



Quorum Technologies

Plasma Etching / Ashing

Technical Brief



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- ∞ Carbon and sputter coaters
- ∞ Plasma reactor for ashing and etching
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- ∞ Critical point dryers
- ∞ Freeze dryers for electron microscopy
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Disclaimer

The components and packages described in this document are mutually compatible and guaranteed to meet or exceed the published performance specifications. No performance guarantees, however, can be given in circumstances where these component packages are used in conjunction with equipment supplied by companies other than Quorum Technologies.



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1 What is a Plasma

Key words:

- ∞ Radio Frequency (RF)
- ∞ Ionisation
- ∞ Glow discharge
- ∞ Excitation
- ∞ Dissociation

A plasma is a partially ionised gas consisting of equal numbers of positive and negative charges and a different number of unionised neutral molecules.

When a gas is subjected to a D.C. or radio frequency (RF) potential at reduced pressure this is usually accompanied by glow which is known as glow discharge. The words glow discharge and plasma tend to be used synonymously, although glow discharges are not perfect plasmas but for the purposes of this text they will not be differentiated. The characteristic glow of these plasmas is due to electronically excited species producing optical emission in the ultraviolet or visible regions of the spectrum and is characteristic of the composition of the glow discharge gas. For example argon gives a bright blue colour and air or nitrogen gives a pink colour that is due to excited nitrogen molecules.

1.1 Ionisation

In the context of plasma enhanced chemistry reactors, the plasma is created in a vacuum chamber which contains a constant flow of a gas at reduced pressure which is typically in the order of 1 mbar. This gas is exposed to a radio frequency (RF) potential which results in the partial ionisation of the gas. In the ionisation process, a bound electron in an atom is ejected from that atom. For example, the ionisation of an argon atom is expressed as follows:



1.2 Excitation

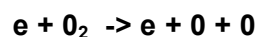
A less dramatic transfer of energy allows the electron the jump to a higher energy level within the atom. This process is known as excitation.

The excited state of an atom is conventionally shown by an asterisk:-



1.3 Dissociation

A further process which can occur is the dissociation of a molecule. If oxygen, for example, is the gas subjected to the RF potential, the oxygen molecule can be dissociated into two oxygen atoms whereas a monatomic gas such as argon cannot be dissociated at all:-



A normal result of dissociation is an enhancement of chemical reactivity since the products are usually more reactive than the parent molecule. Dissociation may or may not be accompanied by ionisation, for example:-



1.4 To Summarise:

The effect of exposing a gas to the RF potential at reduced pressure, a plasma is created which contains active species, for example, in the case of oxygen, atomic oxygen. Oxygen atoms will oxidise organic molecules more readily than oxygen molecules. So typically a cellulose material can be converted to carbon dioxide, carbon monoxide and water at room temperature, rather than elevated temperatures (e.g. burning) and furthermore the oxidation is more controllable.

2 Types of Reactor System

Key words:

- ∞ Barrel reactor
- ∞ Parallel plate reactor
- ∞ Reactive Ion Etching
- ∞ Isotropic
- ∞ Anisotropic

There are many types of reactors available. They are all glow discharge systems but vary considerably in terms of excitation frequency (5 kHz - 5GHz), operating pressure (1 mbar - atmospheric pressure) and electrode arrangement. However, there are only two generic types of reactor, namely the **Barrel Reactor** (see figure 1) and the **Parallel Plate Reactor** (see figure 2). The parallel plate reactor usually consists of a grounded plate onto which the specimens are placed and an insulated parallel plate to which the RF power is applied. The reverse of this arrangement where the specimens are placed on the non-grounded electrode is generally known as "**Reactive Ion Etching**" (RIE). Etching in this type of reactor is inherently directional whereas the former can be both directional (anisotropic) or isotropic. The barrel reactor usually etches isotropically.

The barrel reactor, as the name implies, is a cylindrical container which can be evacuated. The RF power, usually at 13.56 MHz frequency is applied to the system via internal or external electrodes by capacitive or inductive coupling. This type of reactor is used for the plasma ashing process and also for the plasma etching process, although the disadvantage in the latter for some users is that the process is not completely isotonic so that undercutting can occur.

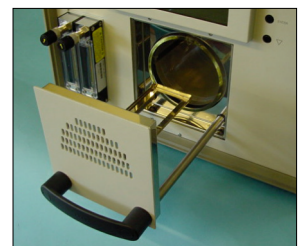
2.1 A Barrel System: Quorum K1050X

Key words:

- ∞ Quartz chamber
- ∞ Boron contamination
- ∞ Vacuum pump
- ∞ "Forward and reflected" power
- ∞ Impedance matching
- ∞ 'Auto tuning'

The K1050X Plasma Reactor from Quorum Technologies is a barrel system using capacitive coupling of the RF power to the gas. The barrel reactor cylinders can be made of Pyrex (Borosilicate) glass or quartz. The use of the quartz barrel and window option is really only for the microelectronics user where the problem of boron contamination might be a problem. Borosilicate glass contains boron which might be extracted in a CF_4 flow. In all other applications there is no problem with Borosilicate glass.

