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[54] **PROCESS AND MATERIAL FOR MANUFACTURING SEMICONDUCTOR DEVICES**

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Related U.S. Patent Documents

Reissue of:
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[52] **U.S. Cl.** .... **156/643;** 156/646; 156/659.1; 204/192 E; 252/79.1

[58] **Field of Search** .... 156/643, 646, 657, 659, 156/662, 659.1; 252/79.1; 204/192 E, 192 EC, 298, 164, 165, 168, 169, 170; 250/531; 219/121 P

[56] **References Cited**

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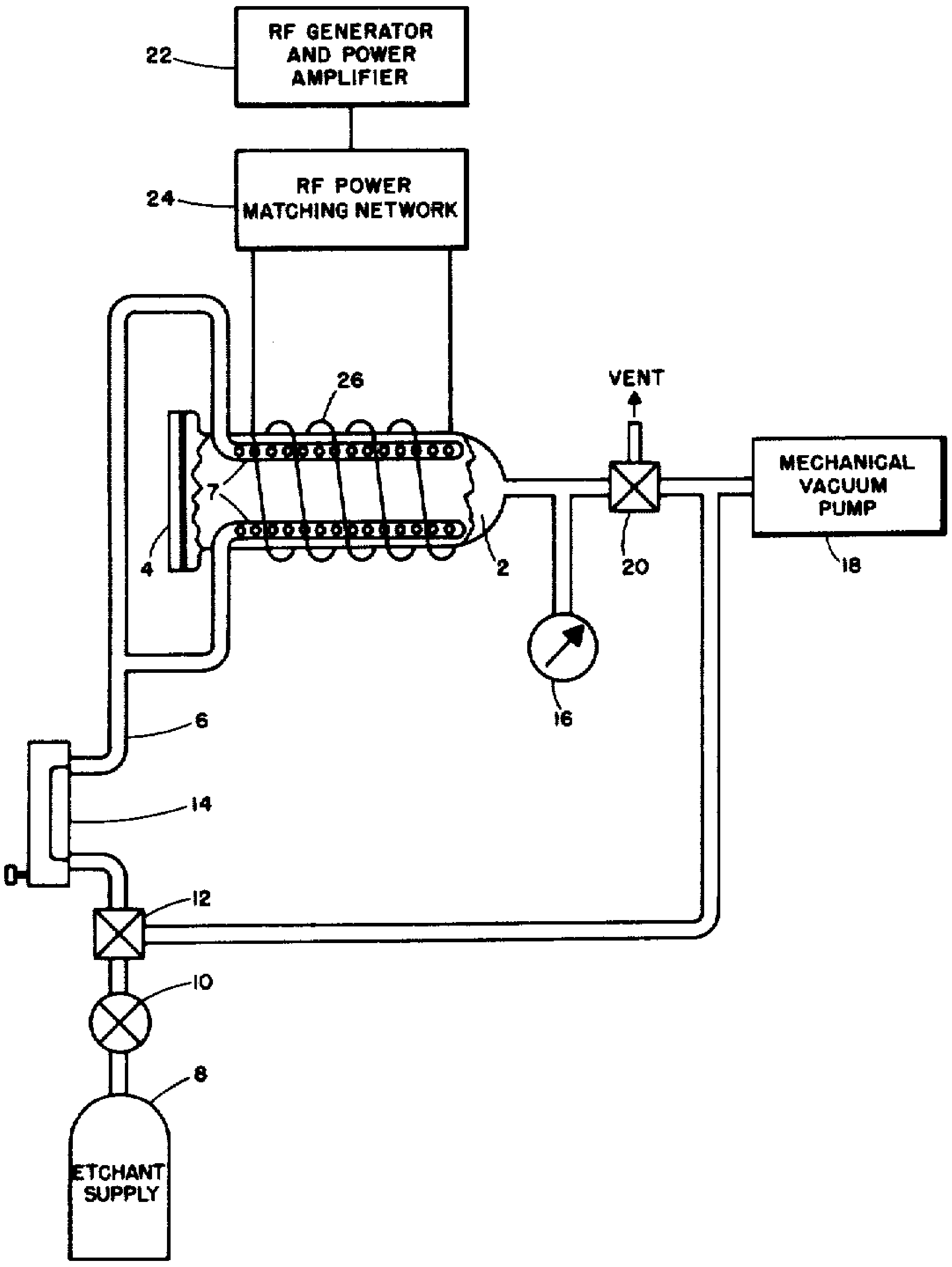
[57] **ABSTRACT**

A process step and material for use in the manufacture of semiconductor devices. To facilitate the etching of unmasked silicon dioxide, silicon nitride, silicon monoxide, bare silicon layers, or various refractory metals on preselected portions of a semiconductor slice, the material is exposed to a low pressure RF generated "cold" plasma (under 325° C.) produced from a homogeneous gaseous binary mixture of oxygen and a halocarbon. The halocarbon is preferably a gas having one carbon atom per molecule and is preferably fully fluorine-substituted.

