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(54) Titre : PROCEDE DE BRULAGE DE MATERIAUX ORGANIQUES PRESENTS A LA SURFACE DE SUBSTRATS
(54) Title: PROCESS FOR ASHING ORGANIC MATERIALS FROM SUBSTRATES

(57) **Abrégé/Abstract:**

Ashing of an organic film from a substrate is carried out by providing a plasma comprising a gas or gas mixture selected from the following groups: (a) sulfur trioxide alone; (2) sulfur trioxide plus one supplemental gas; and (3) sulfur trioxide plus at least two supplemental gases. Any of the following gases may be employed as the supplemental gas: water vapor, ozone, hydrogen, nitrogen, nitrogen oxides, or a halogenide such as tetrafluoromethane, chlorine, nitrogen trifluoride, hexafluoroethane, or methyltrifluoride.



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(21) International Application Number: PCT/US99/01560 (22) International Filing Date: 26 January 1999 (26.01.99) (30) Priority Data: 09/014,695 28 January 1998 (28.01.98) US (71) Applicant: ANON, INC. [US/US]; 621-B River Oaks Parkway, San Jose, CA 95134 (US). (72) Inventors: LEVENSON, Eric, O.; 1235 Monte Verde Court, Los Altos, CA 94024 (US). WALEH, Ahmad; 2344 Emerson Street, Palo Alto, CA 94301 (US). (74) Agent: COLLINS, David, W.; 711 West Los Altos Road, Tucson, AZ 85704 (US).		(81) Designated States: CA, CN, IL, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR ASHING ORGANIC MATERIALS FROM SUBSTRATES (57) Abstract Ashing of an organic film from a substrate is carried out by providing a plasma comprising a gas or gas mixture selected from the following groups: (a) sulfur trioxide alone; (2) sulfur trioxide plus one supplemental gas; and (3) sulfur trioxide plus at least two supplemental gases. Any of the following gases may be employed as the supplemental gas: water vapor, ozone, hydrogen, nitrogen, nitrogen oxides, or a halogenide such as tetrafluoromethane, chlorine, nitrogen trifluoride, hexafluoroethane, or methyltrifluoride.		

5 PROCESS FOR ASHING ORGANIC MATERIALS FROM SUBSTRATES

BACKGROUND OF THE INVENTION10 1. Field of the Invention.

The present invention relates generally to the removal of organic materials on various substrates, and, more particularly, to an ashing method for removing organic films and materials temporarily formed on various substrate layers during fabrication of semiconductor, flat panel display, read/write heads, and other related devices.

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2. Description of the Related Art.

Removal of the photoresist film is an important part of the process of fabricating semiconductor devices. The use of ashing methods, in particular, using a gas with high oxygen content, for removing organic films, such as resists and polyimides has been known for some time.

20 The advances in plasma tools and the related processing techniques, over the last decade, have managed to keep up with the challenges of successive generations of Very Large Scale Integration (VLSI) and Ultra Large Scale Integration (ULSI) devices. However, as the size of the features and the thickness of films in these devices continue to decrease, the manufacturing challenges are also renewed with every generation of Integrated Circuits (ICs).

25 As the dramatic shrinking of IC geometries continues, the ashing methods are continuously faced with two problems: (a) achieving higher rates of residual-free resist removal and (b) lowering the amount of damage caused in the substrate layers underlying the resist film. These generally conflicting objectives are addressed by changing either the physical conditions of the plasma medium or the chemical conditions of the ashing process. For example, one can achieve
30 higher rates of processing by either generating a dense plasma environment or by using or generating, in the plasma environment, chemical species that react more efficiently with the resist.

Substrate damage can likewise be attributed to both physical and chemical conditions of the plasma. For example, charging and ion bombardment effects are directly related to the physical properties of the plasma. Energetic ions can drive small quantities of heavy metal (i.e., Fe, Cu

and Pb) and alkaline metal (i.e., Na and K) atoms, which are generally present as impurities in the resist films, into the substrate layer underneath the resist. The heavy metal contamination and in particular the subsequent permeation and migration of heavy metals into other substrates (e.g. silicon) layers can affect the minority carrier lifetime to the detriment of the device properties.

