. In an embodiment, the non-volatile product 462U' may be a metal halide or a metal oxy halide with a chemical formula of MX_x or MO_yX_x , where M is a metal or semimetal, X is a halide, x is 1-6 and y is 1-5.

30 In an embodiment, the halogenating agent is a metal halide with a formula MX_a or MX_aL_b , where M is a metal or semimetal (e.g., Mo, W, Ta, Nb, Sn, V, Ti, or Si), X is a halide (e.g., Cl or Br), L is a volatile ligand (e.g., alkyls ethylenediamine, or Cp), a is 1-6 and b is 1-5. For example, the metal halide may comprise $MoCl_5$, $TaCl_5$, $NbCl_5$ or WCl_5 .

In an additional embodiment, the halogenating agent is a metal oxy halide with a formula MO_aX_b or $MO_aX_bL_c$, where M is a metal or semimetal (e.g., Mo, W, Ta, Nb, Sn, V, Ti, or Si), X is a halide (e.g., Cl or Br), L is a volatile ligand (e.g., alkyls ethylenediamine, or Cp), a is 1-5, b is 1-5, and c is 1-5. For example, the metal oxy halide may comprise $MoOCl_4$, MoO_2Cl_2 ,

5 $WOCl_4$, or WO_2Cl_2 .

In yet another additional embodiment, the halogenating agent may be an organic halogenating agent. For example, the halogenating agent may comprise thionyl chloride ($SOCl_2$), methanesulfonyl chloride (CH_3SO_2Cl), trichloromethanesulfonyl chloride (CCl_3SO_2Cl), 4-toluenesulfonyl chloride (tosyl chloride), oxalyl chloride ($ClCOCOCl$), *tert*-butyl hypochlorite
 10 $((CH_3)_3COCl)$, N-chlorophthalimide, 1,3-dichloro-5,5-dimethylhydantoin, trimethylsilyl chloride, HCl , Cl_2 , PCl_5 , BCl_3 , HBr , Br_2 , CCl_3Br , CBr_4 , 1,2-dibromo-1,1,2,2-tetrachloroethane ($Cl_2CBrCBrCl_2$), BBr_3 , PBr_3 , *N*-bromosuccinimide, *N*-bromoacetamide, 2-bromo-2-cyano-*N,N*-dimethylacetamide, 1,3-dibromo-5,5-dimethylhydantoin, 2,4,4,6-tetrabromo- 2,5-cyclohexadienone, or trimethylsilyl bromide.

15 In an embodiment, the halogenating agent may be diluted with an inert gas. For example, inert gases such as Ar, N_2 , or He may be used to dilute the halogenating agent. In an embodiment, the pressure may be between approximately 1 torr and approximately 100 torr. In a particular embodiment, the pressure may be between approximately 5 torr and approximately 10 torr. In an embodiment, the substrate 461 may have a controlled temperature during operation 334. For
 20 example, the temperature may vary between approximately $0^\circ C$ and approximately $500^\circ C$. In a particular embodiment, the temperature may vary between approximately $50^\circ C$ and approximately $150^\circ C$.

In an embodiment, process 330 may continue with operation 335, which comprises purging the vacuum chamber with an inert purge. In an embodiment, the purging process removes any
 25 byproducts and unreacted halogenating agent.

In an embodiment, process 330 may continue with operation 336, which comprises vaporizing a ligand into the vacuum chamber. In an embodiment, the ligand reacts with the non-volatile product 462U' to produce a volatile byproduct. That is, the reaction between the vaporized ligand and the non-volatile product 462U' results in the removal of the unexposed regions from
 30 the substrate 461, as shown in Figure 4C. In cases when the non-volatile product is generated from the exposed regions 462E, the exposed regions may be removed from the substrate 461. In an embodiment, the ligand is a protonated ligand, such as amine. In an embodiment, the ligand may be diluted with an inert gas such as Ar, N_2 , or He. In an embodiment, the volatile byproduct may have the chemical formula MX_xLy or MO_xXyLz , where M is a metal or semimetal (e.g.,

Mo, W, Ta, Nb, Sn, V, Ti, or Si), X is a halide (e.g., Cl or Br), L is a volatile ligand (e.g., amine), x is 1-5, y is 1-5, and z is 1-5.

In an embodiment, the pressure may be between approximately 1 torr and approximately 100 torr. In a particular embodiment, the pressure may be between approximately 5 torr and

5 approximately 10 torr. In an embodiment, the substrate 461 may have a controlled temperature during operation 336. For example, the temperature may vary between approximately 0°C and approximately 500°C. In a particular embodiment, the temperature may vary between approximately 50°C and approximately 150°C.

10 In an embodiment, process 330 may continue with operation 337, which comprises purging the vacuum chamber. Purging with an inert gas may result in the removal of volatile byproducts and remaining vaporized ligands.

In an embodiment, operations 334-337 may define a cycle. The cycle may be repeated any number of times in order to fully (or substantially) remove the unexposed regions 462U of the metal oxo photoresist. For example, a cycle may comprise a sequence including a pulse of a
15 vaporized halogenating agent being introduced into the vacuum chamber, followed by an inert purge, followed by a pulse of a vaporized ligand being introduced into the vacuum chamber, followed by an inert purge. In other embodiments, a single cycle may be used. In such embodiments, a soak of the vaporized halogenating agent may be introduced into the vacuum chamber, followed by an inert purge, followed by a soak of a vaporized ligand into the vacuum
20 chamber, followed by an inert purge.

Generally, it has been shown that the etch selectivity of the unexposed regions of the photoresist 462U relative to the exposed regions of the photoresist 462E increases with increases in pressure. Additionally, it has been generally shown that increased substrate temperatures during one or more of operations 334-337 provide an increase in the etch selectivity of the unexposed regions
25 of the photoresist 462U relative to the exposed regions of the photoresist 462E.

Referring now to Figure 5, a flowchart describing a process 540 for patterning a metal oxo photoresist is shown, in accordance with an embodiment of the present disclosure. Figures 6A-6B are corresponding cross-sectional illustrations depicting various processing operations in process 540. In an embodiment, process 540 may be similar to the process 120, with the
30 exception that the halogenating agent is replaced with a vaporized organic acid. That is, an organic acid is vaporized to a vacuum chamber, where the organic acid reacts with either the unexposed or exposed regions of the metal oxo photoresist to produce a volatile byproduct. In an embodiment, process 540 may begin with operation 541, which comprises providing a substrate with a metal oxo photoresist. In an embodiment, the substrate and metal oxo

photoresist may be substantially similar to the substrate and metal oxo photoresist described above with respect to operation 121 of process 120.

