

Mechanism of etching, polymerization and deposition in R.F. (radio frequency) discharges

R. d'Agostino, P. Capezzuto, G. Bruno and F. Cramarossa

Centro di Studio per la Chimica dei Plasmi. CNR. Dipartimento di Chimica,
 Università di Bari - Via Amendola, 173 - 70126 Bari (Italy).

Abstract - Homogeneous and heterogeneous chemical mechanisms in discharges fed with halogenated gases are examined in systems for etching or for deposition of polymeric and inorganic films. In particular, it is emphasized the importance of plasma parameters and of feed additives in changing the relative amounts of species active for etching and for deposition.

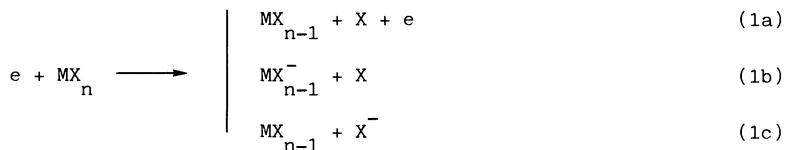
INTRODUCTION

A great deal of work has been produced in the last years in the field of plasma etching and deposition of inorganic and polymeric films. These processes have, in fact, a growing technological relevance in the fields of integrated electronics, optical circuits and film depositions for the treatment of surfaces and for photovoltaic applications.

Etching and deposition of organic and inorganic films are processes based on interactions between plasma produced reactive species and solid surfaces. However, it is a hard task to deal with all possible mechanisms, because the argument has become increasingly too wide to be examined in details. We shall therefore limit our attention to some aspects of the chemical mechanisms involved in discharges fed with halogen bearing gases. Cold plasmas of these gases, and of their mixtures with various additives, revealed to be versatile tools allowing both etching and deposition conditions to be reached inside the same type of reactors. In fact, most halogenated gases ($C F_{n-2n+2}$, CCl_4 , SF_6 , $SiCl_4$, SiF_4 , etc.) can give, under plasma conditions, both building blocks for polymer layers (CF_x , CCl_x , SF_x , $SiCl_x$, SiF_x , etc.) and etchant species (F , Cl , Cl_2 , etc). The importance of plasma parameters and feed additives on the predominant etch or deposition character of the discharge will be emphasized. Particular attention will be given to conditions in which processes involving neutral species prevail with respect to those involving charged particles.

GENERAL PICTURE

When a low-pressure glow discharge is fed with electronegative halogenated gases, many atomic, radicalic and ionic fragments are formed through channels involving electron-neutral interactions. A general scheme of decomposition processes is given by:



where X is for the halogen atom. Processes (1b) and (1c) can also occur through the intermediate formation of unstable MX_n^- .

In most etching and deposition plasmas, average electron energy is lower than 10 eV (ref. 1) and resonant dissociative attachment is likely to dominate in electron impact collision

(ref. 2). Some examples are the formation of SF_5^- , CCl_3^- , CCl_2^- , Cl^- , F^- (refs. 2-4). Electrons can also excite, through resonant processes, neutrals into electronic emitting states; this allows their "in-situ" monitoring by means of emission spectroscopy. Electrons are also responsible of the first step in vibrational excitation of neutrals by means of processes (ref. 5):



The vibrational quanta introduced by this way can be redistributed through collisional energy transfer processes, as vibration-vibration and vibration-translation processes. Therefore, two different channels, namely direct electron impact (eqs. 1) and vibrational excitation, can contribute to the overall dissociation processes in the discharge. A third contribution can come from a joint vibrational-electronic mechanism; in this case dissociation can occur through electron impact on vibrationally excited molecules (ref. 6).

The relative importance of the three pathways is linked to the electron energy distribution function in the discharge and vibrational channels are expected to prevail at low electron energies and reduced electric fields (E/N). Recently, some works appeared in literature (ref. 7,8) concerning modelling of discharges utilized for etching and deposition.

