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(71) Applicant: **LAM RESEARCH CORPORATION** [US/US]; 4650 Cushing Parkway, Fremont, California 94538-6470 (US).

(72) Inventors: **SINGHAL, Akhil N.**; 4556 NW 132nd Avenue, Portland, Oregon 97229 (US). **AUSTIN, Dustin Zachary**; 1903 NW Taylor Avenue, Corvallis, Oregon 97330 (US). **GANANY, Alon**; 6482 NW Wenmarie Drive, Portland, Oregon 97229 (US). **BOATRIGHT, Daniel**; 18859 S. Springwater Road, Estacada, Oregon 97023 (US).

(74) Agent: **SCHEER, Bradley W.** et al.; Schwegman, Lundberg & Woessner, P.A., P. O. Box 2938, Minneapolis, Minnesota 55402 (US).

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(54) Title: ETCHING METAL-OXIDE AND PROTECTING CHAMBER COMPONENTS

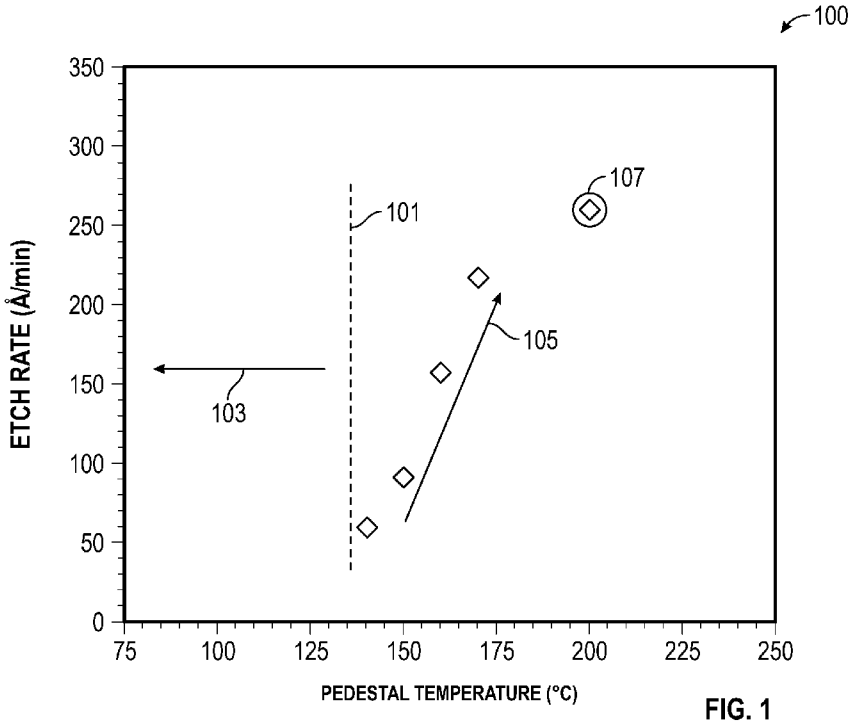

FIG. 1

(57) Abstract: Various embodiments include methods and chemistries to etch metal-oxide films. In one embodiment, a method of etching tin oxide (SnO_2) films includes using thionyl chloride ($SOCl_2$) chemistry to produce an etch rate of the SnO_2 films of up to 10-times higher as compared with Cl_2 chemistry for similar flow-rates and process conditions, and gettering oxygen species from the SnO_2 films by using the $SOCl_2$, thereby forming volatile SO_2 and volatile $SnCl_4$ to provide human safety and machine safety and operations. Other methods, chemistries, and techniques are disclosed.

[Continued on next page]

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ETCHING METAL-OXIDE AND PROTECTING CHAMBER COMPONENTS

CLAIM OF PRIORITY

[0000] This patent application claims priority to U. S. Provisional Application Serial Number 62/734,648, entitled, "ETCHING METAL-OXIDE FILMS AND PROTECTING CHAMBER COMPONENTS FROM HALOGEN (CHLORINE) CHEMISTRIES," filed 21 September 2018; the disclosure of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0001] The subject matter disclosed herein relates to etching of various films used in the semiconductor and allied industries. More specifically, the disclosed subject matter relates to removing tin oxide films from plasma process chambers and other surfaces.

BACKGROUND

[0002] As is known to a person of ordinary skill in the art, tin oxide (SnO_2) films are used for a variety of applications including, for example, extreme ultraviolet (EUV) hard masks, patterning spacers and mandrels for double and quad patterning, gap-fill metal oxides, hard masks, and etch stop layers. Consequently, tin oxide films are deposited on various substrate types in a process chamber via, for example, capacitively-coupled plasma (CCP) techniques. For tin oxide to be able to serve in high-volume manufacturing (HVM), the process chamber should periodically be cleaned of the as-deposited tin oxide film, leaving little to no tin oxide residue on walls and other surfaces within the process chamber. As is known to a person of ordinary skill in the art, tin oxide residues can cause contamination and defects on fabricated devices. For example, if the tin oxide film is not etched or otherwise cleaned or removed from the process chamber, the unremoved tin oxide can result in defects on a substrate as a result of the tin oxide film peeling off chamber components (e.g., due to poor adhesion as a result of buildup of in-film stress).

[0003] Typically, metal oxide films, such as tin oxide, may be etched with various chemistries known in the art such as, for example, hydrogen (H_2), methane (CH_4), chlorine (Cl_2), hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2). Many contemporaneous process chambers comprise aluminum (Al) or aluminum-alloy components. Most of the above-listed chemistries (with the exception of hydrogen and methane) cannot be used in process chambers (e.g., CCP chambers) having aluminum components as each of the listed chemistries attacks Al, thus forming one or more volatile aluminum-halide byproducts (e.g., chloride, bromide, or iodide). The volatile byproducts can produce severe metal contamination on substrates (e.g., silicon wafers) and lead to chamber degradation. Therefore, unless properly removed, the tin oxide could produce a completely non-manufacturable solution. Out of the above-listed halide chemistries, chlorine chemistry would be the most favorable for etching tin oxide, because of the high vapor pressure of a resulting tin tetrachloride ($SnCl_4$). However, using chlorine etchants requires changing materials used to produce the process chambers from aluminum to, for example, expensive ceramic parts or including yttrium coatings within the process chambers.

[0004] Chlorine chemistries, especially when operating in CCP chambers, reactive-ion etch (RIE) plasma-based chamber, or other types of plasma-based chambers known in the art, leads to formation of chloride ions. Chloride ions erode aluminum components by formation of volatile aluminum-chloride salts.

[0005] The information described in this section is provided to offer the skilled artisan a context for the following disclosed subject matter and should not be considered as admitted prior art.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 is a graph exemplifying a motivation for chemical-etch testing;

[0007] FIGS. 2A through 2F show of tables and related graphs from various design-of-experiment (DOE) analyses used to determine etch rates and etch selectivity for various embodiments of the disclosed subject matter;

[0008] FIG. 3 shows possible chemical reactions of chemicals used in some of the DOE analyses o FIGS. 2A through 2F;

[0009] FIGS. 4A and 4B show cross-sectional, scanning-electron microscopy images of remaining film thicknesses in accordance with embodiments of the disclosed subject matter;

[00010] FIGS. 5A through 5D show coupons from aluminum (Al) material compatibility studies;

[00011] FIG. 6 shows cross-sectional, scanning-electron microscopy images of effects of etch on anodized aluminum;

[00012] FIG. 7 shows cross-sectional, scanning-electron microscopy images of anodization cracks on aluminum;

[00013] FIG. 8A shows cross-sectional, scanning-electron microscopy images of limited to no effects of thionyl chloride ($SOCl_2$), in accordance with various embodiments disclosed herein, with various materials overlaying aluminum;

[00014] FIG. 8B shows possible chemical reactions of the $SOCl_2$ chemicals used in etching SnO_2; and

[00015] FIG. 8C provides a graphical summary of conclusions in accordance with various embodiments of the disclosed subject matter.

DETAILED DESCRIPTION

[00016] The disclosed subject matter will now be described in detail with reference to a few general and specific embodiments as illustrated in various ones of the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the disclosed subject matter. It will be apparent, however, to one skilled in the art, that the disclosed subject matter may be practiced without some or all of these specific details. In other instances, well-known process steps or structures have not been described in detail so as not to obscure the disclosed subject matter.

[00017] FIG. 1 is a graph 100 exemplifying a motivation for chemical-etch testing. For example, in contemporaneous cleaning methods, capacitively-coupled plasma (CCP) chambers are often cleaned with a combination of methane and hydrogen. As indicated by the graph 100, at low pedestal temperatures (e.g., less than approximately 135 °C as indicated by a direction 103 from a line 101 extending vertically from 135 °C), the cleaning process is dominated by carbon deposition or tin (Sn) powder. The carbon deposition is due to the methane (CH_4) breaking down readily. The tin formation is due to a low CH_4 plasma-gas concentration. Consequently, overall etch rates for tin oxide films is low.

[00018] With continued reference to FIG. 1, however, at higher temperatures (e.g., greater than approximately 135 °C), as indicated by an increased etch-rate versus increased pedestal temperature, trendline 105, a sustained CH_4 concentration can be maintained. (One outlier 107 from the trendline 105 indicates a point that may not be optimized for CH_4 processes.) An increased or maximum-achievable etch rate is then limited by an upper temperature of the process tool. Due to, for example, deposition temperatures of approximately 65 °C and etch temperatures of approximately 170 °C (or greater) in a typical process tool, a CH_4 plus H_2 cleaning process results in significant thermal cycling. Consequently,

there may be eventual problems due to thermal cycling between a wide-temperature range between deposition and cleaning temperatures.

[00019] To prevent erosion of aluminum, anodized coatings on aluminum are typically used. However, anodized coatings also have limitations, as discussed in more detail with reference to FIG. 7 below, which indicates substantial anodization cracking, suggesting that anodization may not be an effective barrier to a Cl_2-based CCP etch. The anodization cracking may be due to the quality and nature of anodized coatings that are available for fabrication. For example, all or nearly all anodized coatings are prone to some types of pores and/or cracks. Chlorine species can penetrate through those pores and cracks and have a negative impact on underlying aluminum features, parts, or components. Issues pertaining to use of chlorine as an etch gas have therefore warranted the use of expensive ceramic components, including chlorine-resistant alloys such as, for example, nickel-chromium-based alloys (e.g., Inconel®, available from, for example, Huntington Allows Corporation, 3200 Riverside Drive, Huntington, West Virginia, USA 25720) and nickel-molybdenum-chromium-based alloys (e.g., Hastelloy®, available from, for example, Haynes Stellite Company, P.O. Box 9013, 1020 West Park Avenue, Kokomo, Indiana, USA 46904), as well as expensive ceramic coatings such as yttrium oxide-based (Y_2O_3, or simply yttria) coatings, which still has possible physical limitations. Further, yttria-based coatings result in a large price increase for the manufacturing cost of the tool.