11 Claims, 2 Drawing Figures



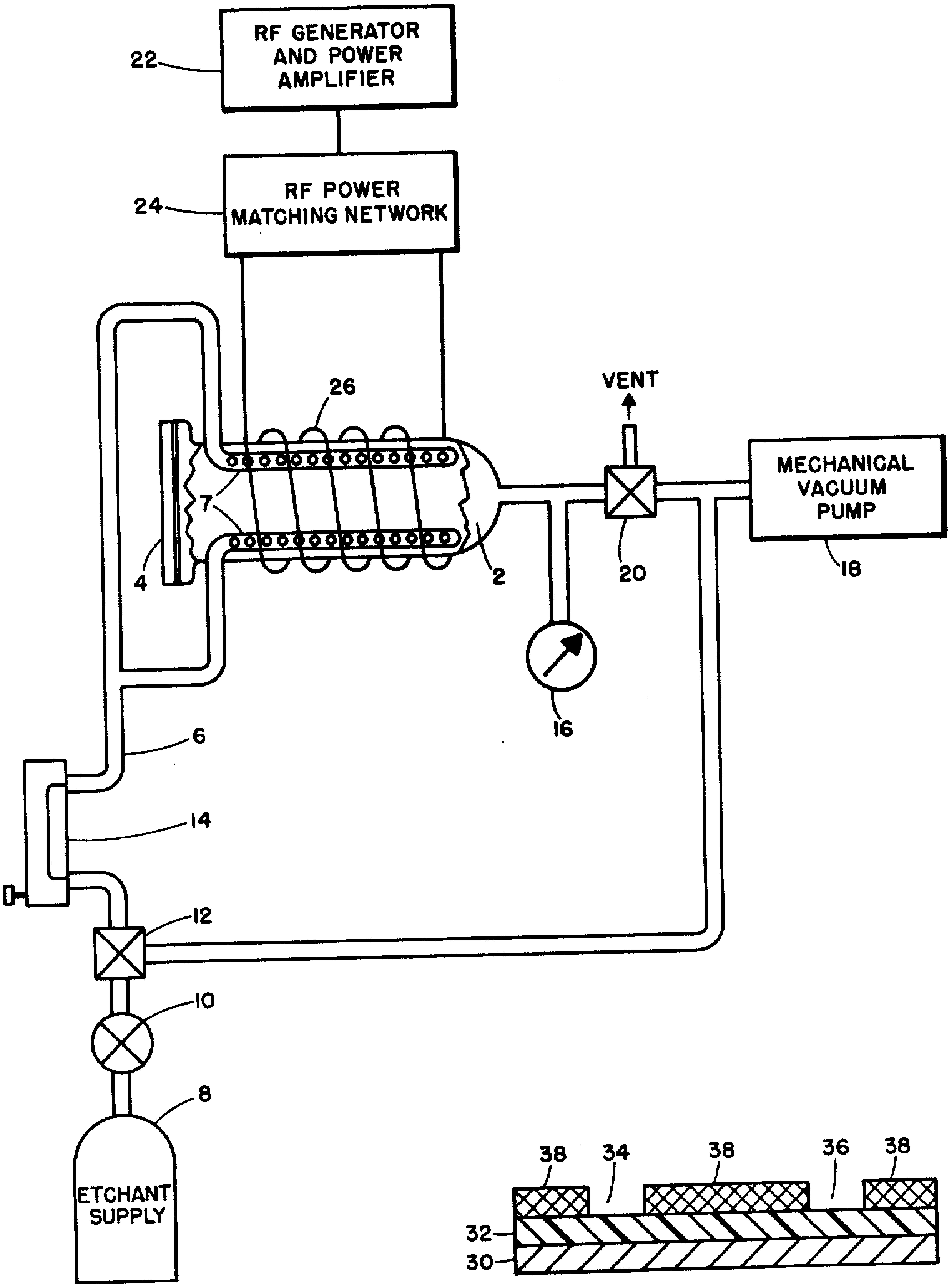


FIGURE 1

FIGURE 2

PROCESS AND MATERIAL FOR MANUFACTURING SEMICONDUCTOR DEVICES

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

FIELD OF THE INVENTION

This invention relates in general to a process and material useful in analytical procedures, and more particularly to a process and material useful in the manufacture of semiconductor devices, enabling the etching of various metals (molybdenum, tungsten, tantalum, etc.) and common passivation or diffusion barrier materials (e.g., SiO, SiO_2, Si_3N_4) during the processing of such devices.

BACKGROUND OF THE INVENTION

In the conventional technique for the manufacture of semiconductor devices, a slice of semiconductor material (p- or n-type) accepts a relatively thin layer, typically 5,000 to 10,000 A., of an insulating film grown or deposited on one or both of its surfaces. A layer of photoresist material is then spun onto the insulating layer of one side, and is subsequently exposed to UV light through a mask having openings corresponding to those areas on the semiconductor slice where it is desired to generate semiconductor junctions. After exposure of the photoresist material through the mask, the mask is removed and the layer of photoresist is developed and processed by means of a suitable solvent, exposing select areas of the underlying insulating layer. A wet acid-based dip is then used to etch the insulating layer from the surface of the semiconductor slice in the exposed areas, the remaining photoresist material serving as an etch-mask for the surface covered by it. Following the wet etching process, a water rinse and a drying step are implemented. The remainder of the photoresist material is subsequently removed, followed by an acid dip required for the removal of inorganic residues. The photoresist material can also be removed by a plasma process utilizing the halocarbon-oxygen gaseous mixtures disclosed by the present inventor in his U.S. Pat. application, Ser. No. 173,537, filed Aug. 20, 1971. Following a further drying step, diffusion of dopant material into the exposed areas of the semiconductor slice (where there is no insulating layer) is commenced to produce a predetermined junction.

Among the problems and drawbacks associated with the etching step used in this particular technique are:

