Plasma etching—A discussion of mechanisms

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The purpose of the present paper is to review the salient features of our understanding of phenomena which occur in plasma etching situations. The etching process is discussed in terms of three basic steps: adsorption, product formation, and product desorption. Experiments performed in well-defined (nonplasma) environments are discussed with the goal of clarifying the relative importance of these three steps in the etching process. An attempt is made to relate the resulting concepts to several phenomena generally observed in plasma situations (e.g. etching anisotropy, selective etching, the loading effect, and the role of additive gases). Moreover, the glow discharge, in addition to generating active species which initiate the chemical reactions, also causes the etched surface to be subjected to energetic particle (ions, electrons) bombardment. The role of this radiation in the etching process is emphasized. Speculative comments relating to plasma etching parameters and apparatus are also given.

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I. INTRODUCTION

Plasma etching, which is expected to play an important role in the manufacture of semiconductor and other devices requiring fine-line lithography, involves using a glow discharge to generate chemically reactive species from relatively inert molecular gases.[1] These reactive species combine chemically with certain solid materials to form volatile compounds which are removed by the vacuum pumping system. Although the general concept is relatively simple, the complexities of the glow discharge itself and of the associated parameter space, have impeded the development of a detailed understanding of the chemical reactions involved in the process, which in turn has impeded the implementation of plasma etching in device manufacture.

In this paper we will discuss some fundamental concepts which we believe determine the etching behavior of surfaces exposed to reactive glow discharges. Plasma etching can be divided, for conceptual purposes, into two processes: (1) the generation of chemically reactive species (e.g. F atoms) in the gas phase as a consequence of the interaction between the glow discharge and the undissociated parent gas (e.g. CF_4) and (2) the subsequent interaction of these chemically reactive species with the surrounding surfaces. The approach taken in this paper is to identify the species present in the gas phase in the glow discharge and then to investigate the types of reactions which occur between these species and the surface under well-defined conditions (i.e., in the absence of a glow discharge). The extent to which experimentally observed plasma-surface phenomena can be understood in terms of these basic gas–surface interactions will then be described.

The advantages, disadvantages and applications of plasma etching as well as the apparatus used have been discussed recently[2,3] and therefore will not be included here. However, we will define briefly some of the terminology which is used to describe various plasma processes in order to reduce possible confusion in this area. The factors which are useful in categorizing plasma processes are (a) the nature of the discharge gas, (b) the extent to which surfaces in the discharge are subjected to energetic particle bombardment, and (c) the volatility of the gas–surface reaction product. These factors are used to classify the various plasma processes in Table I. The terminology defined in Table I is a consequence of historical processes and is unnecessarily complicated. Therefore, in this paper the term "plasma etching" will often be used in a general sense and will include processes that other authors would define as "reactive ion etching," "reactive sputter etching," or "plasma ashing." Whereas the plasma processes of greatest interest in this discussion are those leading to volatile gas–surface reaction products, much of what will be said is applicable to systems where the gas–surface reaction product is involatile. When the reaction product is involatile and the surface is not subjected to energetic ion bombardment (e.g. plasma anodization[4]) the reaction will stop when the reaction product reaches a certain limiting thickness determined by the mobility of the constituents through the product layer. This limiting thickness can be controlled by changing the environment (e.g., temperature of reaction product or electric field across the thin film of reaction product). If the involatile reaction product is subjected to energetic ion bombardment, the overall removal of the surface will continue indefinitely but the product layer will reach a steady state thickness determined by a competition between the reaction rate and the sputtering rate. This concept has been used successfully to grow very thin oxide layers with impressive thickness control and reproducibility.[5]

II. GAS–SURFACE INTERACTIONS

The complexity of the glow discharge and the vast parameter space associated with glow discharge equipment have made it very difficult to develop an understanding of the basic processes which are responsible for a wide variety of experimental observations. Therefore, in this section we will describe the results of several simple nondischarge experiments which can be related quite directly to a glow discharge environment.

