



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C23F 4/00, H01L 21/3213</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/29640</b> <b>(43) International Publication Date:</b> 25 May 2000 (25.05.00)
<b>(21) International Application Number:</b> PCT/US99/26267 <b>(22) International Filing Date:</b> 11 November 1999 (11.11.99) <b>(30) Priority Data:</b> 09/190,435                      12 November 1998 (12.11.98)      US <b>(71) Applicant:</b> APPLIED MATERIALS, INC. [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US). <b>(72) Inventors:</b> WEBB, Timothy, R.; 430 Highland Avenue, San Mateo, CA 94401 (US). NANJANGUD, Savitha; 1771 Valhalla Court, San Jose, CA 95132 (US). LI, Marlene; 5784 Trowbridge Way, San Jose, CA 95138 (US). STOKES, Jeffrey; 4623 Mia Circle, San Jose, CA 95136 (US). <b>(74) Agents:</b> BERNADICOU, Michael, A. et al.; Blakely, Sokoloff, Taylor & Zafman LLP, 7th floor, 12400 Wilshire Boulevard, Los Angeles, CA 90025 (US).		<b>(81) Designated States:</b> JP, KR.  <b>Published</b> <i>With international search report.  Before the expiration of the time limit for amending the  claims and to be republished in the event of the receipt of  amendments.</i>
<b>(54) Title:</b> METHOD FOR RESIDUE-FREE ANISOTROPIC ETCHING OF ALUMINUM AND ITS ALLOYS		
<b>(57) Abstract</b>  The present invention is a method for essentially residue-free anisotropic etching of aluminum or aluminum alloys using a plasma generated from a source gas which includes a chlorine-comprising gas and a hydrocarbon-comprising gas. Etching takes place in a processing apparatus which provides separate power control for the plasma generation source and for a substrate biasing means. Etching is performed using a high density plasma (at least $10^{11}$ e-/cm <sup>3</sup> ) and a low substrate bias (less than about 200V). The method of the invention provides an acceptable etch rate and good etch profile, while prolonging the lifetime of the masking layer. The method of the invention is particularly useful for etching aluminum alloys having high (i.e., greater than about 0.5 %) alloy content. The method of the invention is also especially useful for essentially residue-free etching of aluminum or aluminum alloy layers deposited on substrates having large open areas (i.e., where open areas comprise greater than about 65 % of the surface area of the wafer).		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

1                                    METHOD FOR RESIDUE-FREE ANISOTROPIC ETCHING  
2                                    OF ALUMINUM AND ITS ALLOYS

3                                    **BACKGROUND OF THE INVENTION**

4            1.     Field of the Invention

5                    The present invention pertains to a method for residue-free anisotropic etching of  
6                    aluminum and aluminum alloys.

7            2.     Brief Description of the Background Art

8                    Various methods of etching aluminum and aluminum alloys are disclosed in the  
9                    art. Several of these methods are described below.

10                  U.S. Patent No. 4,618,398, issued October 21, 1986 to Nawata et al., discloses a  
11                  dry etching method wherein an etchant source gaseous mixture of boron trichloride,  
12                  chlorine and a hydrocarbon is converted into a plasma to etch aluminum or its alloys.  
13                  The invention makes it possible to accomplish the anisotropic etching of aluminum or its  
14                  alloys at high speeds with low plasma RF power density.

15                  U.S. Patent No. 5,277,750, issued January 11, 1994 to Frank, discloses a method  
16                  for anisotropic dry etching of metallization layers containing aluminum or aluminum  
17                  alloys, in integrated semiconductor circuits, using an etching mask. Etching is  
18                  performed with a strictly anisotropically attacking etching gas mixture containing an  
19                  iodine compound being volatile under normal conditions, wherein an accurately defined  
20                  vertical profile of the conduction lines is formed.

21                  U.S. Patent No. 5,298,112, issued March 29, 1994 to Hayasaka et al., discloses a  
22                  method and apparatus for removing a composite material to be treated by dry ashing  
23                  using a gas including a halogen element and a gas including a hydrogen element or using

1 a gas including fluorine, a gas including oxygen, and a gas including chlorine in a  
2 reaction chamber containing the material therein for use in manufacturing a  
3 semiconductor device.

4 U.S. Patent No. 5,779,926, issued July 14, 1998 to Ma et al., discloses a method  
5 of etching a multicomponent aluminum alloy on a substrate, without forming etchant  
6 residue on the substrate. In the method, the substrate is placed in a process chamber  
7 comprising a plasma generator and plasma electrodes. A process gas having a  
8 volumetric flow ratio  $V_r$  of (i) a chlorine-containing gas capable of ionizing to form  
9 dissociated  $Cl^+$  plasma ions and non-dissociated  $Cl_2^+$  plasma ions, and (ii) an inert gas  
10 capable of enhancing dissociation of the chlorine-containing gas, is introduced into the  
11 process chamber. The process gas is ionized to form plasma ions that energetically  
12 impinge on the substrate by (i) applying RF current at a first power level to the plasma  
13 generator, and (ii) applying RF current at a second power level to the plasma electrodes.  
14 The combination of the volumetric flow ratio  $V_r$  of the process gas and the power ratio  $P_r$   
15 of the first power level to the second power level is selected so that the chlorine-  
16 containing etchant gas ionizes to form dissociated  $Cl^+$  plasma ions and non-dissociated  
17  $Cl_2^+$  plasma ions in a number ratio of at least about 0.6 : 1. The increased amount of  
18 dissociated  $Cl^+$  ions relative to non-dissociated  $Cl_2^+$  ions etches the multicomponent alloy  
19 on the substrate at an etch rate of at least about 500 nm per minute, without forming  
20 etchant residue on the substrate.

21 It is known in the art that, in order to obtain an acceptable etch profile when  
22 etching aluminum or its alloys, it is important to passivate the etched sidewall in order to  
23 protect the walls of etched features from further etching by incident reactive species  
24 during continued vertical etching of the feature through a mask. Passivating films are  
25 formed by gaseous compounds (*i.e.*, sidewall passivating agents) which react to form a

1 protective film over the sidewalls of etched features as they are formed. Nitrogen (N<sub>2</sub>)  
2 gas is a commonly used sidewall passivating agent. Although nitrogen passivation  
3 provides an acceptable etch profile, the use of nitrogen gas can result in the production of  
4 undesirable residues, such as silicon nitride or copper nitride (when etching aluminum-  
5 copper alloys), which can be difficult to remove. If left in place, these residues can  
6 bridge between metal interconnect lines, causing electrical problems (*e.g.*, shorts) in the  
7 device.

8 Hydrocarbons (such as CH<sub>4</sub>) have been used as sidewall passivating agents.  
9 However, in a typical plasma etch chamber, the use of hydrocarbons as passivating  
10 agents slows the etch rate of the aluminum to an unacceptable level (*i.e.*, below about  
11 5,000 Å per minute). When a high power density (*i.e.*, greater than about 5 mW/cm<sup>2</sup>, or  
12 about 1 mA/cm<sup>2</sup>) is employed during etching, to improve the aluminum etch rate in a  
13 capacitively coupled or inductively coupled etch chamber, this leads to ion bombardment  
14 of the substrate surface, resulting in rapid etching of the mask layer as well as the  
15 aluminum layer. If the mask layer thickness is increased to compensate, it is difficult to  
16 achieve the desired etched feature profile.

17 It would be desirable to provide a method for etching aluminum and aluminum  
18 alloys that provides an acceptable selectivity for the aluminum over the masking layer,  
19 provides the desired etch profile, and provides an acceptable aluminum etch rate, while  
20 providing an etched surface which is essentially residue-free.

## 21 SUMMARY OF THE INVENTION

22 In a typical plasma processing apparatus, the power for the plasma generation  
23 source is under common control with the power for the substrate biasing means. For  
24 example, in a parallel plate plasma chamber, an increase in plasma source power

1 automatically increases power to the substrate pedestal which biases the substrate.

2 We have used a plasma generating apparatus having a plasma source power  
3 control which is separate from the power control to the substrate biasing device, in order  
4 to provide increased selectivity toward aluminum over surrounding etch masking  
5 materials during the etch process while avoiding damage to substrate devices. Further,  
6 we have discovered that use of the separate power controls described above enables the  
7 addition of a hydrocarbon-comprising material into the etch process, while maintaining a  
8 satisfactory etch rate for aluminum.

9 We have discovered that using a separate power control apparatus for the plasma  
10 generation source and for the device used to bias the substrate, in combination with the  
11 addition of a hydrocarbon to either the plasma source gas or to the process chamber (or  
12 both) in which a substrate is etched, enables a simultaneous improvement of the  
13 selectivity of etching for aluminum over adjacent masking materials, while protecting the  
14 sidewalls of an etched aluminum feature (*i.e.*, providing sidewall passivation. The  
15 polymer formed on the sidewalls of the etched feature as a result of the presence of the  
16 hydrocarbon-comprising material is adequate to protect the etched aluminum sidewalls  
17 under anisotropic etch conditions.

18 By increasing the power to the plasma generation source, the number of reactive  
19 species present on the feature surfaces can be greatly increased. By separately  
20 controlling the substrate bias, this bias can be set to produce anisotropic etch conditions  
21 without causing heavy ion bombardment of all horizontal feature surfaces. As a result,  
22 the etchant species composition (rather than ion bombardment) controls selectivity  
23 toward aluminum over adjacent masking materials, while sufficient substrate bias to  
24 produce anisotropic etch conditions is achieved. By simultaneously adding hydrocarbon  
25 to plasma species at the feature surface, a thin layer of polymer is deposited on the

1 sidewall and in the bottom of the feature. Because the feature sidewalls are not as  
2 exposed to etchant species during anisotropic etching, the thin layer of polymer serves to  
3 protect the sidewall surfaces from being etched while the polymer layer at the bottom of  
4 the feature is removed (the thin layer of polymer that was deposited on the horizontal  
5 surfaces, *i.e.*, on the field surface and in the bottom of the feature, is removed during  
6 anisotropic etching.)

7 The method of the present invention comprises anisotropically etching aluminum  
8 or an aluminum alloy using a plasma generated from a plasma source gas which  
9 comprises a chlorine-comprising gas and a hydrocarbon-comprising gas. Etching takes  
10 place in a processing apparatus having separate power controls for the plasma generation  
11 source and substrate biasing means.

12 Preferably, the chlorine-comprising gas is selected from the group consisting of  
13  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{BCl}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CHCl}_2\text{F}$ , and combinations thereof. More  
14 preferably, the chlorine-comprising gas does not comprise fluorine. Most preferably, the  
15 chlorine-comprising gas is  $\text{Cl}_2$ .

16 The hydrocarbon-comprising gas preferably has the chemical formula  $\text{C}_x\text{H}_y$ ,  
17 where  $x$  typically ranges from about 1 to about 5, when  $y$  ranges from about 1 to about  
18 12. More preferably,  $x$  ranges from 1 to 3, and  $y$  ranges from 1 to 6. Most preferably,  
19 the hydrocarbon-comprising gas is  $\text{CH}_4$ .

20 The atomic ratio of chlorine : carbon in the plasma source gas preferably ranges  
21 from about 5 : 1 to about 200 : 1; more preferably, from about 10 : 1 to about 20 : 1. The  
22 atomic ratio of hydrogen : carbon in the hydrocarbon preferably ranges from about 1 : 1  
23 to about 4 : 1.

1 The plasma source gas may also comprise an additive gas which aids in etch  
2 profile control. The additive gas is preferably selected from the group consisting of  
3  $\text{BCl}_3$ ,  $\text{N}_2$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_4\text{F}_8$ ,  $\text{CHF}_3$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{C}_2\text{Cl}_2\text{F}_4$ ,  $\text{CBrF}_3$ ,  
4  $\text{CBr}_2\text{F}_2$ ,  $\text{O}_2$ , and combinations thereof. However, other similar additive gases may be  
5 used for profile control. More preferably, the additive gas does not comprise oxygen.  
6 Most preferably, the additive gas is  $\text{BCl}_3$ .