5 Such bombardment effects become more severe as the resist films become thinner towards the end of the ashing process, particularly as the thickness of sensitive substrates are designed to be thinner.

Substrate damage also results from the chemical properties of plasma, such as etching or other poisonous effects on the layer underneath the resist. For example, etching of silicon oxide
10 (SiO_2) occurs because of fluorine (F), when halogenated gas mixtures such as oxygen (O_2) and tetrafluoromethane (CF_4) are used to increase the rate of plasma ashing. Similarly, energetic oxygen ions can contribute to the formation water inside the surface layers of spin-on-glass (SOG) films, resulting in an increase in the dielectric constant or in the related via-poisoning phenomenon.

15 These considerations apply, to various degrees depending on the application, to all conventional dry-etch plasma etchers, e.g., barrel, down-stream or parallel-electrode configurations, with the down-stream ashing being the most widely used method. To increase the processing rates and minimize the problem of ion damage, techniques for higher plasma densities and lower ion energies may be employed. The new generations of advanced plasma sources achieve these
20 objectives by decoupling the control of the plasma density from the control of ion energy in the plasma by such techniques as Electronic Cyclotron Resonance (ECR) or Inductively Coupled Plasma (ICP) in microwave or radio frequency power regimes. The art of these and other types of plasma technologies and plasma tools are well known and have been the subject of many US patents.

25 Independent of the nature and the regime of the plasma employed, the rate and completeness of ashing as well as any unwanted etching or damage to the substrate layer, in the conventional ashing tools, are strongly influenced by the chemical reactions between the resist and the substrate layer and the reactive ionic, neutral and radical species generated in the plasma. In a typical down-stream or other conventional asher, the nature of the plasma gas mixture is the
30 primary determinant of the ashing rate which is also sensitive to the "ashing temperature". The nature of the gas mixture also influences the activation energy of ashing which is a measure of the sensitivity of the ashing rate to the ashing temperature.

The activation energy is obtained from the gradient of the Arrhenius plot which is a line plot of the ashing rate as a function of the inverse ashing temperatures. Therefore, a small activation energy (small slope of the Arrhenius plot) indicates that ashing rate is less sensitive to ashing temperature, and that the ashing process will be more stable and uniform. Lower activation energies also imply that the ashing temperature can be lowered without significant loss of ashing rate. This is particularly useful where VLSI or ULSI fabrication requires lower processing temperatures and yet where acceptable practical levels of ashing rates (i.e., $> 0.5 \mu\text{m}/\text{min}$) must be maintained.

A thorough discussion of ashing rates and activation energies for a series of gas mixtures consisting of one or more of the following oxygen, hydrogen, nitrogen, water vapor and halogenide gases is given in the US Patent 4,961,820. It is shown that addition of nitrogen to oxygen plasma does not change the activation energy (0.52 eV for oxygen) and improves the rate of ashing only slightly (from 0.1 to 0.2 $\mu\text{m}/\text{min}$ at 160°C). However, addition of 5 to 10% hydrogen or water vapor to oxygen reduces the activation energy to about 0.4 eV with a similar improvement in the ashing rate as in the case of nitrogen addition. Addition of both nitrogen and 5 to 10% of either hydrogen or water vapor to oxygen plasma has a synergistic effect of increasing the ashing rate to a more practical level of 0.5 $\mu\text{m}/\text{min}$ (at 160°C).

The most dramatic improvements in the activation energy (down to 0.1 eV) and the ashing rate ($> 1.5 \mu\text{m}/\text{min}$) are obtained when a halogenide (e.g., tetrafluoro-methane) is added to the oxygen plasma. However, in this case, CF_4 also results in etching of such substrate layers as silicon oxide, polysilicon and aluminum due to fluorine reaction. It is reported that inclusion of water vapor in the reactant gas mixture will reduce the damage by CF_4 apparently as a result of the reaction of water with CF_4 , thus suppressing the halogen action.