[00020] As noted above, contemporary technologies typically employ chlorine and chlorine-based chemistries to etch various metal oxides. In situations where chlorine does not react well with metal-oxide films, BCl_3 is added to a gas mixture to etch the metal-oxide films. The use of such chemistries always or nearly always results in challenges associated with corrosion of anodized aluminum and aluminum components. For example, BCl_3 may etch metal-oxide films better than Cl_2. However, BCl_3 also reacts with aluminum more violently than Cl_2. Consequently, process chambers

which deploy Cl_2 or BCl_3, as etch or clean gases, always or nearly always use ceramic components or expensive coatings (e.g., yttria) as noted above.

[00021] Consequently, there is a need for a chemistry that can etch tin oxide and other metal-oxide films, while continuing to use materials, such anodized aluminum and aluminum, in order to produce processing tools with a significantly lower cost as compared with using ceramic components and other expensive coatings.

[00022] In the disclosed subject matter, $SOCl_2$ was considered as a chemistry to remove tin oxide while not etching aluminum and aluminum alloys. As discussed in greater detail below, $SOCl_2$ has a lower corrosive impact on anodized aluminum and aluminum as compared with a chlorine-based chemistry.

[00023] Referring now to FIGS. 2A and 2B, chlorine etch rates were considered for various process conditions as shown in the table 200 of FIG. 2A and accompanying graph 210 of FIG. 2B in a particular type of CCP process chamber. The graph 210 of FIG. 2B indicates etch rates as function of Cl_2 volumetric flow rate [sccm], pressure [mTorr], and power [W]. The etch rate [Å/min] refers to the etch rate of tin oxide. As shown in the table 200, etch rates of approximately 180 Å/min were achieved for run 16 at the process conditions shown.

[00024] In FIGS. 2C and 2D, chlorine was coupled with hydrogen for etch testing as shown in the table 220 of FIG. 2B and accompanying graph 230 of FIG. 2D. The etch rates were considered for various process conditions as shown in the table 220 and the accompanying graph 230 in the CCP process chamber. As shown in the table 220, etch rates of approximately 730 Å/min were achieved for run 16 at the process conditions shown. Also, the combination of chlorine and hydrogen also had a higher selectivity to ALD oxide while most conditions showed no powder (as discussed above with reference to FIG. 1).

[00025] In FIGS. 2E and 2F, $SOCl_2$ was used for etch testing. The etch rates were considered for various process conditions as shown in table 240 of FIG. 2E and precursor and argon (Ar) carrier flow rates in the CCP process chamber are shown in an accompanying graph 250 in FIG. 2F, which shows precursor flow [sccm] as a function of Ar carrier flow [sccm]. As shown in the table 240, etch rates exceeding approximately 3000 Å/min were achieved for several test-runs with various process condition. Also, the combination of $SOCl_2$ and argon also had a higher selectivity to ALD oxide. Therefore, a summary of FIGS. 2A through 2F indicates etch rates as follows:

Cl_2 (approximately 180 Å/min)
$Cl_2 + H_2$ (approximately 730 Å/min)
$SOCl_2$ (over 3000 Å/min).

[00026] Possible reactions using the $SOCl_2$ combined with tin oxide or silicon dioxide are shown in FIG. 3. As indicated, a reaction using two thionyl chloride ($SOCl_2$) molecules to etch tin oxide (SnO_2) produces tin tetrachloride ($SnCl_4$) plus two sulfur dioxide (SO_2) molecules. A reaction using two thionyl chloride ($SOCl_2$) molecules to etch silicon dioxide (SiO_2) produces silicon tetrachloride ($SiCl_4$) plus two sulfur dioxide (SO_2) molecules. Consequently, the results indicate that metal-oxide films, for example, SnO_2 films, can be etched at significantly higher etch-rates compared to chlorine with this $SOCl_2$ chemistry. Apart from the higher etch-rates, the skilled artisan will also recognize that this chemistry with CCP chambers shows little or no damage on anodized aluminum and very minor damage on aluminum, whereas the chlorine chemistry showed significantly higher damage as shown and described in detail below.

[00027] For example, FIGS. 4A and 4B show cross-sectional, scanning-electron microscopy (X-SEM) images 400, 410 of remaining film thicknesses. In the X-SEM image 400 of FIG. 4A and the X-SEM image 410 of FIG. 4B, measurements of remaining film thicknesses by X-SEM

(e.g., as indicated at approximately 41.6 nm to about 42.8 nm, and at about 155.0 nm to about 155.6 nm, respectively) are in good agreement with measurements performed using ellipsometry (e.g., indicating thicknesses of approximately 45 nm and approximately 148 nm for FIGS. 4A and 4B, respectively).

[00028] FIGS. 5A – 5D show coupons comprised of aluminum (Al) material for chemistry compatibility-studies. FIG. 5A shows incoming coupons 500 of Al material used to test etching of Cl_2 versus $SOCl_2$ prior to any etching being performed. Both aluminum 6061 and 3003 alloys were considered as these aluminum alloys are commonly used in construction of process chambers as well as other process tools in the semiconductor industry.

[00029] FIG. 5B shows the results 510 of a post etch test using Cl_2 on the aluminum coupons after 0 days and 7 days when each of the aluminum coupons were etched for 22 minutes, 110 minutes, and 720 minutes, respectively, in Cl_2. The etching in Cl_2 clearly indicates extreme corrosion of the aluminum coupons etched in Cl_2.

[00030] FIG. 5C shows the results 520 of a post etch test using $SOCl_2$ on the aluminum coupons after 0 days and 7 days when each of the aluminum coupons were etched for 22 minutes, 110 minutes, and 720 minutes, respectively, in $SOCl_2$. The etching in $SOCl_2$ indicates little to no corrosion of the aluminum coupons etched in $SOCl_2$ with only minor discoloration for the aluminum samples etched in $SOCl_2$ for 720 minutes.

[00031] FIG. 5D shows incoming test pieces 530 of anodized aluminum samples including Al/a-Al and Al/a-Al/Oxide compared with etching in Cl_2 and $SOCl_2$ for 720 minutes each. The samples etched in Cl_2 each show a more significant color change than the samples etched in $SOCl_2$.

[00032] Referring now to FIG. 6, cross-sectional, scanning-electron microscopy images of effects of etch on anodized aluminum are shown. The

samples were each etched in either Cl_2 or $SOCl_2$ for 720-minute exposures. The exposures to Cl_2 (in the top row) clearly indicate extreme corrosion of aluminum under the anodization. However, very little to no corrosion was observed with the anodized aluminum samples, in the bottom row, exposed to $SOCl_2$.

[00033] FIG. 7 shows cross-sectional, scanning-electron microscopy images of anodization cracks on aluminum. FIG. 7 indicates that anodization fails to be an effective barrier to Cl_2. FIG. 7 also indicates that cracks 701, 703 can allow corrosive gases to penetrate through an anodization layer and attack underlying aluminum Corners and other abruptly changing feature morphologies especially tend to incur a large amount of anodization cracking. Therefore, anodization techniques do not provide an effective barrier to Cl_2 in, for example, a Cl2 CCP etch process.

[00034] FIG. 8A shows cross-sectional, scanning-electron microscopy images showing limited to no effects of thionyl chloride ($SOCl_2$), in accordance with various embodiments disclosed herein, with various materials overlaying aluminum. The $SOCl_2$ exhibited little to no attack of the aluminum under the anodized aluminum, even with a 720-minute exposure to $SOCl_2$. The ALD oxide shows a low etch rate, in accordance with the DOE analysis presented above.

[00035] FIG. 8B shows possible chemical reactions of the $SOCl_2$ chemicals used in etching SnO_2. Therefore, the $SOCl_2$ seems to be reacting as a surface reaction and not dissociating before the surface reaction since, as noted above, there is no observed attack of the aluminum by the $SOCl_2$.

[00036] FIG. 8C provides a graphical summary of conclusions. As noted above, the etch rates from the DOE analysis indicated CCP chamber etch rates as follows:

Cl_2 (approximately 180 Å/min)
$Cl_2 + H_2$ (approximately 730 Å/min)
$SOCl_2$ (over 3000 Å/min).

[00037] The Cl_2 had an increasing selectivity with an increasing etch rate. The material compatibility analysis indicated that Cl_2 exhibited a strong attack of aluminum even through anodization and oxide with an exposure to Cl_2 of 720 minutes. In contrast, the $SOCl_2$ showed little to no attack of aluminum through anodization even at a 720-minute exposure.

[00038] One hypothesis for the higher etch rate observed with $SOCl_2$ is its ability to getter oxygen out of the metal-oxide film to form SO_2 (a volatile byproduct) along with the formation of the volatile chemical tin tetrachloride ($SnCl_4$). In the case of using chlorine chemistry, the oxygen in the metal-oxide film leads to formation of $SnOCl_2$ or $SnOCl_4$ which is not as volatile as $SnCl_4$ and thus leads to a slowdown in reaction rates.

[00039] A hypothesis for the $SOCl_2$ chemistry showing less attack on aluminum and anodized aluminum is the possibility of oxygen species acting as a self-passivation species, leading to formation of aluminum oxide instead of aluminum chloride when both oxygen species and chlorine species are present. There is also a possibility that the breakdown of $SOCl_2$ in a plasma state is such that S=O bonds absorbs a lot of the energy, leading to formation of chloride ions with lower energy, which are not that harmful on the anodized components.

[00040] Although the results were conducted in CCP chambers, the skilled artisan will recognize that similar results should be expected in RIE plasma, high-density plasma (HDP)-based devices and tools, inductively-coupled plasma (ICP)-based devices and tools, and others, as a way to etch metal-oxide films and also a way to use chlorine-based chemistry with anodized aluminum and aluminum parts.

[00041] Therefore, the use of $SOCl_2$ as a way to supply chloride ions/species to clean/etch metal oxides in, for example, CCP or RIE chambers in such a way that it etches the metal oxide at significantly higher etch rates compared with chlorine itself. Also, the ability of the $SOCl_2$ to provide these high etch-rates while not attacking the anodized aluminum and minimal attack on aluminum components is unique and provides an opportunity to use this chemistry to etch metal-oxide films with anodized parts, without the need of going to ceramic parts or yttrria-coated parts which are extremely expensive.

[00042] Use of the chemistry $SOCl_2$ provides unique advantages in terms of etching metal-oxide films with chlorine ions while not attacking the anodization and aluminum components of the chambers in which such films are formed. Not attacking aluminum components is in stark contrast with chlorine or BCl_3 chemistries that are typically used by the semiconductor and related industries.

[00043] As noted herein, when comparing etch rates of SnO_2 films in chlorine and $SOCl_2$ in CCP chambers, an etch rate of SnO_2 of up to 10-times higher in $SOCl_2$ chemistry compared to Cl_2 chemistry for similar volumetric flow-rates and process conditions. The high etch-rate observed for SnO_2 in $SOCl_2$ stems from the fact that the $SOCl_2$ is able to getter the oxygen species from the SnO_2 films, thereby forming volatile SO_2 and volatile $SnCl_4$.

$$2\ SOCl_2 + SnO_2 \rightarrow SnCl_4 + 2\ SO_2$$

An additional factor to consider is that, for a given application, the boiling point of $SnCl_4$ is 114 °C.

[00044] In the case of Cl_2, the reaction produces less volatile $SnOCl_4$.

$$SnO_2 + Cl_2 \rightarrow Cl_2OSn + OCl_2$$

with decomposition 1/2 Cl_2.