(1) Physical degradation of a photoresist etch mask.
(2) Finite chemical degradation of a metallic etch mask.
(3) Impairment of line-line resolution due to (1) and/or (2).
(4) Enhanced undercutting effects creating undesirable slopes of the etched channel.
(5) Severe chemical degradation (corrosion) of underlying metalization layers; e.g., aluminum in multileveled structures.
(6) Slow and technically elaborate etching of silicon monoxide and silicon nitride.
(7) Required post-etch water rinse and drying steps invariably reducing production yields.
(8) Short shelf-life of etching solution due to inevitable contamination.
(9) Generally very hazardous to personnel and undesirably polluting.

Accordingly, the general object of the present invention is to provide an improved process and new material that overcome the aforementioned problems and provide uniform etching reactions at a rapid rate.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a gas discharge flow apparatus adapted to form a gaseous plasma within a reaction chamber. It has been discovered that if the generated plasma comprises reactive species resulting from the decomposition and excitation of a gaseous binary mixture of oxygen and a halocarbon that includes flourine as a major substituent, passivation layers or diffusion barriers (e.g., SiO, SiO_2, Si_3N_4) can be etched in excess of 3000 A./min. without degradation of an organic photoresist etch mask. Polycrystalline and single crystals of silicon, and a variety of metals (e.g., molybdenum, tantalum, tungsten, etc.) can be etched in excess of 2000 A./min. under similar conditions. While the above etch rates are commensurate with the preservation of an organic photoresist etch mask in this chemically hostile environment, appreciably higher etch rates can be achieved with the utilization of metallic etch masks (e.g., aluminum, gold, etc.). Metallic etch masks are normally attacked by aqueous acidic etch solutions currently in use; however, they are chemically inert to the etching plasma disclosed herein.

DESCRIPTION OF THE DRAWING

In the drawing:

FIG. **1** is an illustration in diagrammatic form of a gas discharge flow system useful in the process of this invention; and

FIG. **2** is an illustration in cross-sectional view of a typical semiconductor slice at an intermediate stage of the manufacturing process.