The barrel chamber electrodes are on the outside of the chamber in a quadrant format (see figure 1). The work chamber is evacuated to about 0.05 mbar and then the "Reactive" gas is allowed to bleed into the chamber to obtain an operating pressure of about 0.5 Mbar. The RF power is then applied and the gas is "ionised".



Under these conditions the chemical reactions occur and the subsequent volatile products are removed by the vacuum pump. The two front panel meters monitor the "Forward" and "Reflected Power". The "forward" power is the power into the work chamber whereas the "reflected" power is the power reflected back into the power supply. The reflected power is a result of mismatching the power supply impedance with the reaction chamber impedance and this level should always be kept at a minimum. In practice balance is achieved by tuning so that the forward power reaches a maximum as the reflected power drops to a minimum. The K1050X has a built in 'auto tuning' facility that ensures that RF power is

automatically impedance matched to any variation the system or loading, this is important as it gives faster reaction times, reproducibility of results and protects the power supply.

The K1050X has a 100mm dia. x 150mm Quartz chamber, 100-Watt power supply, two gas flow channels and metering of vacuum and power. The system is semi automatic; one button initiates a sequence of pump down and ingress of process gas. A second button switches on the plasma (for a period pre-set by the timer). At the completion of the process the chamber is evacuated again prior to venting to atmospheric pressure. This is an important safety feature as it ensures that any potentially harmful gases are evacuated by the rotary pump before the chamber door is opened.

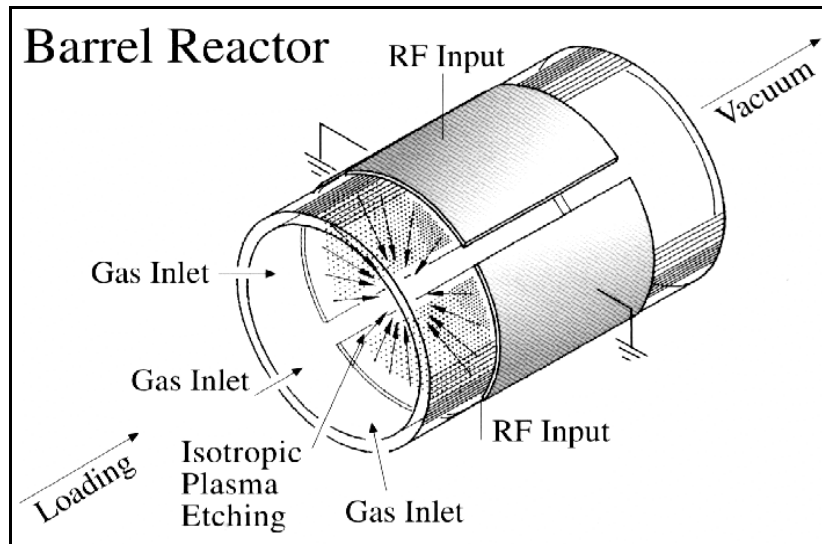


Figure 1 - Barrel Reactor

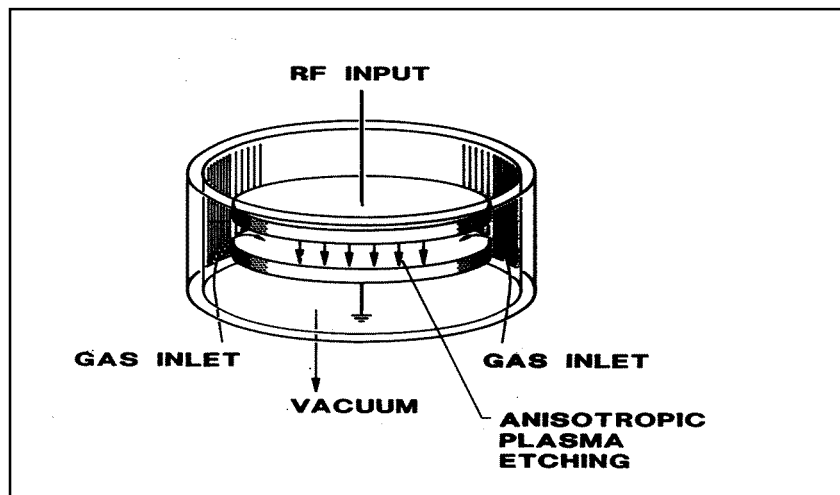


Figure 2 – Planar Reactor

3 Applications of Plasma

3.1 Plasma Ashing

The process of plasma ashing, plasma stripping or micro-incineration is usually restricted to the total removal of organic matter by an oxygen plasma, the products being carbon oxides and water vapour which are volatile and pumped away by the vacuum system. Historically, the first application was for the removal of photoresist in the microelectronics industry, photoresist is composed of organic compounds, essentially consisting of carbon, hydrogen and oxygen. Exposure to an oxygen plasma eventually removes all the photoresist as volatiles leaving no residues unless there are inorganic contaminants in the photoresist. This shows the process can be a totally dry process and also a means of concentrating inorganic contaminants in organic materials.

