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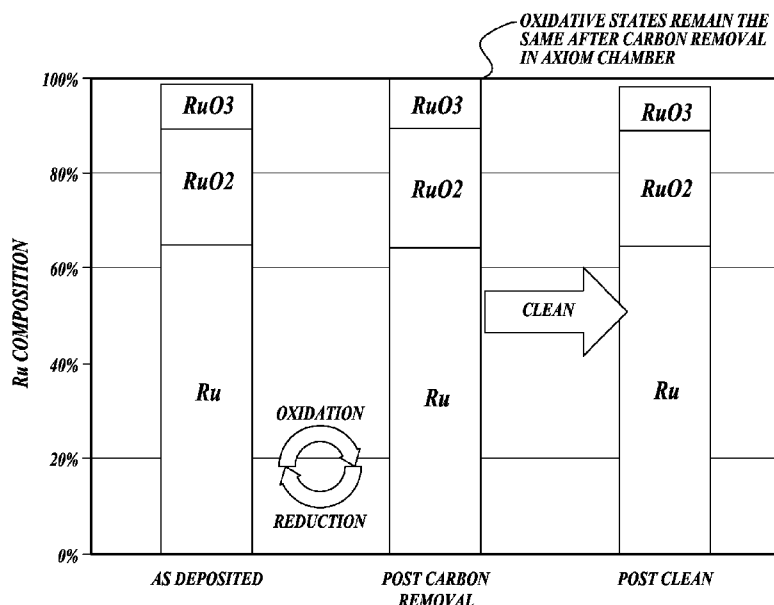
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Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a
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- as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: PROCESS FOR REMOVING CONTAMINATION ON RUTHENIUM SURFACE

**FIG. 4**

(57) Abstract: A method for pretreating an EUVL photomask having an exposed ruthenium surface includes subjecting the photomask to surface treatment in an oxidizing and reducing environment. Another method for pretreating an EUVL photomask having an exposed ruthenium surface includes subjecting the photomask to surface treatment in an oxidizing and reducing environment, and cleaning the photomask with a cleaning solution.

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PROCESS FOR REMOVING CONTAMINATION ON RUTHENIUM SURFACE

BACKGROUND

5 In extreme ultra-violet lithography (EUVL), an EUVL lithography reflection photomask is used. In contrast with a conventional lithography transmission photomask (compare FIGURES 5A and 5B), EUVL photomasks use a multi-layer stack to maximize reflective power of the short (13.5 nm) wavelength projecting a pattern onto the workpiece.

10 To maintain the highest level of reflectivity, the EUVL photomask is periodically cleaned to remove surface contamination. Aggressive cleaning can damage the surface and shorten the lifetime of the mask. However, insufficient cleaning can allow contamination to build and decrease the reflectivity in the EUVL photomask.

Therefore, there exists a need for an improved process for cleaning an EUVL
15 photomask to optimize the lifetime of the mask.

SUMMARY

This summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This summary is not intended to identify key features of the claimed subject matter, nor is it intended to be
20 used as an aid in determining the scope of the claimed subject matter.

In accordance with one embodiment of the present disclosure, a method for pretreating an EUVL photomask having an exposed ruthenium surface is provided. The method includes subjecting the photomask to surface treatment in an oxidizing and reducing environment.

25 In accordance with another embodiment of the present disclosure, a method for cleaning an EUVL photomask having an exposed ruthenium surface is provided. The method includes subjecting the photomask to surface treatment in an oxidizing and reducing environment, and cleaning the photomask with a cleaning solution.

In any of the embodiments described herein, subjecting the photomask to an
30 oxidizing and reducing environment may include treatment with water vapor plasma.

In any of the embodiments described herein, subjecting the photomask to an oxidizing and reducing environment may include treatment with hydroxyl OH* and hydrogen radicals H*.

In any of the embodiments described herein, the surface treatment may oxidize carbon on the surface on the photomask.

In any of the embodiments described herein, the surface treatment may reduce the exposed ruthenium layer.

5 In any of the embodiments described herein, the cleaning solution may include ammonium hydroxide, hydrogen peroxide, and deionized water.