7 The plasma source gas typically includes a non-reactive, diluent gas selected  
8 from the group consisting of argon, helium, xenon, krypton, and combinations thereof,  
9 with argon being preferred due to its lower cost.

10 The electron density of the plasma is preferably at least  $10^{11}$  e/cm<sup>3</sup>, most  
11 preferably, about  $10^{12}$  e/cm<sup>3</sup>. The substrate bias is preferably less than about  
12 - 200 V. Most preferably, the substrate bias ranges from about - 50 V to about - 150 V.

13 The method of the invention is particularly useful for etching aluminum alloys,  
14 such as aluminum-copper and aluminum-copper-silicon alloys, which tend to produce  
15 more undesirable residues than pure aluminum.

16 The method of the invention is especially useful for essentially residue-free  
17 etching of aluminum or aluminum alloy layers deposited on substrates having large open  
18 areas (*i.e.*, where open areas comprise greater than about 65% of the surface area of the  
19 wafer).

## 20 BRIEF DESCRIPTION OF THE DRAWINGS

21 Figure 1 is a cross-sectional schematic of an Applied Materials' CENTURA®  
22 etch system, which is an example of an etch processing apparatus useful in the present  
23 invention.



1           Figure 2a is a detailed schematic of an individual metal etch decoupled plasma  
2 source (DPS) chamber of the type used in the Applied Materials' CENTURA® etch  
3 system shown in Figure 1.

4           Figure 2b is a vertical cross-sectional schematic of an individual metal etch DPS  
5 chamber, as taken from U.S. Patent No. 5,779,926. This schematic shows independent  
6 power controls 268 for the plasma source power and 270 for the bias power.

7           Figure 3 is an illustration of a feature 306 etched in an aluminum layer 308 which  
8 has been deposited on a substrate 310. This illustration is provided to show how the etch  
9 profile of an aluminum line sidewall is measured, with reference to an included angle  
10 varying from the desired perpendicular wall (90°).

11           Figure 4 is a graph showing the effects of increasing the source gas flow rate 402,  
12 the Cl<sub>2</sub> : CH<sub>4</sub> ratio 404, the process chamber pressure 406, and the source power 408 on  
13 the aluminum etch endpoint time, which is an indicator of the aluminum etch rate (*i.e.*,  
14 the shorter the endpoint time, the faster the etch rate).

15           Figure 5 is a graph showing the effects of increasing the source gas flow rate 502,  
16 the Cl<sub>2</sub> : CH<sub>4</sub> ratio 504, the process chamber pressure 506, and the source power 508 on  
17 the etch profile angle of an aluminum line sidewall.

18           Figure 6 is a graph showing the effects of increasing the source gas flow rate 602,  
19 Cl<sub>2</sub> : H<sub>4</sub> ratio 604, process chamber pressure 606, and the source power 608 on the  
20 etch profile microloading, Δ° (*i.e.*, the difference between the average etch profile angle  
21 of a dense array of lines and the average etch profile angle of isolated lines on the same  
22 substrate).

23           Figure 7 is a graph showing the effects of increasing the source gas flow rate 702,  
24 the Cl<sub>2</sub> : CH<sub>4</sub> ratio 704, the process chamber pressure 706, and the source power 708 on  
25 the amount of residue remaining after etching. The amount of residue remaining after

1 etching is shown in arbitrary units that were assigned after comparative evaluation of  
2 scanning electron micrographs (SEMs) taken at 20k magnification, where the number of  
3 deposits present on a given surfaces area were compared and rated on a scale from 1 to  
4 10.

5 Figure 8 is a graph showing the effects of increasing the bias power, while  
6 maintaining a constant source power of 1800 W, on the total amount of photoresist  
7 remaining in the center and at the edge of a wafer after completion of etch.

8 Figure 9 is a graph showing the effects of varying the  $\text{Cl}_2$  flow rate 902,  $\text{BCl}_3$   
9 flow rate 904, Ar flow rate 906, and  $\text{CH}_4$  flow rate 908 on the aluminum alloy etch  
10 endpoint time, which is an indicator of the aluminum alloy etch rate.

11 Figure 10 is a graph showing the effects of varying the  $\text{Cl}_2$  flow rate 1002,  $\text{BCl}_3$   
12 flow rate 1004, Ar flow rate 1006, and  $\text{CH}_4$  flow rate 1008 on the amount of residue  
13 remaining after etching. Residue was quantified by counting the number of deposits  
14 observed in an area of approximately  $2 \mu\text{m}^2$  as shown on an SEM taken at 20k  
15 magnification.

16 Figure 11 is a graph showing the effects of varying the  $\text{Cl}_2$  flow rate 1102,  $\text{BCl}_3$   
17 flow rate 1104, Ar flow rate 1106, and  $\text{CH}_4$  flow rate 1108 on the photoresist etch rate.

## 18 DETAILED DESCRIPTION OF THE INVENTION

19 We have discovered an improved method for essentially residue-free etching of  
20 aluminum and aluminum alloys in semiconductor devices, including interconnect  
21 structures and contacts. The method itself and preferred process parameters for  
22 performing the method of the invention are described in detail below.

## 1 I. DEFINITIONS

2 As a preface to the detailed description, it should be noted that, as used in this  
3 specification and the appended claims, the singular forms "a", "an", and "the" include  
4 plural referents, unless the context clearly dictates otherwise.

5 Specific terminology of particular importance to the description of the present  
6 invention is defined below.

7 The term "aluminum alloy" includes alloys of aluminum of the kind typically  
8 used in the semiconductor industry. Such alloys include, but are not limited to,  
9 aluminum-copper alloys, and aluminum-copper-silicon alloys, for example. Typically,  
10 the aluminum content of the alloy is 90% or greater.

11 The term "anisotropic etching" refers to etching which does not proceed in all  
12 directions at the same rate. If etching proceeds exclusively in one direction (*e.g.*, only  
13 vertically), the etching process is said to be completely anisotropic.

14 The term "aspect ratio" generally refers to the ratio of the height dimension to the  
15 width dimension of a particular feature. In situations where the feature has more than  
16 one width, the minimum width is used in calculating the aspect ratio.

17 The term "bias power" refers to the power applied to the substrate support platen  
18 to produce a negative voltage on the substrate surface. Typically, the negative voltage is  
19 used to control ion bombardment energy and the directionality of ions toward a substrate.

20 The term "chlorine" as used herein is intended to encompass  $\text{Cl}_2$  as well as other  
21 chlorine-comprising compounds which are capable of producing reactive etchant species.

22 The term "decoupled plasma source" refers to a plasma generation apparatus  
23 which has separate controls for power input to a plasma source generator and to a  
24 substrate bias device. Typically, the plasma source power controller controls the supply  
25 of inductively coupled RF power which is used to generate the plasma and determines

1 the plasma density and the bias power controller controls the supply of RF power which  
2 is used to generate a DC bias voltage on the semiconductor substrate surface. The bias  
3 voltage affects the ion bombardment energy on the substrate surface. This decoupled  
4 plasma source typically incorporates measures to separate (decouple) the influence of the  
5 source and bias on one another. The ENDURA® metal deposition systems and  
6 CENTURA® metal etch systems available from Applied Materials, Inc. of Santa Clara,  
7 California, which include decoupled plasma source power and bias power control, are  
8 referred to as “DPS” systems. Similar equipment available from other manufactures may  
9 be referred to by different nomenclature.

10 The term “etch profile” generally refers to, but is not limited to, the cross-  
11 sectional profile of the sidewall of an etched aluminum line. In many instances herein,  
12 the etch profile is described in terms of an angle between the sidewall and the underlying  
13 substrate. When the angle is  $90^\circ$ , the sidewall is perpendicular to the substrate. This is  
14 generally preferred. When the angle is greater than  $90^\circ$  (positive), the line sidewall is  
15 said to be tapered (*i.e.*, the line is wider at its base where it contacts the substrate). When  
16 the angle is less than  $90^\circ$  (negative), the line sidewall is said to be retrograde or undercut  
17 (*i.e.*, the line is more narrow at its base than at its upper surface). Figure 3 illustrates  
18 positive and negative angle line sidewall profiles.

19 The term “etch profile microloading” refers to the difference between the average  
20 etch profile angle of a dense array of lines and the average etch profile angle of isolated  
21 lines on the same substrate. For example, if the average etch profile angle of a dense  
22 array of lines is  $90^\circ$ , and the average etch profile angle of isolated lines on the same  
23 substrate is  $85^\circ$ , the etch profile microloading is  $5^\circ$  (*i.e.*,  $90^\circ - 85^\circ = 5^\circ$ ).

24 The term “feature” refers to, but is not limited to, interconnects, contacts, vias,  
25 trenches, and other structures which make up the topography of the substrate surface.

1           The term "feature size" typically refers to the smallest dimension of a feature.

2           The term "high density plasma" refers to, but is not limited to, a plasma having  
3 an electron density of at least  $10^{11}$  e/cm<sup>3</sup>.

4           The term "hydrocarbon" refers to, but is not limited to, a hydrogen and carbon-  
5 comprising compound having the general formula C<sub>x</sub>H<sub>y</sub>, where *x* preferably ranges from  
6 about 1 to about 5, and *y* preferably ranges from about 1 to about 12.

7           The term "ion bombardment" refers to, but is not limited to, physical  
8 bombardment of a substrate surface by ions (and other excited species of atoms which  
9 are present with the ions). Ion bombardment is frequently used to remove atoms from a  
10 substrate surface, where physical momentum transfer is used to achieve the atom  
11 removal.

12           The term "open areas" refers to the areas of the substrate into which openings  
13 have been formed (*e.g.*, the substrate has been patterned and etched to form contact vias,  
14 trenches, etc.). A substrate having large open areas is a substrate in which openings have  
15 been formed over a large percentage (*i.e.*, greater than about 65%) of the substrate  
16 surface.

17           The term "oxide loss" refers to disappearance of the silicon oxide layer which is  
18 typically sandwiched between the substrate and a diffusion barrier layer.

19           The term "plasma" refers to a partially ionized gas containing an essentially equal  
20 number of positive and negative charges, as well as some other number of non-ionized  
21 gas particles.

22           The term "sidewall passivation" refers to protecting the sidewall of an etched  
23 feature from further etching by incident reactive species during continued vertical  
24 etching of the feature through a mask.

1           The term "source power" refers to the power used to generate plasma ions and  
2 neutrals, whether directly in an etching chamber or remotely, as in the case of a  
3 microwave plasma generator.

## 4           II.     AN APPARATUS FOR PRACTICING THE INVENTION

5           An apparatus having separate controls for power to the plasma generation source  
6 and the substrate biasing means was described by Yan Ye et al. at the Proceedings of the  
7 Eleventh International Symposium of Plasma Processing (May 7, 1996) and published in  
8 the *Electrochemical Society Proceedings* (Volume 96-12, pp. 222 - 233, 1996).

9           Figure 1 shows a cross-sectional schematic of an etch processing apparatus that  
10 can be used in the practice of the present invention, the Applied Materials' CENTURA®  
11 etch system (Applied Materials, Inc., Santa Clara, CA). The CENTURA® etch system is  
12 a fully automated semiconductor fabrication system, employing a single-wafer, multi-  
13 chamber design which accommodates 200-mm wafers. As shown in Figure 1, the  
14 CENTURA® etch system includes decoupled plasma source (DPS) chambers 102;  
15 advanced strip-and-passivation (ASP) chambers 104; wafer orienter chamber 106;  
16 cooldown chamber 108; and independently operated loadlock chambers 110. The  
17 experiments described in Examples One and Two, below, were performed using a  
18 System 2982 CENTURA® etch system. The System 2982 differs from the generic  
19 CENTURA® etch system shown in Figure 1 in that the System 2982 includes only one  
20 ASP chamber.

