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(54) Title: ENHANCED CLEANING PROCESS OF CHAMBER USED PLASMA SPRAY COATING WITHOUT DAMAGING COATING

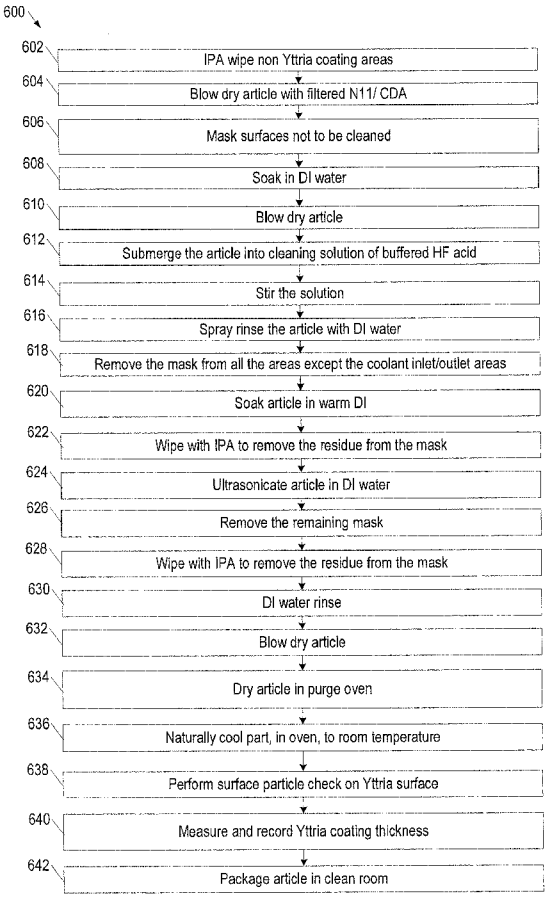

FIG. 6

(57) Abstract: A method including immersing a ceramic coated article into a bath including an HF acid solution having NH_4F with a molar concentration of about 0.1M to 1.0M for a time period to remove a deposition, and rinsing the ceramic coated article.

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ENHANCED CLEANING PROCESS OF CHAMBER USED PLASMA SPRAY COATING WITHOUT DAMAGING COATING

TECHNICAL FIELD

[0001] Embodiments of the present invention relate, in general, to a cleaning process that may be used to clean ceramic articles and ceramic coated articles.

BACKGROUND

[0002] A deposition of SiOx can form over time on plasma spray coated components used in semiconductor manufacturing. It is preferable to clean this SiOx deposition without damaging the plasma spray coating on the components. However, a conventional method of using pure HF acid to remove the SiOx deposition can also attack the coating surface causing damage to the plasma spray coating.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] The present invention is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings in which like references indicate similar elements. It should be noted that different references to "an" or "one" embodiment in this disclosure are not necessarily to the same embodiment, and such references mean at least one.

[0004] Figure 1 illustrates remaining silicon deposits on a chamber component over immersion time in a cleaning solution according a method of one embodiment.

[0005] Figure 2A illustrates a cross-sectional transmission electron microscope (TEM) view of an article prior to cleaning.

[0006] Figure 2B illustrates a cross-sectional TEM view of an article subsequent to cleaning according to a method of one embodiment.

[0007] Figure 3 illustrates top scanning electron microscope (SEM) views of articles after various immersion times in a cleaning solution according to a method of one embodiment.

[0008] Figure 4A illustrates cross-sectional TEM views of articles after various immersion times in a cleaning solution according to a method of one embodiment.

[0009] Figure 4B illustrates cross-sectional TEM views of articles after various immersion times in a cleaning solution according to a method of one embodiment.

[0010] Figure 5 illustrates cross-sectional TEM views of articles after various immersion times in a cleaning solution according to a method of one embodiment.

[0011] Figure 6 illustrates a method of cleaning according to one embodiment.

DETAILED DESCRIPTION

[0012] Embodiments are directed to a process for cleaning a ceramic article or an article that has a ceramic coating. Embodiments of the present invention provide a buffered HF acid

chemistry that maintains a SiOx removal effectiveness while minimizing and/or alleviating substrate damage (e.g., damage to a ceramic coating). A method according to one embodiment can include immersing a ceramic coated article into a bath including an HF acid solution having NH_4F with a molar concentration of about 0.1M to 1.0M for a time period to remove a deposition; and rinsing the ceramic coated article.

[0013] During processing, semiconductor manufacturing chamber components that are exposed to plasma can receive a deposition of SiOx. The chamber components may be, for example, lids, showerheads, chucks, chamber walls, nozzles, gas delivery hub, liner kit parts, and so forth. These chamber components may be ceramic components or may be ceramic coated components. This SiOx layer on the chamber components may periodically be cleaned using a wet clean or dry clean process.

[0014] HF acid may be used to clean semiconductor manufacturing components with a plasma spray coating, but it is highly acidic (e.g., pH equals about 2), which can damage the plasma spray coating. Additionally, use of HF acid may damage the surface of semiconductor manufacturing components that include bulk ceramics. It is preferable to clean the SiOx deposition on the components without damaging the underlying coating surface (e.g., to remove the SiOx layer without damaging the ceramic coating) or bulk ceramic surface. According to one embodiment, a buffered acid solution, which is a mixture of acid, a buffer and H_2O_2, may be used to clean the deposition of SiOx. One example buffer that may be used is NHF4.

[0015] In one embodiment, the pH of HF acid is increased by adding a buffer. This may result in a buffered HF acid mixture having a pH of about 4. By increasing the pH of the solution, Zeta potential is increased. Zeta potential is electrokinetic potential in colloidal systems. Change of the Zeta potential reduces the surface charge on cleaned components to lessen damage to the component caused by the HF. Additionally, change of the Zeta potential helps clean very small surface particles from the component.