Among the various ground and excited species which are produced in a plasma, a distinction should be made between neutrals such as MX and X, and charged particles, since these species play different roles in the interaction with surfaces. Charged particles are responsible of electron impact induced dissociations, excitations in gas phase and various types of bombardments of substrates to be etched or covered with deposits. The nature of the bombarding particles, as well as their flow and energy, depends on the substrate position (either over the electrodes or floating) and on the additional bias, on discharge frequency and on many other parameters, such as feed, pressure, etc. (refs. 9-11). The charged particle bombardment should, in principle, affect both etching and deposition processes, either for the induced alteration of bond strengths in the solid network and for the creation of dangling bonds, unsaturated and active sites. When a discharge is working in a pressure range of 10^{-1} -1 torr, charged particles can affect surface processes in which, however, the predominant role is played by neutrals (ref. 12). At lower pressures, 10^{-3} - 10^{-1} torr, an ionic regime is established and charged particles are expected to have a dominant role in the surface processes. Halogen atoms and/or molecules can react with solid surfaces and lead to volatile etch products, such as SiF_4 and $AlCl_3$, in the interaction with silicon compounds and aluminum; they can also react with radicals and unsaturated in the gas phase leading to various stable products. Halogenated radicals, besides leading themselves to stable addition compounds in the gas phase, interact with solid surfaces as bricks for building polymer layers. Noticeable exceptions to this simple picture can be found in the interaction of some radicals with particular substrates, which produces etching instead of deposition. Table I lists the most important species active for etching and deposition of organic and inorganic films, which are produced in a plasma fed with gases containing fluorine, chlorine and bromine. Examples of the dual role played by some radicals are shown in the Table.

Since a discharge fed with halogenated gases of Table I can give both radicals and atoms, it has variable ability to act as etch or polymerizing medium. The shift to one or the other of the two plasma characters depends essentially on the $[X]/[MX]$ ratio in the plasma phase. This ratio can be changed by introducing feed additives, such as H_2 , O_2 , unsaturated, which can scavenge either halogens or radicals. Some examples of the additive effects will be given in the next section.

The study of the interactions between a plasma and a solid surface presents a more complicate picture because different steps in the overall process can introduce limitations in the kinetics. One or more of the following steps can cause kinetics limitations:

- active species production;
- mass-transfer;
- absorption;
- surface reactive process.

The first two steps control the chemical active particles supplied to the surface. The production of active species depends on the dissociation and recombination processes in the discharge, as well as on the type and amount of eventual additives. As an example, addition of O_2 to a freon increases the F atom production by scavenging CF_x radicals, while addition of H_2 increases radicals by scavenging F atoms. Under conditions in which the supply of active species to surface is the rate-limiting step, etching or deposition processes are regulated by their diffusion rates. These conditions are evidenced by the presence of a load effect, *i.e.* etch or deposition rates decrease with increasing the area of the surface. Mass transfer limitations can also occur when the surface is hindered by its coverage with films. This limitation can be due to the diffusion of species towards or from the surface through film bulk. When limitations due to species supply occur, the macroscopic kinetics of the interaction process do not reflect the "true" kinetics of the reaction on the surface. On the contrary, the "true" kinetics is observed when either absorption or surface reactive process represent the rate limiting steps. In this last case the overall kinetic data, plotted in the Arrhenius form, show an apparent activation energy which is a rather complex function of both the enthalpy variation of absorption/desorption process, ΔH , and of the true activation energy of the reactive process, E . In a plasmachemical system, charged particle bombardment can, at least in principle, affect ΔH and E values; hence, the apparent activation energy reflects this additional complication.

DIAGNOSTIC TECHNIQUES

Many diagnostic techniques are utilized with the purpose of monitoring stable and unstable species in the gas phase during etching or deposition processes in plasmas (ref. 13). Among the various techniques, the most utilized are probably Laser Induced Fluorescence (LIF), Actinometric Optical Emission Spectroscopy (AOES) and mass spectrometry.

LIF allows space and time resolved monitoring of some unstable species, such as CF_2 , CCl , Cl , Cl_2 , $HSiF$, etc. (refs. 13-18). The technique is precise, but not very versatile and needs sophisticated and expensive instrumentation.