21           Figure 2a shows a detailed schematic of an individual metal etch DPS chamber  
22 102 of the type used in the CENTURA® etch system. The metal etch DPS chamber 102  
23 includes a ceramic dome 202, a standard monopolar electrostatic chuck (ESC) 204, and a  
24 1.0-inch focus ring 206. The dome 202 is maintained at a constant temperature to

1 control the formation of particulates during processing. Gas is introduced into the  
2 chamber via four ceramic gas injection nozzles 208 for uniform gas distribution.  
3 Chamber pressure is controlled by a closed-loop pressure control system 210 with a  
4 unique plunger-style throttle valve 212.

5 The DPS etch chamber 102 uses an inductive plasma source, frequency tuned at  
6 approximately 2 MHz, to generate and sustain a high density plasma (*i.e.*, having an  
7 electron density of at least  $10^{11}$  e/cm<sup>3</sup>). The wafer is biased with a 13.56 MHz RF  
8 power source. The decoupled nature of the plasma source allows independent control of  
9 ion energy and ion density, which provides highly uniform plasma (< 5% variation) with  
10 a wide process window over changes in source and bias power, pressure, and metal etch  
11 gas chemistry.

12 Figure 2b is a vertical cross-sectional schematic of an individual metal etch DPS  
13 chamber 102. In the etching process, a substrate 225 is placed in the processing chamber  
14 102 and held in place by means of an electrostatic chuck 273. The electrostatic chuck  
15 273 overlies a cathode plasma electrode 257, which is connected to an independently  
16 controlled plasma electrode (RF) power source 270. The walls 263 of the chamber are  
17 electrically grounded to form an anode plasma electrode 258. A plasma source gas is  
18 introduced into and distributed throughout the processing chamber 102 by means of a gas  
19 distributor 265 peripherally disposed above the substrate 225. Plasma ions are formed  
20 from the plasma source gas by applying an RF current to an inductive coil plasma  
21 generator 255, which is connected to an independently controlled plasma generator (RF)  
22 power source 268. The cathode electrode 257 is electrically biased with respect to the  
23 anode electrode 258 by applying an RF voltage to the cathode electrode 257 via power  
24 source 270, so that the plasma ions formed in the chamber 102 are attracted toward,  
25 energetically impinge upon, and etch the substrate 225. Spent process gas and etchant

1 byproducts are exhausted from the process chamber 102 through an exhaust system 274.  
2 A throttle valve 276 is provided in the exhaust for controlling the pressure in the  
3 chamber 102. A more detailed description of the metal etch DPS chamber 102 is found  
4 in U.S. Patent No. 5,779,926, issued July 14, 1998 to Ma et al., the disclosure of which is  
5 hereby incorporated by reference herein in its entirety.

6 The experiments described in Examples Three, Four, and Five, below, were  
7 performed using an Applied Materials' System 5084 prototype etch processing system.  
8 The System 5084 is a fully automated semiconductor fabrication system, employing a  
9 single-wafer, multi-chamber design which is very similar to the System 2982  
10 CENTURA® Etch System, but which accommodates 150-mm wafers. The System 5084  
11 supports three processing chambers (two prototype DPS chambers and one ASP  
12 chamber), which are attached to a central loadlock chamber. The System 5084 apparatus  
13 is able to perform the same functions in a similar manner to the Applied Materials'  
14 System 2982 apparatus.

### 15 III. THE METHOD FOR RESIDUE-FREE ANISOTROPIC ETCHING OF 16 ALUMINUM AND ITS ALLOYS

17 The method of the invention comprises anisotropic etching of aluminum or  
18 aluminum alloys using a plasma generated from a plasma source gas which includes  
19 reactive, chlorine-comprising species and a hydrocarbon-comprising gas, in combination  
20 with an independently controlled plasma generation source and substrate biasing means.  
21 The etch processing chamber may utilize an externally or locally generated plasma  
22 source with or without an RF coupled internal coil to increase plasma ion content.



1           The chlorine-comprising species is typically generated from a gas which is  
2 preferably selected from the group consisting of  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{BCl}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{CHCl}_3$ ,  
3  $\text{CCl}_2\text{F}_2$ ,  $\text{CHCl}_2\text{F}$ , and combinations thereof. More preferably, the chlorine-comprising  
4 species is generated from a gas which does not comprise fluorine. Most preferably, the  
5 chlorine-comprising species is generated from  $\text{Cl}_2$ .

6           The hydrocarbon-comprising gas, used to provide sidewall passivation for the  
7 etched aluminum feature surfaces, is typically added to the other gases which make up  
8 the plasma source gas. The hydrocarbon-comprising gas preferably has the chemical  
9 formula  $\text{C}_x\text{H}_y$ , where  $x$  typically ranges from about 1 to about 5, when  $y$  ranges from  
10 about 1 to about 12. More preferably,  $x$  ranges from 1 to 3, and  $y$  ranges from 1 to 6.  
11 Most preferably, the hydrocarbon-comprising gas is  $\text{CH}_4$ .

12           As used herein, the term "sidewall passivation" refers to protecting the sidewall  
13 of an etched feature from further etching by incident reactive species during continued  
14 vertical etching of the feature through a mask. In addition, by adjusting the relative  
15 ratios of chlorine, carbon, and hydrogen in the plasma source gas, it is possible to obtain  
16 the additional benefit of passivating the entire feature surface after completion of  
17 etching, thereby providing improved corrosion resistance during subsequent processing  
18 and device use. The chlorine or chlorine-comprising gas and the hydrocarbon-  
19 comprising gas are preferably provided in relative quantities such that the atomic ratio of  
20 chlorine : carbon in the plasma source gas is within the range of about 5 : 1 to about  
21 200 : 1; more preferably, from about 10 : 1 to about 10 : 1. The atomic ratio of hydrogen  
22 : carbon in the hydrocarbon preferably ranges from about 1 : 1 to about 4 : 1.

23           The plasma source gas may further comprise an additive gas which assists in  
24 profile control, where the additive gas is preferably selected from the group consisting of  
25  $\text{BCl}_3$ ,  $\text{N}_2$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_4\text{F}_8$ ,  $\text{CHF}_3$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{F}$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{C}_2\text{Cl}_2\text{F}_4$ ,  $\text{CBrF}_3$ ,

1 CBr<sub>2</sub>F<sub>2</sub>, O<sub>2</sub>, and combinations thereof. However, other similar additive gases may be  
2 used for profile control. More preferably, the additive gas does not comprise oxygen.  
3 The presence of oxygen in the plasma source gas can lower the selectivity of the plasma  
4 source gas for the preferential etching of aluminum relative to the photoresist masking  
5 material, resulting in an undesirable etch rate for the photoresist masking layer. The  
6 most preferred additive gas is BCl<sub>3</sub>.

7 The plasma source gas typically includes a non-reactive, diluent gas, where the  
8 non-reactive, diluent gas is selected from the group consisting of argon, helium, xenon,  
9 krypton, and combinations thereof, with argon being preferred due to its lower cost.

10 Etching is performed using a process apparatus in which the plasma source power  
11 is separately controlled from the substrate bias power. A general description of which is  
12 provided in Section II, above. The electron density of the plasma is preferably at least  
13  $10^{11}$  e/cm<sup>3</sup>, and more preferably, about  $10^{12}$  e/cm<sup>3</sup>.

14 In order to provide anisotropic etching, while reducing the amount of ion  
15 bombardment on the surface of the etch masking layer, the substrate bias power is  
16 carefully controlled. In the apparatus described herein, the bias power is preferably less  
17 than about 300 W; more preferably, less than about 200 W; most preferably, less than  
18 about 100 W.

19 Table 1, below, provides preferred process conditions for essentially residue-free  
20 etching of aluminum and/or its alloys according to the method of the invention, using  
21 the Applied Materials' System 2982 CENTURA® Etch System, which is shown in  
22 Figures 1 and 2 and described in Section II, above.

1 Table 1. Preferred Process Conditions for Etching Aluminum and its Alloys

2

Process Parameter	Preferred Process Conditions	More Preferred Process Conditions	Optimum Known Process Conditions
3 Plasma Source Power (W)	300 - 2000	800 - 1600	800 - 1200
4 Substrate Bias Power (W)	50 - 300	50 - 200	50 - 100
5 Cl <sub>2</sub> Flow Rate (sccm)	50 - 200	50 - 100	50 - 90
6 CH <sub>4</sub> Flow Rate (sccm)	1 - 100	1 - 50	1 - 20
7 BCl <sub>3</sub> Flow Rate (sccm)	0 - 200	0 - 100	0 - 50
8 Ar Flow Rate (sccm)	0 - 200	20 - 200	20 - 100
9 Typical Total Gas Flow (sccm)	50 - 350	50 - 200	80 - 180
10 Process Chamber Pressure (mT)	5 - 50	5 - 25	8 - 12
11 Pedestal Temperature (°C)*	10 - 80	20 - 60	30 - 50
12 Process Chamber Wall Temp. (°C)	20 - 100	40 - 100	80

13 \* The substrate temperature is typically about 40 - 50°C higher than the pedestal  
 14 temperature. For example, a pedestal temperature of about 50°C would typically result  
 15 in a substrate temperature of about 90 - 100°C).

16 EXAMPLE ONE:

17 Experiments were conducted to compare aluminum alloy etch rates for an etchant  
 18 species mixture of Cl<sub>2</sub> and BCl<sub>3</sub>, which was held constant, while nitrogen and methane  
 19 were added to the plasma source gas in varying amounts.

20 The process work was performed in an Applied Materials' System 2982 etch  
 21 processing apparatus, which is shown in Figures 1 and 2 and described in section II,  
 22 above.

23 The following film stack, from top to bottom, was used for this study: 1.8 μm  
 24 i-line photoresist (supplied by TFI of Fremont, CA); 450 Å TiN ARC (anti-reflective  
 25 coating); 11,500 Å Al - 0.5% Cu; 700 Å Ti barrier layer; and 1.12 μm silicon oxide, on a

1 silicon wafer substrate.

2 All substrates were patterned using an i-line photoresist mask having a lines and  
3 spaces pattern, with a feature size of about 0.4  $\mu\text{m}$  and an aspect ratio of about 2.5 : 1.  
4 The TiN ARC was patterned using a commercially available i-line stepper.

5 The aluminum alloy and the titanium barrier layer were etched using the  
6 following process parameters: 100 sccm  $\text{Cl}_2$ , 40 sccm  $\text{BCl}_3$ , and 5 or 10 sccm of  $\text{N}_2$  or  
7  $\text{CH}_4$ ; 1200 W source power; 150 W bias power; 10 - 20 mT process chamber pressure;  
8 7 T helium back pressure on the backside of the substrate wafer; 45°C substrate  
9 temperature; and an 80°C process chamber wall and dome temperature.

10 The height of each line (*i.e.*, etch depth) was approximately 1  $\mu\text{m}$ . The endpoint  
11 time required to reach this etch depth was recorded. The endpoint times for etching,  
12 using the different plasma source gases, process chamber pressures, and flow rates, are  
13 recorded in Table 2, below.

14 Table 2. A Comparison of Aluminum Alloy Etch Rates for Nitrogen-comprising and  
15 Methane-comprising Plasma Source Gases

Pressure (mT)	$\text{N}_2$ Flow (sccm)	$\text{CH}_4$ Flow (sccm)	Endpoint Time (seconds)	Etch Rate ( $\text{\AA}$ / minute)
10	5	--	34	14,100
10	--	5	45	10,680
10	10	--	34	14,100
10	--	10	53	9,000
20	5	--	32	15,000
20	--	5	42	11,400
20	10	--	31	15,480
20	--	10	48	10,020

1           Although the aluminum alloy etch rate was significantly slower when the etch  
2           plasma contained methane than when the etch plasma contained nitrogen, the etch rate  
3           obtained using a methane-comprising source gas was still well above the 5,000 Å per  
4           minute minimum acceptable etch rate at each of the different process chamber pressures  
5           and source gas flow rates.