In an embodiment, process 540 may continue with operation 542, which comprises exposing portions of the metal oxo photoresist to create exposed regions and unexposed regions. In an embodiment, the exposure process of operation 542 may be substantially similar to the exposure process of operation 122 of process 120. Figure 6A provides a cross-sectional illustration of the substrate 661 and exposed regions of the photoresist 662E and unexposed regions of the photoresist 662U.

In an embodiment, process 540 may continue with operation 543, which comprises placing the substrate into a vacuum chamber. The vacuum chamber used in process 540 may be substantially similar to the vacuum chamber used in process 120.

In an embodiment, process 540 may continue with operation 544, which comprises vaporizing an organic acid into the vacuum chamber. In an embodiment, the organic acid reacts with either the unexposed regions 662U or the exposed regions 662E to produce a volatile byproduct. That is, the reaction between the organic acid and the unexposed regions 662U results in the removal of the unexposed regions 662U from the substrate 661 (as shown in Figure 6B), or the reaction between the organic acid and the exposed regions 662E results in the removal of the exposed regions 662E from the substrate 661.

In an embodiment, the organic acid may be a carboxylic acid with a chemical formula RCO_2H .

For example, R may be H, CH_3 , tBu, or iPr. In an embodiment, the byproduct of the reaction is a volatile carboxylate. For example, the carboxylate may have a chemical formula $\text{M}(\text{RCO}_2)_x$, where M is the metal from the metal oxo photoresist and R is the R used in the organic acid.

In an embodiment, the organic acid may be diluted with an inert gas. For example, inert gases such as Ar, N_2 , or He may be used to dilute the organic acid. Generally, it has been shown that

the etch selectivity of the unexposed regions of the photoresist 262U relative to the exposed regions of the photoresist 262E increases with increases in pressure. In an embodiment, the pressure may be between approximately 1 torr and approximately 100 torr. In a particular embodiment, the pressure may be between approximately 5 torr and approximately 10 torr.

In an embodiment, the substrate 661 may have a controlled temperature during operation 544.

For example, the temperature may vary between approximately 0°C and approximately 500°C . In a particular embodiment, the temperature may vary between approximately 50°C and approximately 150°C . Generally, it has been shown that increased substrate temperatures provide an increase in the etch selectivity of the unexposed regions of the photoresist 662U relative to the exposed regions of the photoresist 662E.

In an embodiment process 540 may continue with operation 545 which comprises purging the vacuum chamber. Purging the vacuum chamber removes the byproducts from the reaction in operation 544 from the vacuum chamber. In an embodiment, operation 544 may be implemented as a soak followed by a single purge in operation 545. In alternative embodiments, operations 5 544 and 545 may define a cycle comprising a pulse of the organic acid followed by a purge. In such embodiments, a plurality of cycles may be repeated in order to clear the unexposed regions of the photoresist 662U.

Accordingly, embodiments described herein include thermal vapor phase processes for developing a metal oxo photoresist. As such, embodiments disclosed herein may not require 10 vacuum chambers with the ability to form a plasma. The removal of a plasma process also reduces damage to the metal oxo photoresist. This is especially beneficial at low photoresist thicknesses (e.g., at photoresist thicknesses of approximately 15nm or smaller). At low photoresist thicknesses plasma damage may result in poor LER/LWR or even broken line patterns when the pattern is transferred into the underlayer.

15 Additionally, wet chemistries are avoided, and byproducts generated by the reactions disclosed herein may be destroyed with abatement systems typical of the semiconductor manufacturing industry. As such, waste streams are significantly reduced. Furthermore, vapor phase processes allow for fewer defects and impurities in the resulting developed metal oxo photoresist, especially at small feature sizes, since wet chemistries are not used.

20 Figure 7 is a schematic of a vacuum chamber configured to develop the unexposed regions of a metal oxo photoresist, in accordance with an embodiment of the present disclosure. Vacuum chamber 700 includes a grounded chamber 705. In an embodiment, the chamber 705 may be temperature controlled. That is, walls of the chamber 705 may be actively cooled or heated during processes disclosed herein. A substrate 710 is loaded through an opening 715 and 25 positioned on a temperature controlled pedestal 720.

Process gases, are supplied from gas sources 744 through respective mass flow controllers 749 to the interior of the chamber 705. In certain embodiments, a gas distribution plate 735 provides for distribution of process gases 744, such as, for example, halogenating agents, ligands, organic acids, and/or inert gases. Chamber 705 is evacuated via an exhaust pump 755.

30 The vacuum chamber 700 is controlled by controller 770. The controller 770 may comprise a CPU 772, a memory 773, and an I/O interface 774. The CPU 772 may execute processing operations within the vacuum chamber 700 in accordance with instructions stored in the memory 773. For example, one or more processes such as processes 120, 330, and 540 described above may be executed in the vacuum chamber by the controller 770.

While the vacuum chamber 700 is described above as not having features suitable for forming a plasma within the chamber, it is to be appreciated that embodiments of the present disclosure may be implemented in a vacuum chamber 700 that is capable of generating a plasma within the chamber.

5 Figure 8 illustrates a diagrammatic representation of a machine in the exemplary form of a computer system 800 within which a set of instructions, for causing the machine to perform any one or more of the methodologies described herein, may be executed. In alternative
embodiments, the machine may be connected (e.g., networked) to other machines in a Local Area Network (LAN), an intranet, an extranet, or the Internet. The machine may operate in the
10 capacity of a server or a client machine in a client-server network environment, or as a peer machine in a peer-to-peer (or distributed) network environment. The machine may be a personal computer (PC), a tablet PC, a set-top box (STB), a Personal Digital Assistant (PDA), a cellular telephone, a web appliance, a server, a network router, switch or bridge, or any machine capable of executing a set of instructions (sequential or otherwise) that specify actions to be taken by that
15 machine. Further, while only a single machine is illustrated, the term “machine” shall also be taken to include any collection of machines (e.g., computers) that individually or jointly execute a set (or multiple sets) of instructions to perform any one or more of the methodologies described herein.

The exemplary computer system 800 includes a processor 802, a main memory 804 (e.g., read-
20 only memory (ROM), flash memory, dynamic random access memory (DRAM) such as synchronous DRAM (SDRAM) or Rambus DRAM (RDRAM), etc.), a static memory 806 (e.g., flash memory, static random access memory (SRAM), MRAM, etc.), and a secondary memory 818 (e.g., a data storage device), which communicate with each other via a bus 830.