3.1.1 Asbestos Detection

This is a major market for plasma units. The exact protocols vary from country to country but in the UK the following is a summary of the recommended method. The technique requires that a sample of filtered air (or water) is collected from a known volume on MF series filter (mixed cellulose acetate and nitrate). The filter is then transferred to a microscope slide and after treatment with a clearing solution and dried is transferred to the plasma unit. The asbestos fibres are then exposed by partial ashing of the filter by treatment in oxygen plasma for typically seven minutes. This removes surface layers of the filter leaving the asbestos fibres exposed but still attached. The fibres can be counted and identified by light microscopy, light contrast microscopy, SEM and EDX.

3.1.2 Coal Ashing

Small samples can be ground and distributed in a Petri dish to produce maximum surface area. The coal dust can be ashed by oxygen plasma at low temperatures compared to those generally used in a muffle furnace for this process. Volatile elements such as selenium are retained and therefore a more accurate calorific and ash value can be produced. These problems in estimating the required values are a result of the structure of coal which includes organic materials and hence convertible material together with inorganic materials which are inert all being included in the overall matrix.

Plasma chemistry is a surface reaction so the ashing of coal requires that new surfaces are exposed. Physical stirring of the sample is recommended every 1-2 hours and the complete ashing of a one gram sample can be completed in 12-24 hours.

3.1.3 Detection of Metals In Blood

The use of plasma ashing as a pre-treatment for, say, atomic absorption analysis (AAS) is another application. In this case one is normally looking for metals such as lead, cadmium, zinc and mercury in trace quantities in organic materials such as vegetables, dairy products or animal tissue. A specific example involves the treatment of multiple samples of human blood exposed to a CF_4/O_2 plasma. The organic materials in this application can be removed in 15 minutes leaving only the metallic contaminants to be analysed for cadmium.

3.1.4 Ashing of Biological Material Food Stuffs Etc.

Plasma ashing has also been successfully used to ash materials as varied as post mortem lung tissue (for asbestos) bread (to determine type and distribution of iron) and samples of school dinners (for man made mineral fibres). Samples need to be dried prior to ashing and their size kept to a minimum.

3.1.5 Organic/Inorganic Composites

Similar problems are encountered in composite materials such as paints, vehicle tyres and brake linings, contaminated oils and the application of clays onto paper.

In paints, the organic binder can be removed to leave the inorganic pigment in its original distribution.

In paper, the clay platelet distribution and adhesion can be investigated after the ashing of the paper and binder.

Similarly epoxy composite materials can be investigated.

3.2 Plasma Etching

Plasma ashing and plasma etching basically rely on the same principles. Plasma Etching is usually confined to the semiconductor industry and more often than not uses carbon tetrafluoride (with oxygen) as the plasma process gas. Probably the most frequent application is the etching of silicon, silicon oxides, silicon nitrate as well as glass passivation layers.

Failure Analysis of integrated circuits is also an important application of plasma processing. Oxygen gas is used to remove epoxy encapsulates or CF_4/O_2 is used to remove glass filters in the encapsulates so as to uncover devices which have failed. Inspection by, say, SEM is then possible.

When etching, it should always be remembered that not only the required surface may be removed. The choice of gas is made so that preferential etching of the required surface is attained.

Plasma Etching is a chemical process where the RF discharge generates species which react with the material being etched to form a volatile product which is swept away by the gas flow. Since reactive species are being formed the reactant gas is chosen to give the highest concentration of the etching species involved.

For example, CF_4 and CF_4/O_2 mixtures produce very reactive fluorine and CF_3 radicals and ions. Similarly, other gases and volatile compounds have been investigated and used to etch a wide variety of materials. These include CCl_4 , $CFC1_3$, C_2Cl_6 , C_2F_6 , SF_6 , SIF_4 , and mixtures of these gases with H_2 , O_2 , Ar, He, CO_2 , CO, N_2 etc.

3.3 Surface Treatment Of Plastics

A number of applications of plasma involve the surface treatment of plastic materials, prior to a subsequent process. An example is the treatment of reinforcing fibres that are to be integrated into an epoxy structure. By treatment in an oxygen plasma for say five minutes at 50-100 watts the surface roughness of the fibres by the creation of pits is enhanced and consequently a good mechanical bond is produced with enhanced rigidity and strength.