6           EXAMPLE TWO:

7           Experiments were conducted to measure the aluminum alloy etch rate, etch  
8           profile, etch profile microloading, thickness of the photoresist masking layer remaining  
9           after etch, and the amount of residue remaining after etching of aluminum alloy lines and  
10          spaces, each as a function of plasma source gas composition (*i.e.*, varying the ratio of  
11          Cl<sub>2</sub> : CH<sub>4</sub>), total gas flow rate, process chamber pressure, and source power.

12          The process work was performed in an Applied Materials' System 2982 etch  
13          processing apparatus, which is shown in Figures 1 and 2 and described in section II,  
14          above.

15          The following film stack, from top to bottom, was used for this study: 1.8 μm  
16          i-line photoresist (supplied by TFI of Fremont, CA); 450 Å TiN ARC; 11,500 Å  
17          Al - 0.5% Cu; 700 Å Ti barrier layer; and 1.12 μm silicon oxide, on a silicon wafer  
18          substrate.

19          All substrates were patterned using an i-line photoresist mask having a lines and  
20          spaces pattern, with a feature size of about 0.4 μm and an aspect ratio of about 2.5 : 1.  
21          The TiN ARC was patterned using a commercially available i-line stepper.

22          The aluminum alloy and the titanium barrier layer were etched using the  
23          following process parameters: 800 - 1600 W source power; 150 W bias power; 8 - 16  
24          mT process chamber pressure; 7 T helium back pressure on the backside of the substrate

1 wafer; 45°C substrate temperature; and an 80°C process chamber wall and dome  
2 temperature. The Cl<sub>2</sub>/CH<sub>4</sub> ratio was varied from 6 : 1 to 33 : 1. No additive gas (such as  
3 BCl<sub>3</sub>) was used in this set of experiments.

4 The height of each line (*i.e.*, etch depth) was approximately 1 μm. The endpoint  
5 time required to reach this etch depth was recorded. The etch profile angle for the wall  
6 of the etched aluminum line, relative to the underlying substrate, was measured in  
7 degrees (with a vertical, *i.e.*, 90°, etch profile being ideal). Etch profile microloading  
8 (Δ°) was measured by comparing the average etch profile angle of a dense array of lines  
9 with the average etch profile angle of isolated lines on the same substrate.

10 The etch endpoint times, etch profile angles, etch profile microloading, and  
11 photoresist thickness at completion of etching are provided in Table 3, below, as a  
12 function of the following process variables: Cl<sub>2</sub> : CH<sub>4</sub> ratio of the plasma source gas;  
13 total flow rate of the plasma source gas; process chamber pressures; and source power  
14 (the bias power was held constant at 150 W).

Table 3. Effect of Varying  $\text{Cl}_2 : \text{CH}_4$  Ratios and Other Process Variables  
on Aluminum Alloy Etch Results

$\text{Cl}_2 : \text{CH}_4$ Ratio	Total Flow Rate (sccm)	Etch Chamber Pressure (mT)	Source Power (W)	Endpoint Time (s)	Etch Profile Angle ( $^\circ$ )	Etch Profile Micro- loading ( $\Delta^\circ$ )	Remaining Photoresist Thickness ( $\text{\AA}$ )
6 : 1	100	8	800	67	89	14	6000
6 : 1	100	24	1600	47	90	11	6400
6 : 1	140	8	1600	58	88	8	6250
6 : 1	140	24	800	50	86	12	6900
19.5 : 1	120	16	1200	34	89	6	7000
19.5 : 1	120	16	1200	34	91	8	6750
33 : 1	100	8	1600	38	91	3	7500
33 : 1	100	24	800	37	86	5	7000
33 : 1	140	8	800	35	91	6	6750
33 : 1	140	24	1600	29	94	8	6700

Etch profile angles which are described subsequently herein are best illustrated with reference to Figure 3. Figure 3 shows a cross-sectional schematic of a pattern of lines 302 and spaces 304 upon a substrate 306. The etch profile in general refers to the cross-sectional profile of an aluminum line sidewall 308. An etch profile angle,  $\alpha$ , is the angle between a line sidewall 308 and the surface 310 of the underlying substrate 306. The angle  $\alpha$  is measured from the substrate surface 310 interior of the line 302 toward the line sidewall 308. For example,  $\alpha_1$  is approximately  $85^\circ$  and represents a "tapered" line sidewall profile, where the line is broader at its base (adjacent to substrate surface 310). By comparison,  $\alpha_2$  is  $90^\circ$ , so that the line sidewall forms a perpendicular

1 intersection with substrate surface 310. Further,  $\alpha_3$  is  $105^\circ$  and represents a retrograde  
2 or undercut line sidewall profile, where the line is more narrow at its base than at its top.

3 The effects of varying the process variables of plasma source gas  $\text{Cl}_2 : \text{CH}_4$  ratio;  
4 the source gas flow rate; the process chamber pressure; and the source power on etch  
5 performance variables, including etch endpoint time; etch profile angle; amount of  
6 residue remaining after etching; and etch profile microloading are shown in Figures 4 - 8,  
7 respectively. The general effects of increasing each of the process variables on the  
8 aluminum etch rate; etch profile angle; etch profile microloading; and the amount of  
9 residue remaining after etching are summarized in Table 4, below.

10 Table 4. General Effects of Increasing Various Process Variables  
11 on Aluminum Alloy Etch Results

Process Parameter	Aluminum Alloy Etch Rate	Etch Profile Angle	Etch Profile Microloading	Residue Remaining After Etching
Total Flow	↑	↑	→	↑
$\text{Cl}_2/\text{CH}_4$ Ratio	↑↑	↑↑	↓↓	↑↑
Pressure	↑	↓	↑	↑↑
Source Power	↑	↑↑	↓	↑

17 ↑ = increases; ↑↑ = increases strongly; ↓ = decreases; ↓↓ = decreases strongly;  
18 → = essentially no change.

19 Mean etch endpoint time was used as the indicator of the aluminum alloy etch  
20 rate. The shorter the endpoint time, the faster the etch rate. Figure 4 shows the effects of  
21 increasing the source gas flow rate 402, the  $\text{Cl}_2 : \text{CH}_4$  ratio 404, the process chamber  
22 pressure 406, and the source power 408 on the etch endpoint time. As shown in Figure 4,



1 increasing the  $\text{Cl}_2$  :  $\text{CH}_4$  ratio 404 resulted in a dramatic increase in the aluminum alloy  
2 etch rate (indicated by a decrease in etch endpoint time). Increasing the process chamber  
3 pressure 406 also produced a significant increase in the aluminum alloy etch rate.  
4 Increasing the source gas flow rate 402 and the source power 408 produced more  
5 moderate increases in the aluminum alloy etch rate.

6 Figure 5 shows the effects of increasing the source gas flow rate 502, the  
7  $\text{Cl}_2$  :  $\text{CH}_4$  ratio 504, the process chamber pressure 506, and the source power 508 on the  
8 etch profile angle of an aluminum line sidewall. As shown in Figure 5, increasing the  
9 source power 508 resulted in a dramatic increase in the etch profile angle (*i.e.*, brought  
10 the etch profile angle closer to  $90^\circ$ ). Increasing the  $\text{Cl}_2$  :  $\text{CH}_4$  ratio 504 also produced a  
11 significant increase in the etch profile angle. Increasing the source gas flow rate 502  
12 produced a more moderate increase in the etch profile angle, while increasing the process  
13 chamber pressure 506 decreased the etch profile angle.

14 Figure 6 shows the effects of increasing the source gas flow rate 602, the  
15  $\text{Cl}_2$  :  $\text{CH}_4$  ratio 604, process chamber pressure 606, and the source power 608 on the etch  
16 profile microloading. As shown in Figure 6, increasing the  $\text{Cl}_2$  :  $\text{CH}_4$  ratio 604 resulted  
17 in a dramatic decrease in etch profile microloading. Increasing the source power 608  
18 produced a moderate decrease in etch profile microloading. Increasing the source gas  
19 flow rate 602 had no significant effect on the etch profile microloading.

20 Increasing the process chamber pressure 606 moderately increased the etch  
21 profile microloading. This is thought to be due to increased residence time of the  
22 chlorine gas when higher chamber pressures are used. Chlorine gas etches the aluminum  
23 line sidewall, and an increased residence time results in an increased profile angle. This  
24 effect is observed to a greater extent in isolated lines than in lines located within a dense  
25 array, thereby increasing the etch profile microloading.

1           Figure 7 shows the effects of increasing the source gas flow rate 702, the  
2           Cl<sub>2</sub> : CH<sub>4</sub> ratio 704, the process chamber pressure 706, and the source power 708 on the  
3           amount of residue remaining after etching. The amount of residue remaining after  
4           etching is shown in arbitrary units that were assigned after comparative evaluation of  
5           scanning electron micrographs (SEMs) taken at 20k magnification, where the number of  
6           deposits present on a given surface area were compared and rated on a scale from 1 to  
7           10. Residues remaining after aluminum alloy etch are typically compounds of aluminum  
8           or copper. As shown in Figure 7, increasing the Cl<sub>2</sub> : CH<sub>4</sub> ratio 704 and the process  
9           chamber pressure 706 resulted in significant increases in the amount of residue  
10          remaining after etching. Increasing the source gas flow rate 702 and the source power  
11          678 resulted in modest increases in the amount of residue remaining after etching.

### 12          EXAMPLE THREE:

13                 Experiments were conducted to measure the effects of varying the CH<sub>4</sub> flow rate,  
14                 source power, bias power, and process chamber pressure on the etching of an aluminum  
15                 alloy (0.5% Cu) feature.

16                 This process work was performed in an Applied Materials' System 5084  
17                 prototype etch processing apparatus. The System 5084 had equivalent features to the  
18                 Applied Materials' System 2982 etch processing apparatus shown in Figures 1 and 2.  
19                 The etch chamber included a metal decoupled plasma source (DPS) with a mechanical  
20                 clamp for 150-mm wafer processing.

21                 The following film stack, from top to bottom, was used for this study: 1.4 μm  
22                 i-line photoresist (supplied by TFI of Fremont, CA); 250 Å TiN ARC; 8000 Å Al - 0.5%  
23                 Cu; 1000 Å TiN barrier layer; and approximately 1 μm silicon oxide, on a silicon wafer  
24                 substrate.

1 All substrates were patterned using an i-line photoresist mask having a lines and  
2 spaces pattern, with a feature size of about  $0.6\ \mu\text{m}$  and an aspect ratio of about 2.5 : 1.  
3 The TiN ARC was patterned using a commercially available i-line stepper.

4 After patterning of the photoresist mask, the substrates were baked in a  
5 convection oven at  $110^\circ\text{C}$  for at least one hour prior to etching.

6 The aluminum alloy and the titanium nitride barrier layer were etched using the  
7 following process parameters: 90 sccm  $\text{Cl}_2$ , 0 - 25 sccm  $\text{BCl}_3$ , 0 - 20 sccm  $\text{CH}_4$ , 75 sccm  
8 Ar; 1200 - 1800 W source power; 100 - 160 W bias power; 10 - 15 mT process chamber  
9 pressure; 8 T helium back pressure on the backside of the substrate wafer;  $60^\circ\text{C}$  substrate  
10 temperature and a  $40 - 65^\circ\text{C}$  process chamber wall temperature. Etch endpoint times  
11 were recorded.