DESCRIPTION OF THE DRAWINGS

The foregoing aspects and many of the attendant advantages of this disclosure will become more readily appreciated by reference to the following detailed description, when
10 taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is an exemplary EUVL reflection photomask blank including multiple layers of different materials, in accordance with embodiments of the present disclosure;

FIGURE 2 is a fabricated EUVL reflection photomask showing exposed capping layer, in accordance with embodiments of the present disclosure;

15 FIGURE 3 is a comparative graph showing Ru composition and oxidative state of the capping layer on the EUVL photomask of FIGURE 2, as deposited, post carbon removal, and post clean using a previously developed carbon removal technology;

FIGURE 4 is a comparative graph showing Ru composition and oxidative state of the capping layer on the EUVL photomask of FIGURE 2, as deposited, post carbon
20 removal, and post clean in accordance with embodiments of the present disclosure;

FIGURE 5A is a previously developed conventional lithography transmission photomask showing absorption; and

FIGURE 5B is an EUVL reflection photomask showing reflection.

DETAILED DESCRIPTION

25 The present disclosure relates to methods for cleaning extreme ultra-violet lithography (EUVL) photomasks.

In contrast with convention lithography transmission photomasks, EUVL photomasks are reflection photomasks. Referring to FIGURE 1, an exemplary EUVL reflection photomask 20 may include multiple layers of different materials. The layers
30 include a backside coating layer 22, a substrate 24, a Bragg reflector 26 including multiple layers, a capping layer 28, an absorber layer 30, an anti-reflective coating layer 32, and a photoresist layer 34. Referring to FIGURE 2, when fabricated, the capping layer 28 may be exposed on the EUVL photomask.

Ruthenium is typically used as the capping layer 28. In one non-limiting example, the ruthenium capping layer has a thickness of 2.5 nm. One drawback of a ruthenium capping layer, is its tendency to oxidize quickly.

The most common contamination on an EUVL photomask is carbon. The carbon
5 layer grows on the exposed surface of the mask as it is exposed to air over time. In addition, other process-induced contaminations on mask surfaces may include residual photoresist, metalorganic compounds, and sub-micrometer particles during patterning. The most common way to remove carbon from the surface is to oxidize the surface. However, such oxidation for carbon removal also oxidizes the ruthenium capping surface
10 of the EUVL photomask to the various oxidative states of RuO_2 , RuO_3 , and RuO_4 .

The higher oxidative states of ruthenium have higher etch rates in conventional mask cleaning chemistry causing loss of the total ruthenium thickness and reducing the lifespan of the EUVL photomask. As can be seen in FIGURE 3, RuO_4 material is lost from the capping layer during the clean. The formation of oxides and increase in surface
15 roughness as a result to material loss can negatively impact the reflectivity of the ruthenium capping layer.

In accordance with one embodiment of the present disclosure, the EUVL photomask is pre-treated in a reducing and oxidizing environment prior to cleaning. Such treatment has the effect of oxidizing carbon on the surface of the EUVL photomask, while reducing the ruthenium surface to maintain lower oxidative states on the ruthenium
20 surface.

In one embodiment of the present disclosure, the EUVL photomask is pre-treated using a water vapor plasma prior to cleaning. The treatment uses OH^* and H^* radicals to produce both a reducing and oxidizing environment. The oxidizing nature of the plasma
25 removes the carbon contamination, while the competing reducing reaction maintains the ruthenium layer oxidative state. As can be seen in FIGURE 4, the ruthenium material oxidative state of RuO_3 remains the same after carbon removal.

After such treatment, the EUVL photomask can be cleaned using an SCI cleaning solution, which may include ammonium hydroxide, hydrogen peroxide, and de-ionized
30 water. Other cleaning solutions are also within the scope of the present disclosure.

In accordance with embodiments of the present disclosure, oxide reduction can be achieved at a lower temperature using water plasma to reduce the metal oxide and also remove carbon from the seed layer surface. The hydrogen plasma includes H^* radicals

that can be used to uniformly reduce oxides and clean the seed layer surface in the feature.

EXAMPLE

5 An exemplary EUVL reflection photomask includes 106 layers of eight different materials. The layers include a backside coating having a thickness of about 70 nm, a substrate having a thickness of about 6.35 mm, a Bragg reflector multilayer having 100 layers and a total thickness of about 275nm, a capping layer of about 2.5 nm, a bulk absorber having a thickness of about 55 nm, an anti-reflective coating layer having a
10 thickness of about 15 nm, and a photoresist layer having a thickness of about 100 nm.

While illustrative embodiments have been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the disclosure.

15

CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for pretreating an EUVL photomask having an exposed ruthenium surface, the method comprising:

subjecting the photomask to surface treatment in an oxidizing and reducing environment.

2. The method of Claim 1, wherein subjecting the photomask to an oxidizing and reducing environment includes treatment with water vapor plasma.