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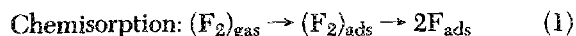
TABLE I. Classification of plasma processes.

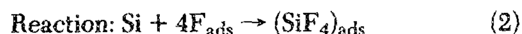
Extent of ion bombardment \ Type of discharge	Inert gas discharge	Reactive gas discharge: Involatile gas–surface product	Reactive gas discharge: Volatile gas–surface product
Minimal (sample on ground plane)	Plasma cleaning	Plasma anodization (oxygen plasma)	Plasma etching Plasma ashing (oxygen plasma)
Extensive (sample on target electrode)	Sputter etching	Reactive sputter etching	Reactive sputter etching Reactive ion etching

In this work, the fluorocarbon etching of silicon and its compounds has been used as a typical example of a process which forms a volatile reaction product and therefore many of the experiments described in this paper are directed toward understanding this system. However, it is anticipated that the concepts which have evolved will be applicable to other chemical systems.

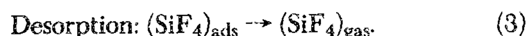
It is instructive to consider the steps which must occur during the etching of a surface with active gaseous species. A necessary first step is that the gas-phase species chemisorb on the surface. In the case of molecular gases this chemisorption will often involve dissociation of the molecule. However, even in cases where chemisorption is nondissociative, the radiation necessarily present in the glow discharge will usually cause the adsorbed molecule to fragment. The second step is the formation of the volatile reaction product and the third step is the desorption of the reaction product into the gas phase. These steps are illustrated below using the etching of Si with molecular fluorine as an example:



$$\text{Chemisorption: } (F_2)_{gas} \rightarrow (F_2)_{ads} \rightarrow 2F_{ads} \tag{1}$$



$$\text{Reaction: } Si + 4F_{ads} \rightarrow (SiF_4)_{ads} \tag{2}$$



$$\text{Desorption: } (SiF_4)_{ads} \rightarrow (SiF_4)_{gas}. \tag{3}$$

It is apparent that any of these steps could be rate limiting in the etching process and if any of these steps do not occur, then the surface will not be etched.

A. Gas–surface interactions without radiation

In order to understand the dominant processes in plasma etching, it is important to know to what extent the etching gas itself (e.g. CF_4) reacts with the surface to be etched in the absence of the plasma or radiation (ions, electrons, photons). If there is no etching without the plasma, as is almost always the case, it is important to learn which of the etching steps discussed above is blocking the reaction.

Recently a study has been made[6] of the adsorption characteristics of several halocarbon gases (CF_4, CF_3H, CF_3Cl, CF_2Cl_2, CCl_4) on silicon, silicon dioxide, and silicon nitride and it was concluded that dissociative chemisorption is not important in these systems, thus identifying the chemisorption step as the reason etching does not occur spontaneously. This conclusion obviously does not apply to all gas–surface combinations used in plasma etching. For example, it has been shown that chlorine chemisorbs on silicon[7,8] and exists as a *stable* structure at room temperature which suggests that etching does not spontaneously occur. Therefore in this case the step which blocks the etching is not chemisorption but is probably the second step, the formation of the reaction product $SiCl_4$. It is apparent that each chemical system must be studied individually in order to determine which step in the etching process is the rate limiting or blocking step.

There are some situations in which spontaneous etching does take place but the etch gases required are usually very toxic and corrosive and consequently are not used extensively in dry etching technology. For example, molecular fluorine will etch silicon spontaneously at room temperature but with a very low reaction coefficient ($\sim 10^{-5}$–10^{-6}).[9,10] The etch rate is proportional to the fluorine pressure so in this case, although chemisorption is not blocking the reaction, it is the rate limiting step. Recently[11] it has been reported that XeF_2 will etch silicon spontaneously with a reaction coefficient approximately four orders of magnitude larger than that of F_2 on silicon. Even in this case the etch rate is proportional to the XeF_2 pressure, indicating that chemisorption is still the rate limiting step. Clearly, for the silicon–fluorine system the product formation step and the product desorption step proceed spontaneously at room temperature at very high rates.