12 After etching (with no photoresist stripping), wafers were baked in a convection  
13 oven at  $110^\circ\text{C}$  for at least 8 hours for volatilization of residual chlorine. Half of the  
14 wafers were then stripped of photoresist in a commercially available plasma asher and  
15 dipped in a commercially available solvent at  $65^\circ\text{C}$  for 20 minutes for polymer removal.

16 The unstripped wafers were evaluated for amount of photoresist remaining after  
17 etch. The stripped wafers were evaluated for oxide loss (in open areas and dense arrays),  
18 sidewall surface roughness (*i.e.*, pitting), sidewall profile angle, and amount of residue  
19 remaining after etching. The effects of changes in the  $\text{CH}_4$  flow rate, source power, bias  
20 power, and process chamber pressure on each of the above criteria were analyzed.

21 Figure 8 and Table 5, below, show the effect of increasing the bias power (100,  
22 130, 160 W), while maintaining a fixed source power (1800 W) during etch, on the total  
23 amount of photoresist masking material remaining in the center 802 and at the edge 804  
24 of the wafer after completion of etch. Process parameters for each run were as follows:  
25 90 sccm  $\text{Cl}_2$ , 0 - 25 sccm  $\text{BCl}_3$ , 20 sccm  $\text{CH}_4$ , 75 sccm Ar; 10 mT process chamber

1 pressure; 8 T helium back pressure on the backside of the wafer substrate; 60°C substrate  
 2 temperature; and a 65°C process chamber wall temperature, except for the 100 W bias  
 3 power run, which had a wall temperature of 40°C (previously conducted experiments  
 4 have shown that varying the process chamber temperature has little effect on aluminum  
 5 etch results).

6 Table 5. Effect of Increasing Bias Power on Total Remaining Photoresist

7 Source Power (W)	1800	1800	1800
8 Bias Power (W)	100	130	160
9 Total Photoresist 10 Remaining - Center (Å)	8700	7700	6300
11 Total Photoresist 12 Remaining - Edge (Å)	7700	6800	6000

13 As shown in Figure 8 and Table 5, above, increasing the bias power by only a  
 14 small amount (increments of 30 W) at a fixed source power of 1800 W resulted in a  
 15 dramatic decrease in the total amount of photoresist remaining in the center 802 and at  
 16 the edge 804 of the wafer. By extrapolation of the data presented in Figure 8 and Table  
 17 5, it is clear that, in a processing apparatus in which the power to the plasma generation  
 18 source and to the substrate biasing means are under common control, operation at a  
 19 source power adequate to produce a satisfactory aluminum etch rate would result in rapid  
 20 disappearance of the photoresist masking layer.

21 Increasing the bias power increased oxide loss, while sidewall surface roughness  
 22 was relatively unaffected. Increasing the source power had minimal effect on sidewall  
 23 surface roughness, but did result in overetching of aluminum alloy at the bottom of the  
 24 feature (*i.e.*, sidewall profile angles > 90°), apparently due to increased reactive species  
 25 density.

1 No residue was observed on any of the samples.

2 During the etch process development, the effect of varying the CH<sub>4</sub> flow rate was  
3 evaluated, in terms of the sidewall passivation capability, aluminum alloy etch rate,  
4 residue production; and selectivity toward etching aluminum alloy over photoresist.  
5 Initial results demonstrated that CH<sub>4</sub> can provide sufficient passivation for the sidewalls  
6 of aluminum lines in an anisotropic etch process. However, etch endpoint times  
7 increased by about 23 - 35% (from 54 seconds when no CH<sub>4</sub> was used, to 75 - 90  
8 seconds when 20 sccm CH<sub>4</sub> was used). Increasing the process chamber pressure from 10  
9 to 15 mT decreased the etch endpoint time slightly (to 72 seconds, when 20 sccm CH<sub>4</sub>  
10 was used).

#### 11 EXAMPLE FOUR:

12 Experiments were conducted to measure the effects of varying the plasma source  
13 gas composition, process chamber pressure, and bias power on the etching of an  
14 aluminum alloy (1% Cu) feature. The same general process described in Example Three  
15 for etching of aluminum alloy (0.5% Cu) features was used.

16 The following film stack, from top to bottom, was used for this study: 1.4 μm  
17 i-line photoresist (supplied by TFI of Fremont, CA); 250 Å TiN ARC; 8000 Å Al - 1%  
18 Cu; 1000 Å TiN barrier layer; and approximately 1 μm silicon oxide, on a silicon wafer  
19 substrate.

20 All substrates were patterned using an i-line photoresist mask having a lines and  
21 spaces pattern, with a feature size of about 0.4 μm and an aspect ratio of about 2.5 : 1.  
22 The TiN ARC was patterned using a commercially available i-line stepper.

1 Etching was performed using the Applied Materials' System 5084 prototype etch  
 2 processing apparatus described in Example Three, above. The aluminum alloy and the  
 3 titanium nitride barrier layer were etched using the following process parameters:  
 4 90 - 100 sccm Cl<sub>2</sub>, 25 sccm BCl<sub>3</sub>, 10 - 20 sccm CH<sub>4</sub>, 0 - 75 sccm Ar; 1500 W source  
 5 power; 75 - 100 W bias power; 10 - 15 mT process chamber pressure; 8 T helium back  
 6 pressure on the backside of the substrate wafer; 60°C substrate temperature; and a  
 7 65°C process chamber wall temperature. Etch endpoint times were recorded.

8 The effects of varying the plasma source gas composition, process chamber  
 9 pressure, and bias power on the etch endpoint time and the amount of residue remaining  
 10 after etch were analyzed. (No residue had been observed on the 0.5% Cu features after  
 11 etching.) The results are presented in Table 6 and discussed below.

12 Table 6. Effects of Varying Aluminum Alloy Etch Process Parameters  
 13 on Residue Control and Etch Endpoint Time

14 Cl <sub>2</sub> (sccm)	90	90	90	100
15 BCl <sub>3</sub> (sccm)	25	25	25	25
16 CH <sub>4</sub> (sccm)	20	20	20	10
17 Ar (sccm)	75	0	75	40
18 Pressure (mT)	10	10	15	10
19 Bias Power (W)	100	100	100	75
20 Etch Endpoint 21 Time (s)	100	82	78	65
22 Residue - Center	No	Yes (open surfaces)	Yes (open surfaces)	Yes (all surfaces)
23 Residue - Edge	No	Yes (open surfaces)	Yes (open surfaces)	Yes (all surfaces)

1           The effect of increasing the process chamber pressure from 10 to 15 mT on the  
2 aluminum etch rate was investigated. Although the endpoint times decreased 18 - 22%,  
3 some residue was seen in the open area surfaces of the wafer.

4           The contribution of argon to the aluminum etch rate and residue control was  
5 investigated. When argon was omitted from the plasma source gas composition, the  
6 aluminum etch rate increased, but some residue was observed in the open area surfaces  
7 of the wafer. The presence of argon provided increased surface bombardment with  
8 excited argon species, which provided a surface cleaning action

9           While simultaneously increasing the flow rate of  $\text{Cl}_2$  (from 90 sccm to 100 sccm),  
10 decreasing the flow rates of  $\text{CH}_4$  (from 20 sccm to 10 sccm) and argon (from 75 sccm to  
11 40 sccm), and decreasing the bias power (from 100 W to 75 W) resulted in a 35%  
12 decrease in endpoint time, residue was observed on all areas of the surface.

13           In summary, the results of the experiments described in Examples Three and  
14 Four, above, showed that  $\text{CH}_4$  can be used to passivate sidewalls of etched aluminum  
15 alloy features at the expense of decreased, but still acceptable, aluminum alloy etch rates.  
16 Increased plasma source powers (1200  $\rightarrow$  1800 W) resulted in overetching of aluminum  
17 at the bottom of the feature (*i.e.*, sidewall profile angles  $> 90^\circ$ ). Higher bias powers  
18 (100  $\rightarrow$  160 W) significantly shortened the lifetime of photoresist masking layers, while  
19 increasing etch rate microloading. Higher process chamber pressures (10  $\rightarrow$  15 mT)  
20 increased substrate etch rates in general. Higher process chamber pressures also resulted  
21 in increased residue (typically copper compounds) being deposited on aluminum alloy  
22 (1% Cu) feature surfaces. The presence of argon in the plasma source gas was  
23 demonstrated to assist in residue removal from etched aluminum alloy feature surfaces.

1           EXAMPLE FIVE:

2           A ten run designed experiment (1/2 replicate of four factors in eight experiments,  
3 plus two centerpoint runs), which varied the flow rates of CH<sub>4</sub>, Cl<sub>2</sub>, BCl<sub>3</sub>, and Ar was  
4 conducted to investigate the main effects of gas flows on the etching of aluminum alloy  
5 (1% Cu) features. The main effects on aluminum alloy etch caused by varying the flow  
6 rate of each gas were clear; however, the interactions between the various gases were  
7 unclear.

8           Two centerpoint runs were included for a total of ten wafer runs. The centerpoint  
9 recipe was selected based on the one-dimensional experiments on aluminum alloy (0.5%  
10 Cu) features described in Example Three, above. The factors and levels used in this  
11 experiment are set forth in Table 7, below.

12                               Table 7. Factors and Levels for Two-level Experiment  
13                               on Aluminum Alloy (1% Cu) Features

Factor	Cl <sub>2</sub> Flow (sccm)	BCl <sub>3</sub> Flow (sccm)	Ar Flow (sccm)	CH <sub>4</sub> Flow (sccm)
Low	70	15	40	10
Center	90	30	70	15
High	110	45	100	20

18           The following film stack, from top to bottom, was used for this study: 1.4 μm  
19 i-line photoresist (supplied by TFI of Fremont, CA); 250 Å TiN ARC; 8000 Å Al - 1%  
20 Cu; 1000 Å TiN barrier layer; and approximately 1 μm silicon oxide, on a silicon wafer  
21 substrate.



1 All substrates were patterned using an i-line photoresist mask having a lines and  
 2 spaces pattern, with a feature size of about  $0.4 \mu\text{m}$  and an aspect ratio of about 2.5 : 1.  
 3 The TiN ARC was patterned using a commercially available i-line stepper.

4 Etching was performed using the Applied Materials' System 5084 prototype etch  
 5 processing apparatus described in Example Three, above. The aluminum alloy and the  
 6 titanium nitride barrier layer were etched using the following process parameters:  
 7 12 mT process chamber pressure; 1500 W source power; 100 W bias power; 8 T helium  
 8 back pressure on the backside of the substrate wafer;  $60^\circ\text{C}$  cathode temperature; and a  
 9  $65^\circ\text{C}$  process chamber wall temperature,.

10 Curves showing the effects of varying the flow rates of  $\text{CH}_4$ ,  $\text{Cl}_2$ ,  $\text{BCl}_3$ , and Ar on  
 11 the aluminum alloy etch endpoint time, the amount of residue remaining after etching,  
 12 and the photoresist etch rate are provided in Figures 9 - 11, respectively. The main  
 13 effects of increasing the flow rate of each gas on the etch results are summarized in Table  
 14 8, below.

15 Table 8. Main Effects of Increasing the Flow Rates of Various Etchant Gases  
 16 on Aluminum Alloy Etch Results

Gas	Aluminum Alloy Etch Rate	Residue Remaining After Etching	Photoresist Etch Rate
$\text{Cl}_2$	↑↑	↑↑	↑↑
$\text{BCl}_3$	↓	↓	↓
Ar	↓	↓	↓
$\text{CH}_4$	↓↓	↓	↓↓

22 ↑ = increases; ↑↑ = increases strongly; ↓ = decreases; ↓↓ = decreases strongly.