[0016] In one embodiment, a concentration of less than about 1% HF acid (e.g., about 0.5% HF acid) is buffered in a solution including NH_4F, with a molar concentration in a range from about 0.1M to about 1M (e.g., about 0.5M), and H_2O_2 in a range from about 1% to about 15% (e.g., about 10%). SiOx deposition can more effectively be removed if it is in an SiO_2 form. When H_2O_2 reacts with SiOx, it aids in the formation of SiO_2 and eases the removal of the overall deposition

[0017] In one embodiment the substrate can be ceramic, metal (such as Al), or another material. A coating on the substrate can be Yittria (Y_2O_3) a Yittria based High Performance Material (HPM), Yttria stabilized zirconia (YSZ), $Y_3Al_5O_{12}$ (YAG,) Alumina, YF_3, $Y_4Al_2O_9$ Al_2O_3 (YAM), Quartz, SiC, Si_3N_4, AlN, ZrO_2, or other ceramics. The HPM may be composed

of a compound $Y_4Al_2O_9$ (YAM) and a solid solution Y_2-xZr_xO_3 (Y_2O_3-ZrO_2 solid solution). In one embodiment, the HPM ceramic composite contains 77% Y_2O_3, 15% ZrO_2 and 8% Al_2O_3. In another embodiment, the HPM ceramic composite contains 63% Y_2O_3, 23% ZrO_2 and 14% Al_2O_3. In still another embodiment, the HPM ceramic composite contains 55% Y_2O_3, 20% ZrO_2 and 25% Al_2O_3. Other distributions of these ceramic powders may also be used for the HPM material. The ceramic coating may be pure yttrium oxide or a yttrium oxide containing solid solution that may be doped with one or more of ZrO_2, Al_2O_3, SiO_2, B_2O_3, Er_2O_3, Nd_2O_3, Nb_2O_5, CeO_2, Sm_2O_3, Yb_2O_3, or other oxides. In one embodiment, the ceramic coating is a yttrium oxide containing ceramic or other yttrium containing oxide that is deposited on a metal or ceramic substrate using a thermal spraying technique or plasma spraying technique. In alternative embodiments, chamber components that are composed of a bulk ceramic may also be cleaned. Such bulk ceramics may be any of the above mentioned ceramics.

[0018] In one embodiment, the components can be submerged into the acid solution during the cleaning process. Complete submersion of the component can improve repeatability and be an effective technique to clean the component. However, this mixture can also be applied on the surface with cloth (e.g., by wiping) to remove a buildup of SiOx.

[0019] Figure 1 shows the effectiveness of removing SiOx deposition using a buffered HF acid solution as a percentage of remaining Si on a surface of a cleaned chamber component over time. Here, a semiconductor manufacturing component was submerged in a cleaning solution according to one embodiment. After 120 seconds of submersion, the deposition was removed. In one embodiment, the time period for submersion is about 90 seconds (e.g., about 90 seconds for each 60 nm of deposition or about 0.6 nm/second). However, effectiveness of the cleaning solution may deteriorate with use, and the cleaning solution may be replaced after a number of uses (e.g., after 20-25 components have been cleaned using the buffered HF solution).

[0020] Figure 2A illustrates a cross-sectional TEM view of a component prior to cleaning. Here, a layer of SiOx deposition 202 that has built up with use in a semiconductor manufacturing chamber can be seen over a Yttria coating 204 on the component. Further, a presence of Si on the component is shown in the energy-dispersive x-ray spectroscopy (EDS) analysis.

[0021] Figure 2B illustrates a cross-sectional TEM view of a component subsequent to cleaning using a buffered HF acid solution according to a method of one embodiment. Here, the layer of SiOx deposition is not present on the Yttria coating 204. Further, EDS analysis does not indicate the presence of Si on the component.

[0022] So that performance of the component is not adversely affected, the cleaning process should cause minimal or no damage to the coating surface during removal of the surface deposition of SiO_x. Figure 3 illustrates top scanning electron microscope (SEM) views at 4kx

and 10kx of components after various immersion times in a buffered HF acid solution according to a method of one embodiment. Here, plasma spray Yttria coupons have been exposed to the buffered HF cleaning solution for various time periods, including at 0 seconds (or no exposure), at 60 seconds, at 120 seconds, and at 180 seconds. The SEM images indicate no detectable surface damage.

[0023] Figures 4A illustrates cross-sectional TEM views of components with no SiO_x deposition pre-cleaning and at 90 seconds, 120 seconds, and 300 seconds of cleaning in a buffered HF solution. The TEM images indicate no detectable surface damage. Figures 4B and 4C illustrate cross-sectional TEM views of components with a Yttria coating 412 (i.e., a plasma spray coating) both pre-cleaning and after various immersion times in a buffered HF bath according to a method of one embodiment. In Figure 4B, at 90 seconds, the SiO_x deposition 410 is still present on the Yttria coating 412. However, at 120 seconds, 150 seconds, and 300 seconds, SiO_x deposition is not present and the Yttria coating 412 is undamaged.

[0024] Figure 5 shows a crack in the Yttria coating 512 that was present prior to the cleaning process. Figure 5 shows that the crack is still present and visibly unaffected at 90 seconds, at 120 second, at 150 second and at 300 seconds. The SiOx deposition 510 is still present on the Yttria coating 512 at 90 seconds, but is removed at 120 seconds, 150 seconds, and 300 seconds, and the Yttria coating 512 appears to be undamaged, including no change in the number or size of the cracks, even after 300 seconds of immersion in the buffered HF acid solution.

[0025] Semiconductor manufacturing components, including chamber lower liner and upper liner kit components, may be cleaned via the cleaning process described herein. Further, these components may be installed in a semiconductor manufacturing chamber to test for particles. A test for particle performance over time of an article pre-cleaning and post-cleaning according to a method of one embodiment has shown that particle adders (i.e., particles dislodged from components during semiconductor manufacturing that may degrade semiconductor performance) do not increase after the component has been cleaned. For example, particle adders at 45nm ranged from about 1 to about 20 pre-cleaning, and particle adders at 45nm ranged from about 0 to about 35 post-cleaning. Accordingly, cleaning in the buffered HF acid solution does not damage the surface of the plasma spray coating.

[0026] Figure 6 illustrates a method of cleaning processor chamber components using a buffered HF acid solution according to one embodiment. For example, the cleaning process can be used for cleaning an aluminum component with a ceramic coating (e.g., a Yttria (Y_2O_3) plasma spray coating). The cleaning method may be used for Yttria coated components used in, for example, conductor etch chambers. Conductor etch is one example of a form of plasma processing used to fabricate integrated circuits on conductive materials, such as metal wafers,

with a high-speed stream of plasma of an appropriate gas mixture directed at a substrate. This procedure covers the recycle cleaning of chamber-used Y_2O_3 spray-coated aluminum components, but may also be applied to other ceramic coated articles.

[0027] Tools and materials that may be used to perform the cleaning process include chemical resistant gloves, eye protection, a deionized (DI) water tank or sink, an ultrasonic cleaning tank, compressed hot dry nitrogen, polyester heat-sealed polynet class 10 cloth wipes, a vacuum oven or nitrogen purge oven, a particle counter, a 6 mils polyethylene bag, a 4 mils polyethylene bag, IPA (electronic grade), acetone (electronic grade), HF (electronic grade), H_2O_2 (electronic grade), NH_4F (electronic grade), an ultrasonic tank with cover and proper ventilation, and ultrasonic power (40 KHz, 50 Watt/gallon).