3. The method of Claim 1, wherein subjecting the photomask to an oxidizing and reducing environment includes treatment with hydroxyl OH* and hydrogen radicals H*.

4. The method of Claim 1, wherein the surface treatment oxidizes carbon on the surface on the photomask.

5. The method of Claim 1, wherein the surface treatment reduces the exposed ruthenium layer.

6. A method for cleaning an EUVL photomask having an exposed ruthenium surface, the method comprising:

(a) subjecting the photomask to surface treatment in an oxidizing and reducing environment; and

(b) cleaning the photomask with a cleaning solution.

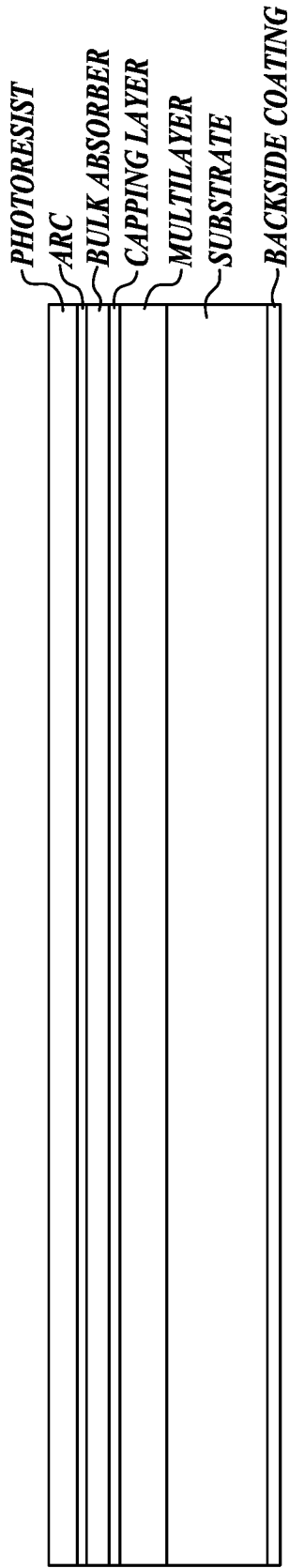
7. The method of Claim 6, wherein subjecting the photomask to an oxidizing and reducing environment includes treatment with water vapor plasma.

8. The method of Claim 6, wherein subjecting the photomask to an oxidizing and reducing environment includes treatment with hydroxyl OH* and hydrogen radicals H*.

9. The method of Claim 6, wherein the surface treatment oxidizes carbon on the surface on the photomask.

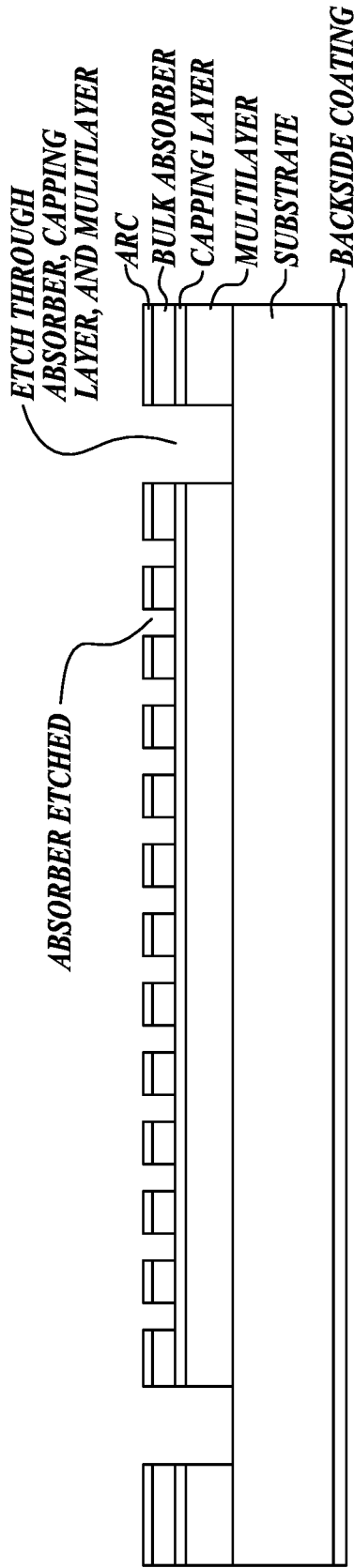
10. The method of Claim 6, wherein the surface treatment reduces the exposed ruthenium layer.