SnO_2+ $SnCl_4$

[00045] Decomposition of Cl2OSn reaction would happen with additional chlorine and would lead to formation of:

$SnCl_4$ and SnO_2 → SnO_2 + $SnCl_4$

The reaction of Cl_2 is unfavorable due to the formation of less-volatile $SnOCl_2$ while the reaction with $SOCl_2$ is more favorable and, consequently, etch rates are higher with $SOCl_2$.

[00046] In addition to higher etch rates seen with $SOCl_2$ chemistry compared to Cl_2 chemistry with SnO_2 film, the $SOCl_2$ chemistry doesn't attack anodized aluminum and very minimally attacks aluminum. As disclosed herein, this behavior is very different than what was observed with Cl_2 chemistry where aluminum components were corroded heavily and even completely destroyed. Even anodized aluminum showed signs of erosion in the aluminum layer below the anodized layer (anodization also suffered a loss in thickness).

[00047] The ability to use this $SOCl_2$ chemistry provides a pathway to etch and clean metal-oxide films such as SnO_2 from process chambers while still using anodization components, while not resorting to ceramic components or yttria-based coatings which are typically extremely expensive and can make the entire tool cost highly prohibitive.

Examples of the Disclosed Subject Matter

[00048] In a first example, the disclosed subject matter includes a method of etching tin oxide (SnO_2) films from surfaces. The method includes using thionyl chloride ($SOCl_2$) chemistry to etch at least a portion of the SnO_2 films, and gettering oxygen species from the SnO_2 films by using the $SOCl_2$ chemistry, thereby forming volatile SO_2 and volatile $SnCl_4$.

[00049] A second example includes the method of the first example,

where the surfaces comprise at least one material including materials of aluminum and anodized aluminum.

[00050] A third example includes any one of the preceding examples, and where the $SOCl_2$ chemistry used to etch at least a portion of the SnO_2 films produces an etch rate of the SnO_2 films of up to ten-times higher as compared with chlorine Cl_2 chemistry for comparable flow-rates and process conditions.

[00051] A fourth example includes any one of the preceding examples, and further includes avoiding using one or more of the following chemistries to avoid forming one or more volatile aluminum-halide byproducts, the chemistries including chlorine (Cl_2), hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2).

[00052] A fifth example includes any one of the preceding examples, where the surfaces include interior portions of plasma-based processing chambers.

[00053] A sixth example includes any one of the preceding examples, where the $SOCl_2$ chemistry does not etch anodized aluminum.

[00054] In a seventh example, the disclosed subject matter includes a method of cleaning tin oxide from interior portions of a plasma-based processing chamber. The method includes introducing methane into the processing chamber, maintaining a temperature of greater than about 135 °C within the processing chamber to maintain a concentration level of the methane, and introducing thionyl chloride into the processing chamber and avoiding introducing chlorine into the processing chamber.

[00055] An eighth example includes the method of the seventh example, where the interior portions of the plasma-based processing chamber comprise at least one material including materials of aluminum and anodized aluminum.

[00056] A ninth example includes the method of the eighth example, and further includes avoiding introducing one or more of the following chemistries into the processing chamber to avoid forming one or more volatile aluminum-halide byproducts, the chemistries including hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2).

[00057] In a tenth example, the disclosed subject matter includes a method for removing metal-oxide films from aluminum and aluminum-based surfaces of plasma-based processing chambers. The method includes introducing methane (CH_4) into the processing chamber, introducing hydrogen (H_2) into the processing chamber, maintaining a temperature of greater than about 135 °C within the processing chamber to maintain a concentration level of the methane, and introducing thionyl chloride ($SOCl_2$) into the processing chamber and avoiding introducing chlorine (Cl_2) into the processing chamber.

[00058] An eleventh example includes the method of the tenth example, and further includes avoiding introducing one or more of the following chemistries into the processing chamber to avoid forming one or more volatile aluminum-halide byproducts, the chemistries including hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2).

[00059] A twelfth example includes any one of the preceding examples, where the metal-oxide film is tin oxide (SnO_2).

[00060] A thirteenth example includes the method of the twelfth example, where a reaction using two thionyl chloride ($SOCl_2$) molecules to etch the tin oxide (SnO_2) produces tin tetrachloride ($SnCl_4$) plus two sulfur dioxide (SO_2) molecules.

[00061] A fourteenth example includes any one of the preceding examples, and further includes etching dielectric materials from the

surfaces of the of plasma-based processing chambers.

[00062] A fifteenth example includes the method of the fourteenth example, where the dielectric material is silicon dioxide (SiO_2).

[00063] A sixteenth example includes the method of the fifteenth example, where a reaction using two thionyl chloride ($SOCl_2$) molecules to etch the silicon dioxide (SiO_2) produces silicon tetrachloride ($SiCl_4$) plus two sulfur dioxide (SO_2) molecules.

[00064] Throughout this specification, plural instances may implement components, operations, chemistries, or structures described as a single instance. Although individual operations of one or more methods are illustrated and described as separate operations, one or more of the individual operations may be performed concurrently, and nothing requires that the operations be performed in the order illustrated. Structures and functionality presented as separate components in example configurations may be implemented as a combined structure or component. Similarly, structures and functionality presented as a single component may be implemented as separate components. These and other variations, modifications, additions, and improvements fall within the scope of the subject matter herein.

[00065] Certain embodiments may be described herein as including logic or a number of components, modules, mechanisms, or particular chemistries. In various embodiments, one or more computer systems (e.g., a standalone computer system, a client computer system, or a server computer system) or one or more hardware modules of a computer system (e.g., a processor or a group of processors) may be configured by software (e.g., an application or application portion) as a hardware module that operates to perform certain operations (e.g., various process recipes) as described herein.

[00066] As used herein, the term "or" may be construed in an inclusive or exclusive sense. Further, other embodiments will be understood by a person of ordinary skill in the art upon reading and understanding the disclosure provided. Further, upon reading and understanding the disclosure provided herein, the person of ordinary skill in the art will readily understand that various combinations of the chemistries, techniques, and examples provided herein may all be applied in various combinations.

[00067] Although various embodiments are discussed separately, these separate embodiments are not intended to be considered as independent techniques or designs. As indicated above, each of the various portions may be inter-related and each may be used separately or in combination with other portions and embodiments discussed herein. For example, although various embodiments of methods, operations, chemistries, and processes have been described, these methods, operations, chemistries, and processes may be used either separately or in various combinations.

[00068] Consequently, many modifications and variations can be made, as will be apparent to a person of ordinary skill in the art upon reading and understanding the disclosure provided herein. Functionally equivalent methods and devices within the scope of the disclosure, in addition to those enumerated herein, will be apparent to the skilled artisan from the foregoing descriptions. Portions and features of some embodiments may be included in, or substituted for, those of others. Such modifications and variations are intended to fall within a scope of the appended claims. Therefore, the present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

[00069] The Abstract of the Disclosure is provided to allow the reader to quickly ascertain the nature of the technical disclosure. The abstract is submitted with the understanding that it will not be used to interpret or limit the claims. In addition, in the foregoing Detailed Description, it may be seen that various features may be grouped together in a single embodiment for the purpose of streamlining the disclosure. This method of disclosure is not to be interpreted as limiting the claims. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment.

CLAIMS

What is claimed is:

1. A method of etching tin oxide (SnO_2) films from surfaces, the method comprising:

using thionyl chloride ($SOCl_2$) chemistry to etch at least a portion of the SnO_2 films; and

gettering oxygen species from the SnO_2 films by using the $SOCl_2$ chemistry, thereby forming volatile SO_2 and volatile $SnCl_4$.

2. The method of claim 1, wherein the surfaces comprise at least one material including materials of aluminum and anodized aluminum.

3. The method of claim 1, wherein the $SOCl_2$ chemistry used to etch at least a portion of the SnO_2 films produces an etch rate of the SnO_2 films of up to ten-times higher as compared with chlorine Cl_2 chemistry for comparable flow-rates and process conditions.

4. The method of claim 1, further comprising avoiding using one or more of the following chemistries to avoid forming one or more volatile aluminum-halide byproducts, the chemistries including chlorine (Cl_2), hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2).

5. The method of claim 1, wherein the surfaces include interior portions of plasma-based processing chambers.

6. The method of claim 1, wherein the $SOCl_2$ chemistry does not etch anodized aluminum.

7. A method of cleaning tin oxide from interior portions of a plasma-based processing chamber, the method comprising:

introducing methane into the processing chamber;

maintaining a temperature of greater than about 135 °C within the processing chamber to maintain a concentration level of the methane; and

introducing thionyl chloride into the processing chamber and avoiding introducing chlorine into the processing chamber.

8. The method of claim 7, wherein the interior portions of the plasma-based processing chamber comprise at least one material including materials of aluminum and anodized aluminum.

9. The method of claim 8, further comprising avoiding introducing one or more of the following chemistries into the processing chamber to avoid forming one or more volatile aluminum-halide byproducts, the chemistries including hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2).

10. A method for removing metal-oxide films from aluminum and aluminum-based surfaces of plasma-based processing chambers, the method comprising:

introducing methane (CH_4) into the processing chamber;

introducing hydrogen (H_2) into the processing chamber;

maintaining a temperature of greater than about 135 °C within the processing chamber to maintain a concentration level of the methane; and

introducing thionyl chloride ($SOCl_2$) into the processing chamber and avoiding introducing chlorine (Cl_2) into the processing chamber.

11. The method of claim 10, further comprising avoiding introducing one or more of the following chemistries into the processing chamber to avoid forming one or more volatile aluminum-halide byproducts, the chemistries including hydrochloric acid (HCl), bromide (Br), hydrobromic acid (HBr), boron trichloride (BCl_3), hydrogen iodide (HI), and iodine (I_2).

12. The method of claim 10, wherein the metal-oxide film is tin oxide (SnO_2).

13. The method of claim 12, wherein a reaction using two thionyl chloride ($SOCl_2$) molecules to etch the tin oxide (SnO_2) produces tin tetrachloride ($SnCl_4$) plus two sulfur dioxide (SO_2) molecules.

14. The method of claim 10, further comprising etching dielectric materials from the surfaces of the of plasma-based processing chambers.

15. The method of claim 14, wherein the dielectric material is silicon dioxide (SiO_2).

16. The method of claim 15, wherein a reaction using two thionyl chloride ($SOCl_2$) molecules to etch the silicon dioxide (SiO_2) produces silicon tetrachloride ($SiCl_4$) plus two sulfur dioxide (SO_2) molecules.