Processor 802 represents one or more general-purpose processing devices such as a
25 microprocessor, central processing unit, or the like. More particularly, the processor 802 may be a complex instruction set computing (CISC) microprocessor, reduced instruction set computing (RISC) microprocessor, very long instruction word (VLIW) microprocessor, processor implementing other instruction sets, or processors implementing a combination of instruction sets. Processor 802 may also be one or more special-purpose processing devices such as an
30 application specific integrated circuit (ASIC), a field programmable gate array (FPGA), a digital signal processor (DSP), network processor, or the like. Processor 802 is configured to execute the processing logic 826 for performing the operations described herein.

The computer system 800 may further include a network interface device 808. The computer system 800 also may include a video display unit 810 (e.g., a liquid crystal display (LCD), a light
35 emitting diode display (LED), or a cathode ray tube (CRT)), an alphanumeric input device 812

(e.g., a keyboard), a cursor control device 814 (e.g., a mouse), and a signal generation device 816 (e.g., a speaker).

The secondary memory 818 may include a machine-accessible storage medium (or more specifically a computer-readable storage medium) 832 on which is stored one or more sets of instructions (e.g., software 822) embodying any one or more of the methodologies or functions described herein. The software 822 may also reside, completely or at least partially, within the main memory 804 and/or within the processor 802 during execution thereof by the computer system 800, the main memory 804 and the processor 802 also constituting machine-readable storage media. The software 822 may further be transmitted or received over a network 820 via the network interface device 808.

While the machine-accessible storage medium 832 is shown in an exemplary embodiment to be a single medium, the term “machine-readable storage medium” should be taken to include a single medium or multiple media (e.g., a centralized or distributed database, and/or associated caches and servers) that store the one or more sets of instructions. The term “machine-readable storage medium” shall also be taken to include any medium that is capable of storing or encoding a set of instructions for execution by the machine and that cause the machine to perform any one or more of the methodologies of the present disclosure. The term “machine-readable storage medium” shall accordingly be taken to include, but not be limited to, solid-state memories, and optical and magnetic media.

In accordance with an embodiment of the present disclosure, a machine-accessible storage medium has instructions stored thereon which cause a data processing system to perform a method of developing a metal oxo photoresist on a substrate with vapor phase processes. The method includes exposing a metal oxo photoresist to provide exposed and unexposed regions, and placing a substrate with the exposed photoresist into a vacuum chamber. In an embodiment, a gas reactive to the unexposed regions of the photoresist is vaporized into the vacuum chamber. For example, the reactive gas may comprise one or more of a halogenating agent, a ligand, and an organic acid. The reactive gas and the unexposed regions of the metal oxo photoresist react to form a volatile byproduct. The byproduct may be removed from the chamber with an inert gas purge.

Thus, methods for forming a developing a metal oxo photoresist using vapor phase processes have been disclosed.

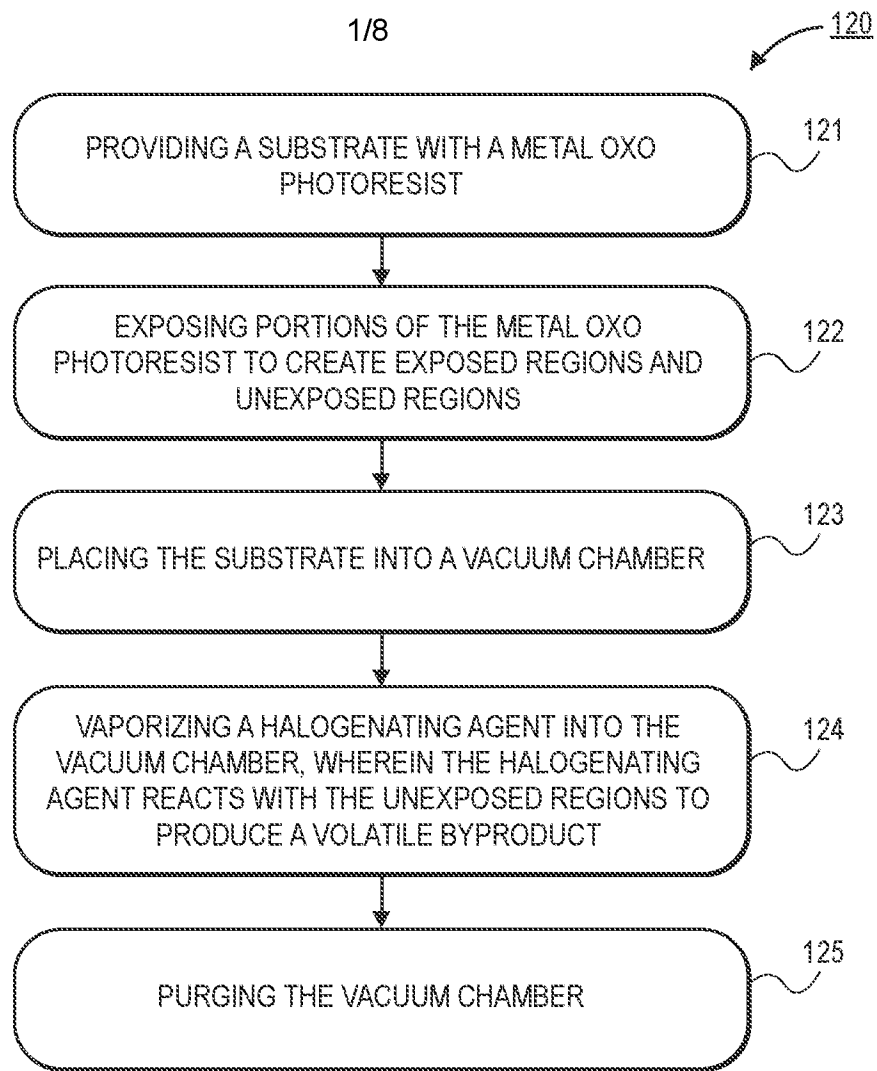
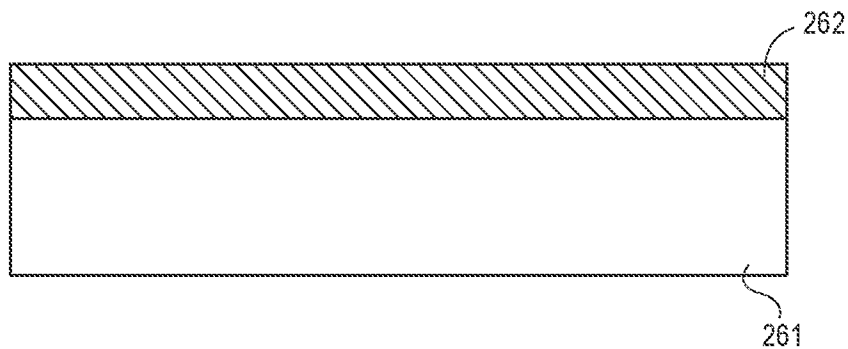
CLAIMS