The relatively inert nature of the halocarbon gases with respect to silicon and its compounds serves to emphasize the major role of the glow discharge—*to generate reactive radicals by dissociating the halocarbon molecule*.

It is believed that dissociative processes in a CF_4 plasma produce primarily[12] CF_3^+, CF_3, F, CF_3^-, and F^-. The negative ions (CF_3^-, F^-) do not usually contribute to etching since the plasma potential prevents them from reaching surfaces. On the other hand, it has been shown that both the CF_3 radical[6] and CF_3^+ ion[13] react readily with clean silicon. The reaction probability for CF_3^+ is near unity while the reaction probability of CF_3 is about 0.25. Therefore, the presence of CF_3^+ and CF_3 will strongly influence the etching reaction; however, the etching action of these radicals by themselves is impeded by the carbon residue resulting from dissociative chemisorption. That is, the CF_3 radical impinging on Si cannot be thought of as a viable source of etching species because the system CF_3–Si is very much fluorine deficient with respect to the anticipated volatile products of SiF_4 and CF_4. Stated differently, fluorine from a given CF_3 radical is most certainly used to form SiF_4 at the silicon surface but the resulting carbon

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must then be removed by fluorine from another source. The question of the role of carbon, or involatile residues in general, will be discussed later.

The last and most important radical is the F atom. It is well known that F atoms react efficiently with silicon and a commercially available etching apparatus[14] has been developed in which F atoms, generated in a microwave discharge, are directed onto the silicon substrates, which are located in a region free from any energetic radiation. Large etch rates can be obtained in this apparatus. Similar conclusions about the large reactivity of fluorine atoms with silicon can be drawn from the fact that XeF_2 reacts very rapidly with silicon at room temperature.[6]

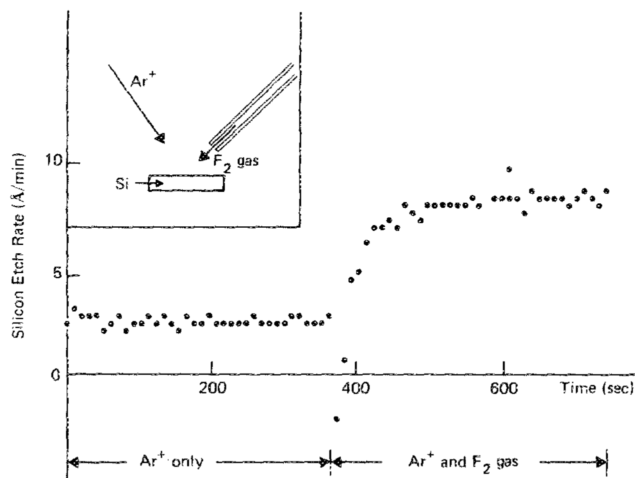

FIG. 1. Ion-assisted etching of Si by Ar^+ and F_2. Ar^+ energy = 500 eV; Ar^+ current = 1.0 μA; F_2 flow is 0 (for $t < 365$ s) and 1.36×10^{16} molecules/s (for $t > 365$ s). (The Ar^+ current density and the F_2 flux are not uniform over the Si surface. The effective area for the Ar^+ current and the F_2 flux are estimated at 0.1 and 0.3 cm^2, respectively).

B. Gas–surface interactions with radiation

The dissociation of the often relatively inert etching gas molecules into chemically active radicals is not the only role that the glow discharge plays in plasma etching. Inevitably, any surface immersed in a glow discharge will be subjected to fluxes of ions, electrons, and photons. The relative intensities and energies of the charged particles will be strongly dependent on the electrical potential of the surface with respect to potential of the glow discharge. This energetic particle bombardment has a large influence on the reaction rate for many gas–surface interactions. Not only will such radiation increase the reaction rate of spontaneously occurring process, but also it enables reactions to occur which do not occur without radiation.