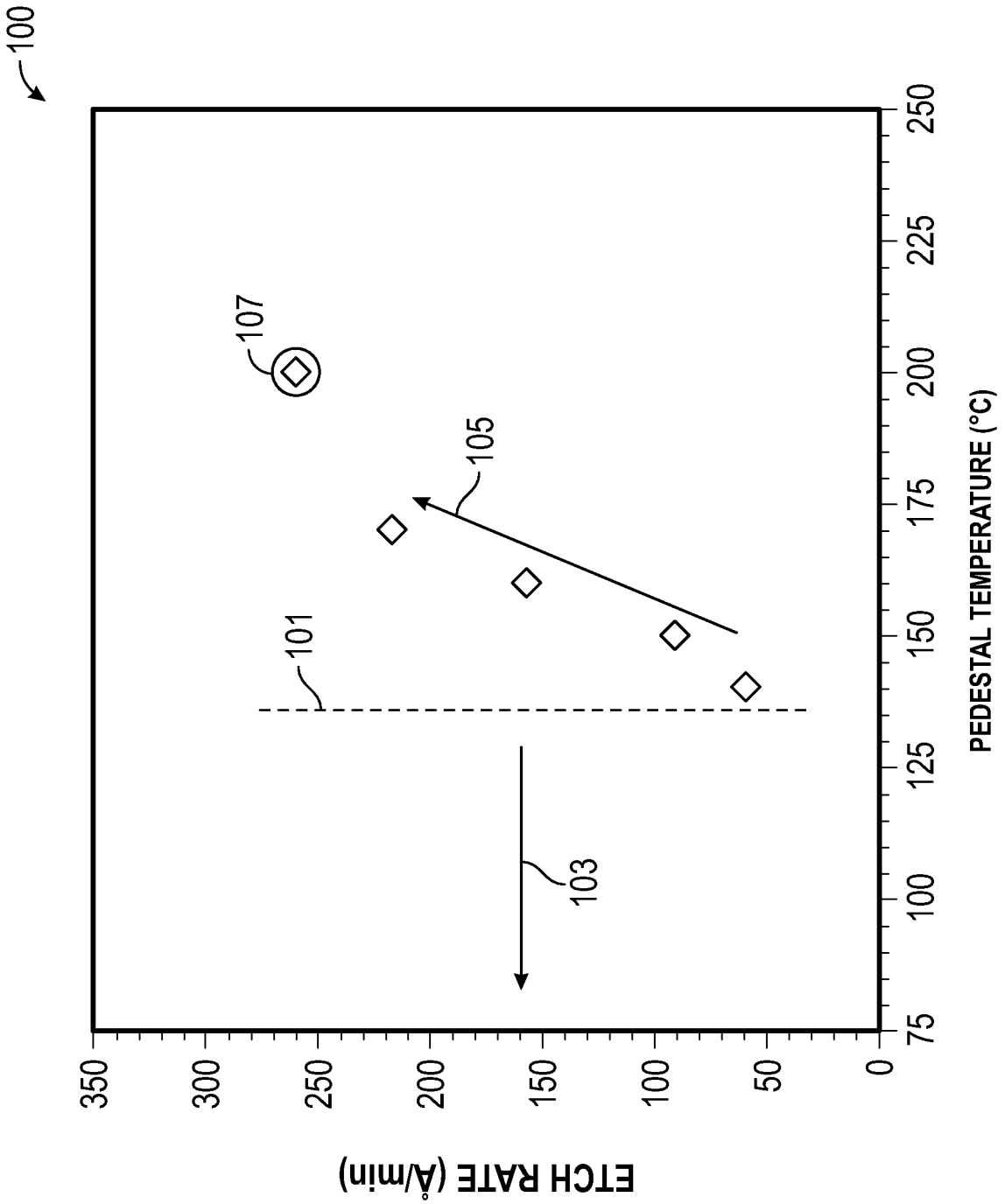

100
107
105
101
103
ETCH RATE (Å/min)
0
50
100
150
200
250
300
350
75
100
125
150
175
200
225
250
PEDESTAL TEMPERATURE (°C)

FIG. 1

200

RUN	PATTERN	CL_2 FLOW	Ar FLOW	He FLOW	PRESSURE	CCP POWER	ETCH RATE
		sccm	sccm	sccm	mTorr	W	Å/min
1	111	100	500	500	500	50	7
2	113	100	500	500	500	200	19
3	122	100	500	500	1250	125	26
4	131	100	500	500	2000	50	6
5	133	100	500	500	2000	200	60
6	212	200	500	500	500	125	35
7	221	200	500	500	1250	50	11
8	222	200	500	500	1250	125	43
9	222	200	500	500	1250	125	41
10	223	200	500	500	1250	200	100
11	232	200	500	500	2000	125	79
12	311	300	500	500	500	50	13
13	313	300	500	500	500	200	76
14	322	300	500	500	1250	125	62
15	331	300	500	500	2000	50	13
16	333	300	500	500	2000	200	184

FIG. 2A

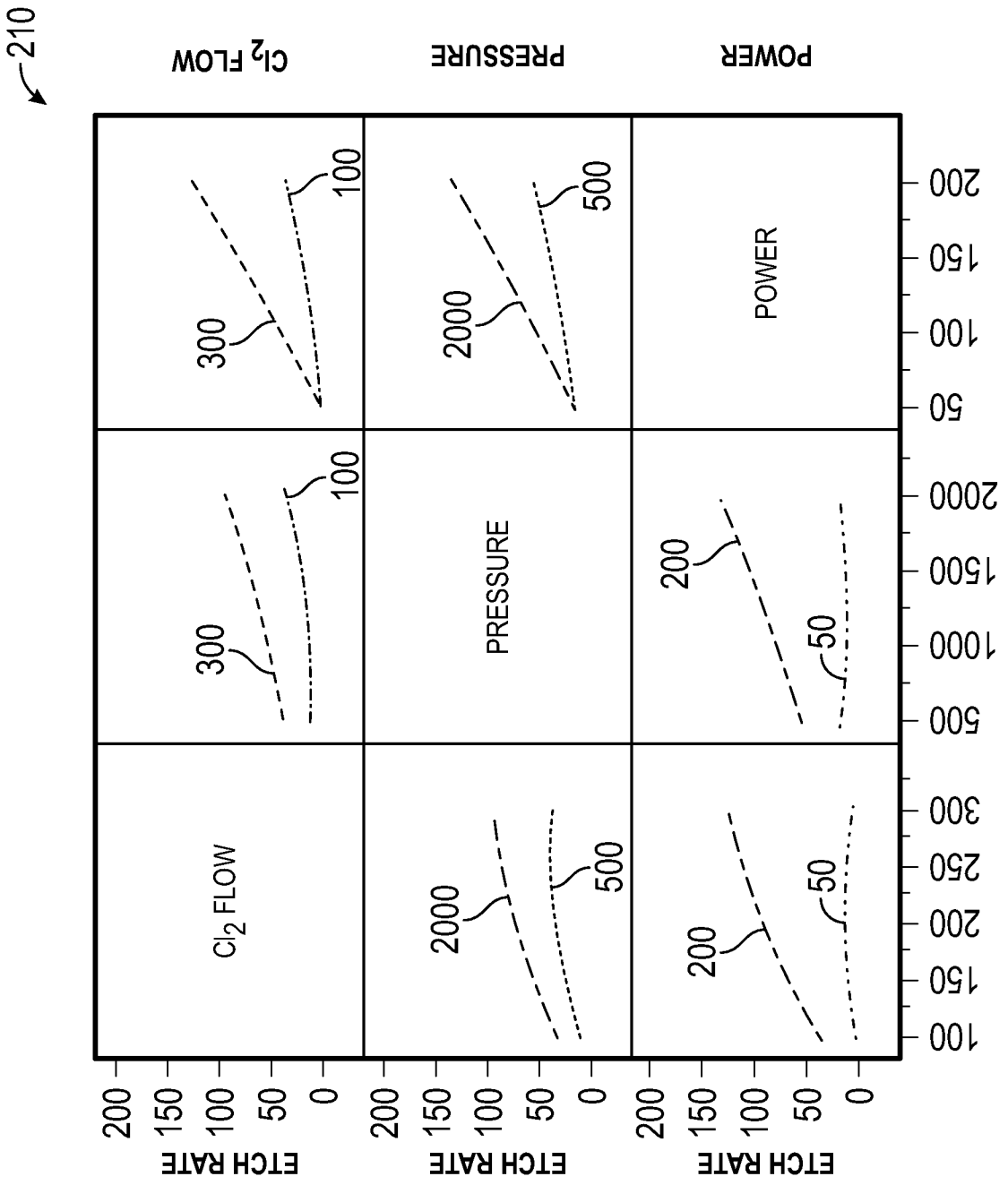

210
Cl_2 FLOW
PRESSURE
POWER
ETCH RATE
Cl_2 FLOW
PRESSURE
POWER
300
100
2000
500
200
50
0
50
100
150
200
250
300
500
1000
1500
2000

FIG. 2B

220

RUN	PATTERN	CL_2 FLOW	Ar FLOW	He FLOW	H_2 FLOW	PRESSURE	CCP POWER	ETCH RATE
		sccm	sccm	sccm	sccm	mTorr	W	Å/min
1	111	20	500	500	50	500	200	40
2	113	20	500	500	600	500	200	126
3	122	20	500	500	325	1250	200	130
4	131	20	500	500	50	2000	200	114
5	133	20	500	500	600	2000	200	399
6	212	160	500	500	325	500	200	138
7	221	160	500	500	50	1250	200	244
8	222	160	500	500	325	1250	200	465
9	222	160	500	500	325	1250	200	463
10	223	160	500	500	600	1250	200	455
11	232	160	500	500	325	2000	200	447
12	311	300	500	500	50	500	200	93
13	313	300	500	500	600	500	200	167
14	322	300	500	500	325	1250	200	503
15	331	300	500	500	50	2000	200	495
16	333	300	500	500	600	2000	200	735