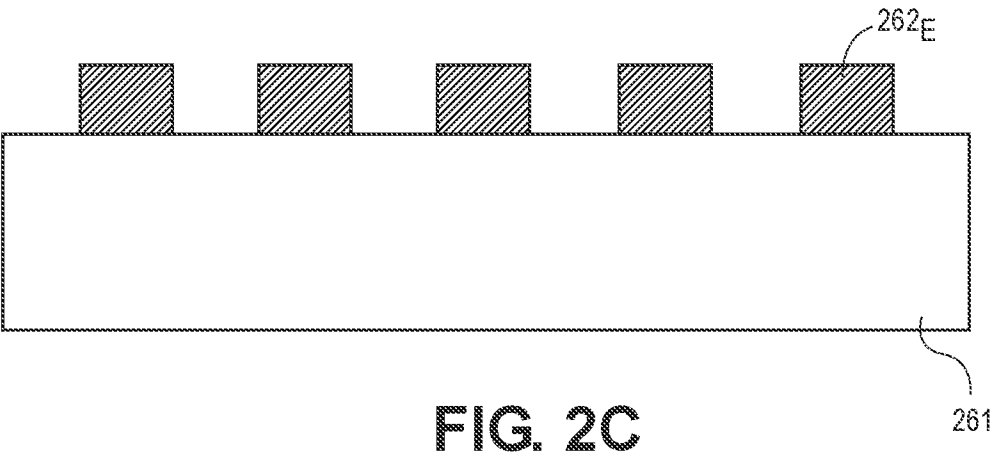
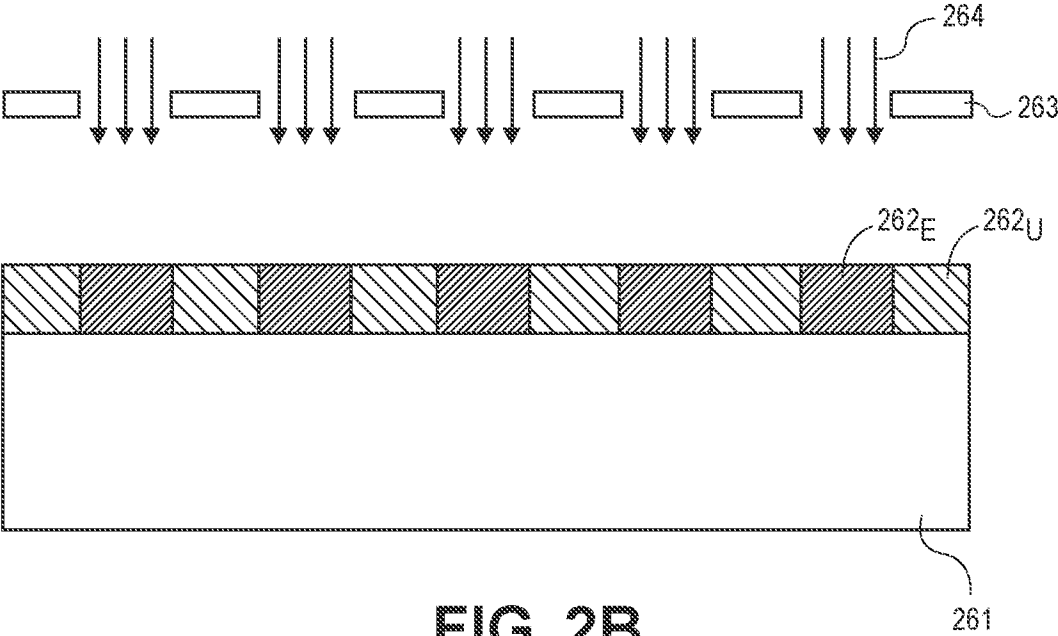
What is claimed is:

1. A method of developing a metal oxo photoresist, comprising:
 - 5 providing a substrate with the metal oxo photoresist into a vacuum chamber, wherein the metal oxo photoresist comprises exposed regions and unexposed regions, and wherein the unexposed regions comprise a higher carbon concentration than the exposed regions;
 - vaporizing a halogenating agent into the vacuum chamber, wherein the halogenating agent reacts with either the unexposed regions or the exposed regions to produce a volatile
 - 10 byproduct; and
 - purging the vacuum chamber.
2. The method of claim 1, wherein the halogenating agent comprises a metal halide.
- 15 3. The method of claim 2, wherein the metal halide has the chemical formula MX_a or MX_aL_b , wherein M is a metal, X is a halogen, L is a volatile ligand, a is 1-6, and b is 1-5.
4. The method of claim 3, wherein the metal halide comprises $MoCl_5$, $TaCl_5$, $NbCl_5$, or WCl_5 .
- 20 5. The method of claim 1, wherein the halogenating agent comprises a metal oxy halide.
6. The method of claim 5, wherein the metal oxy halide has the chemical formula MO_aX_b or $MO_aX_bL_c$, wherein M is a metal, X is a halogen, L is volatile ligand, a is 1-5, b is 1-5, and c is 1-5.
- 25 7. The method of claim 6, wherein the metal oxy halide comprises $MoOCl_4$, MoO_2Cl_2 , WO_2Cl_2 .
8. The method of claim 1, wherein the halogenating agent comprises thionyl chloride ($SOCl_2$), methanesulfonyl chloride (CH_3SO_2Cl), trichloromethanesulfonyl chloride (CCl_3SO_2Cl), 4-toluenesulfonyl chloride (tosyl chloride), oxalyl chloride ($ClCOCOCl$), *tert*-butyl hypochlorite ($((CH_3)_3COCl)$), N-chlorophthalimide, 1,3-dichloro-5,5-dimethylhydantoin, trimethylsilyl chloride, HCl, Cl_2 , PCl_5 , BCl_3 , HBr, Br_2 , CCl_3Br , CBr_4 , 1,2-dibromo-1,1,2,2-tetrachloroethane ($Cl_2CBrCBrCl_2$), BBr_3 , PBr_3 , N-bromosuccinimide, N-bromoacetamide, 2-bromo-2-cyano-N,N-dimethylacetamide, 1,3-dibromo-5,5-dimethylhydantoin, 2,4,4,6-tetrabromo- 2,5-cyclohexadienone, or trimethylsilyl bromide.
- 35