As seen from the above discussion, the search for a satisfactory reactant gas mixture, with reasonably high ashing rate and without any deleterious effect on the substrate layer underneath the resist film, continues. Furthermore, as the constraints of the VLSI and ULSI fabrication become more stringent, lower ashing temperatures and ashing-process stability (lower activation energy) increasingly become major requirements of a satisfactory reactant gas mixture.

The present inventors have successfully used anhydrous sulfur trioxide (SO_3) in non-plasma resist removal applications at temperatures substantially lower than 200°C. Experiments have shown that exposure of resist-covered substrate surfaces to SO_3 leaves polysilicon and metal substrates surfaces intact without any deleterious effect. Exposed silicon and metal surfaces are also protected because of passivation action of sulfur trioxide. Therefore, sulfur trioxide

appears as a suitable candidate, either alone or in a reactant gas mixture, for plasma ashing applications. Particularly in the presence of oxygen plasma, it is expected that SO_3 will enhance the oxygen radical formation, thus significantly improving the rate of the ashing reaction.

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SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved process for ashing organic materials, including photoresist residues, from substrates by including sulfur trioxide gas as a part of the reactive gas mix. This can be accomplished by employing one of three groups of gas mixes in the ashing process. These mixes include (1) Group 1 gas, which comprises only sulfur trioxide gas; (2) Group 2 gases, which comprise a mixture of sulfur trioxide and a supplemental gas such as water vapor, ozone, hydrogen, nitrogen, nitrogen oxides, or a halogenide such as tetrafluoro-methane (CF_4), chlorine (Cl_2), nitrogen trifluoride (NF_3), hexafluoroethane (C_2F_6), or methyltrifluoride (CHF_3); and (3) Group 3 gases, which comprise a mixture of sulfur trioxide and at least two of the foregoing supplemental gases.

In accordance with one aspect of the present invention there is provided a process for removing an organic material from a surface of a substrate comprising the steps of:

(a) creating a plasma from a reactant gas comprising sulfur trioxide and optionally, from 5 to 99 volume percent of at least one supplemental gas selected from the group consisting of water vapor, ozone, hydrogen, nitrogen, nitrogen oxides, and halogenides; and

(b) allowing said plasma to impinge upon said surface of said substrate containing said organic material for a time sufficient to ash said organic material but insufficient to attack said surface of said substrate.

As is well-known in the art, when certain of these supplemental gases are added to the main reactive ashing gas in the appropriate quantities and at the appropriate time in the process, they promote favorable ashing process characteristics and organic film removal performance. Such favorable characteristics and performance includes (a) higher ashing rates, (b) lower activation energies, and (c) absence of ground layer etching during the organic removal process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Stripping and plasma ashing of organic photoresists, using one of the three groups of gases described above, are carried out with a conventional down-flow, barrel, downstream, direct, or other type of plasma ashing tool which is known in the prior art. The present invention pertains to the nature of the gases used in the ashing process and has application in all conventional ashing tools. The down-flow, barrel, direct, and downstream and other types of plasma ashing tools are well-known in this art and form no part of this invention.

The basic concept behind this invention is that sulfur trioxide gas, under the appropriate volumes and processing conditions, and with the optional addition of certain supplemental gases required to either reduce the activation energy, increase the speed of the ashing process, lower the operating temperature of the ashing process, or otherwise improve the effectiveness or efficiency

of the ashing process, is used in gaseous form as a reactant gas mixture to plasma ash, or otherwise react with, all types of organic coatings, films, layers and residues, including process-hardened photoresists, so as to cause them to be substantially removed, cleaned, or stripped from the surface of the substrate. In all embodiments of the present invention, the sulfur trioxide is provided in a source container from which sulfur trioxide gas is supplied to the processing chamber in the quantities and at the appropriate time in the ashing process. Within the source container, sulfur trioxide may be a mix of solid, liquid or gas, with the solid material in alpha form, beta form, gamma form or a mixture thereof.

Specifically, the following organic materials, in the form of coatings, films, layers, and residues, may be removed by the process of the present invention: polymerized and non-polymerized photoresists, photoresist residues, photosensitive and non-photosensitive organic compounds, paints, resins, multilayer organic polymers, organo-metallic complexes, sidewall polymers, and organic spin-on-glass. The photoresists may comprise positive optical photoresists, negative optical photoresists, electron beam photoresists, X-ray photoresists, and ion-beam photoresists.