FIG. 2C

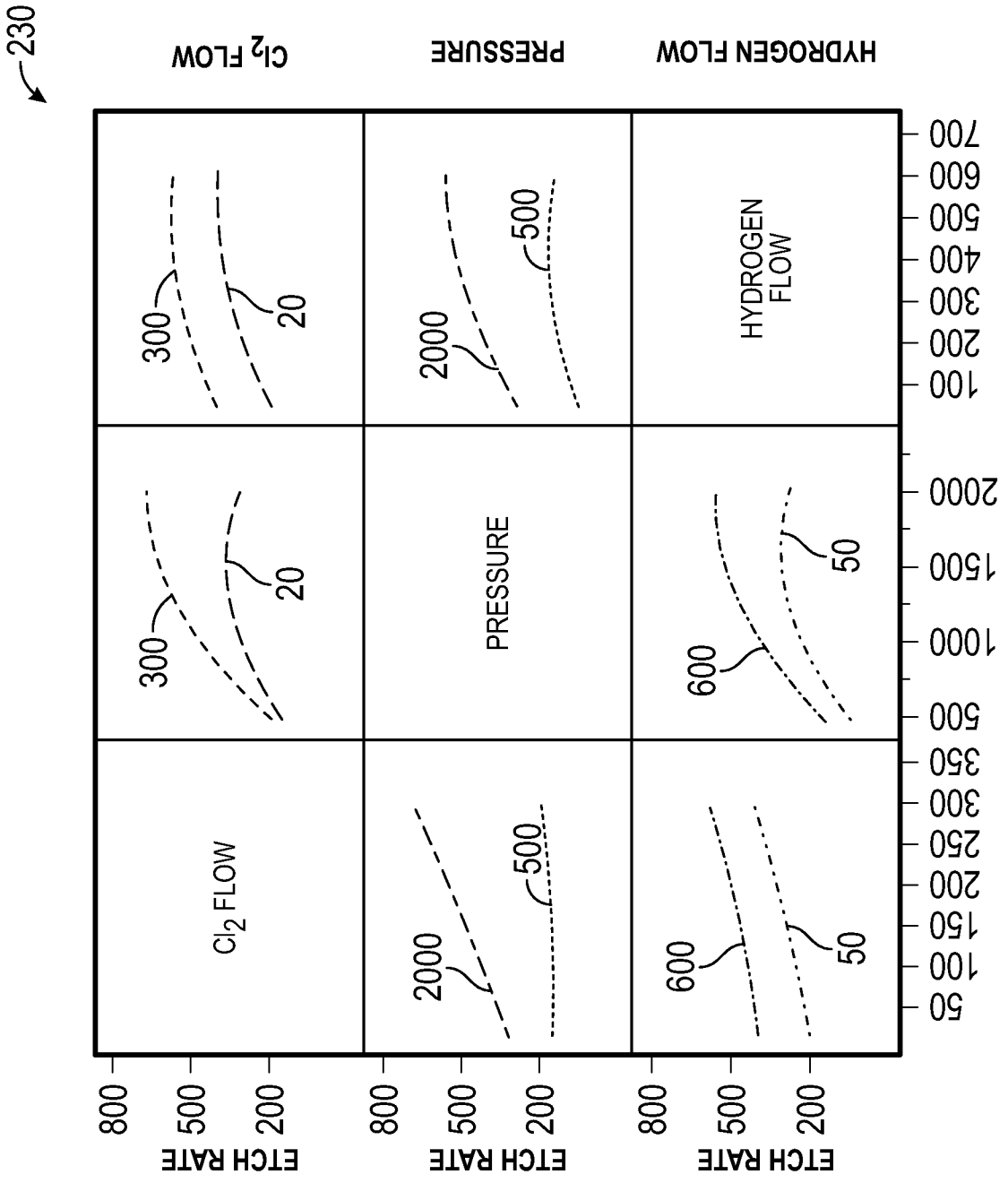

230
Cl_2 FLOW
PRESSURE
HYDROGEN FLOW
ETCH RATE
800
500
200
300
20
2000
500
600
50
Cl_2 FLOW
PRESSURE
HYDROGEN FLOW
50
100
150
200
250
300
350
500
1000
1500
2000
100
200
300
400
500
600
700

FIG. 2D

240

RUN	PATTERN	Ar CARRIER FLOW	Ar FLOW	He FLOW	PRESSURE	CCP POWER	ETCH RATE
		sccm	sccm	sccm	mTorr	W	Å/min
1	111	20	500	500	500	50	606
2	113	20	500	500	500	200	2231
3	122	20	500	500	750	125	3115
4	131	20	500	500	1000	50	1273
5	133	20	500	500	1000	200	2785
6	212	60	500	500	500	125	2191
7	221	60	500	500	750	50	2047
8	222	60	500	500	750	125	3209
9	222	60	500	500	750	125	3264
10	223	60	500	500	750	200	1989
11	232	60	500	500	1000	125	2777
12	311	100	500	500	500	50	455
13	313	100	500	500	500	200	869
14	322	100	500	500	750	125	1422
15	331	100	500	500	1000	50	1493
16	333	100	500	500	1000	200	1109

FIG. 2E

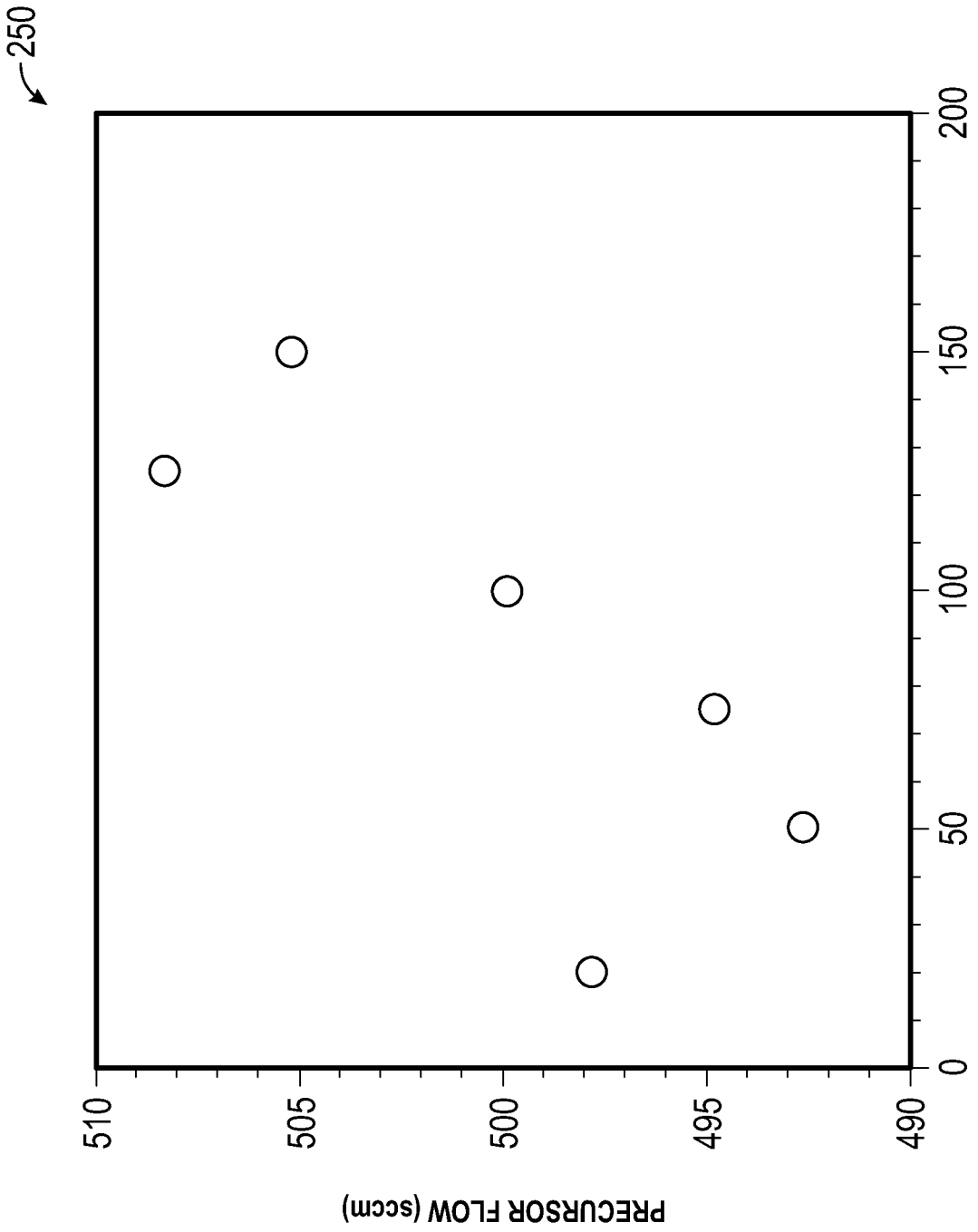

250
510
505
500
495
490
PRECURSOR FLOW (sccm)
0
50
100
150
200
Ar CARRIER FLOW (sccm)