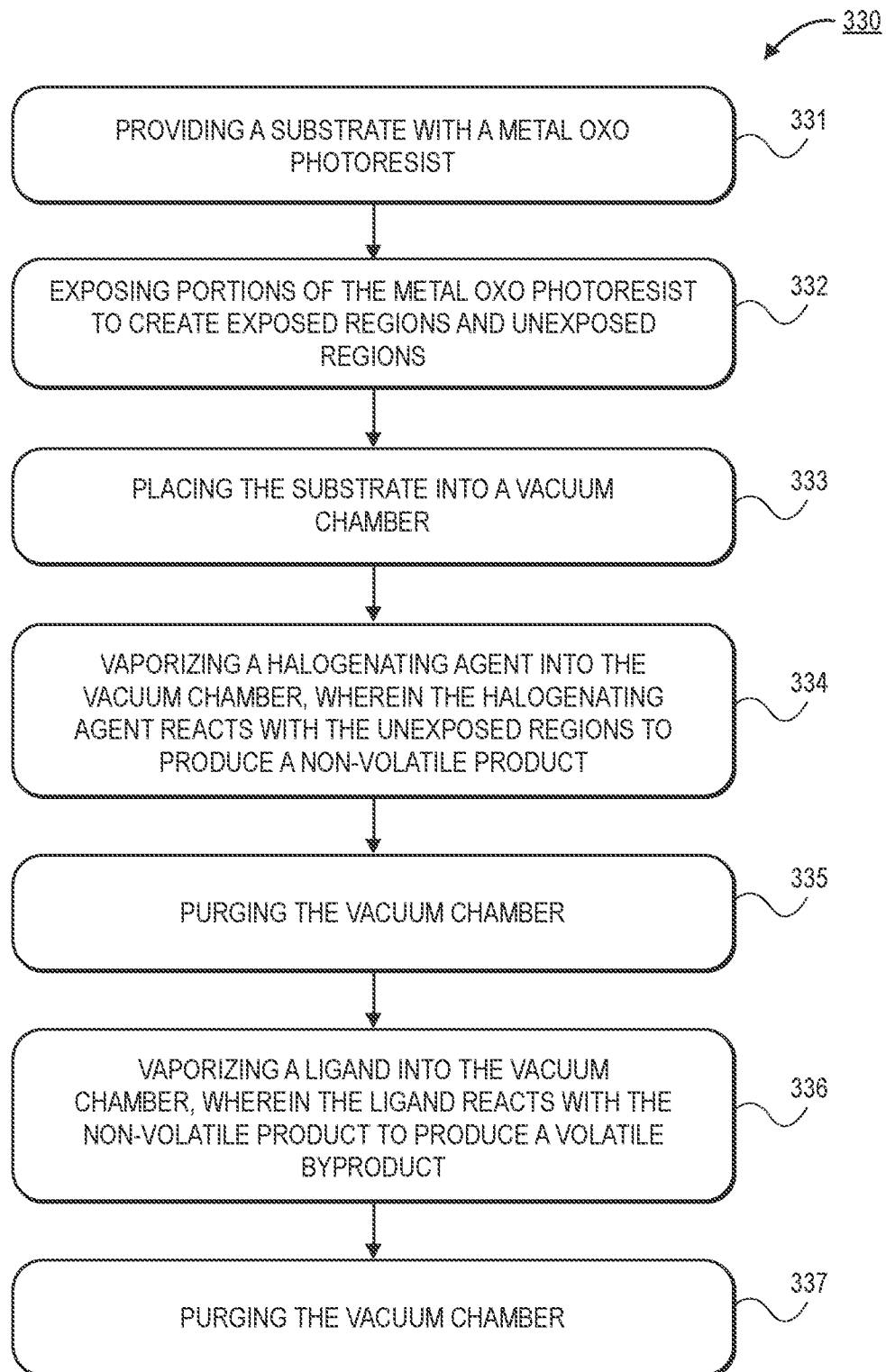
9. The method of claim 1, wherein the halogenating agent comprises one or more of SOBr_2 (thionyl bromide), SO_2Cl_2 (sulfuryl chloride), and SO_2Br_2 (sulfuryl bromide)
10. The method of claim 1, wherein the halogenating agent is diluted with an inert gas.
- 5 11. A method of developing a metal oxo photoresist, comprising:
providing a substrate with the metal oxo photoresist into a vacuum chamber, wherein the metal oxo photoresist comprises exposed regions and unexposed regions, and wherein the unexposed regions comprise a higher carbon concentration than the exposed regions;
10 vaporizing a halogenating agent into the vacuum chamber, wherein the halogenating agent reacts with either the unexposed regions or the exposed regions to produce a non-volatile product;
vaporizing a ligand into the vacuum chamber, wherein the ligand reacts with the non-volatile product to produce a volatile byproduct; and
15 purging the vacuum chamber.
12. The method of claim 11, wherein the halogenating agent comprises a metal halide.
13. The method of claim 11, wherein the halogenating agent comprises a metal oxy halide.
- 20 14. The method of claim 11, wherein the halogenating agent is an organic halogenating agent.
15. The method of claim 11, wherein the ligand is a protonated ligand.
- 25 16. The method of claim 15, wherein the protonated ligand is an amine.
17. A method of developing a metal oxo photoresist, comprising:
providing a substrate with the metal oxo photoresist into a vacuum chamber, wherein the metal oxo photoresist comprises exposed regions and unexposed regions, and wherein the
30 unexposed regions comprise a higher carbon concentration than the exposed regions;
vaporizing an organic acid into the vacuum chamber, wherein the organic acid reacts with either the unexposed regions or the exposed regions to produce a volatile byproduct; and
purging the vacuum chamber.
- 35 18. The method of claim 17, wherein the organic acid is a carboxylic acid (RCO_2H).

19. The method of claim 18, wherein the R group comprises H, CH₃, tBu, or iPr.
20. The method of claim 17, wherein the organic acid is diluted with an inert gas.