1           Figure 9 shows the effects of varying the Cl<sub>2</sub> flow rate 902, BCl<sub>3</sub> flow rate 904,  
2           Ar flow rate 906, and CH<sub>4</sub> flow rate 908 on the aluminum alloy etch endpoint time. As  
3           shown in Figure 9, increasing the Cl<sub>2</sub> flow rate (represented by reference numeral 902)  
4           resulted in a dramatic increase in the aluminum alloy etch rate (indicated by a decrease in  
5           etch endpoint time). Increasing the CH<sub>4</sub> flow rate 908 resulted in a significant decrease  
6           in the aluminum alloy etch rate. Increasing the Ar flow rate 906 resulted in a moderate  
7           decrease in the aluminum alloy etch rate. Increasing the BCl<sub>3</sub> flow rate 904 resulted in a  
8           modest decrease in the aluminum alloy etch rate.

9           Figure 10 shows the effects of varying the Cl<sub>2</sub> flow rate 1002, BCl<sub>3</sub> flow rate  
10          1004, Ar flow rate 1006, and CH<sub>4</sub> flow rate 1008 on the amount of residue remaining  
11          after etching. Residue was quantified by counting the number of deposits observed in an  
12          area of approximately 2 μm<sup>2</sup> as shown on an SEM taken at 20k magnification. As shown  
13          in Figure 10, increasing the Cl<sub>2</sub> flow rate 1002 resulted in a dramatic increase in the  
14          amount of residue remaining after etching. This is thought to be due to increased  
15          aluminum etch rates with higher Cl<sub>2</sub> flows. Because the chlorine - aluminum product  
16          compounds are so much more volatile than the chlorine - copper etch product  
17          compounds, if the aluminum alloy etch rate is particularly high, an increased amount of  
18          copper-containing residue remains after the aluminum alloy feature is completely etched.

19          Increasing the CH<sub>4</sub> flow rate 1008 and BCl<sub>3</sub> flow rate 1004 resulted in a  
20          significant decrease in the amount of residue remaining after etching. Increasing the Ar  
21          flow rate 1006 resulted in a moderate decrease in the amount of residue remaining after  
22          etching, and SEM micrographs visually verified the importance of Ar in controlling  
23          residue. (The necessity of argon addition was previously demonstrated in the experiment  
24          described in Example Four, above). No residue was observed at the edge of the wafer in  
25          any of the runs.

1           Figure 11 shows the effects of varying the Cl<sub>2</sub> flow rate 1102, BCl<sub>3</sub> flow rate  
2           1104, Ar flow rate 1106, and CH<sub>4</sub> flow rate 1108 on the photoresist etch rate. As shown  
3           in Figure 11, increasing the Cl<sub>2</sub> flow rate 1102 resulted in a dramatic increase in the  
4           photoresist etch rate. Increasing the CH<sub>4</sub> flow rate 1108 resulted in a dramatic decrease  
5           in the photoresist etch rate. Increasing the Ar flow rate 1106 also resulted in a significant  
6           decrease in the photoresist etch rate. Increasing the BCl<sub>3</sub> flow rate 1104 resulted in a  
7           moderate decrease in the photoresist etch rate. The reduction in the photoresist etch rate  
8           observed with increased flow rates of CH<sub>4</sub>, Ar, and BCl<sub>3</sub> is likely due to the dilution of  
9           chlorine in the gas mixture.

10           In general, sidewall roughness improved (*i.e.*, sidewall surface was less pitted)  
11           with increased CH<sub>4</sub> flow. The effectiveness of CH<sub>4</sub> for sidewall passivation is more  
12           pronounced during high Cl<sub>2</sub> flow processes, since a greater degree of sidewall attack is  
13           likely to occur due to increased chlorine in the plasma.

14           No profile trends were observed in this experiment.

15           In conclusion, CH<sub>4</sub> provided sufficient sidewall passivation to prevent pitting  
16           without producing residues on the etched feature surfaces. CH<sub>4</sub> addition reduces the  
17           aluminum etch endpoint top times by about 23 - 35%; however, acceptable aluminum  
18           alloy etch rates of at least 8,000 Å per minute can still be obtained. Increasing bias  
19           powers led to increased photoresist etch rates; however, a bias power of less than about -  
20           200 V (preferably ranging from about - 50 V to about - 150 V) was generally found to be  
21           acceptable. Higher plasma source powers generally resulted in slightly greater overetch  
22           of aluminum at the bottom of the feature (which were indicated by undercut or retrograde  
23           etch profile angles of > 90°). Acceptable plasma source powers ranged from about  
24           300 W to about 2000 W; preferably, about 800 W to about 1600 W; most preferably,  
25           about 800 W to about 1200 W. Lower process chamber pressures (5 - 50 mT; preferably,

1 5 - 25 mT; most preferably, 8 - 12 mT) were required for residue control. Argon was  
2 also necessary for residue control. Preferred argon content of the plasma source gas  
3 ranges from about 20 to about 200 sccm. Increasing the Cl<sub>2</sub> flow rate resulted in  
4 significant increases in the aluminum alloy etch rate, photoresist etch rate, and the  
5 amount of residue remaining after etching. Preferred Cl<sub>2</sub> content of the plasma source  
6 gas ranges from about 50 sccm to about 200 sccm. Preferred overall flow rate of the  
7 plasma source gas ranges from about 50 sccm to about 350 sccm.

8 Overall, a residue-free etch process was developed for aluminum alloy etching  
9 which avoided pitting of the etched alloy surface by the addition of a hydrocarbon to the  
10 process chamber during etching.

11 The present invention provides a method for anisotropic etching of aluminum and  
12 aluminum alloys which provides an acceptable etch rate and good etch profile angle,  
13 without disappearance of the mask layer, while providing an essentially residue-free  
14 etched surface.

15 The method of the invention is particularly useful for etching aluminum alloys  
16 having high (*i.e.*, greater than about 0.5%) alloy content.

17 The method of the invention is also especially useful for essentially residue-free  
18 etching of aluminum or aluminum alloy layers deposited on substrates having large open  
19 areas (*i.e.*, where open areas comprise greater than about 65% of the surface area of the  
20 wafer).

21 The above described preferred embodiments are not intended to limit the scope of  
22 the present invention, as one skilled in the art can, in view of the present disclosure,  
23 expand such embodiments to correspond with the subject matter of the invention claimed  
24 below.

## CLAIMS

We claim:

- 1           1.       A method for essentially residue-free anisotropic etching of aluminum or of an  
2 aluminum alloy, wherein said method comprises etching said aluminum or said  
3 aluminum alloy using a plasma generated from a plasma source gas comprising a  
4 chlorine-comprising gas and a hydrocarbon-comprising gas, and wherein etching takes  
5 place in a processing apparatus which provides for separate power control of a plasma  
6 generation source and a substrate biasing means.
  
- 1           2.       The method of Claim 1, wherein said chlorine-comprising gas is selected from  
2 the group consisting of  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{BCl}_3$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CHCl}_2\text{F}$ , and  
3 combinations thereof.
  
- 1           3.       The method of Claim 2, wherein said chlorine-comprising gas does not comprise  
2 fluorine.
  
- 1           4.       The method of Claim 3, wherein said chlorine-comprising gas is  $\text{Cl}_2$ .
  
- 1           5.       The method of Claim 1, wherein said hydrocarbon-comprising gas has the  
2 chemical formula  $\text{C}_x\text{H}_y$ , where  $x$  ranges from about 1 to about 5, and  $y$  ranges from about  
3 1 to about 12.
  
- 1           6.       The method of Claim 5, wherein  $x$  ranges from 1 to 3, and  $y$  ranges from 1 to 6.

- 1           7.       The method of Claim 6, wherein said hydrocarbon gas is CH<sub>4</sub>.
- 1           8.       The method of Claim 1, wherein the atomic ratio of chlorine : carbon in said  
2 plasma source gas ranges from about 5 : 1 to about 200 : 1.
- 1           9.       The method of Claim 8, wherein the atomic ratio of chlorine : carbon in said  
2 plasma source gas ranges from about 10 : 1 to about 20 : 1, and the atomic ratio of  
3 hydrogen : carbon in said hydrocarbon ranges from about 1 : 1 to about 4 : 1.
- 1           10.      The method of Claim 1, wherein said plasma source gas further comprises an  
2 additive gas selected from the group consisting of BCl<sub>3</sub>, N<sub>2</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>4</sub>F<sub>8</sub>, CHF<sub>3</sub>,  
3 CH<sub>2</sub>F<sub>2</sub>, CHCl<sub>3</sub>, CHCl<sub>2</sub>F, CCl<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>, CBrF<sub>3</sub>, CBr<sub>2</sub>F<sub>2</sub>, O<sub>2</sub>, and combinations thereof.
- 1           11.      The method of Claim 10, wherein said additive gas does not comprise oxygen.
- 1           12.      The method of Claim 11, wherein said additive gas is BCl<sub>3</sub>.
- 1           13.      The method of Claim 1, wherein said plasma source gas further comprises a non-  
2 reactive, diluent gas selected from the group consisting of argon, helium, xenon, krypton,  
3 and combinations thereof.
- 1           14.      The method of Claim 13, wherein said non-reactive, diluent gas is argon.
- 1           15.      The method of Claim 1, wherein the electron density of said plasma is at least  
2 10<sup>11</sup> e/cm<sup>3</sup>.

1           16.    The method of Claim 15, wherein the electron density of said plasma ranges from  
2           about  $10^{11}$  e/cm<sup>3</sup> to about  $10^{12}$  e/cm<sup>3</sup>.

1           17.    The method of Claim 1, wherein the substrate bias is less than about - 200 V.

1           18.    The method of Claim 17, wherein the substrate bias ranges from about - 50 V to  
2           about - 150 V.

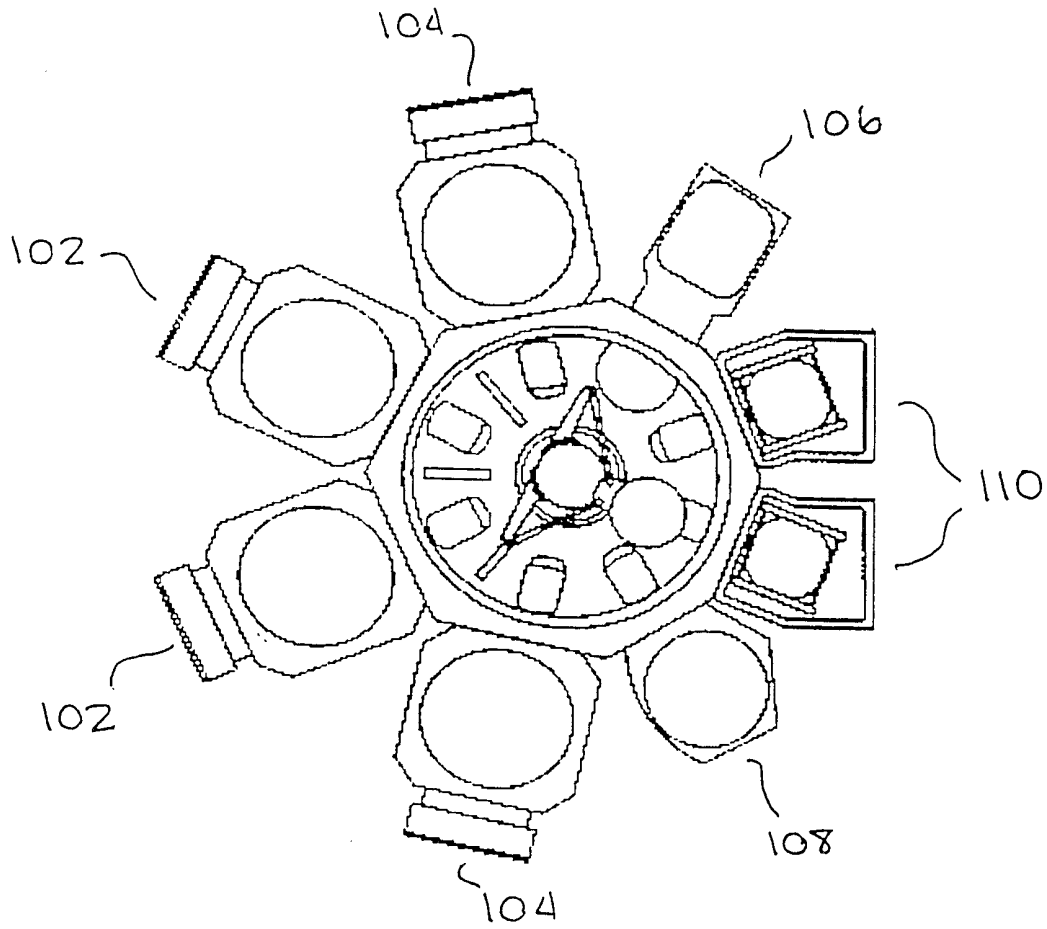


Figure 1  
(PRIOR ART)