DESCRIPTION OF PREFERRED EMBODIMENT

FIG. **1** depicts diagrammatically an apparatus performing the process described in the invention. The apparatus includes a reactor chamber **2**, typically made of quartz, having a cover **4** and a gas inlet manifold **6**. The side of the reactor **2** has been partially broken away in the drawing so as to better illustrate the gas diffusion tubes **7** which are disposed therein and are externally connected to manifold **6**. Such a reactor is disclosed in U.S. Pat. No. 3,619,403, issued on Nov. 9, 1971, and assigned to LFE Corporation.

A pressurized supply **8** of a binary gaseous mixture comprised of oxygen and a halocarbon gas described below is connected through a pressure regulating valve **10**, a three-way solenoid valve **12**, and a flowmeter **14** to manifold **6**. A vacuum gauge **16** provides an indication of total reaction pressure in reactor **2**. At any time, and prior to introduction of the gas mixture to manifold **6**, the corresponding flow lines are constantly evacuated through the three-way solenoid valve **12** leading to the mechanical vacuum pump **18**, this being the case also under conditions where air at atmospheric pressure prevails in reactor **2** through the utilization of the three-way isolation valve **20**. A source of radio frequency power **22** provides exciting energy through a matching network **24** to coil **26** which surrounds reaction chamber **2**. Preferably, inductor **26** consists of a multiturn coil having two coil sections whose respective coil turns are wound in opposite directions, as disclosed in U.S. Pat.

application Ser. No. 186,739, filed on Oct. 5, 1971, now U.S. Pat. No. 3,705,091, and assigned to LFE Corporation. Although the binary gaseous mixture is preferably premixed and supplied to the reactor from a single container **8**, it will be apparent that the oxygen and halocarbon gases may, if desired, be supplied from separate sources via separate flow lines and mixed within either manifold **6** or reactor **2**. In operation, the gaseous mixture is admitted to reaction chamber **2** where the inductively coupled radio frequency energy creates a "cold" plasma. Such a reaction system is commercially available from the Process Control Division of LFE Corporation, under the trade designation PDE-301 or PDE-504. Typically, the RF power employed is between 175 and 225 watts continuous radiation at 13.5 mHz.

The general process is one in which as many as 25 semi-conductor wafers at an appropriate stage of the manufacturing process are placed in reactor **2** and exposed to the plasma generated by the admission of an appropriate gaseous mixture of oxygen and a halocarbon gas. For the appropriate reactions to take place, the reaction chamber is evacuated to a residual pressure of 20 to 50 microns mercury prior to the admission of the gaseous etchant. The process provides rapid and uniform etching of dielectrics (up to 5000 A./min.) across a typical production batch of semiconductor slices with negligible loss of an organic etch mask.

In FIG. 2 there is shown in cross-sectional view a portion of a typical semiconductor device at a suitable processing stage for the utilization of this invention. The semiconductor device consists of a semiconductor material **30**, such as silicon (or GaAs, GaAsP, InSb) having a relatively thin (200 to 10,000 A.) layer of a dielectric material **32** (e.g. SiO, SiO_2, Si_3N_4) either deposited or thermally grown onto it. This dielectric layer **32** (sometimes p or n-type doped) is to be etched at the openings **34** and **36** in the overlying photoresist mask **38**. These openings or windows in the etch mask **38** represent fractional areas of less than 1 percent to 80 percent of the total area of the semiconductor slice, and correspond to positions on the semiconductor slice where it is desired to form a semiconductor junction by a subsequent diffusion of suitable dopants.

If the semiconductor device, as depicted in FIG. 2, is exposed to the prescribed plasma formed from a gaseous mixture of oxygen and a halocarbon gas or vapor, the photoresist material will stay intact while the exposed dielectric film **32** will be etched down to the semiconductor layer **30** in openings **34** and **36**. It has been found that an effective halocarbon should be selected from the group of organohalides no more than two carbon atoms per molecule and in which the carbon atoms are attached to a predominance of fluorine atoms. If a liquid halocarbon is considered, it should have a boiling point between 20° and 120° C. associated with a vapor pressure of at least 50 torr at 25° C. The preferred gaseous mixture is produced from a mixture containing 8.5 percent by volume of oxygen and 91.5 percent tetrafluoromethane gas. This optimum combination can be supplied from a prepared pressurized mixture maintained in a commercially available metal cylinder. Careful and close control of this dry etching

process will permit the manufacture of semiconductor devices with high line-line resolution (0.15 mil.). It also provides a significant reduction in the undercutting of the etch mask, coupled with the option to control the slope of the etched channel. It further provides an efficient and simultaneous means for etching various dielectrics with an insignificant chemical or physical deterioration of over-exposed underlying substrates such as aluminum, gallium arsenide, indium antimonide, garnets, etc. Satisfactory results were achieved with mixtures of up to 25 percent by volume of oxygen. In general, for the mixture combinations in the aforementioned group, an increase in the number of carbon atoms per molecule tends to slow down the etching process, while an increase in the mole fraction of oxygen (up to 0.5) tends to result in an excessive etch rate of the dielectric layer **32** with associated degradation of the photoresist mask and the line-line resolution. Increasing the mole fraction of the halocarbon beyond 0.5 tends to appreciably reduce the average etch rate.