11. The method of Claim 6, wherein the cleaning solution includes ammonium hydroxide, hydrogen peroxide, and deionized water.



EUV MASK BLANK

FIG. 1



FABRICATED EUV MASK

FIG. 2

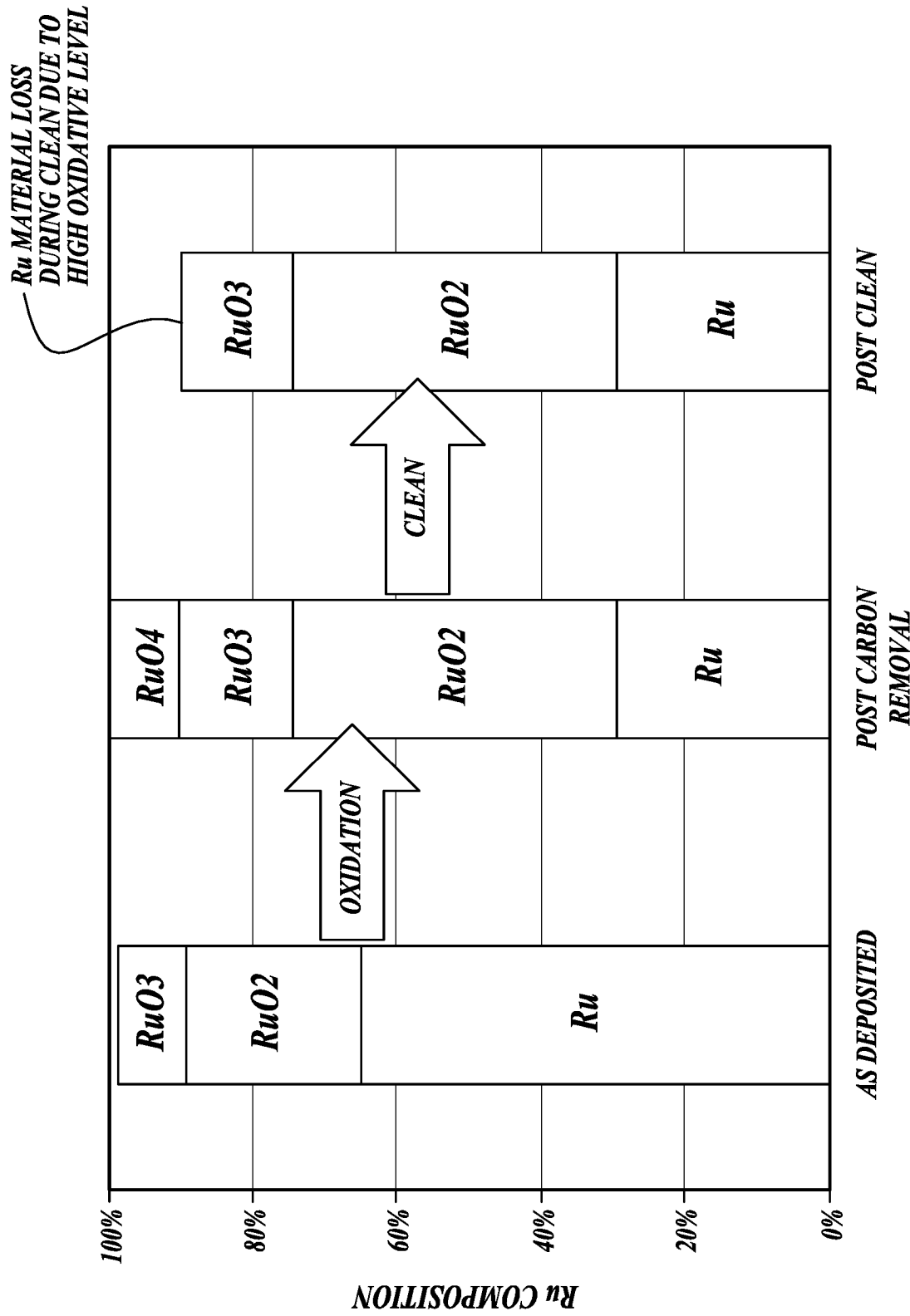


FIG. 3

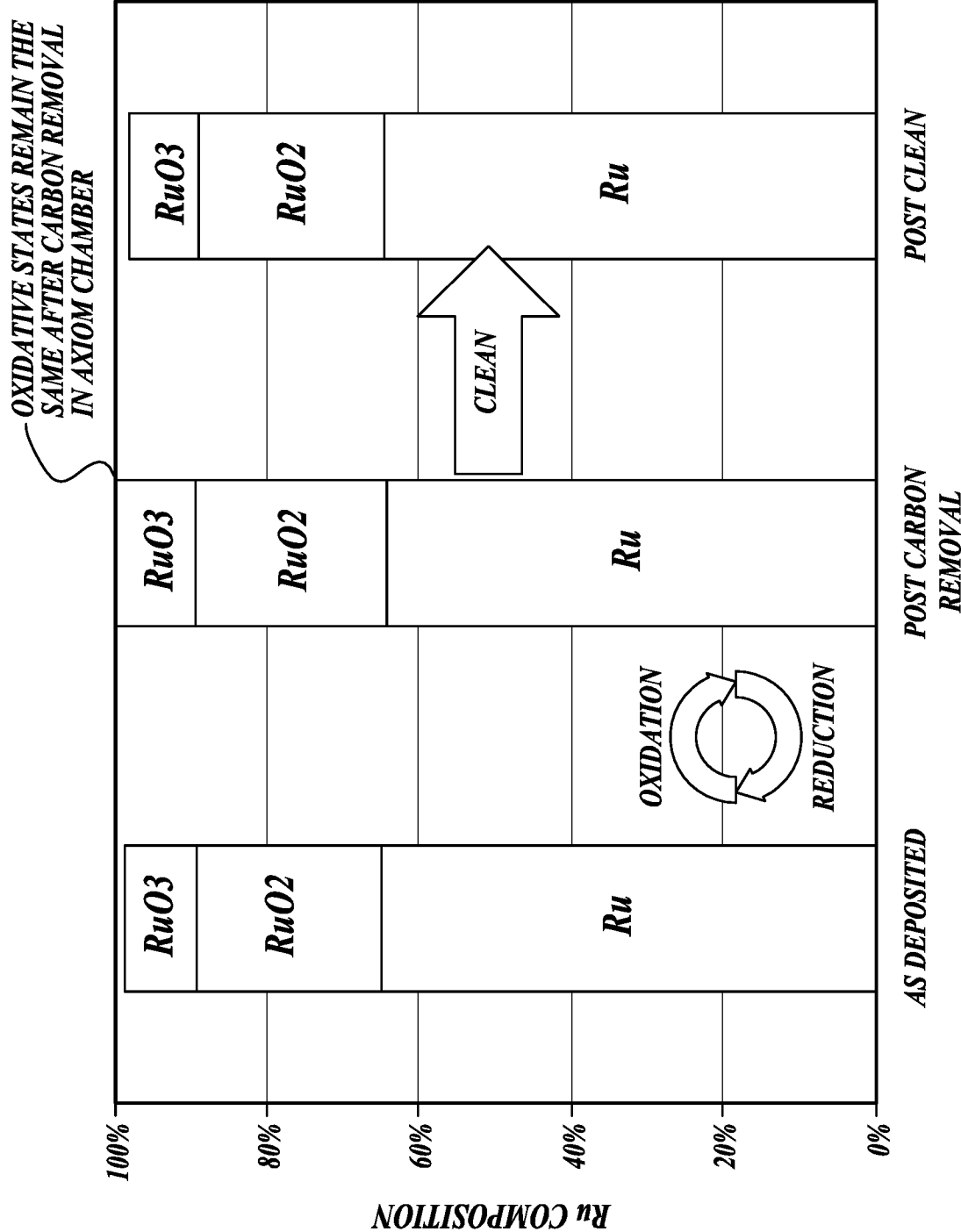


FIG. 4

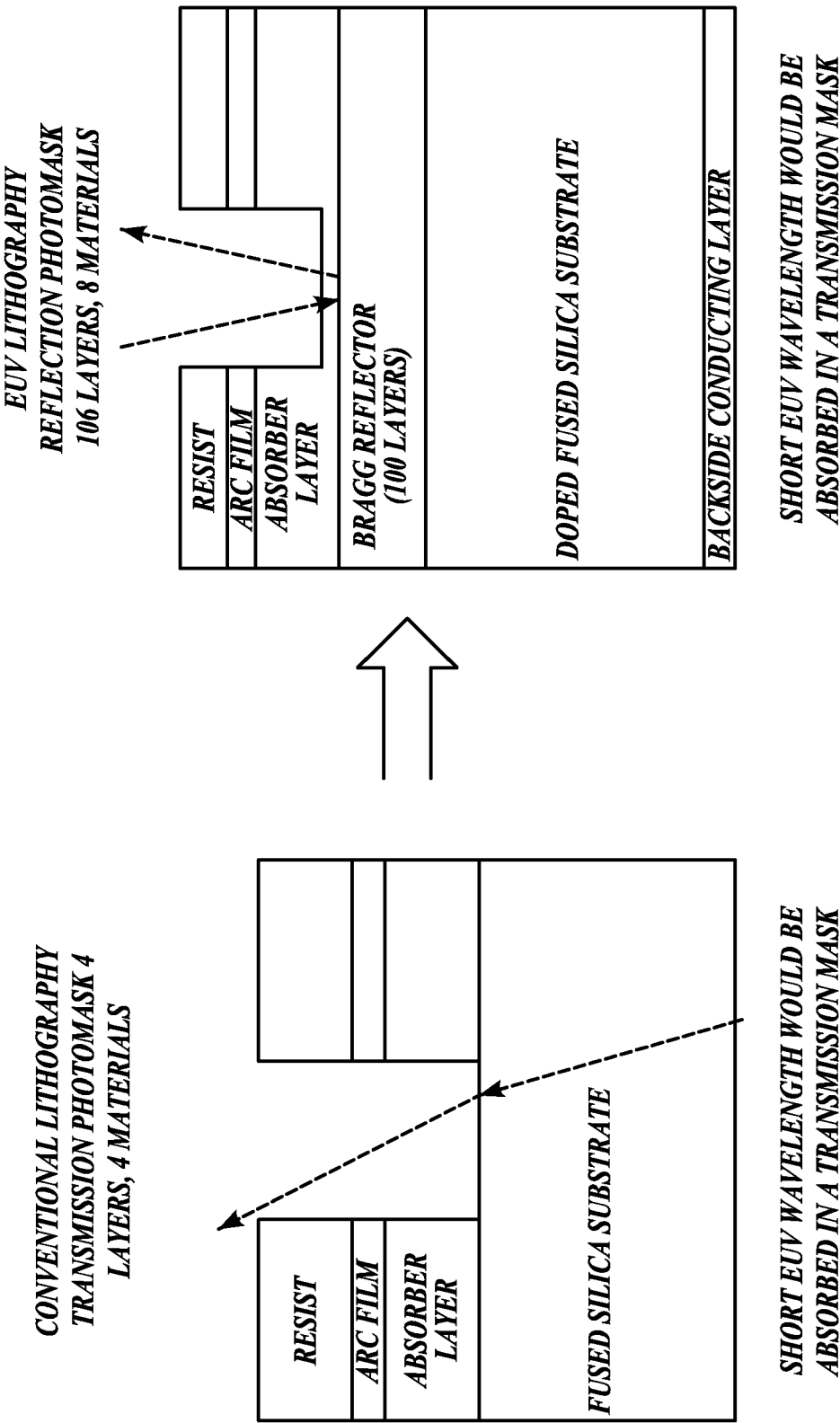


FIG. 5A

FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/038551**A. CLASSIFICATION OF SUBJECT MATTER****G03F 1/22(2012.01)i, G03F 7/20(2006.01)i, G03F 7/004(2006.01)i, G03F 7/26(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 