[0028] At block 602, non-Yttria coating areas may be wiped with IPA. At block 604, the component may be blow dried with filtered N_2/clean dry air (CDA) at room temperature for at least about 2 minutes. At block 606, O ring grooves, RF gasket grooves, weld cover, coolant inlet/outlet areas and Ni plated surfaces may be masked. At block 608, a room temperature DI water soak may be performed for about 10 minutes. At block 610, the component may be blow dried with filtered N_2/CDA at room temperature for at least about 2 minutes.

[0029] At block 612, according to one embodiment, the component is fully submerged into the cleaning solution. In one embodiment, the cleaning solution is less than about 1% HF and about 0.1 to about 1.0 M NH_4F. Optionally, about 1% to about 15% H_2O_2 mixture may also be included in the cleaning solution. The component may be submerged in the cleaning solution for about 90 seconds in one embodiment. Alternatively, the component may be submerged in the cleaning solution for greater than 90 seconds (e.g., 100 seconds, 120 seconds, or longer). At block 614, the solution may be stirred occasionally while the component is immersed in the cleaning solution. This may keep the solution on the component fresh (continuously exposing the component to new HF and NH_4F molecules). At block 616, the component may be spray rinsed with DI water for at least about 10 minutes.

[0030] At block 618, the mask may be removed from all the areas except for coolant inlet/outlet areas of the component. For example, the mask may be left on the inlet/outlet areas of the component to prevent water from entering during the subsequent DI water soak. At block 620, the component may be soaked in warm DI water (e.g., about 38 degrees C to about 42 degrees C) for about 30 minutes. At block 622, the component may be wiped with IPA to remove the residue from the mask.

[0031] At block 624, the component may be ultrasonicated in DI water for about 5 minutes to about 2 hours (e.g., about 40 minutes) at about 10 Watt per square inch (+/- about 2 Watts per square inch). The component may be rotated about every 10 minutes during the ultrasonicating.

[0032] At block 626, the remaining mask may be removed from the component. At block 628, the component may be wiped with IPA to remove the residue from the mask. At block 630, a DI water rinse may be performed for at least 10 minutes. At block 632, the component may be blown dry with filtered N_2/ CDA at room temperature. Note that in one embodiment, for all baking processes, the oven is not pre-heated.

[0033] At block 634, the component may be dried in a filtered N_2 or CDA purge oven (e.g., a vacuum oven) at about 90 degrees C to about 95degrees C for at least about 3 hours. At block 636, the component may be naturally cooled, in the oven, to room temperature. The component may be ramped up to temperature slowly (e.g., about 3 degrees C per minute), baked for the specified time, and cooled slowly (natural cooling) to room temperature, such that the component is not thermally shocked.

[0034] At block 638, a surface particle check may be performed on the Yttria surface. At block 640, the Yttria coating thickness, for each component, may be measured and kept on record at the end of the wet-clean process. At block 742, the component may be packaged in a clean room. In one embodiment, the total ultrasonic time for the entire cleaning process may be recommended to not exceed 1 hour.

[0035] In one embodiment, with regards to the above example cleaning process, the following techniques can be observed. Components and assemblies may be handled with talc free vinyl, clean room gloves. Acid-resistant gloves and clean room gloves may be used during wet cleaning. Gloved hands that touch clean components may touch only clean components. A Class 1000 or better clean room may be employed for final cleaning, drying, final inspection and packaging. Tooling, fixtures and hardware accessories used for cleaning may meet contamination and cleanliness requirements, and be suitable for a cleaning process. The cleaning process may not chip, scratch, pit, or damage the component surface. The baths may be free of any surface films that might contaminate the component on entry or withdrawal from the solution. The tanks may be covered when they are not in use. De-ionized water rinses may have a resistivity of 2 M-Ohms-cm or higher. Nitrogen or clean-dry-air (CDA) used to dry components may be dry, oil-free, and filtered at the point of use with a 0.1 micron filter. Ovens may meet cleanliness requirements, and they may be contamination particle qualified before component drying use.

[0036] Incoming and outgoing inspections may be performed. A bench top visual check can be performed for any chips, crack, scratches, or other unusual features. Any deviations from the usual can be recorded in cleaning logs against the serial number of the component. Similar inspection can be performed after the cleaning is completed, including a check for drying stain.

[0037] The following tests may be performed to assure component cleanliness quality. For contamination qualifications, the post-clean component may analyzed for surface trace metal contamination. Tests may be applied to one component for every ten components shipped in the same lot. The Yttria coated surface (at one location) may also be analyzed for surface trace metals by acidic extraction Inductively Coupled Plasma Mass Sectroscopy (ICP-MS) or another equivalent method. This test can be used to verify that adequate cleaning has occurred. The extraction area can then be rinsed with DI water (e.g., with a 18 Meg-ohm resistivity).

[0038] Before packaging, the components may be verified to be completely dry. In one embodiment, packaging may be done in a class 1000 clean room or better, or a class 100 or better clean room. Each component may be placed separately in an unused polyethylene (PE) bag, and double bagged (e.g., a 4 mil thick PE inner bag and a 6 mils thick PE outer bag). The bag can then be purged with 0.1 micron filtered dry nitrogen and vacuum heat-seal. In an embodiment, antistatic bags are not used. In one example, polyethylene bags should remain inside original bulk shipping container until ready for use, and bags may be pre-qualified for metal impurities and particles and only unpacked in the clean room.

[0039] The preceding description sets forth numerous specific details such as examples of specific systems, components, methods, and so forth, in order to provide a good understanding of several embodiments of the present invention. It will be apparent to one skilled in the art, however, that at least some embodiments of the present invention may be practiced without these specific details. In other instances, well-known components or methods are not described in detail or are presented in simple block diagram format in order to avoid unnecessarily obscuring the present invention. Thus, the specific details set forth are merely exemplary. Particular implementations may vary from these exemplary details and still be contemplated to be within the scope of the present invention.

[0040] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrase "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment. In addition, the term "or" is intended to mean an inclusive "or" rather than an exclusive "or." In one embodiment, the term "about" means plus or minus ten percent.

[0041] Although the operations of the methods herein are shown and described in a particular order, the steps of each method may be altered so that certain steps may be performed in a different order, or not at all, or so that certain steps may be performed, at least in part,

concurrently with other operations. In another embodiment, some steps of the method are not performed.

[0042] It is to be understood that the above description is intended to be illustrative, and not restrictive. Many other embodiments will be apparent to those of skill in the art upon reading and understanding the above description. The scope of the invention should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

CLAIMS

What is claimed is:

1. A method comprising:

submerging a ceramic coated article in a bath comprising an HF acid solution having NH_4F with a molar concentration of about 0.1M to 1.0M for a time period to remove a deposition; and

rinsing the ceramic coated article.