1. *Ion-assisted gas–surface chemistry*

Much of the early evidence for ion-assisted chemical reactions has been obtained from measurements of etch rates in plasma etching systems where it has been consistently observed[15-17] that the etch rate of a surface subjected to energetic ion bombardment (i.e., surfaces located on the target electrode as in reactive ion etching) is much greater than the etch rate of surfaces subjected to low energy ion bombardment (i.e., located on the ground plane).

Ion-assisted chemistry has been observed more directly using an Ar^+ ion beam coincident on a surface with a beam of chemically active gas molecules.[18] The surface which has been used is a quartz-crystal microbalance upon which a thin film of the material to be etched had been deposited by conventional vapor deposition methods. The microbalance is used to measure the etch rate and can be operated during Ar^+ bombardment. With this simple configuration, shown schematically in Fig. 1, ion-enhanced chemical reactions have been observed for a variety of chemical systems. An example is shown in Fig. 1 for Ar^+ and F_2 on Si. Initially at $t = 0$ the Si surface is subjected to only Ar^+ ion bombardment and a steady state sputter-etch rate is achieved. At $t = 365$ s the Si surface was suddenly exposed to a flux of between 10^{15} and 10^{16} F_2 molecules/s cm^2. Initially, there is a slight increase in the mass as chemisorption of the F_2 overwhelms the etch rate. After this transient response, the etch rate reaches a steady state value which is about 3.5 times the sputter-etch rate. It is important to note that when the ion bombardment is terminated, the etch rate drops to zero because at these low fluxes F_2 does not etch Si at a detectable (<0.1 Å/min) rate. The significant conclusion to be drawn from this figure is that the etch rate with the Ar^+ ions and the F_2 molecules simultaneously incident on the Si surface is much larger than the sum of the etch rates obtained with the same fluxes incident separately. It is this type of ion-assisted etching which we believe is responsible for most of the anisotropy obtained in plasma etching and reactive ion etching. Similar results to those depicted in Fig. 1 have been obtained for other systems in which volatile reaction products are formed (e.g., Ar^+ and Cl_2 on Si,[18] Ar^+ and O_2 on C). In contrast, for every case in which the reaction product was involatile, the etch rate decreased upon exposure to the active gas (e.g., Ar^+ and O_2 on Si, Ar^+ and F_2 on Al[18]). This latter effect is well known in glow discharge sputter etching[19,20] and ion milling[21,22] and is due to the presence of chemisorbed gas which decreases the physical sputtering rate of the substrate.

In discussing the processes involved we will assume that we are dealing with an ion-assisted chemical reaction and not a chemically assisted sputtering process[23] even though we are not aware of any data which would completely justify this assumption. We have presented some evidence to support this point of view elsewhere.[18]

Consider the example shown in Fig. 1 for Ar^+ and F_2 on Si. It was concluded earlier that the relatively slow reaction rate between F_2 and Si was caused by a very low probability for the dissociative chemisorption of F_2 on Si. The Ar^+ bombardment greatly increases this probability and at least two mechanisms can be suggested. One possibility is that the Ar^+ bombardment generates a high density of sites capable of nucleating the dissociative chemisorption of F_2. A second possibility is that the Ar^+ bombardment causes the dissociation of F_2 by direct impact while the F_2 is adsorbed on the surface in a relatively weakly bonded molecular state. It is difficult to distinguish between these two possibilities in the present experiment but it should be pointed out that the second mechanism cannot apply in the CF_4 discharge environment because F atoms and not F_2 molecules are the dominant active

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gas-phase species in this case. It is interesting to note that when CF_4 is used in place of F_2 in the experiment depicted in Fig. 1, the etch rate is not affected by the CF_4 gas flow. It has been shown earlier that CF_4 does not dissociatively chemisorb on Si and the observation that CF_4 has no measurable effect on the etch rate during ion bombardment tells us that the steady-state concentration of physically adsorbed CF_4 molecules is low. If an appreciable coverage of CF_4 molecules existed on the surface, dissociation of these adsorbed molecules by direct ion impact would take place and a change in the etch rate would result.