Such coatings, films, layers, and residues may have been formed on a variety of substrates, including, but not limited to, (a) semiconductor wafers and devices comprised of silicon, polysilicon, germanium, III-V materials, and II-VI materials, (b) oxides, (c) nitrides, (d) oxynitrides, (e) inorganic dielectrics, (f) metals and metal alloys, (g) ceramic devices, (h) photomasks, (i) liquid crystal and flat panel displays, (j) printed circuit boards, (k) magnetic read/write heads, and (l) thin film heads.

The ashing process of the invention may be carried out at a temperature within the range of room temperature (about 20°C) up to 350°C. However, the ashing process is preferably carried out at as low a temperature as possible, consistent with maintaining as high an etching rate as possible. More preferably, then, the ashing process is carried out at a temperature less than about 200°C.

1. The First Embodiment.

One embodiment is a plasma ashing process conducted in any of the conventional down-flow, barrel, direct, and downstream and other types of ashing tools known in the prior art. In this first embodiment, the Group 1 gases are employed for the purpose of creating a plasma. In particular, the reactant gases comprise only sulfur trioxide. Sulfur trioxide is supplied to the plasma generating chamber, which is initially evacuated and exhausted to an appropriate vacuum. The

flow rate of the SO₃ gas is controlled by a controller during the process. Microwave power is supplied into the plasma generating chamber where a plasma is created with the reactant gases. Active species which are generated as a plasma, flow down to a process chamber and come into contact with the organic film on the surface of the substrate by one of the methods disclosed in the prior art. As a result of the interaction of the organic film and the plasma, the organic film is either removed or chemically changed so as to render the film removable with subsequent rinsing or cleaning steps in the process. The process limitations, such as flow rate, microwave power, and the like are the same as those conventionally employed in the prior art, such as disclosed in U.S. Patents 4,669,689 and 4,961,820.

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2. The Second Embodiment.

Another embodiment of the present invention is a plasma ashing process conducted in any of the conventional down-flow, barrel, direct, and downstream and other types of ashing tools. In this second embodiment, the Group 2 gases are employed for the purpose of creating a plasma. In particular, the reactant gases comprise sulfur trioxide and one supplemental gas. Sulfur trioxide and the supplemental gas are supplied to the plasma generating chamber, which is initially evacuated and exhausted to an appropriate vacuum. The sulfur trioxide concentration in the Group 2 reactant gas is within the range of about 1 to 95 vol%. The supplemental gas comprises the balance (99 to 5 vol%).

The flow rate of each gas is controlled by a controller during the process. Microwave power is supplied into the plasma generating chamber where a plasma is created with the reactant gases. Active species which are generated as a plasma flow down to a process chamber and come into contact with the organic film on the surface of the substrate by one of the methods disclosed in the prior art. As a result of the interaction of the organic film and the plasma, the organic film is either removed or chemically changed so as to render the film removable with subsequent rinsing or cleaning steps in the process. As above, the process limitations, such as flow rate, microwave power, and the like are the same as those conventionally employed in the prior art.

The supplemental gas may comprise any of the gases selected from the group consisting of water vapor, ozone, hydrogen, nitrogen, nitrogen oxides, or a halogenide such as tetrafluoromethane (CF_4), chlorine (Cl_2), nitrogen trifluoride (NF_3), hexafluoroethane (C_2F_6), or methyltrifluoride (CHF_3). Examples of nitrogen oxides include nitrous oxide (N_2O), nitric oxide (NO), nitrogen trioxide (NO_3), and nitrogen dioxide (NO_2).

3. The Third Embodiment.

Yet another embodiment of the present invention is a plasma ashing process conducted in any of the conventional down-flow, barrel, direct, and downstream and other types of ashing tools. In this third embodiment, the Group 3 gases are employed for the purpose of creating a plasma. In particular, the reactant gases comprise sulfur trioxide and at least two supplemental gases. Sulfur trioxide and the supplemental gases are supplied to the plasma generating chamber, which is initially evacuated and exhausted to an appropriate vacuum. The sulfur trioxide concentration in the Group 3 reactant gas is within the range of about 1 to 95 vol%. The supplemental gas comprises the balance (99 to 5 vol%).