2. The method of claim 1, wherein the article comprises one of an electrostatic chuck, a lid, a showerhead, nozzle, gas delivery hub, chamber liner kit parts, or a chamber wall.

3. The method of claim 1, wherein the bath further comprises about 1% to about 15% H_2O_2.

4. The method of claim 1, wherein the bath comprises less than about 1% HF.

5. The method of claim 1, wherein the NH_4F has a molar concentration of about 0.5M.

6. The method of claim 1, wherein the ceramic coated article comprises at least one of Al, AlN, or Al_2O_3, and wherein the coating comprises Yttria.

7. The method of claim 1, wherein rinsing the ceramic coated article comprises soaking the ceramic coated article de-ionized water at a temperature of about 38 degree C to about 42 degree for an additional time period.

8. A method comprising:

wiping a ceramic coated article with a solution comprising an HF acid solution having NHF_4 with a molar concentration of about 0.1M to 1.0M for a time period to remove a deposition; and

rinsing the ceramic coated article.

9. The method of claim 8, wherein the solution further comprises about 1% to about 15% H_2O_2.

10. The method of claim 8, wherein the solution comprises about less than about 1% HF.

11. An article for use in semiconductor manufacturing, the article having been cleaned by a process comprising:

submerging a ceramic coated article in a bath comprising an HF acid solution having NH_4F with a molar concentration of about 0.1M to 1.0M for a time period to remove a deposition; and

rinsing the ceramic coated article.

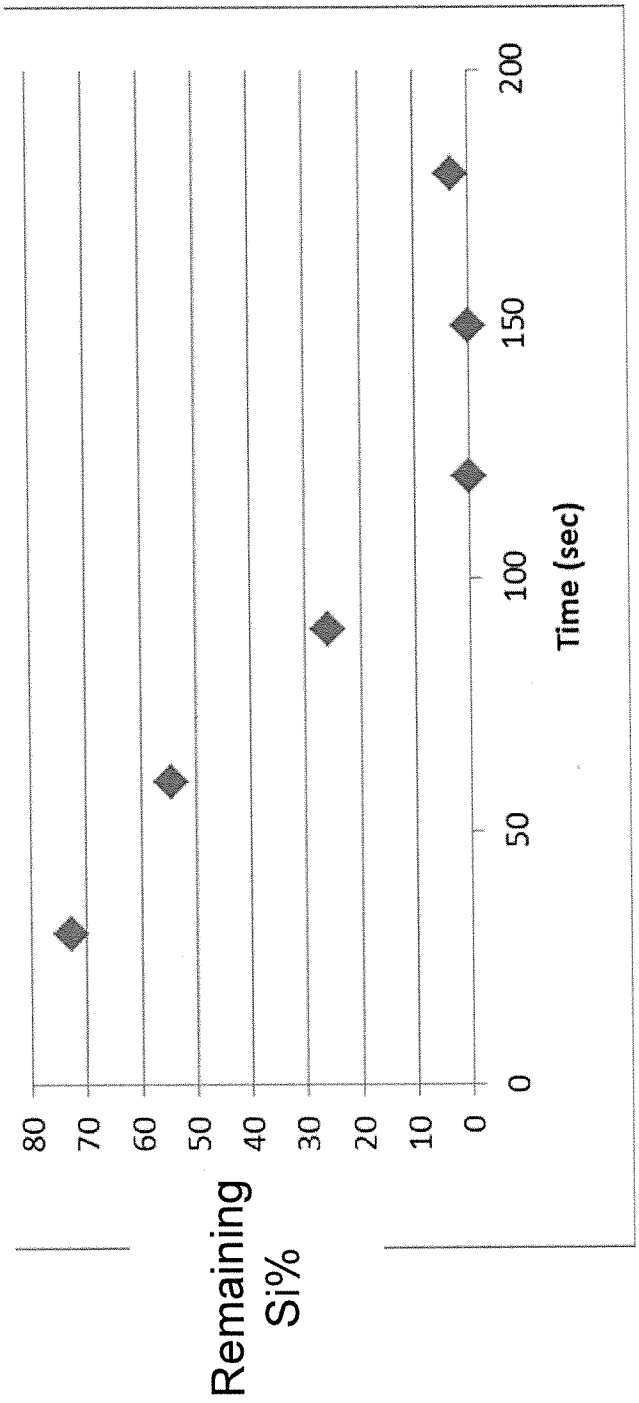
12. The article of claim 11, wherein the article comprises one of an electrostatic chuck, a lid, a showerhead, nozzle, gas delivery hub, chamber liner kit parts, or a chamber wall.

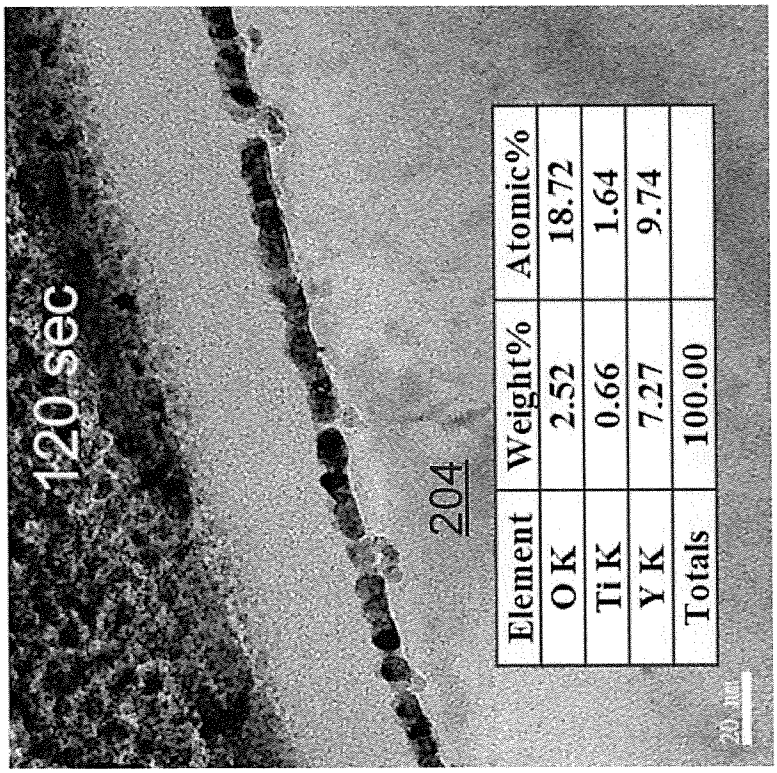
13. The article of claim 11, wherein the bath further comprises about 1% to about 15% H_2O_2.