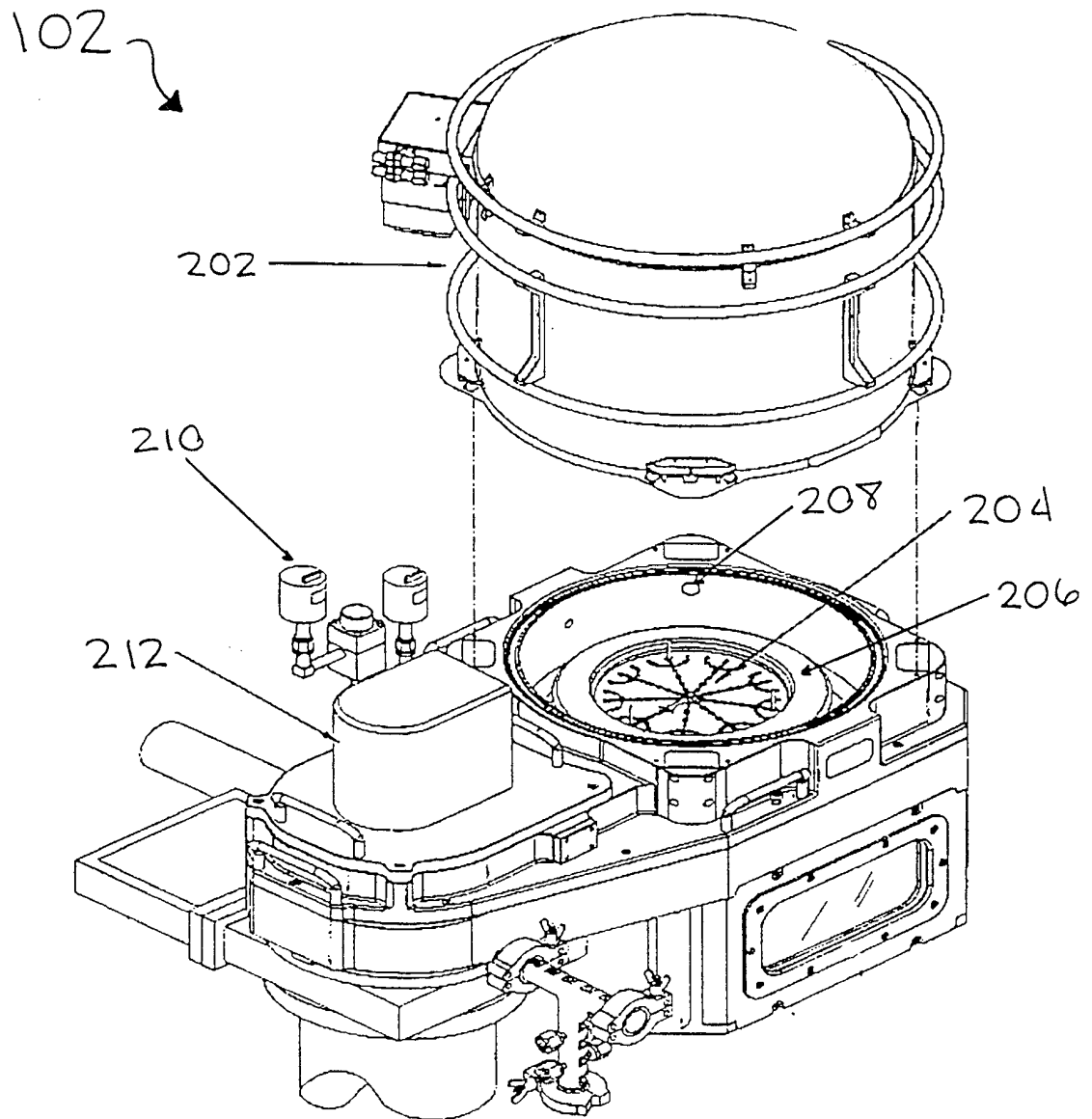


Figure 2a  
(PRIOR ART)

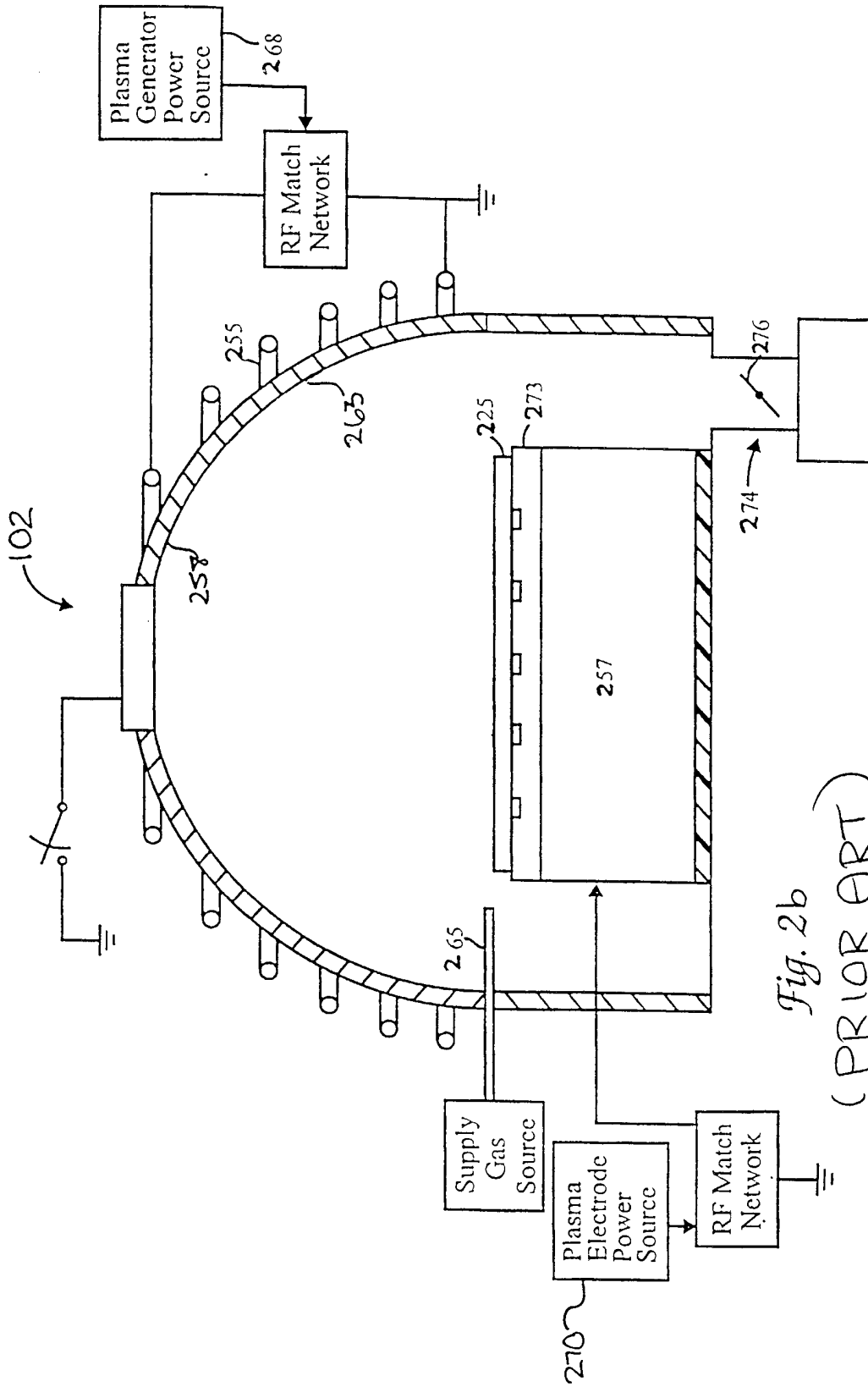


Fig. 2b  
(PRIOR ART)

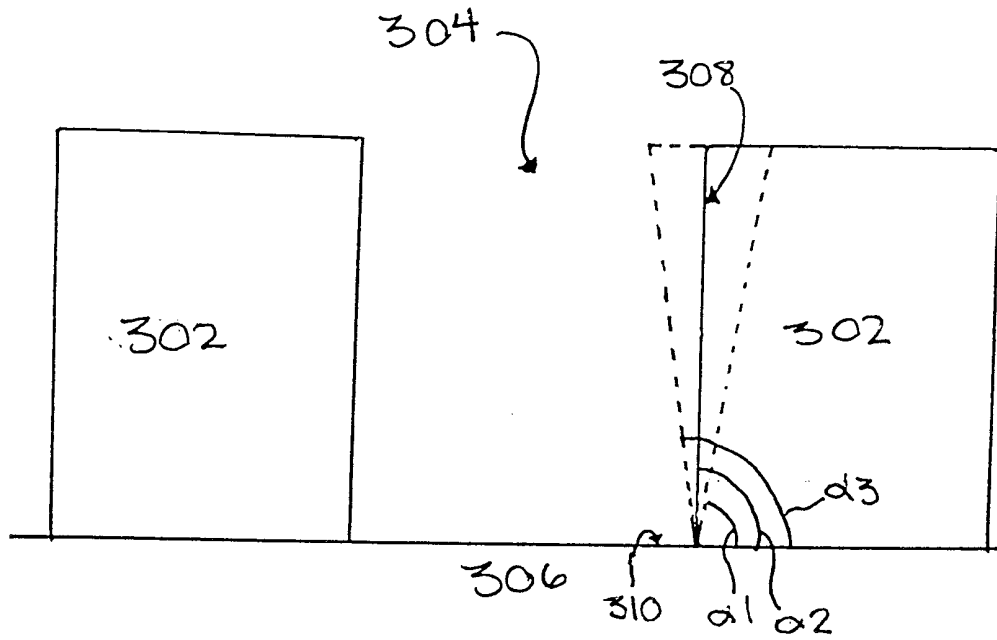
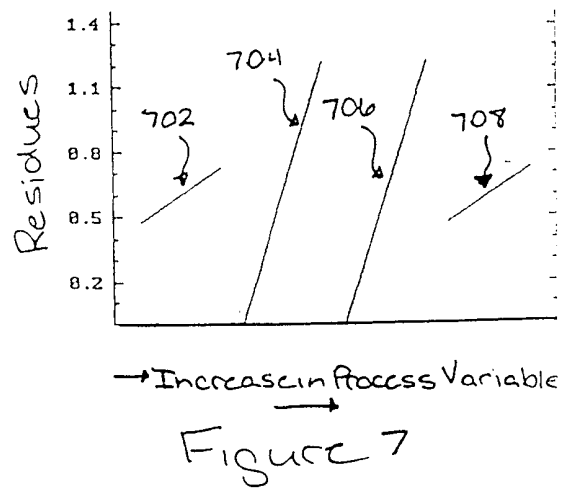
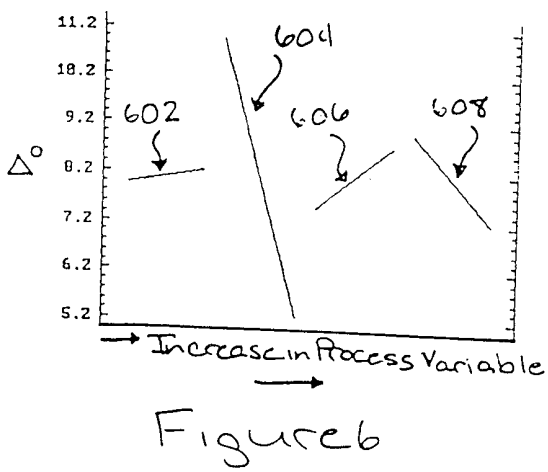
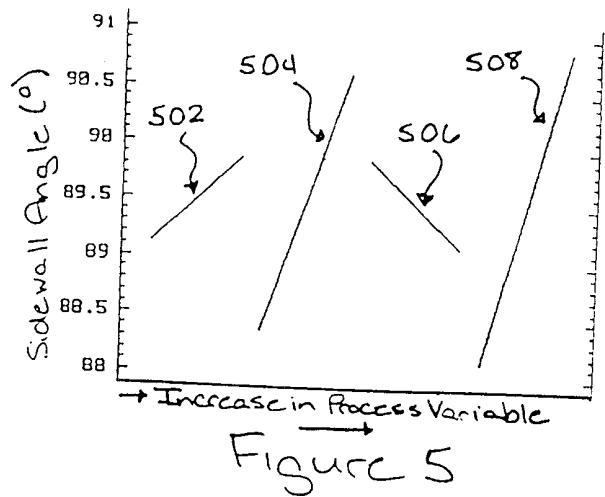
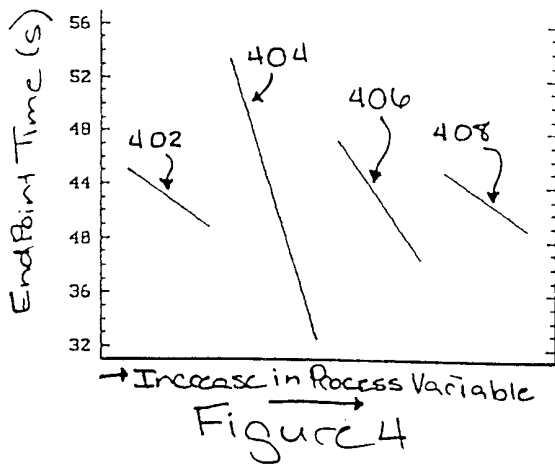