The successful operation of this process is believed to include competitive homogeneous and heterogenous reactions in the plasma such that atomic oxygen, generated by the decomposition of molecular oxygen, reacts with solid silicon dioxide layers to form a reduced silicon oxide entity, e.g., silicon monoxide. This lower oxide of silicon is further converted by the fluorocarbon-based plasma to either volatile silicon tetrafluoride, SiF_4, or to volatile silicon oxyfluoride, Si_2OF_6, that is removed with the main gas stream to the vacuum pump. This reaction path, via the lower oxide of silicon, gives rise to thermochemically preferable reaction products as opposed to products that will ensue from the direct attack of either fluorine atoms or fluorinated hydrocarbon radicals on a silicon dioxide solid film. As a result, the presence of molecular oxygen in the etchant mixture enhances the etching (volatilization) of commonly encountered silicon dioxide films, since this reaction is coupled with a correspondingly higher probability of occurrence. By the same token, it is also believed that etching of silicon nitride layers proceeds via a similar lower oxide of silicon. In this case, the overall reaction is more exothermic, leading to a correspondingly enhanced etching of silicon nitride over silicon dioxide—a much desired result currently unobtainable within the semiconductor industry. It is this very feature of the plasma etch process that enables the direct photoresist masking of silicon nitride layers prior to etching, as opposed to indirect masking of such films by silicon dioxide and photoresist films in a multistep procedure currently employed with wet chemical etchants.

It has been found that the mixtures and operating parameters set forth below produce acceptable results in the described process. These parameters are intended to optimize the etch rate of dielectric films at negligible loss or degradation of any commercially available organic photoresist etch masks. Higher gaseous flow rates, RF power levels, etc., will enable correspondingly higher etch rates which may be used in conjunction with inorganic (e.g., metal) etch masks whose degradation is substantially avoided with this etching process.

Etchant	Etchant flow rate (micromoles sec.$^{-1}$)	Total pressure (microns Hg)	RF power (watts)	Material etched	Percent area etched	No. wafers	Etch rate (A min.$^{-1}$)
CF_4, 1% O_2	42.6	695	200	Th.[1] SiO_2	40	1	390
CF_4, 8.5% O_2	9	220	150	Th.[1] SiO_2	5	1	620
CF_4, 8.5% O_2	52	780	200	Th.[1] SiO_2	40	25	300
CF_4, 8.5% O_2	55	850	250	Th.[1] SiO_2	20	1	1,000
CF_4, 8.5% O_2	22	450	150	Dep.[2] SiO_2 on Al	5	1	2,600
CF_4,8.5% O_2	45	600	200	Molybdenum	70	1	1,500
CF_4, 8.5% O_2	15	340	250	Dep. Si_3N_4	5	20	670
CF_4, 8.5% O_2	55	850	200	Tungsten	70	1	1,000
CF_4,8.5%O_2	55	850	200	Selenium	70	1	1,500
CF_4, 8.5% O_2	15	340	200	Dep. Si_3N_4	5	1	1,300
CF_4, 15.5% O_2	55	770	200	Th. SiO_2	40	1	840
CF_4, 23.5% O_2	28	465	125	Th. SiO_2	40	1	800
CF_4, 29% O_2	100	1,343	300	Th. SiO_2	100	1	5,100
CF_4, 50% O_2	110	1,415	150	Th. SiO_2	100	1	1,890
CF_4, 69% O_2	17	275	300	Th. SiO_2	100	1	1,000
CHF_3, 41% O_2	50	1,365	300	Th. SiO_2	100	1	2,000
CHF_3,55% O_2	38	1,005	125	Th. SiO_2	100	1	1,200
CHF_3, 80.5% O_2	133	3,496	400	Th. SiO_2	100	1	2,800
CHF_3, 93.7% O_2	115	2,996	300	Th. SiO_2	100	1	500
C_2F_6, 50% O_2	108	1,435	300	Th. SiO_2	40	1	500
CF_2ClCCl_2F, 75% O_2	53	710	300	Th. SiO_2	40	1	1,000

[1] Th = Thermally oxidized.