14. The article of claim 11, wherein the bath comprises less than about 1% HF.

15. The article of claim 11, wherein the NH_4F has a molar concentration of about 0.5M.

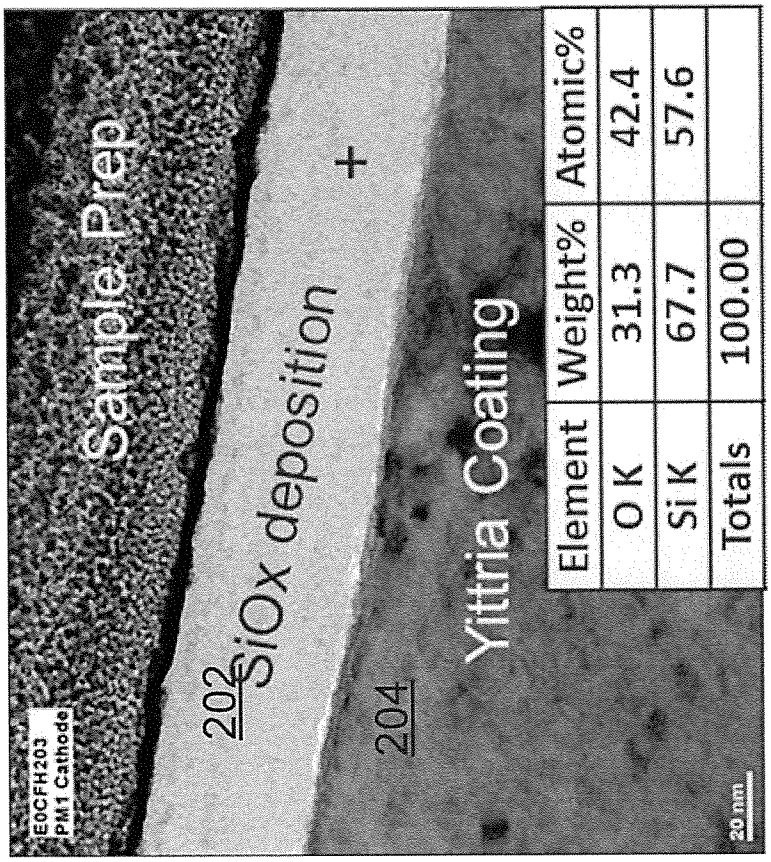
FIG. 1





Element	Weight%	Atomic%
O K	2.52	18.72
Ti K	0.66	1.64
Y K	7.27	9.74
Totals	100.00	