2. *Electron-assisted gas–surface chemistry*

Electron-assisted gas–surface chemistry has been observed in various types of electron microscopy or spectroscopy in the form of electron-stimulated oxidation leading to primarily involatile oxides.[24–31] The electron-beam-induced oxidation of carbon[13,32] is one example of an etching process caused by electron irradiation.

The gas XeF_2 has provided the best examples of electron-assisted gas–surface chemistry in the silicon–fluorine system. The high reactivity of XeF_2 towards Si in the absence of radiation was mentioned earlier. It was found in this same study[11] that XeF_2 does not react appreciably with SiO_2, Si_3N_4, or SiC even though fluorine was observed on these surfaces following XeF_2 exposure. However, all these materials etch quite rapidly when they are subjected to electron bombardment in the presence of XeF_2 vapor. A typical observation of this effect is shown in Fig. 2. In this example etching is obtained only when the sample is subjected simultaneously to a flux of XeF_2 molecules and a flux of energetic electrons.

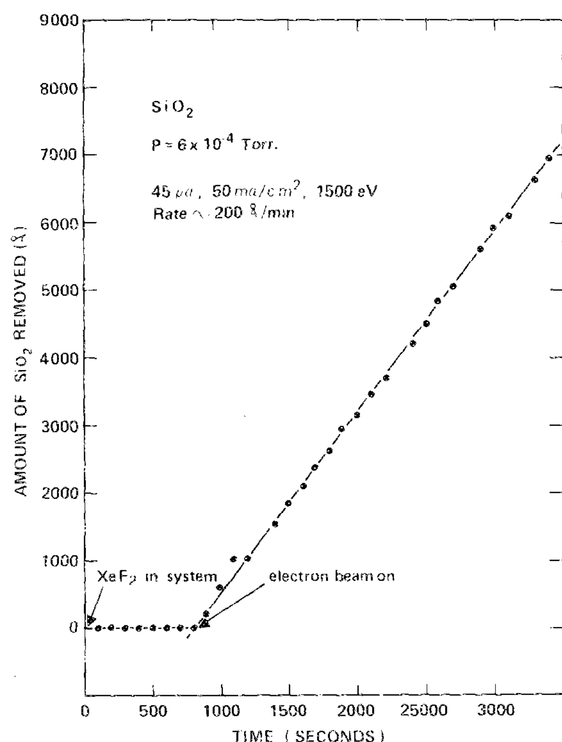

FIG. 2. Electron-enhanced etching of SiO_2 by XeF_2 (gas). P (total) $= 6 \times 10^{-4}$ Torr with most of the ambient gas being xenon. Exposure of SiO_2 to XeF_2 (gas) does not produce etching until an electron beam is activated at $t \sim 800$ s. An etch rate of $\sim$200 Å/min is then observed. The electron beam by itself does not produce sustained etching. Similar data was obtained for Si_3N_4 and SiC. (See Ref. 18.)

The fact that fluorine is observed on SiO_2 following XeF_2 exposure (no Xe could be detected) indicates that XeF_2 does dissociatively chemisorb on the SiO_2 surface (the Xe immediately desorbs following dissociation) and therefore the step which is blocking the etching reaction must be the product formation step. The electron bombardment is able to initiate this product formation step in some way, presumably by breaking Si–O bonds at the surface. In this regard, it is known that electron irradiation of SiO_2 without a partial pressure of reactive gas produces some elemental Si on the surface,[33,34] but continuous etching is *not* observed under these conditions.

The importance of electron-assisted gas–surface chemistry in a glow discharge environment is not clear. It is difficult to intentionally promote energetic electron bombardment of surfaces in a glow discharge in a controllable way because when a positive bias is applied to a surface in contact with a glow discharge, the nature of the discharge, including the plasma potential, is usually influenced significantly.[35] Also the flux of energetic electrons caused by the application of this bias voltage might generate more active species in the gas phase immediately adjacent to the surface being etched thus confusing the interpretation of the resulting etch rate changes. However, secondary electrons formed by ion or photon impact on negatively biased surfaces (e.g. target electrode) will be accelerated into the discharge and can arrive at other surfaces with substantial energy. This will be discussed later.