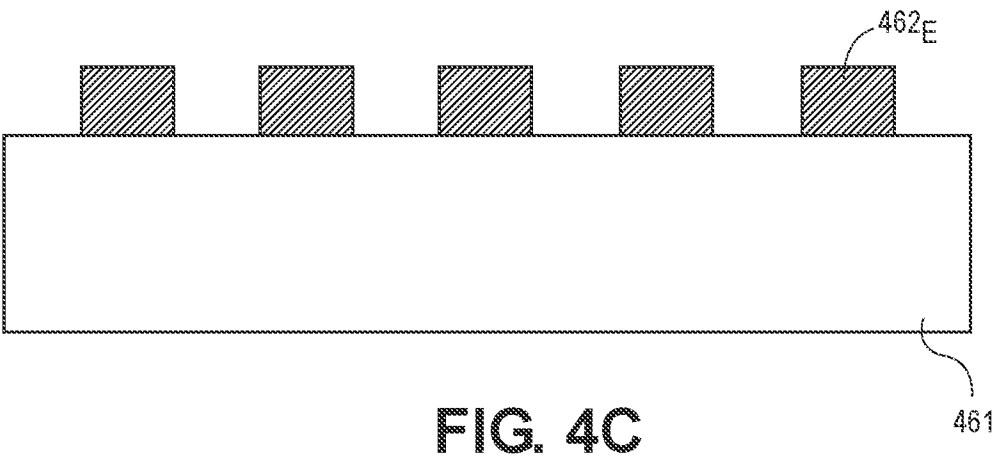
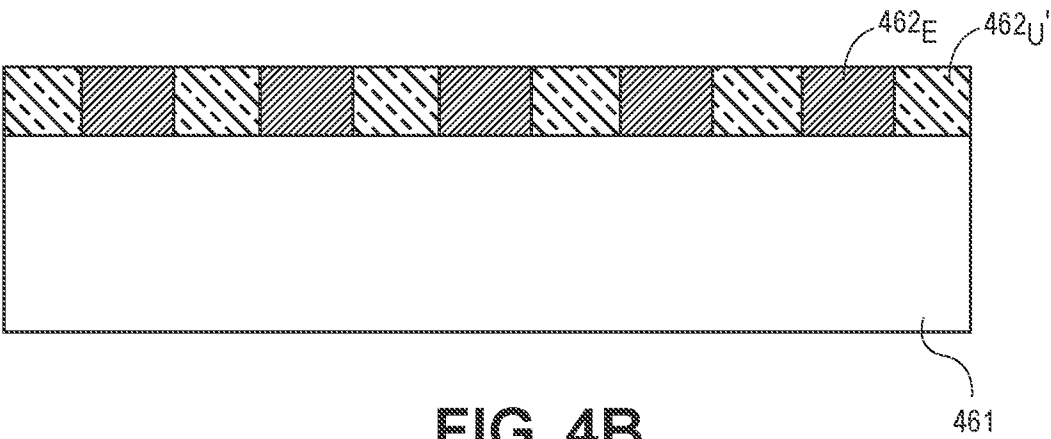
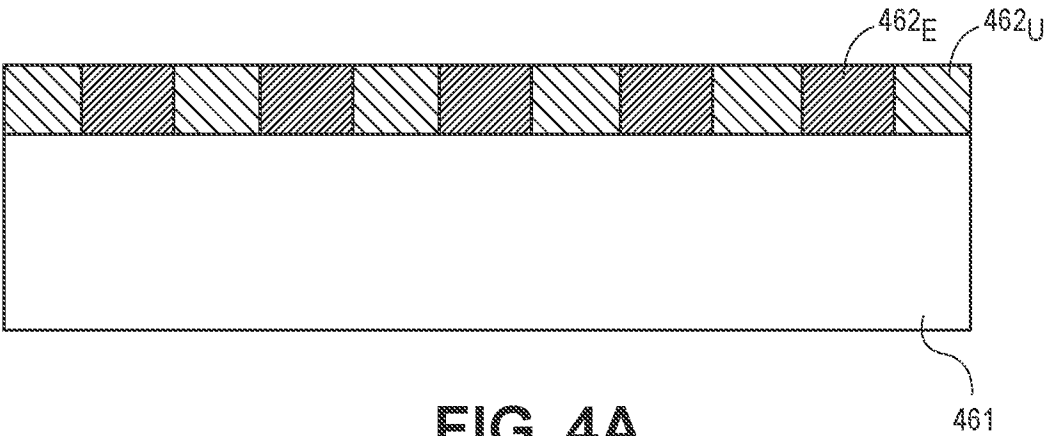
**FIG. 1****FIG. 2A**