FIG.2B



Element	Weight%	Atomic%
O K	31.3	42.4
Si K	67.7	57.6
Totals	100.00	

FIG. 2A

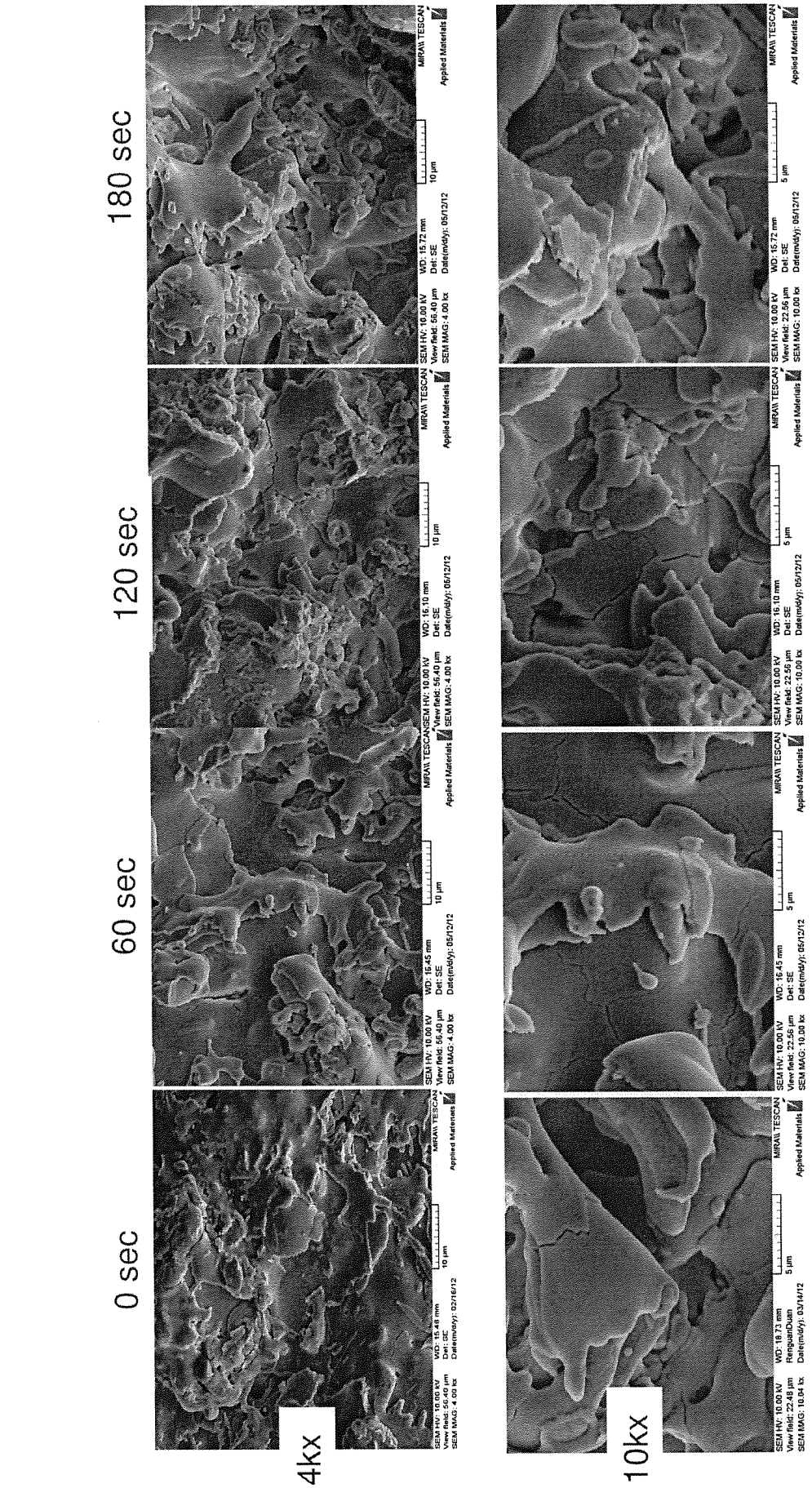


FIG. 3

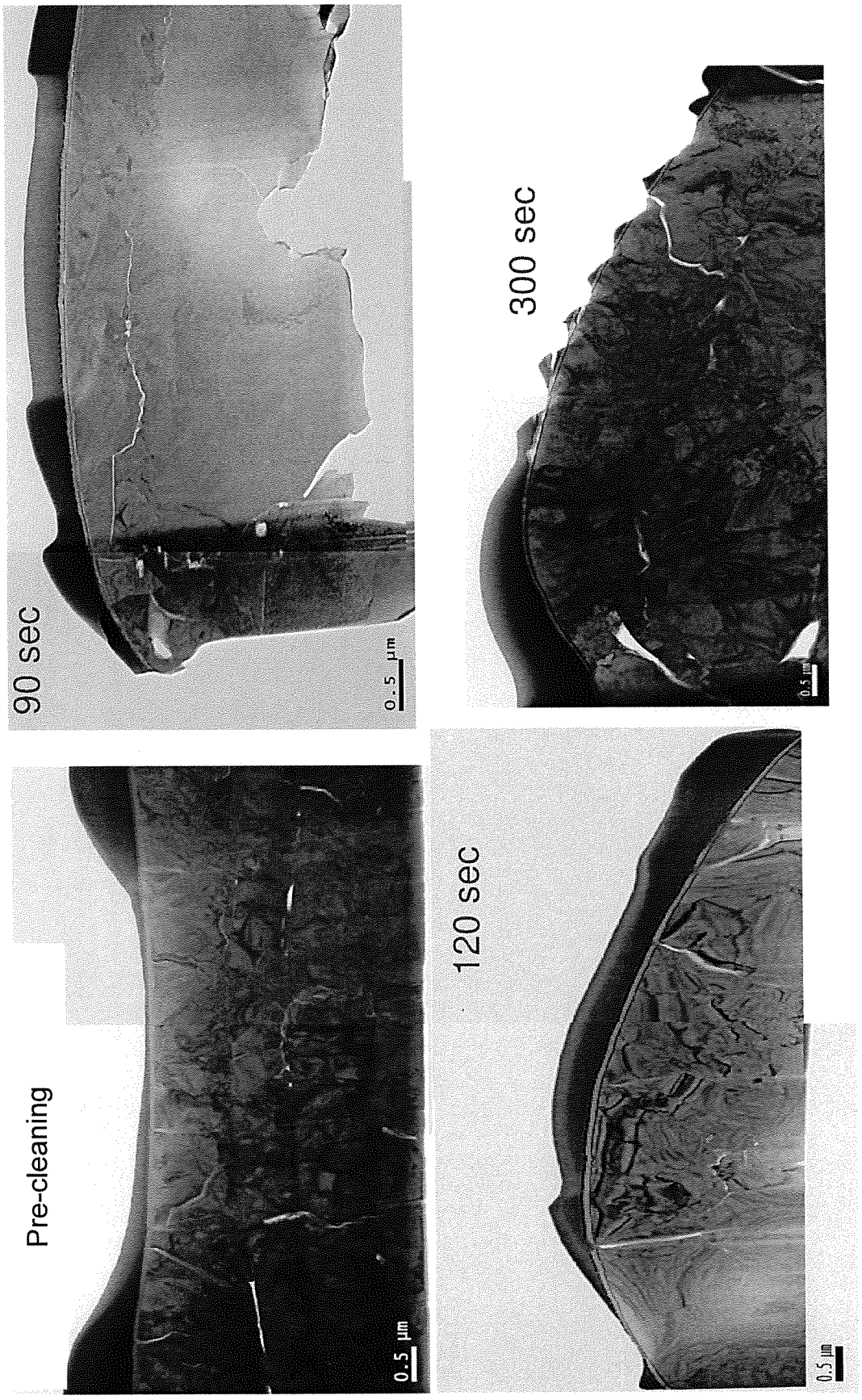


FIG. 4A