1/22; G03F 1/82; B08B 7/00; G03F 1/00; C22B 11/00; G01J 3/10; H01L 21/31; H01L 21/00; G21K 5/10; G03F 7/20; G03F 7/004; G03F 7/26

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: photomask, ruthenium surface, oxidizing and reducing environment, plasma, radical, cleaning solution**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015-0107617 A1 (SAMSUNG ELECTRONICS CO., LTD.) 23 April 2015 See abstract; paragraphs [0040], [0052], [0062], [0066]–[0068], [0090]; claim 1.	1,4,5
Y		2,3,6–11
Y	US 2009-0061327 A1 (SENGUPTA, ARCHITA et al.) 05 March 2009 See abstract; paragraphs [0011], [0014]–[0017], [0029]; claim 1.	2,3,6–11
A	US 2007-0054497 A1 (WEISS, MARKUS et al.) 08 March 2007 See abstract; paragraphs [0016], [0022]; claims 1, 2, 7.	1–11
A	US 7598503 B2 (VAN HERPEN, MAARTEN MARINUS JOHANNES WILHELMUS et al.) 06 October 2009 See abstract; column 11, lines 41–47; claim 1.	1–11
A	US 2008-0241711 A1 (YUN, HENRY K. et al.) 02 October 2008 See abstract; paragraph [0006]; claim 1.	1–11

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2008-0241711 A1	02/10/2008	None	