Plasma processing of plastics to convert a hydrophobic surface to a hydrophilic surface. This type of treatment usually requires short exposure (3-5 minutes) at low power (50 watts). This type of treatment has been applied to the assembly of ink pens to improve the speed of ink filling and transfer, the treatment of electrical wire insulation so that the insulation can be printed upon with regular inks, a similar treatment of car bumpers so that they can be painted and the treatment of textile fibres to improve water retention.

Plasma surface treatment in Biomedical Applications is expanding rapidly. For example, the surface modifications of a polymers to improve blood compatibility. This involves tailoring the polymer surface to minimise blood reaction. Similarly, the internal surfaces of tubing can be modified so that drugs can chemically bond to the surfaces which would allow the drug to be slowly dispensed in a local area.

3.4 Plasma Polymerisation

Plasma polymerisation is the polymerisation of active species generated in a plasma. For example, the introduction of polysiloxanes onto hard contact lenses improves the hydrophilic nature of the surface. Using CF_4 , a fluorinated surface can be deposited on P.E.T. and polypropylene bottles to make the bottles less previous to carbon dioxide in the soft drinks industry. A porous surface can be produced on medical equipment which makes it possible to sterilise the equipment with nitrous oxide whilst remaining impervious to air. Deposition of polymers on implants is also possible so as to improve the bio-compatibility of the implant and prevent rejection.

3.5 Notes:

- (a) The use of the quartz barrel and window option is really only for the microelectronics user where the problem of boron contamination might be a problem. Borosilicate glass contains boron which might be extracted in a CF_4 flow. In all other applications there is no problem with borosilicate glass.
- (b) Rotary vacuum pump. It is recommended by the pump manufacturer that Fomblin oil is used were oxygen is the process gas instead of the regular hydrocarbon based oils. This requires a special version of the pump and has to be ordered as such. Always check that the process gas is compatible with the rotary pump oil.

3.6 Applications of Plasma Techniques

The major applications of plasma techniques are in improving the wettability and adhesion of polymers for surface coatings, inks and dyes (1) self adhesion can also be markedly improved by plasma treatment. (2, 3).

Plasma techniques are widely used in the electronics industry (4) particularly for microelectronics fabrication. Although most of the materials involved in these applications are inorganic, they are of interest to polymer chemists because polymers can be involved as resists, insulators or semiconductors. Operations carried out by plasma techniques include photo-resist removal (5) etching silicon compounds (6) and deposition of polymer films (7, 8). The chief virtue of plasma techniques in microelectronics fabrication is that it permits automated, multi step processing of complex devices (9).

Plasma applications of plasma polymerisation have included the production of protective coatings for metals and other reactive surfaces (12) fabrication of reverse osmosis membranes (13) coatings for optical plastics (14) and the formation of radiation resistant coatings (15).

Other application of plasma polymerisation have included the production of protective coatings for metals and other reactive surfaces (12) fabrication of reverse osmosis membranes (13) coatings for optical plastics (14) and the formation of radiation resistant coatings (15).

Last and by no means least, the application of plasma ashing in the analysis of inorganic materials in an organic matrix in the investigation of asbestos fibres in air and metal contamination of food has been increasingly predominant.

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4 Plasma Chemistry Processes Gas

Application of:

O₂: organic materials

Ashing; Removal of organic materials as volatile products remaining material used for analysis, process times typically 10-30 minutes.

O₂: organic materials

Micro-incineration; Removal of organic materials as volatile products usually from thin sections for SEM/TEM studies, typically 10-30 minutes.

O₂: organic materials

Surface etching; Differential removal of organic material as volatile products usually from thick epoxy sections maintaining the section for SEM surface studies, typically 30 sec's to 2 minutes for etching depths of 10-30nm.

CF₄: silica, silicon nitride and silicon.

Etching; Removal of glass passivity layers as volatile product from semiconductor substrate for circuit investigation. Addition of small amounts of oxygen (~10%) increases etching rate, times typically 30-80 minutes nominal thickness 150nm similarly for silicon nitrate with somewhat slower rate for silicon. Will etch metals Ta, Mo, Ti, W but inert to Al, Cu and Fe metals alternative gases are CHF₃ and C₂F₆ also used for selective etching of silicon nitride and silica on silicon.

SF₆: silicon dioxide

Etching over GaAs, usually with oxygen.

NF₃: silicon dioxide

Etching over GaAs, diluted with argon.

H₂ GaAs, InP, InGaAsp

Etching over silicon, silicon dioxide, metals.

CCl₄: POLY-Si, GaAs, Al₂O₃, Cp

Etching with chlorine as active species, boron tri-chloride can also be used.

O₂: Photoresist

Removal of photoresist in semiconductor manufacture, addition of CF₄ (~10%) will enhance etching rates, typically 20-40 minutes for thickness of about 800 nm