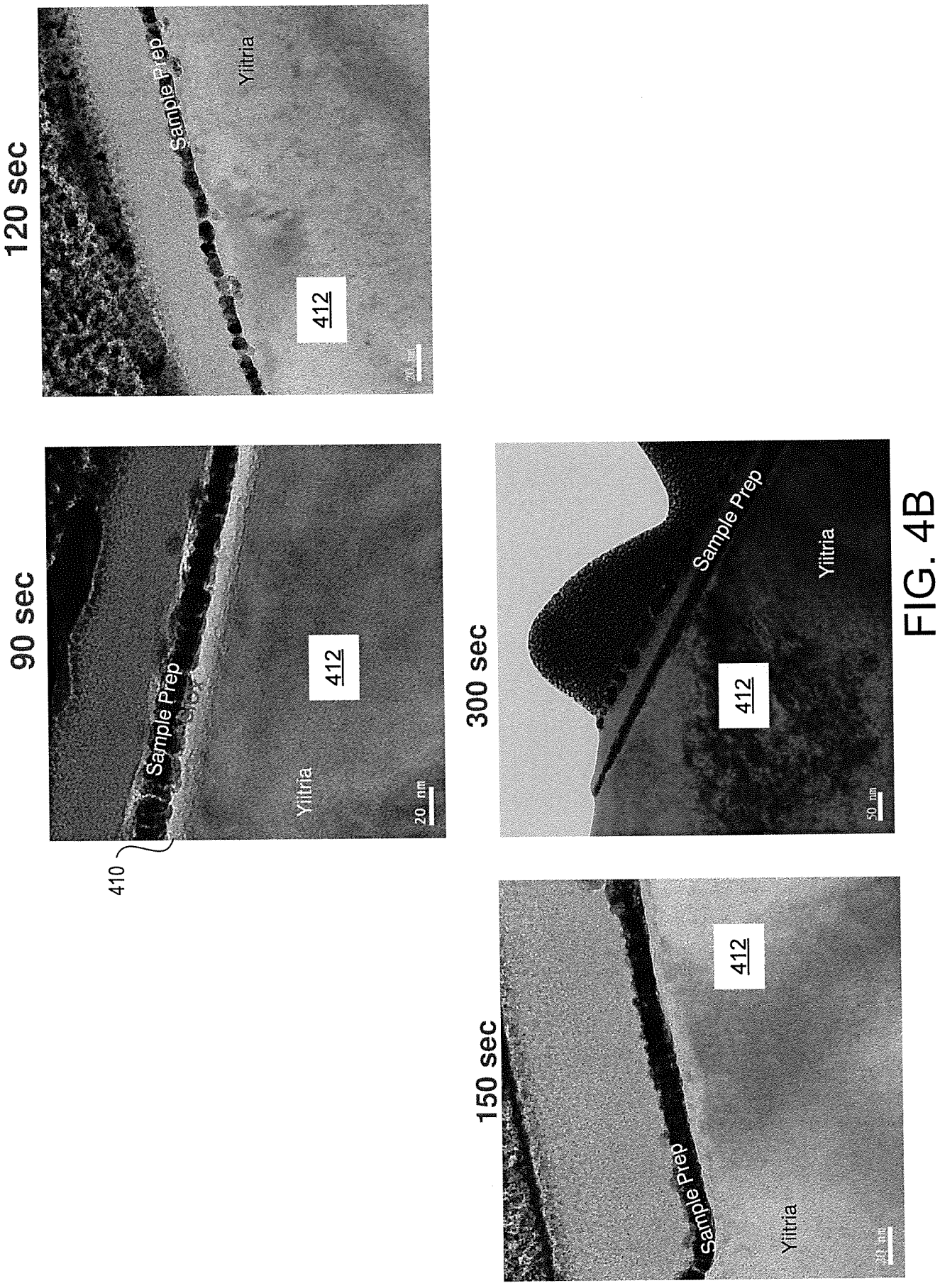

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FIG. 4B

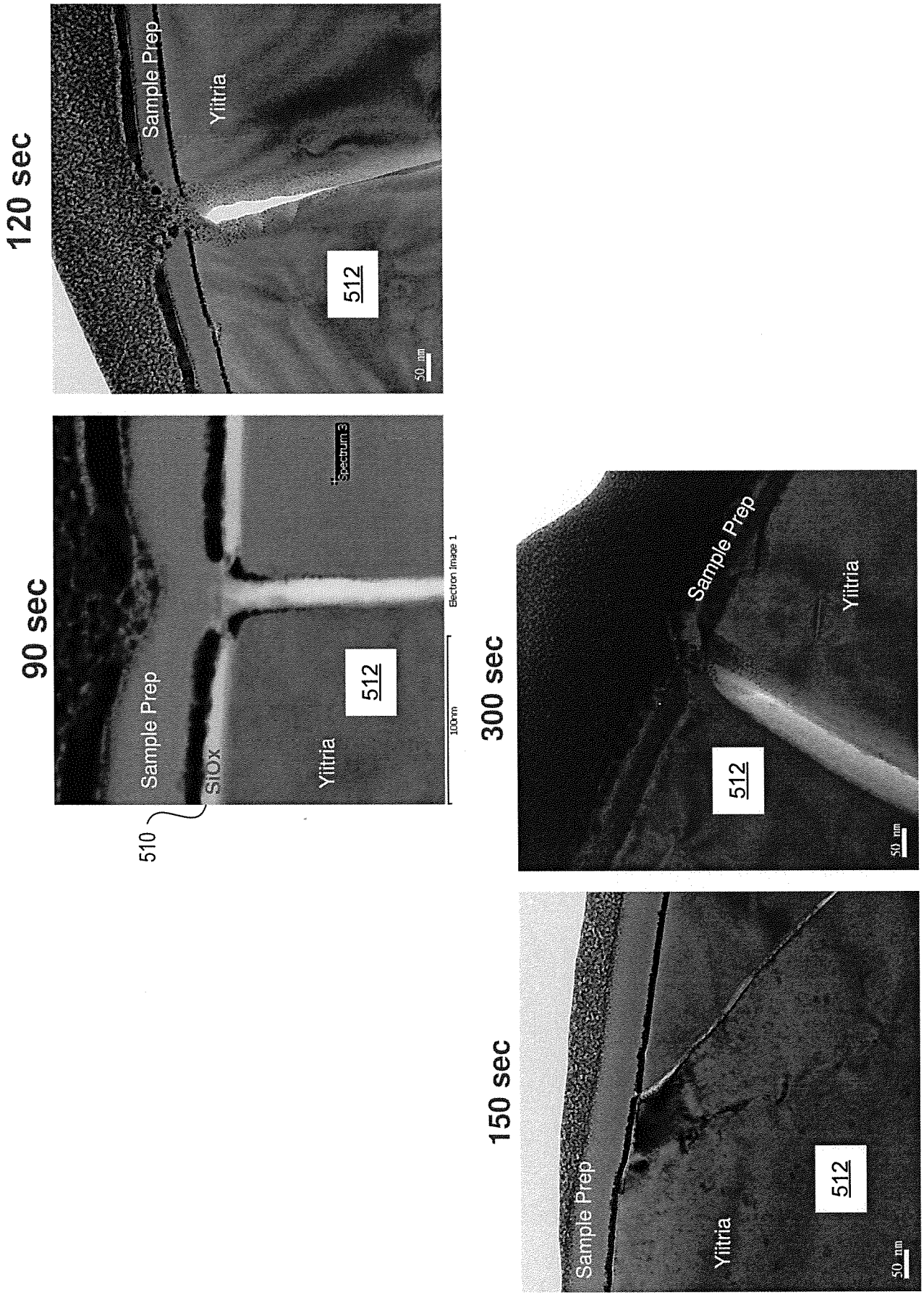
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FIG. 5