The flow rate of the gas is controlled by a controller during the process. Microwave power is supplied into the plasma generating chamber where a plasma is created with the reactant gases. Active species which are generated as a plasma, flow down to a process chamber and come into contact with the organic film on the surface of the substrate by one of the methods disclosed in the prior art. As a result of the interaction of the organic film and the plasma, the organic film is either removed, or chemically changed so as to render the film removable with subsequent rinsing or cleaning steps in the process. As above, the process limitations, such as flow rate, microwave power, and the like are the same as those conventionally employed in the prior art.

The supplemental gases comprises at least two of the gases from the list of supplemental gases given above.

In each of the foregoing embodiments, removal of organic films, including resist layers, is substantially complete, with little or no damage to the underlying ground layer.

Thus, there has been disclosed a process for removing organic materials from the surface of a substrate, employing a plasma ashing process that uses a reactant gas that contains sulfur trioxide. It will be readily apparent to those skilled in this art that various changes and modifications of an obvious nature may be made, and all such changes and modifications are considered to fall within the scope of the appended claims.

What is Claimed is:

1. A process for removing an organic material from a surface of a substrate comprising the steps of:
 - (a) creating a plasma from a reactant gas comprising sulfur trioxide and optionally from 5 to 99 volume percent of at least one supplemental gas selected from the group consisting of water vapor, ozone, hydrogen, nitrogen, nitrogen oxides, and halogenides; and
 - (b) allowing said plasma to impinge upon said surface of said substrate containing said organic material for a time sufficient to ash said organic material but insufficient to attack said surface of said substrate.
2. The process of claim 1, wherein said reactant gas consists essentially of sulfur trioxide gas.
3. The process of claim 1, wherein said reactant gas consists essentially of sulfur trioxide and one said supplemental gas, said sulfur trioxide having a concentration within a range of about 1 to 95 volume percent.
4. The process of claim 1, wherein said reactant gas consists essentially of sulfur trioxide and at least two said supplemental gases, said sulfur trioxide having a concentration within a range of about 1 to 95 volume percent.
5. The process of claim 1, wherein said nitrogen oxides are selected from the group consisting of nitrous oxide (N_2O), nitric oxide (NO), nitrogen trioxide (NO_3), and nitrogen dioxide (NO_2).
6. The process of claim 1, wherein said halogenides are selected from the group consisting of tetrafluoromethane (CF_4), chlorine (Cl_2), nitrogen trifluoride (NF_3), hexafluoroethane (C_2F_6), and methyltrifluoride (CHF_3).

7. The process of claim 1, wherein said organic material comprises a substance selected from the group consisting of polymerized and non-polymerized photoresists, photoresist residues, photosensitive and non-photosensitive organic compounds, paints, resins, multilayer organic polymers, organo-metallic complexes, sidewall polymers, and organic spin-on-glass.

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8. The process of claim 7, wherein said photoresists are selected from the group consisting of positive optical photoresists, negative optical photoresists, electron beam photoresists, X-ray photoresists, and ion-beam photoresists.

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9. The process of claim 1, wherein said substrate is selected from the group consisting of (a) semiconductor wafers and devices comprised of silicon, polysilicon, germanium, III-V materials, and II-VI materials, (b) oxides, (c) nitrides, (d) oxynitrides, (e) inorganic dielectrics, (f) metals and metal alloys, (g) ceramic devices, (h) photomasks, (i) liquid crystal and flat panel displays, (j) printed circuit boards, (k) magnetic read/write heads, and (l) thin film heads.

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10. The process of claim 9, wherein said metals and metal alloys are selected from the group consisting of aluminum and aluminum-silicon-copper alloy.

11. The process of claim 1, wherein the plasma ashing process is carried out at a temperature between room temperature and 350°C.

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12. The process of claim 11, wherein said temperature is less than 200°C.

13. The process of claim 1, wherein said process is carried out in a down-flow, barrel, downstream, or direct ashing apparatus.

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