FIG. 2F

POSSIBLE REACTIONS

$$2\ SOCl_2 + SnO_2 \rightarrow SnCl_4 + 2\ SO_2$$

$$2\ SOCl_2 + SiO_2 \rightarrow SiCl_4 + 2\ SO_2$$

FIG. 3

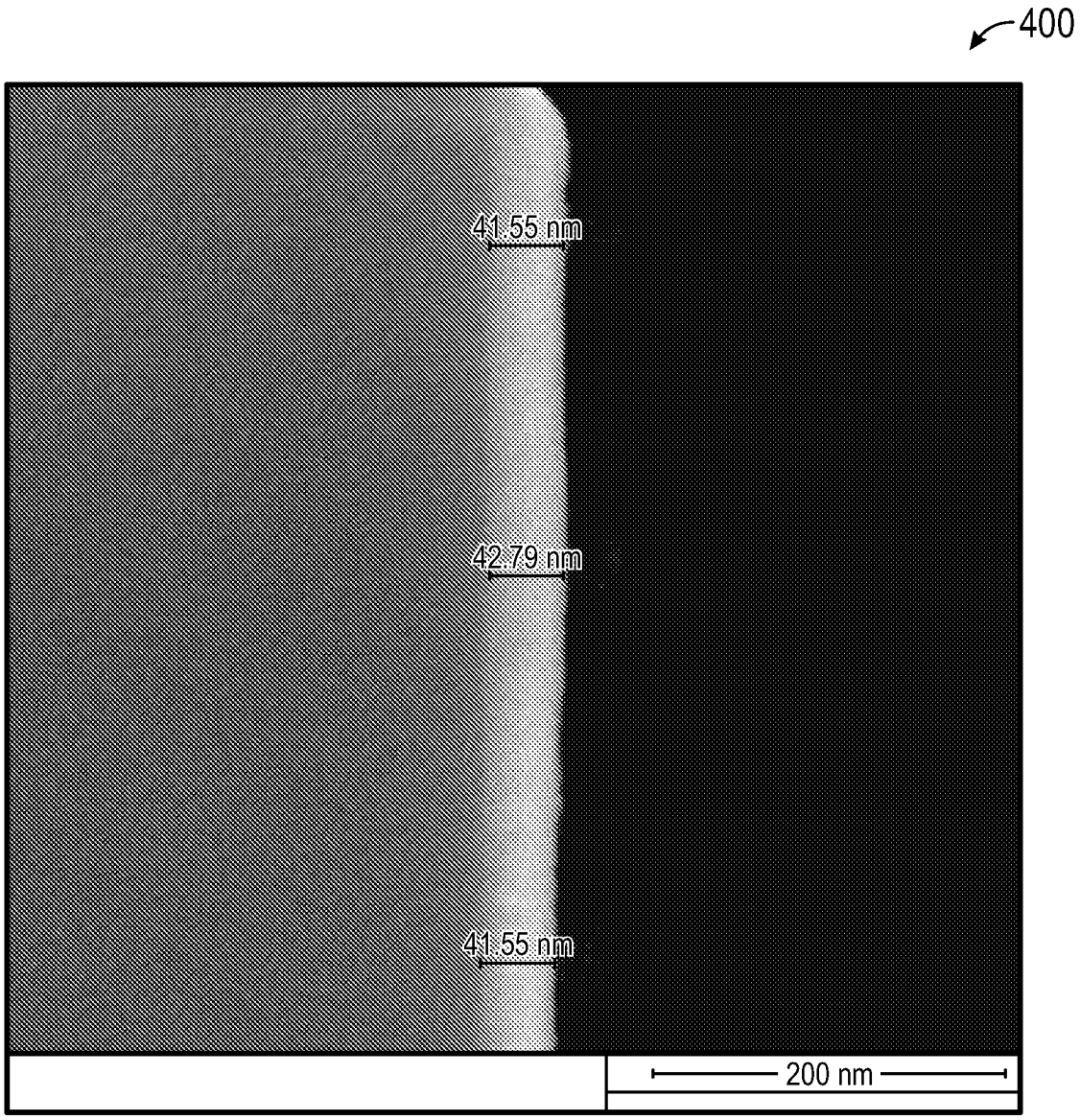


FIG. 4A

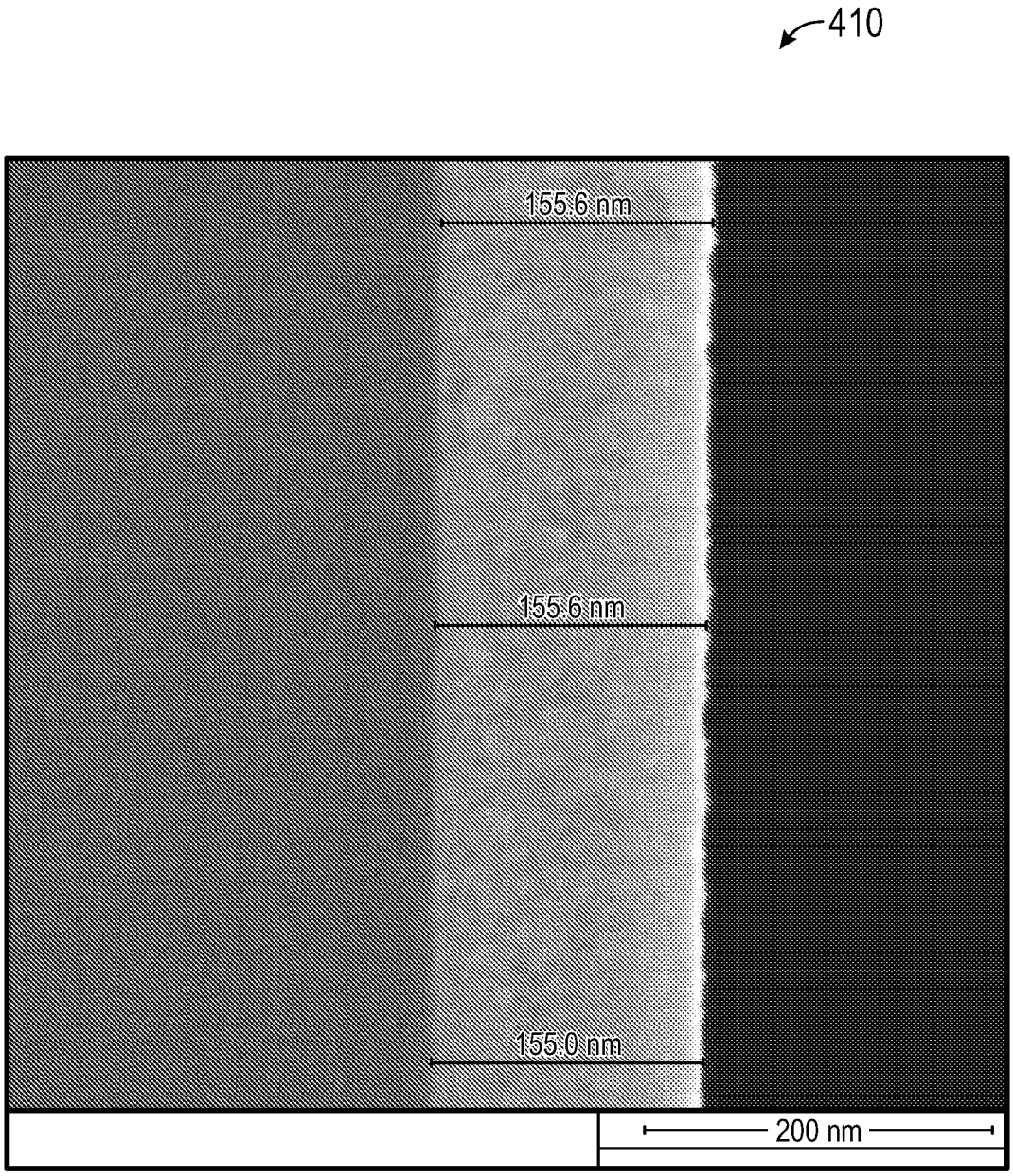


FIG. 4B

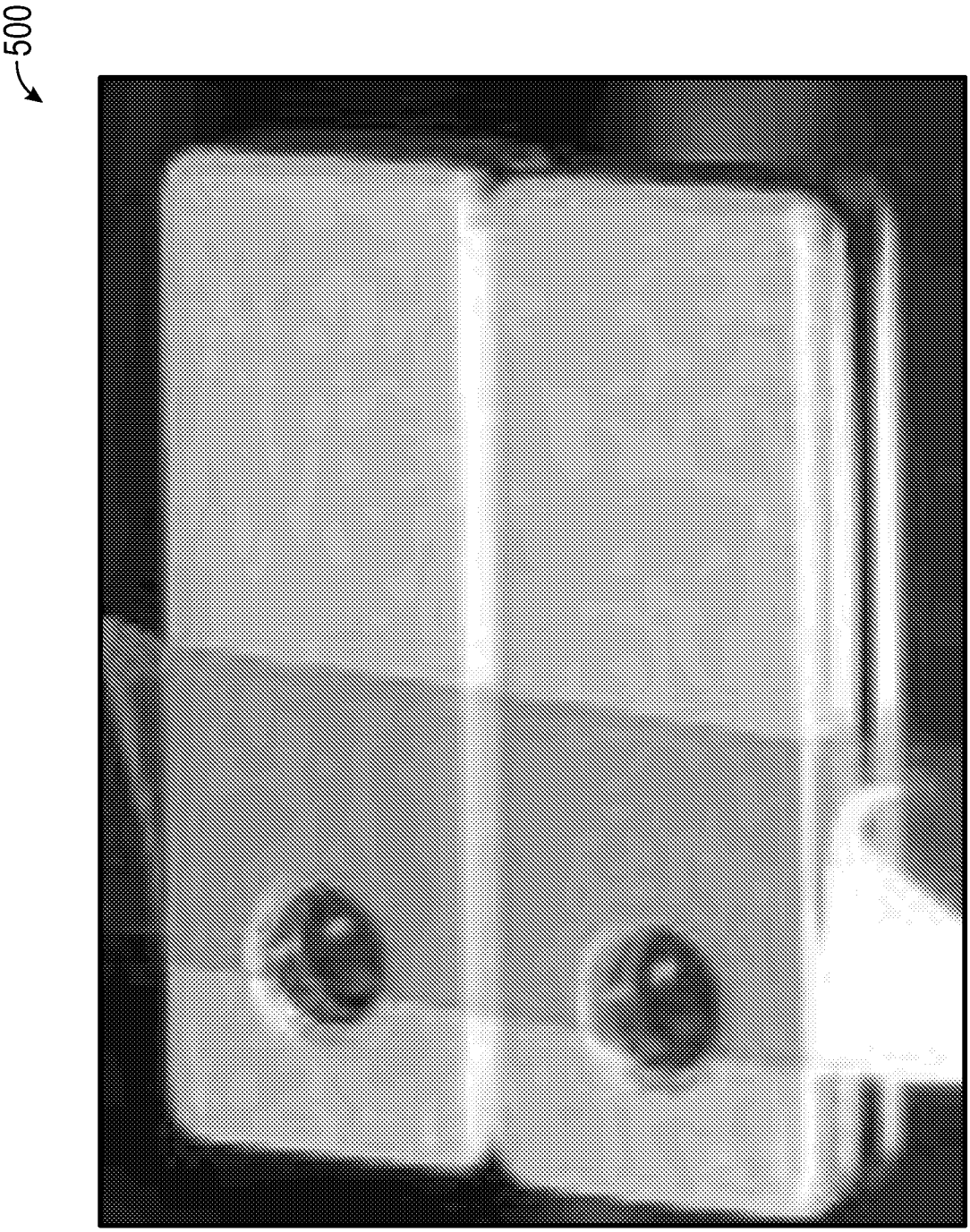


FIG. 5A

510

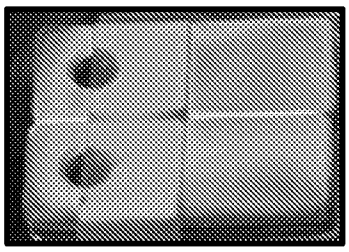
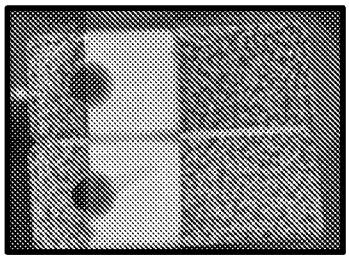
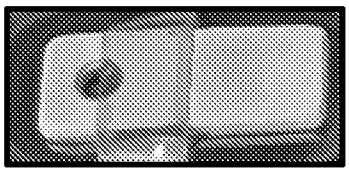
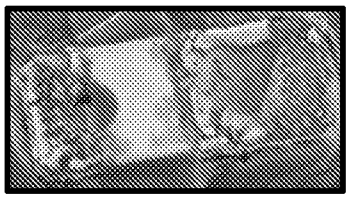
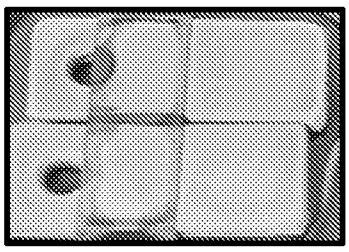
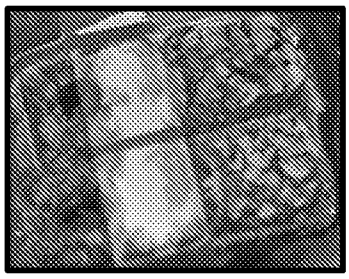
	Cl_2 (333)	
	POST ETCH 0 DAYS	POST ETCH 7 DAYS
22 MINUTES		
110 MINUTES		
720 MINUTES		

FIG. 5B

520

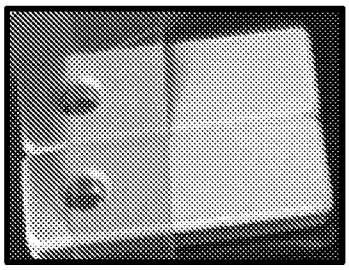
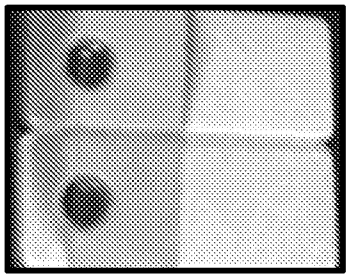
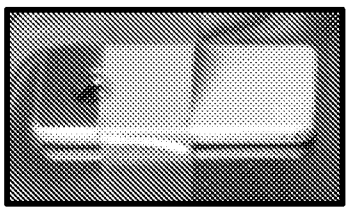
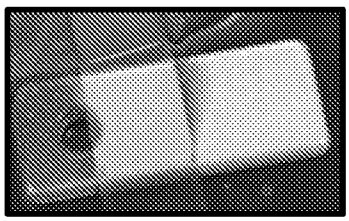
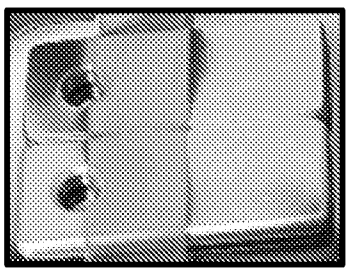
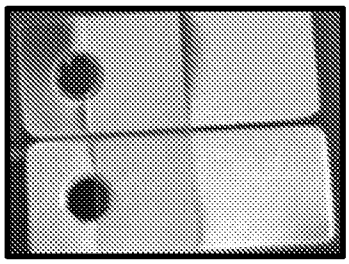
	$SOCl_2$ (222)	
	POST ETCH 0 DAYS	POST ETCH 7 DAYS
22 MINUTES		
110 MINUTES		
720 MINUTES		