C. Involatile residues

Most of the gases used in plasma etching contain an element which itself is involatile and is capable of being deposited on the surface being etched or on fixtures or walls of the vacuum chamber. The deposition of carbon, when halocarbon etch gases are used, is the most common example but other etch gases such as SiF_4 or SF_6 can lead to the deposition of silicon or sulphur, respectively. This process is not to be confused with the formation of an involatile reaction product, nor with the unintentional deposition of materials sputtered from nearby electrodes or surfaces onto the material being etched. The carbon deposited in an etching situation is probably removed quite rapidly in a subsequent reaction, e.g. $4F + C \rightarrow CF_4$ (gas). Nevertheless, the carbon deposition will strongly affect the characteristics of the overall etching reaction and must be considered when attempting to interpret experimental data.

There are several mechanisms which can result in the deposition of carbon on surfaces when halocarbon etching gases are used in a plasma system. One mechanism which was mentioned earlier is the dissociative chemisorption of halocarbon radicals such as CF_3 on the etched surface.[6] A second mechanism is the dissociation by either ion or electron impact of a physically adsorbed molecule of the etching gas. This process was observed for example when a SiO_2 surface was subjected to electron bombardment in the presence of CCl_4 vapor.[6] A large buildup of carbon was observed whereas negligible carbon buildup was seen when the SiO_2 surface was

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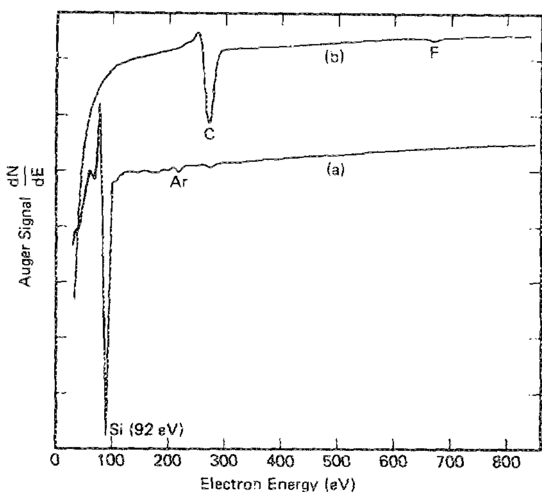

FIG. 3. Auger electron spectrum from (a) Si surface cleaned by 500-eV Ar^+ ion bombardment and (b) same surface as (a) after bombardment with 5×10^{16} CF_3^+ ions/cm² (500 eV). Experiments were performed in an ultrahigh vacuum system using an ion beam which was not mass analyzed. (See Ref. 13.)

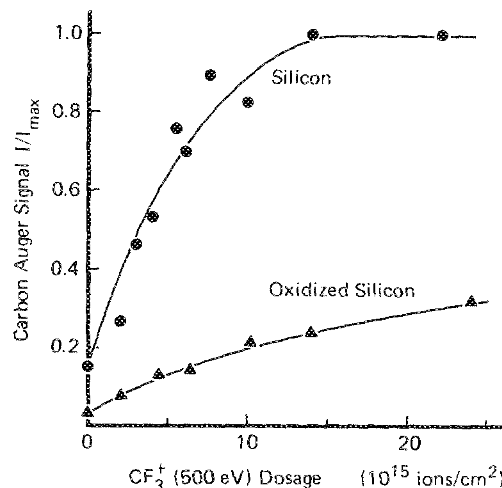

FIG. 4. Carbon Auger intensity I/I_{max} vs 500-eV CF_3^+ dosage. Experiments were performed in an ultrahigh vacuum system using an ion beam which was not mass analyzed. The data for oxidized silicon was obtained for a very thin oxide layer (estimated to be less than 100 Å) and therefore the carbon buildup on pure SiO_2 might be expected to be somewhat less. (See Ref. 13.)