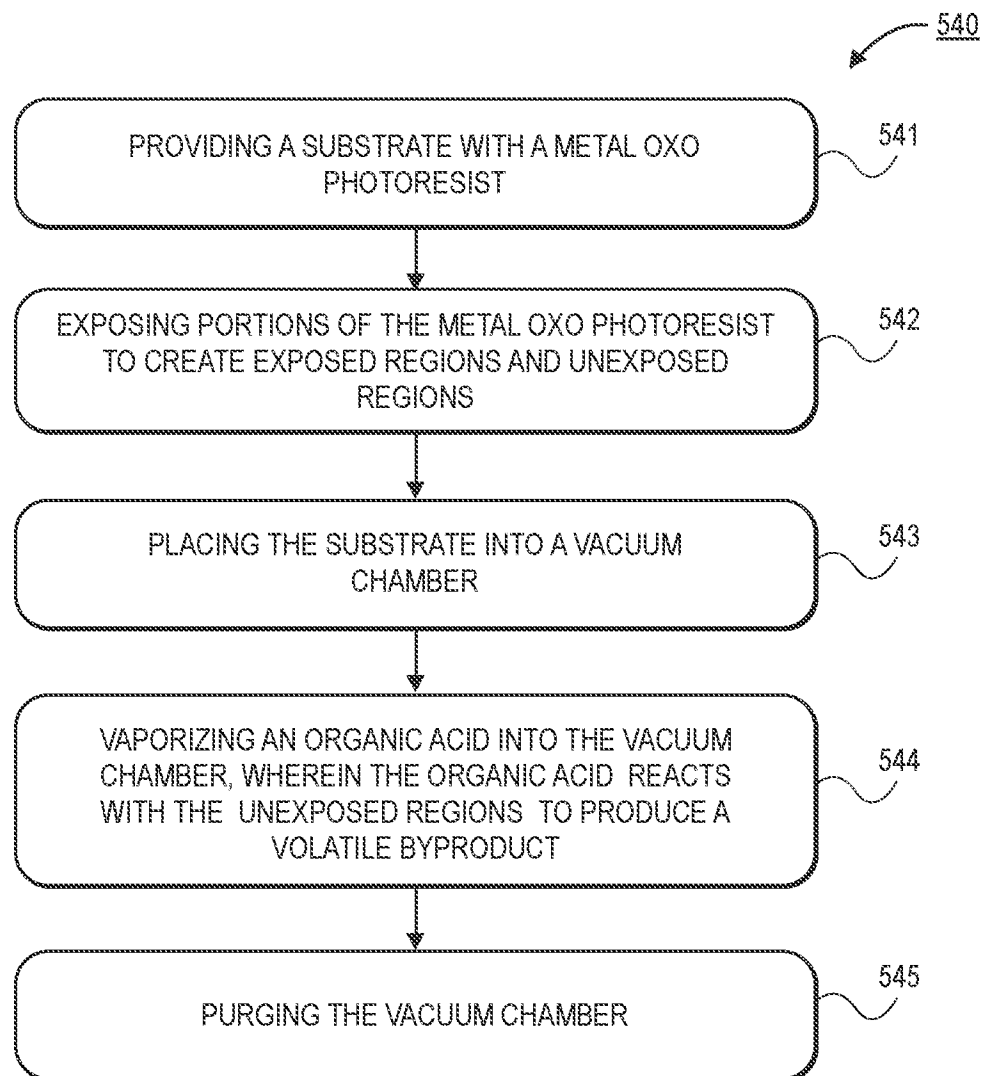
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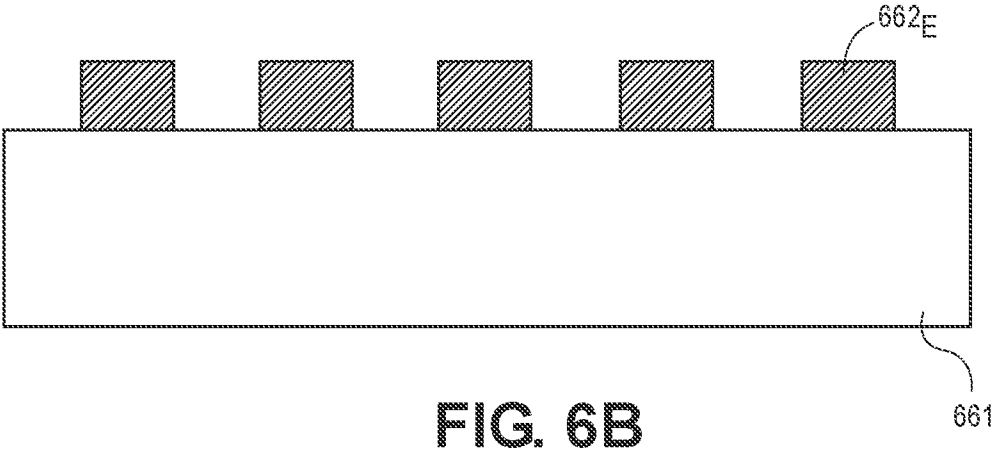
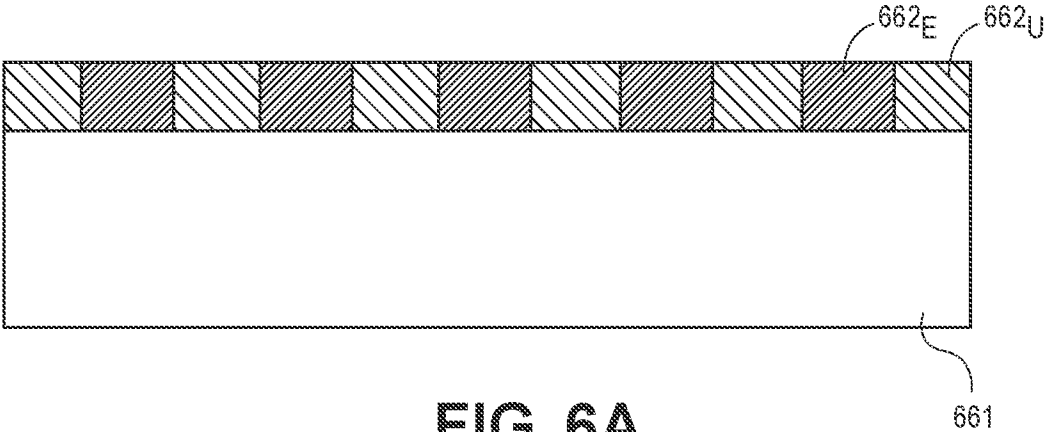
**FIG. 3**