FIG. 5C

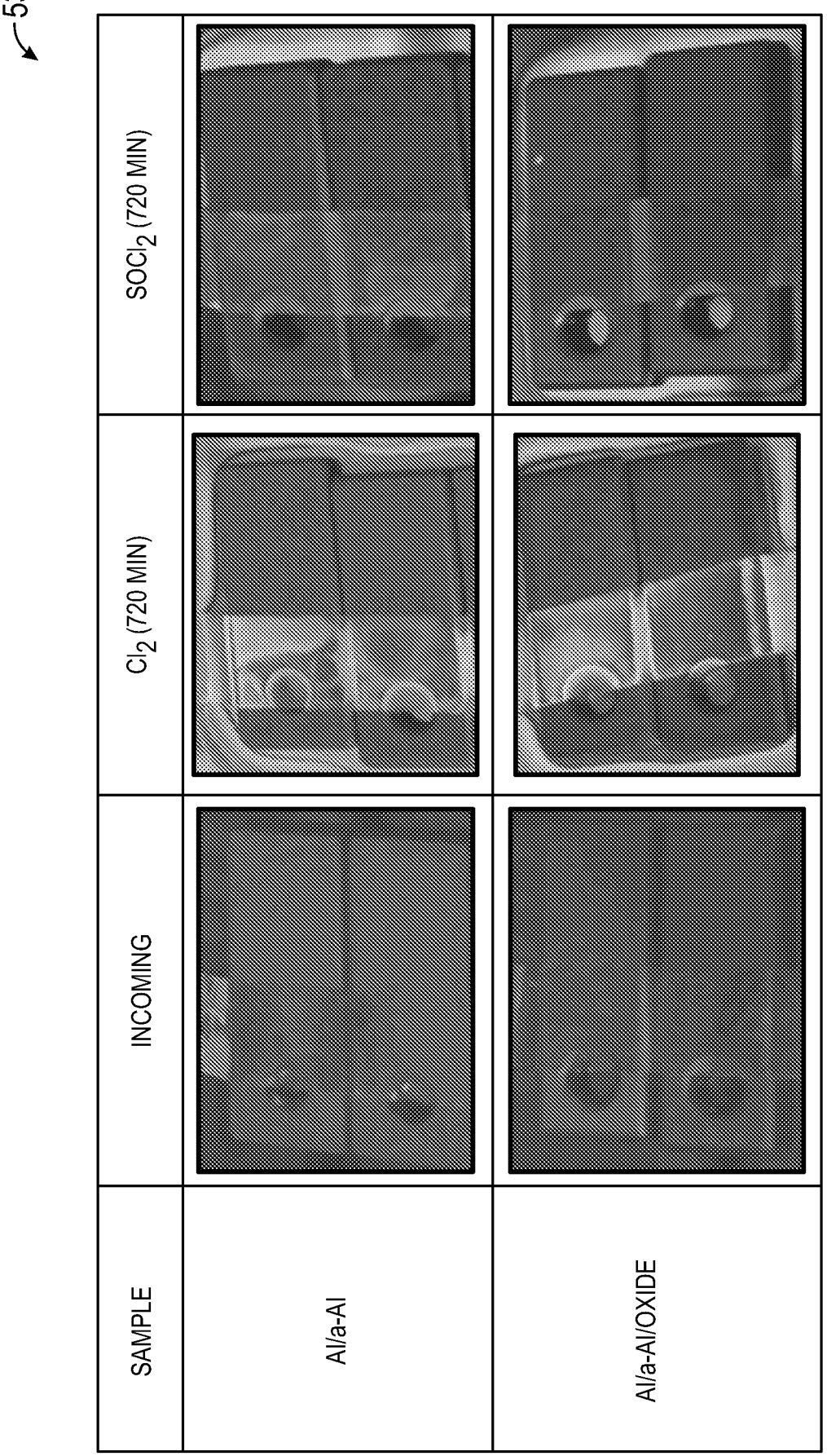

530
SAMPLE
INCOMING
Cl_2 (720 MIN)
$SOCl_2$ (720 MIN)
Al/a-Al
Al/a-Al/OXIDE

FIG. 5D

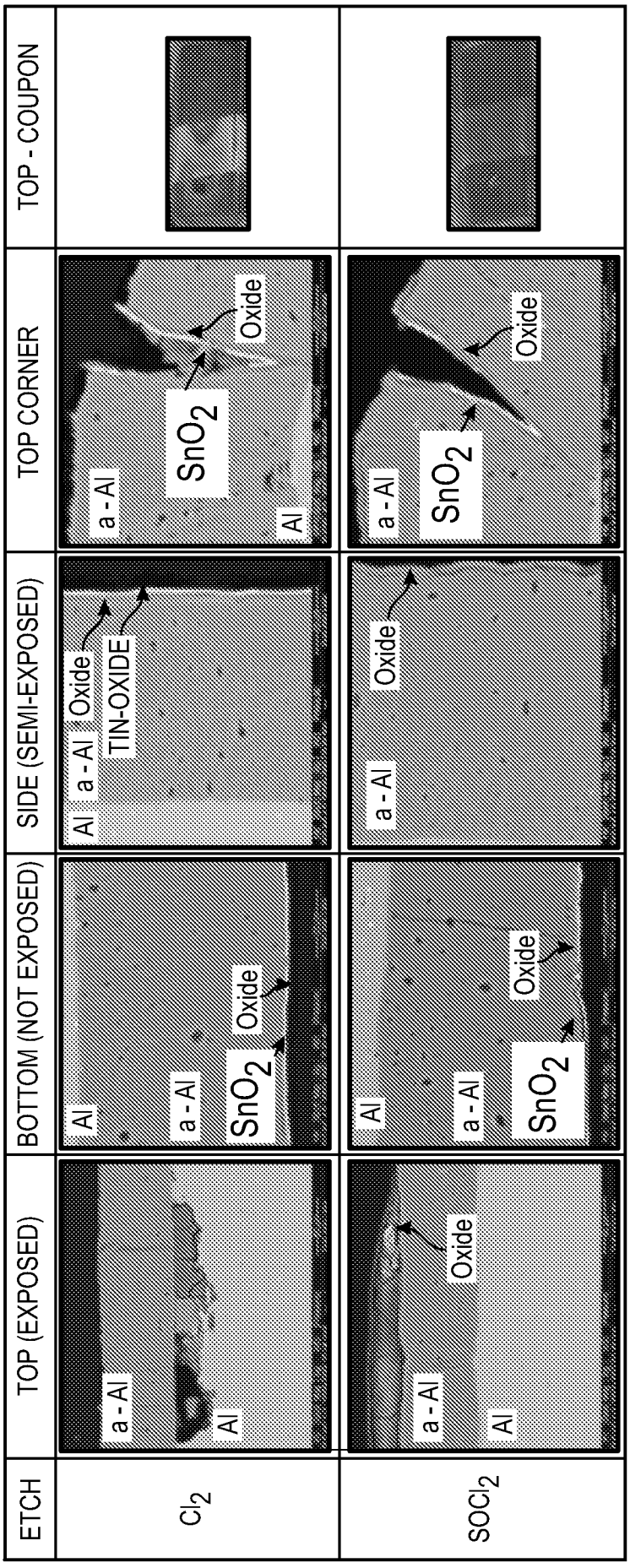

ETCH
TOP (EXPOSED)
BOTTOM (NOT EXPOSED)
SIDE (SEMI-EXPOSED)
TOP CORNER
TOP - COUPON
Cl_2
$SOCl_2$
a - Al
Al
SnO_2
Oxide
TIN-OXIDE

FIG. 6

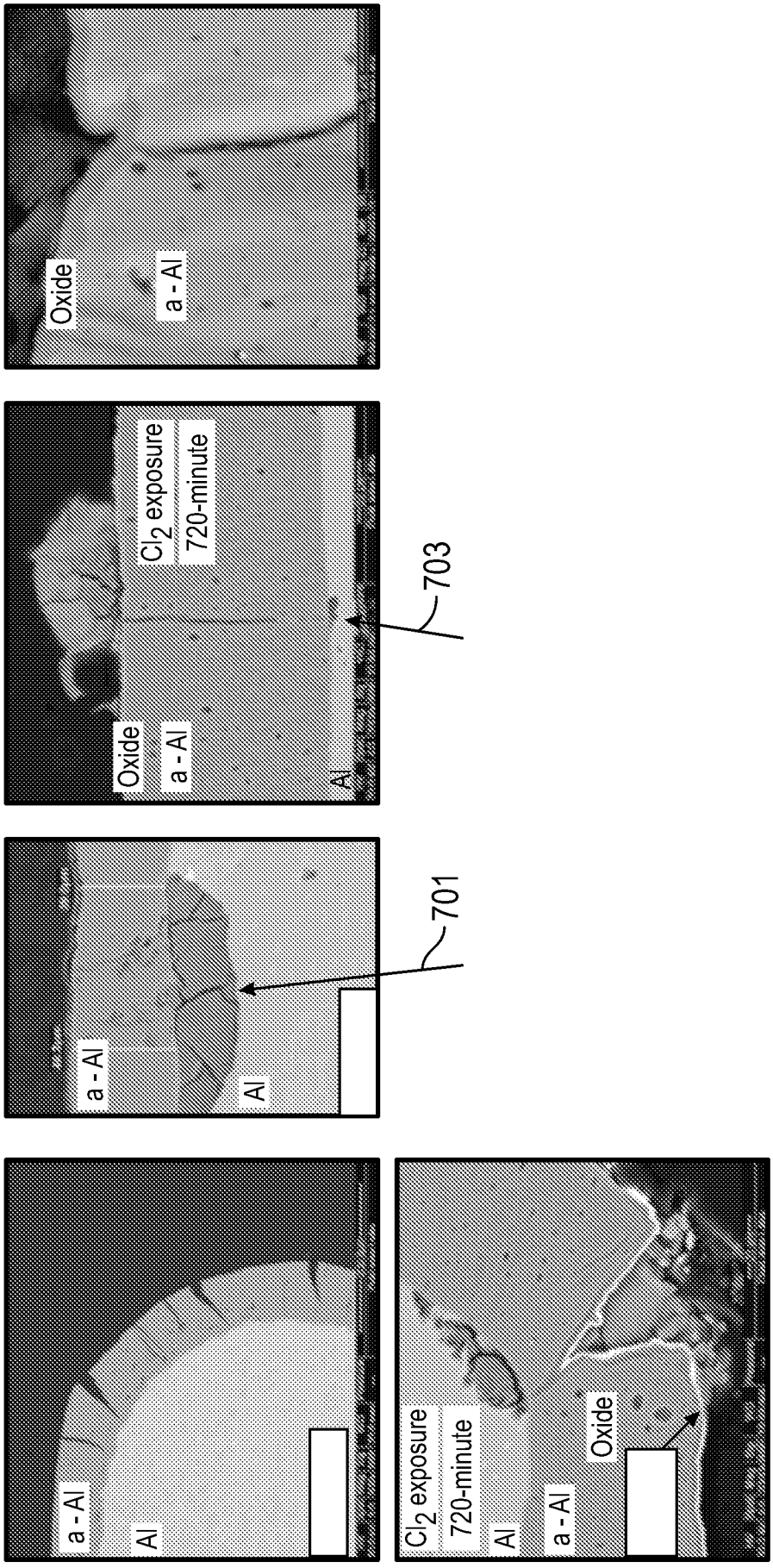

a - Al
Al
a - Al
Al
701
Oxide
a - Al
Al
Cl_2 exposure
720-minute
703
Oxide
a - Al
Cl_2 exposure
720-minute
Al
a - Al
Oxide