[2] Dep. = Vapor deposited.

What is claimed is:

[1. A process for chemically converting material in a plasma environment, comprising the step of:

exposing the material to a gaseous plasma formed from a binary mixture consisting essentially of oxygen and a halocarbon having no more than two carbon atoms per molecule, wherein at least one carbon atom in said molecule is linked to a predominance of fluorine atoms to produce as an intermediate low order oxides.]

2. A process for *chemically* etching *solid* material in a plasma environment comprising the step of:

exposing the material to a gaseous plasma formed from a binary mixture consisting essentially of oxygen and a halocarbon having only one carbon atom per molecule, said carbon atom being linked to a predominance of fluorine atoms to produce as an intermediate a low order oxide.

3. A process as in claim 2 wherein the reaction temperature is within the range of 25 to 300 degrees centigrade.

4. A process as in claim 2 wherein said halocarbon gas includes at least one hydrogen atom.

5. A process as in claim 2 wherein said halocarbon and said oxygen are supplied to a reactor from separate sources.

6. A process as in claim 2 wherein said halocarbon and said oxygen are supplied to a reactor from a common premixed source.

7. A process as in claim 6 wherein said gaseous binary mixture contains 8.5 percent oxygen and 91.5 percent tetrafluoromethane by volume,

said mixture being supplied to said reactor at a total flow rate within the range of 9 to 55 micromoles per second corresponding total pressures of 220 to 850 microns mercury, and having RF energy coupled to said mixture within the range of 20 to 400 watts.

[8. A composition of matter, useful for chemically converting material in a plasma environment, consisting essentially of a binary gaseous mixture of oxygen and a halocarbon having no more than two carbon atoms per molecule, wherein at least one carbon atom in said molecule is linked to a predominance of fluorine atoms.]

9. A composition of matter, useful in a process for *chemically* etching *a silicon containing* material in the presence of an organic etch mask by forming fluorine-based and oxyfluoride-based compounds volatile in a low pressure-low temperature plasma, consisting essentially of a binary gaseous mixture of oxygen and tetrafluoromethane wherein said mixture contains 1 to 25 percent oxygen by volume.

[10. A composition of matter, useful in a process for etching material in the absence of an organic etch mask by forming fluorine-based and oxyfluoride-based compounds volatile in a low pressure-low temperature plasma, consisting essentially of a binary gaseous mixture of oxygen and tetrafluoromethane wherein said mixture contains 1 to 75 percent oxygen by volume.]

[11. A composition of matter, useful in a process for etching material in the presence of a metal etch mask by forming fluorine-based and oxyfluoride-based compounds volatile in a low pressure-low temperature plasma, consisting essentially of a binary gaseous mixture of oxygen and tetrafluoromethane wherein said mixture contains 1 to 75 percent oxygen by volume.]

12. A composition of matter, useful in a process for *etching silicon oxide in the presence of photoresist in* manufacturing semiconductors, comprising a binary gaseous mixture of oxygen and tetrafluoromethane, said oxygen containing 8.5 percent of the mixture by volume.

13. A process for chemically etching solid material in a plasma environment, comprising the step of:

exposing the material to a gaseous plasma at a pressure of at least 220 microns formed from a binary mixture consisting essentially of oxygen and a halocarbon having no more than two carbon atoms per molecule, wherein at least one carbon atom in said molecule is linked to a predominance of fluorine atoms to produce as an intermediate low order oxides.

14. A process for chemically etching solid material in a plasma environment, comprising the step of:

exposing the material to a gaseous plasma formed in an RF field from a binary mixture consisting essentially of oxygen and a halocarbon having no more than two *carbon atoms per molecule, wherein at least one carbon atom in said molecule is linked to a predominance of fluorine atoms to produce as an intermediate low order oxides.*

15. A process for chemically etching solid material in a plasma environment, comprising the step of:

exposing the material to a gaseous plasma formed from a binary mixture consisting essentially of oxygen and a halocarbon having no more than two carbon atoms per molecule, wherein at least one carbon atom in said molecule is linked to a predominance of fluorine atoms to produce as an intermediate low order oxides and wherein said mixture contains 1 to 25% oxygen by volume.

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