exposed to CCl_4 vapor without electron irradiation. A third mechanism for depositing carbon is the bombardment of a surface with energetic halocarbon ions. The extent to which carbon can be deposited in this way has been demonstrated[13] using 500-eV CF_3^+ ions on Si. The Auger spectra in Fig. 3 show that after the CF_3^+ bombardment, the Si surface is completely covered with carbon as indicated by the absence of the Si (92-eV) Auger peak. Furthermore it was noted that the rate of carbon buildup was much slower on an oxidized silicon surface than on a clean Si surface as is shown in Fig. 4. This difference is attributed to oxidation of the carbon by the oxygen in the SiO_2 lattice to form volatile CO and is believed to be responsible for the increase in the SiO_2-to-Si etch-rate ratio noted in fluorocarbon glow discharges which have been made fluorine deficient.[36] This will be discussed in more detail later.

The potential importance of the deposition of carbon in the plasma etching of silicon can be recognized when one considers the relative carbon–fluorine and silicon–fluorine reactivities. Whereas XeF_2 attacks Si spontaneously at a rapid rate,[11] carbon and silicon carbide are not etched by exposure to XeF_2. There is evidence, as might be anticipated, that the carbon–fluorine reactivity is very dependent on the chemical form of the carbon. For example, it has been observed in our laboratory that SiC can be etched in XeF_2 with electron irradiation whereas a graphitic carbon film is not etched under the same conditions.

III. GLOW DISCHARGE PROCESSES

A. Chemical aspects of plasma etching

1. Role of oxygen

It has been recognized by many workers that the addition of chemically active gases to halocarbon plasma etching discharges usually results in significant and often selective changes in the etch rates of various materials of interest in device manufacture. One of the first gases used was oxygen and it has been consistently observed that the addition of oxygen to a CF_4 glow discharge causes the etch rate of silicon to increase.[15,37–41] Independently it has been found that CF_4 does not react with atomic oxygen[42,43] and therefore the chemistry responsible for the increase in the Si etch rate must be a reaction between oxygen and the carbon containing species produced by the electron-impact dissociation of CF_4. There are several ways in which this reaction can take place but the overall consequences are similar—a carbon–oxygen bond is formed (i.e., CO, CO_2, or COF_2 are generated) and since the carbon entered the system as a CF_4 molecule, some fluorine has been made available for etching by the oxidation of the carbon. Harshbarger *et al.*[39] first noted that when oxygen was introduced into a CF_4 glow discharge, there existed a correlation between the increased etch rate of Si and the increased intensity of the F and CO optical emission. More recent data[41] showing this correlation is presented in Fig. 5. These results show clearly that the increased Si etch rate is due

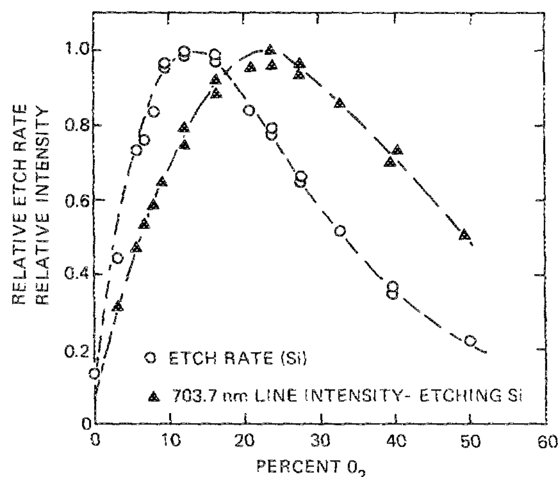

FIG. 5. The normalized etch rate for Si and the normalized intensity of the emission from electronically excited F atoms (703.7-nm line) vs the O_2 concentration in the CF_4–O_2 etch gas (data from Ref. 41).

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