FIG. 7

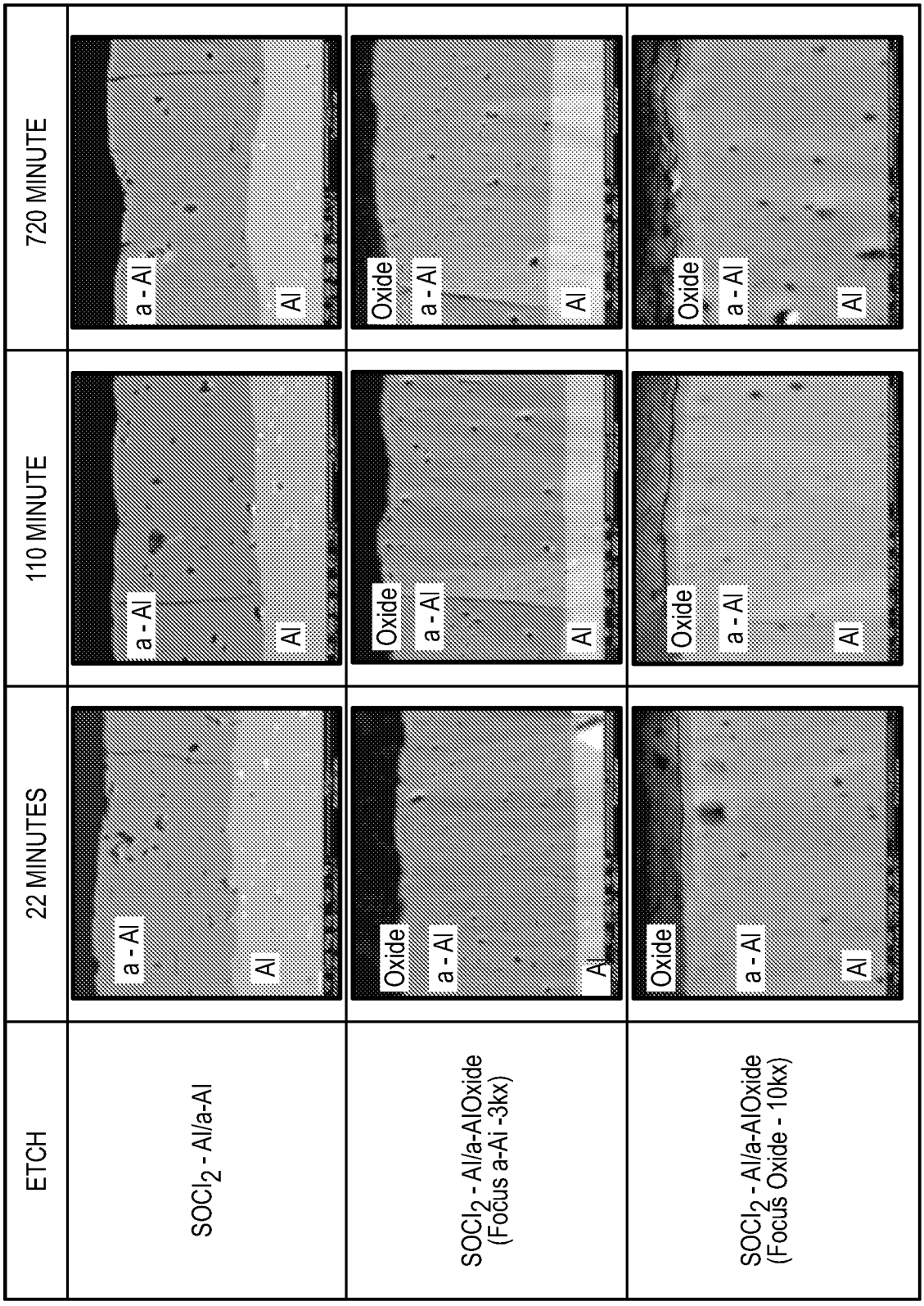

ETCH
22 MINUTES
110 MINUTE
720 MINUTE
SOCl2 - Al/a-Al
SOCl2 - Al/a-AlOxide (Focus a-Ai -3kx)
SOCl2 - Al/a-AlOxide (Focus Oxide - 10kx)
a - Al
Al
Oxide

FIG. 8A

POSSIBLE REACTIONS

$$2\ SOCl_2 + SnO_2 \rightarrow SnCl_4 + 2\ SO_2$$

$$2\ SOCl_2 + SiO_2 \rightarrow SiCl_4 + 2\ SO_2$$

FIG. 8B

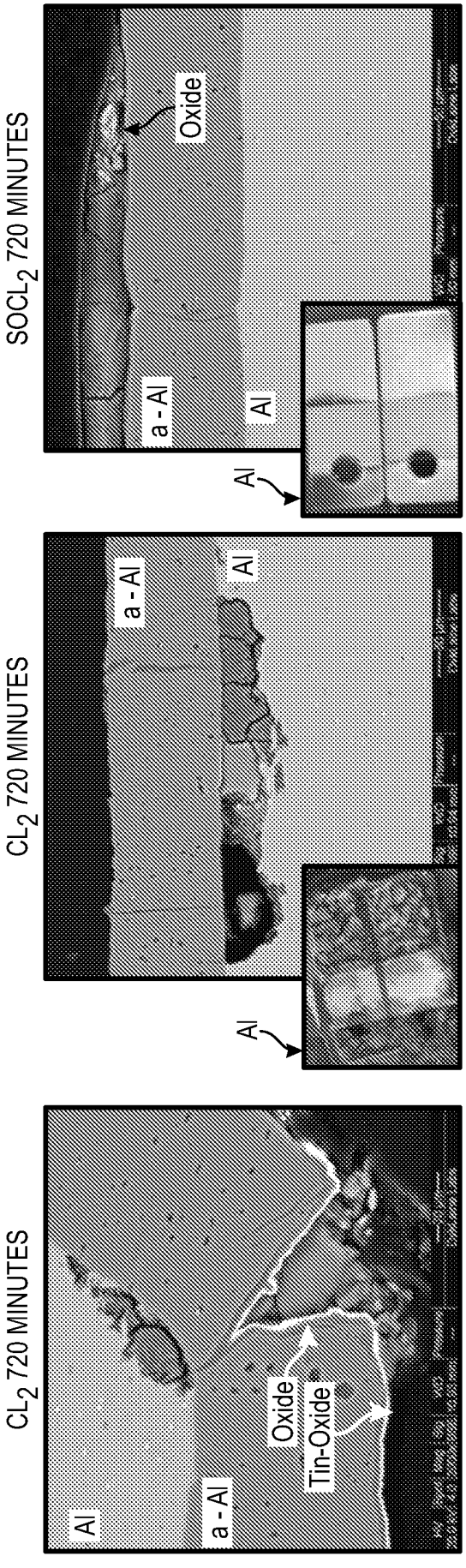

$SOCL_2$ 720 MINUTES
Oxide
a - Al
Al
Al
CL_2 720 MINUTES
a - Al
Al
Al
CL_2 720 MINUTES
Al
a - Al
Oxide
Tin-Oxide

FIG. 8C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/052208

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/3213(2006.01)i, H01L 21/3065(2006.01)i, H01L 21/324(2006.01)i, H01L 21/67(2006.01)i, H05H 1/46(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 21/3213; B08B 7/00; B08B 9/08; C23C 16/44; H01J 37/32; H01L 21/02; H01L 21/033; H01L 21/321; H01L 31/18; H01L 21/3065; H01L 21/324; H01L 21/67; H05H 1/46

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: chamber, tin oxide, thionyl chloride, methane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2011-0088718 A1 (ROBERT TORRES, JR. et al.) 21 April 2011 See paragraphs [0020]-[0043], claim 1 and figures 1-3.	1-6
A		7-16
Y	US 2015-0218695 A1 (SEASTAR CHEMICALS INC.) 06 August 2015 See paragraphs [0007], [0039]-[0049], claim 1 and figure 3.	1-6
A	US 2017-0213709 A1 (APPLIED MATERIALS, INC.) 27 July 2017 See paragraphs [0018]-[0046] and figures 1-3B.	1-16
A	US 2018-0240667 A1 (LAM RESEARCH CORPORATION) 23 August 2018 See claims 1, 5.	1-16
A	WO 98-00874 A1 (LAM RESEARCH CORPORATION) 08 January 1998 See claims 1, 17.	1-16

☐ 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	Date of mailing of the international search report
10 January 2020 (10.01.2020)	**10 January 2020 (10.01.2020)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
JANG, Gijeong
Telephone No. +82-42-481-8364

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/052208

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0088718 A1	21/04/2011	TW 201120209 A	16/06/2011
		WO 2011-047302 A2	21/04/2011
		WO 2011-047302 A3	21/07/2011
US 2015-0218695 A1	06/08/2015	CN 104853855 A	19/08/2015
		EP 2934775 A1	28/10/2015
		JP 2016-516287 A	02/06/2016
		JP 6390977 B2	19/09/2018
		KR 10-1792165 B1	31/10/2017
		KR 10-2015-0095611 A	21/08/2015
		US 10240230 B2	26/03/2019
		WO 2014-094103 A1	26/06/2014
US 2017-0213709 A1	27/07/2017	US 10115572 B2	30/10/2018
US 2018-0240667 A1	23/08/2018	CN 107546106 A	05/01/2018
		CN 108493152 A	04/09/2018
		JP 2018-006742 A	11/01/2018
		JP 2018-142698 A	13/09/2018
		KR 10-2018-0002026 A	05/01/2018
		KR 10-2018-0093798 A	22/08/2018
		KR 10-2019-0110142 A	27/09/2019
		SG 10201704783 A	30/01/2018
		SG 10201801132 A	27/09/2018
		TW 201812834 A	01/04/2018
		TW 201841258 A	16/11/2018
		TW 201842573 A	01/12/2018
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