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**FIG. 5**



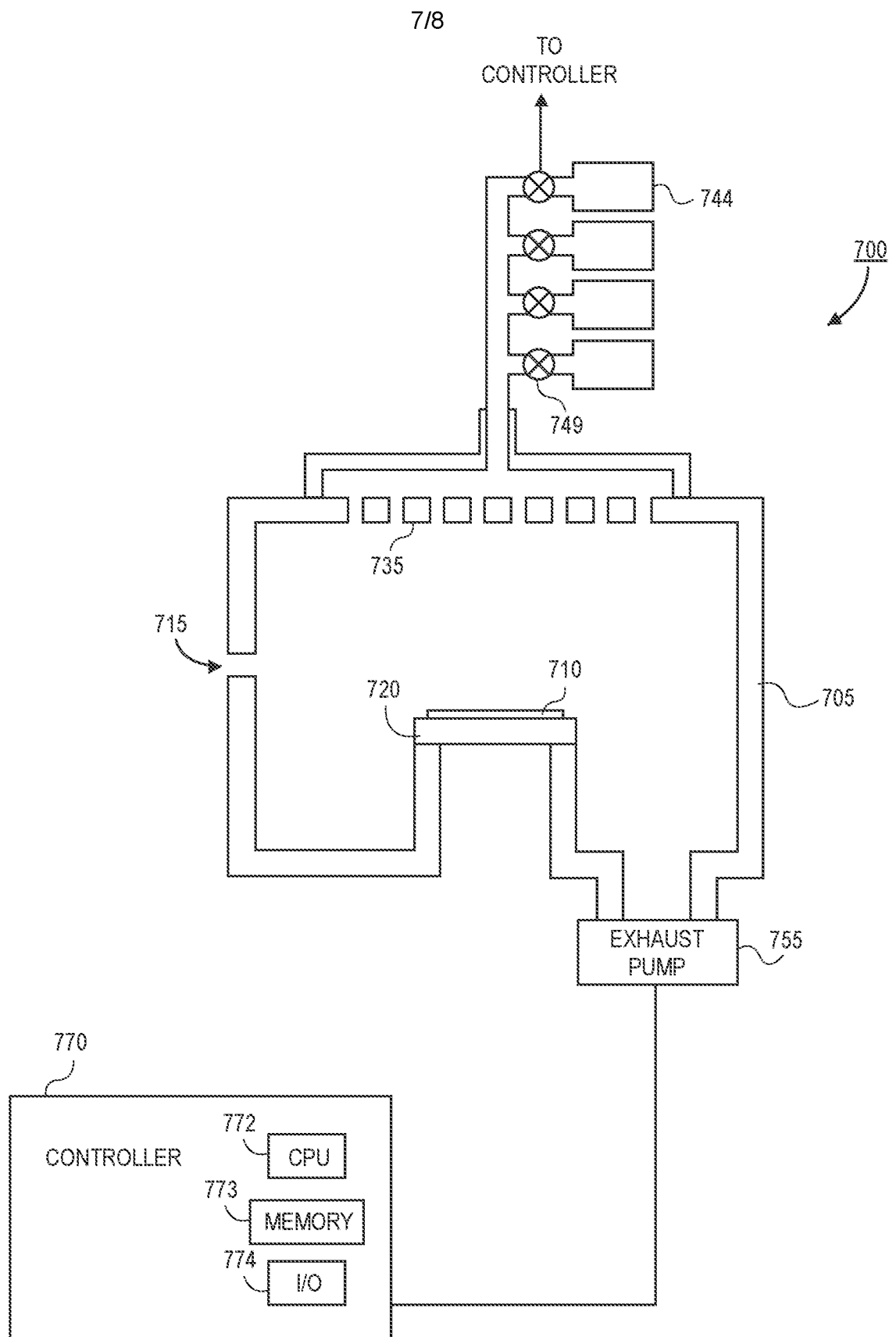


FIG. 7

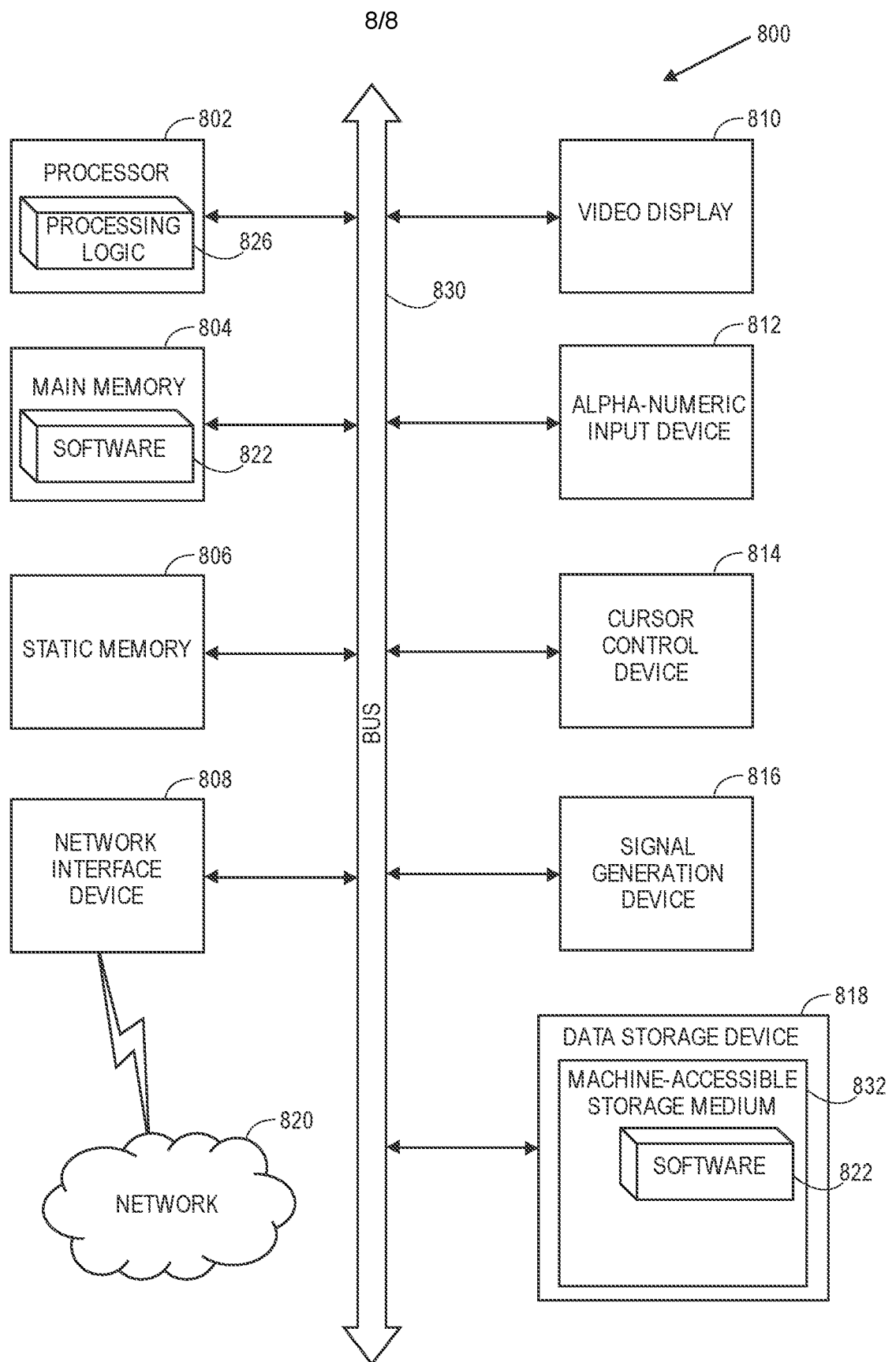


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2021/038424

A. CLASSIFICATION OF SUBJECT MATTER G03F 7/36(2006.01)i; G03F 7/004(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) G03F 7/36(2006.01); G03F 7/004(2006.01); G03F 7/16(2006.01); G03F 7/20(2006.01); G03F 7/32(2006.01); H01L 21/027(2006.01); H01L 21/033(2006.01); H01L 21/311(2006.01) 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: metal oxo photoresist, development, halogenating agent, volatile byproduct		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2020-132281 A1 (LAM RESEARCH CORPORATION) 25 June 2020 (2020-06-25) paragraph [0034], claims 1-8 and figures 1A-1B	1-20
A	US 2017-0146909 A1 (LAM RESEARCH CORPORATION) 25 May 2017 (2017-05-25) paragraphs [0026]-[0034], claim 1 and figures 1A-1D	1-20
A	US 2019-0131130 A1 (LAM RESEARCH CORPORATION) 02 May 2019 (2019-05-02) paragraphs [0039]-[0051] and figure 1	1-20
A	WO 2018-004646 A1 (INTEL CORPORATION) 04 January 2018 (2018-01-04) claim 17	1-20
A	WO 2004-095551 A1 (TOKYO ELECTRON LIMITED et al.) 04 November 2004 (2004-11-04) paragraphs [0021]-[0030] and figures 2-3	1-20
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "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 14 October 2021		Date of mailing of the international search report 14 October 2021
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer JUN, Sun Ae Telephone No. +82-42-481-8150

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2021/038424

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