Figure 3



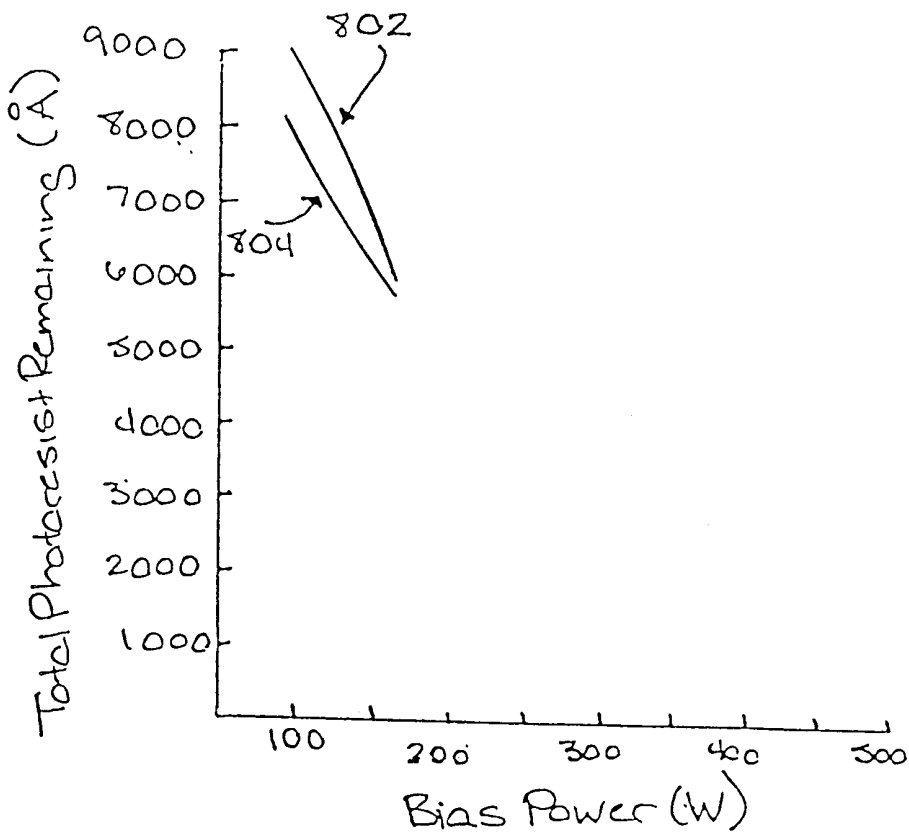


Figure 8

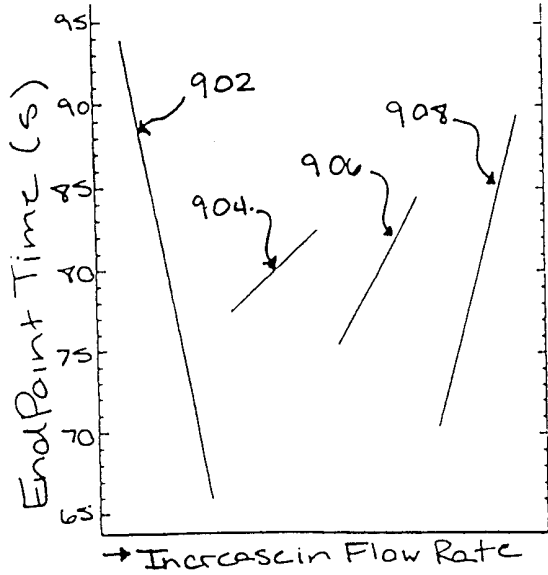


Figure 9

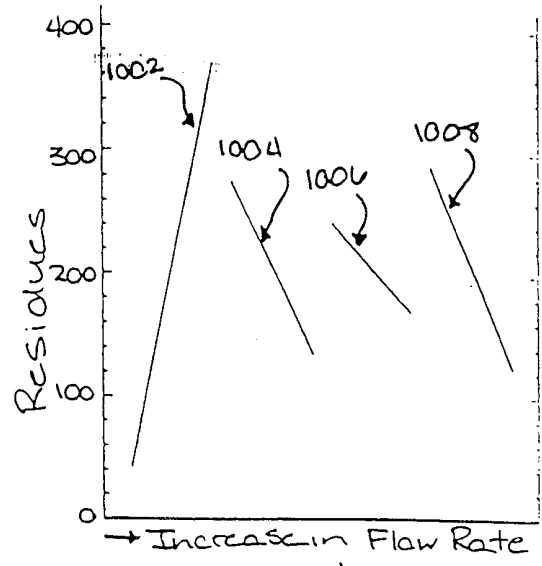


Figure 10

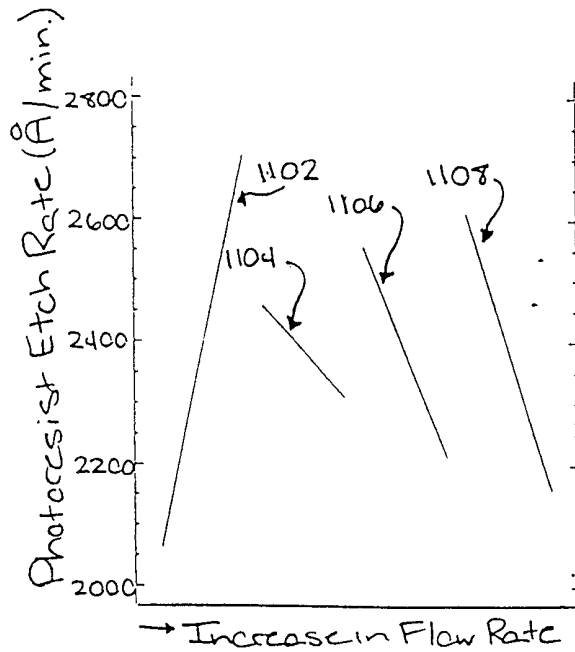


Figure 11



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/26267

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Y YE ET AL: "0.35 MICRON AND SUB-0.035 MICRON METAL STACK ETCH IN A DPS CHAMBER - DPS CHAMBER AND PROCESS CHARACTERIZATION" ELECTROCHEMICAL SOCIETY PROCEEDINGS, vol. 96, no. 12, 5 May 1996 (1996-05-05), pages 222-233, XP002096578 Pennington (US) cited in the application page 231 -page 232	1-14
A	US 4 618 398 A (NISHIUMI MASAHARU ET AL) 21 October 1986 (1986-10-21) cited in the application column 2; claims 1,2	1-12
A	US 4 372 807 A (HALON BERNARD ET AL) 8 February 1983 (1983-02-08) example 1	1-12
A	LUTZE J W ET AL: "ANISOTROPIC REACTIVE ION ETCHING OF ALUMINUM USING Cl <sub>2</sub> , BCl <sub>3</sub> , AND CH <sub>4</sub> GASES" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, US, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, vol. 137, no. 1, 1 January 1990 (1990-01-01), pages 249-252, XP000133077 ISSN: 0013-4651	1-9, 17, 18
A	WO 97 36322 A (LAM RES CORP) 2 October 1997 (1997-10-02) claim 1; figure 3	1
A	US 5 277 757 A (SATO JUNICHI) 11 January 1994 (1994-01-11) column 4, line 1-9	1
A	GB 2 137 143 A (LFE CORP) 3 October 1984 (1984-10-03) table 1	1
A	US 4 844 767 A (OKUDAIRA SADAYUKI ET AL) 4 July 1989 (1989-07-04) claims 1,6	1
A	US 5 779 926 A (TAJIMA DAISUKE ET AL) 14 July 1998 (1998-07-14) cited in the application figure 2; example 1	1
A	US 5 277 750 A (FRANK WOLFGANG) 11 January 1994 (1994-01-11) cited in the application	



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/26267

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0779651	A	18-06-1997	JP 9102484 A JP 9293725 A	15-04-1997 11-11-1997
DE 4317722	A	01-12-1994	US 5480051 A	02-01-1996
US 4618398	A	21-10-1986	JP 1878538 C JP 5087972 B JP 60169140 A KR 9000440 B	07-10-1994 20-12-1993 02-09-1985 30-01-1990
US 4372807	A	08-02-1983	NONE	
WO 9736322	A	02-10-1997	NONE	
US 5277757	A	11-01-1994	JP 4288828 A	13-10-1992
GB 2137143	A	03-10-1984	US 4505782 A DE 3410023 A FR 2543166 A IE 55419 B JP 59229821 A NL 8400937 A	19-03-1985 27-09-1984 28-09-1984 12-09-1990 24-12-1984 16-10-1985
US 4844767	A	04-07-1989	JP 2603217 B JP 62014429 A	23-04-1997 23-01-1987
US 5779926	A	14-07-1998	US 5777289 A US 5753044 A US 5783101 A EP 0788147 A JP 10032191 A EP 0788138 A JP 10027785 A AT 184729 T DE 69604212 D DE 69604212 T EP 0727807 A JP 8321490 A DE 69513758 D EP 0702391 A JP 8172082 A	07-07-1998 19-05-1998 21-07-1998 06-08-1997 03-02-1998 06-08-1997 27-01-1998 15-10-1999 21-10-1999 23-03-2000 21-08-1996 03-12-1998 13-01-2000 20-03-1996 02-07-1996
US 5277750	A	11-01-1994	DE 4107006 A EP 0502523 A FR 2673764 A	10-09-1992 09-09-1992 11-09-1992