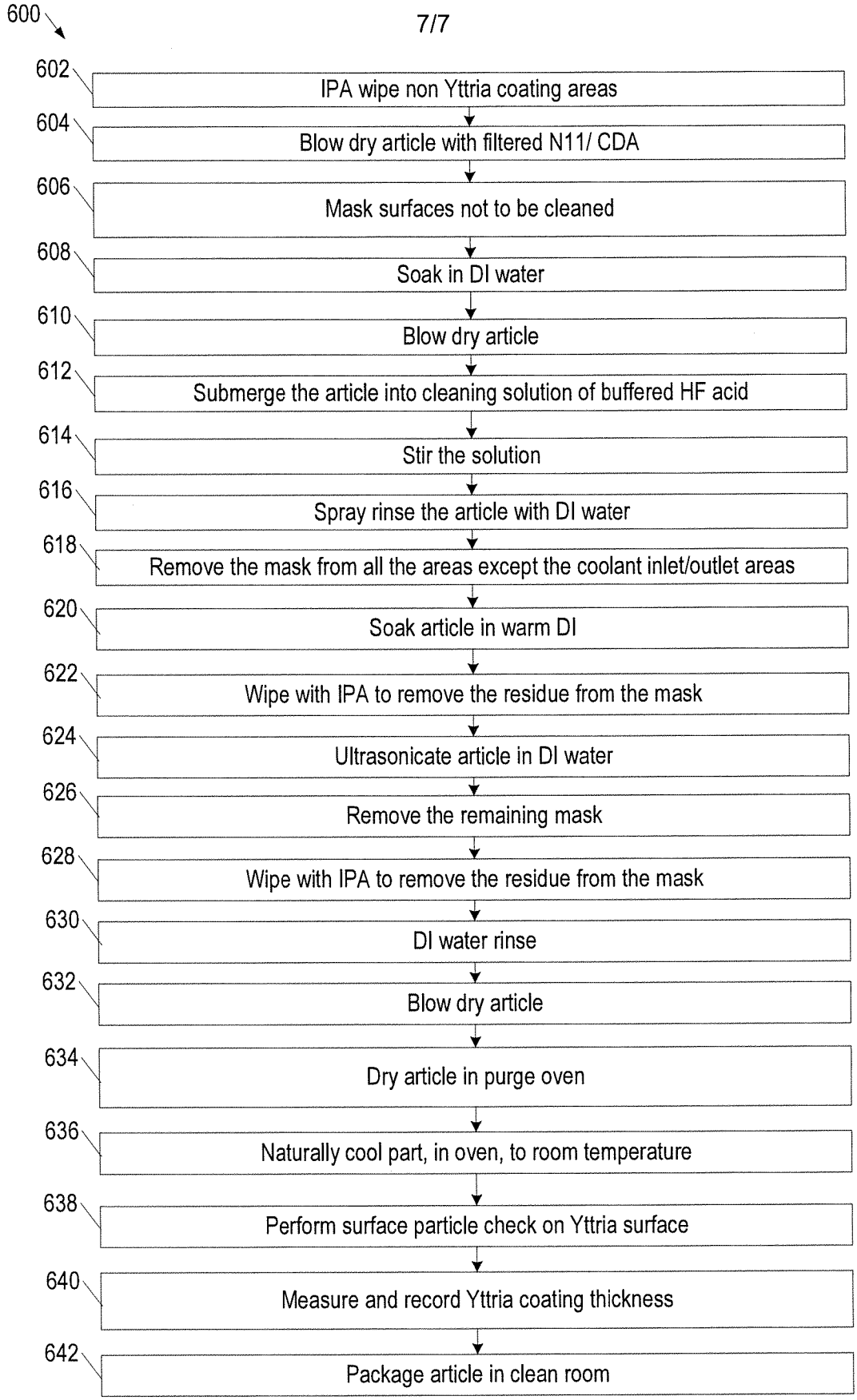
600
602
IPA wipe non Yttria coating areas
604
Blow dry article with filtered N11/ CDA
606
Mask surfaces not to be cleaned
608
Soak in DI water
610
Blow dry article
612
Submerge the article into cleaning solution of buffered HF acid
614
Stir the solution
616
Spray rinse the article with DI water
618
Remove the mask from all the areas except the coolant inlet/outlet areas
620
Soak article in warm DI
622
Wipe with IPA to remove the residue from the mask
624
Ultrasonicate article in DI water
626
Remove the remaining mask
628
Wipe with IPA to remove the residue from the mask
630
DI water rinse
632
Blow dry article
634
Dry article in purge oven
636
Naturally cool part, in oven, to room temperature
638
Perform surface particle check on Yttria surface
640
Measure and record Yttria coating thickness
642
Package article in clean room

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/052202

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/302(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)
H01L 21/302; C25D 5/00; B08B 7/04; H01L 21/306; B08B 3/00; B08B 3/08; B08B 3/12; C23C 16/00; H01L 21/02

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: acid, solution, NH4F, ammonium fluoride, concentration

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5972123 A (STEVEN VERHAVERBEKE) 26 October 1999 See abstract, column 3, lines 7-30, column 5, line 43 - column 6, line 49, claims 1, 6 and figures 1-3.	1-15
A	US 2009-0075486 A1 (HIROHISA KIKUYAMA et al.) 19 March 2009 See abstract, paragraphs [0014]-[0025] and figure 1.	1-15
A	JP 2005-279481 A (OMI TADAHIRO et al.) 13 October 2005 See abstract, paragraphs [0009], [0028], claims 1-2 and figures 1-2.	1-15
A	US 2008-0223725 A1 (NIANCI HAN et al.) 18 September 2008 See abstract, paragraphs [0029]-[0030], claim 1 and figure 3.	1-15
A	US 2006-0054181 A1 (RONALD RAYANDAYAN et al.) 16 March 2006 See abstract, paragraph [0040] and claims 1, 6.	1-15

☐ 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
"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 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	Date of mailing of the international search report
11 November 2013 (11.11.2013)	**12 November 2013 (12.11.2013)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/052202

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5972123 A	26/10/1999	None	
US 2009-0075486 A1	19/03/2009	CN 1608037 A	20/04/2005
		CN 1608037 C0	30/01/2008
		EP 1426346 A1	09/06/2004
		EP 1426346 A4	25/03/2009
		JP 2003-063842 A	05/03/2003
		JP 5132859 B2	30/01/2013
		KR 10-0828112 B1	08/05/2008
		TW I298748 B	11/07/2008
		TW I316973 B	11/11/2009
		US 2007-0029519 A1	08/02/2007
		US 8066898 B2	29/11/2011
		WO 03-018500 A1	06/03/2003
JP 2005-279481 A	13/10/2005	JP 4443976 B2	31/03/2010
US 2008-0223725 A1	18/09/2008	CN 101302610 A	12/11/2008
		CN 101302610 B	25/04/2012
		CN 1620522 A	25/05/2005
		CN 1620522 C0	03/12/2008
		CN 1690254 A	02/11/2005
		CN 1690254 B	13/03/2013
		KR 10-0855531 B1	01/09/2008
		KR 10-0864205 B1	17/10/2008
		TW I307114 A	01/03/2009
		US 2003-0127049 A1	10/07/2003
		US 2004-0191545 A1	30/09/2004
		US 2008-0017516 A1	24/01/2008
		US 2008-0110760 A1	15/05/2008
		US 2012-0135155 A1	31/05/2012
		US 2012-0138472 A1	07/06/2012
		US 6942929 B2	13/09/2005
		US 7371467 B2	13/05/2008
		US 7833401 B2	16/11/2010
		US 8110086 B2	07/02/2012
		US 8114525 B2	14/02/2012
		WO 03-060187 A1	24/07/2003
US 2006-0054181 A1	16/03/2006	JP 2004-519088 A	24/06/2004
		US 2002-0102852 A1	01/08/2002
		US 2005-0227888 A1	13/10/2005
		US 2006-0260647 A1	23/11/2006
		US 2006-0264343 A1	23/11/2006
		US 2006-0270242 A1	30/11/2006
		US 6927176 B2	09/08/2005
		US 7449127 B2	11/11/2008
		US 7456113 B2	25/11/2008
		US 7469883 B2	30/12/2008

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/052202

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		WO 02-01609 A2	03/01/2002
		WO 2006-132989 A2	14/12/2006
		WO 2006-132989 A3	08/03/2007