AOES is based on the comparison of the emissions of some actinometers (N_2 , Ar, He), added to the main gas feedstock, with the emissions of excited species. The technique allows time resolved monitoring of some species, as CF , CF_2 , Cl , Br , F , Cl_2 , etc; it allows also an estimation of the trends of electron densities at various energies (refs. 19-24). The technique is very simple and needs instrumentation cheaper than LIF.

Mass spectrometry is by far the most known and utilized diagnostic technique. Since monitoring of unstable species is often troublesome, the technique is usually utilized for stable products.

HALOGENATED FEEDS FOR PLASMA ETCHING AND DEPOSITION

Freons

Freons are probably the most suitable feeds for etching and for polymerization purposes. Their versatility depends essentially on the possibility of careful control of the $[X]/[MX]$ ratio in the gas phase by either changing the type of pure freon utilized or by admitting various additives, such as O_2 , H_2 , C_2F_4 , etc.

A comparison of various freons. The suitability of freons for producing both etching and polymerizing active species clearly appears from the trends in Fig. 1.

In this figure we have plotted the concentration trends of CF , CF_2 , CF_3 radicals, of F atoms and of fast (≥ 11 eV) electrons, as obtained in discharges fed with C_nF_{2n+2} ($n=1-3$) and CF_3Cl freons. Data for the unsaturated tetrafluoroethylene are also included for comparison. All data have been obtained with actinometric emission spectroscopy, as discussed in refs. 19,21,25 also for other mixtures.

It can be seen from the figure that, with increasing the C/F ratio of the feed, the density of radicals increases and that of atoms decreases. The effect is, however, not linear and variations of orders of magnitude are found. CF_3Cl escapes this simple rule, because it

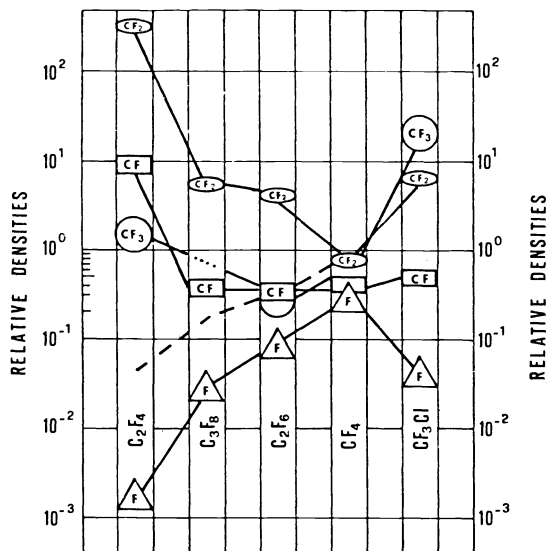


Fig. 1- Density trends of principal unstable species in discharges fed with halocarbons (0.5 torr, 50 watt, 50 sccm, 27 MHz, tubular reactor, discharge volume $\sim 13\text{cm}^3$). Dashed line is proportional to fast electron density.

decomposes in the plasma, leading to CF_3 and Cl fragments. The opposite trends shown by radicals and atoms is a consequence of the fast recombinations of these species, *i.e.* it is impossible to obtain both species in large concentration in the same feed. From the concentration trends of the figure it is possible to classify the various fluorinated feeds with respect to the expected etching ability. The order is: $\text{CF}_4 > \text{C}_2\text{F}_6 > \text{C}_3\text{F}_8 > \text{C}_2\text{F}_4$. Etch rate measurements have confirmed these expectations and C_2F_4 has been found to give rise to polymers over silicon substrates under experimental conditions: 0,5 torr, 50 W, 50 sccm.

Figure 2, where Si-etch rates *vs.* F atom densities are reported, shows that Si-etching depends only on F atoms, despite the large differences in radical and electron density exhibited by the various feeds. This universal etch law can be expressed as:

$$E_{\text{Si}} = k_{\text{Si}} [\text{F}] \quad (3)$$

where E_{Si} and k_{Si} are the etch rate and the etch constant for silicon, respectively. Equation 3 well agrees with experimental finding of Flamm and coworkers (ref. 26), who have found that F atoms (and molecules) chemically interact with Si (and SiO_2) surfaces, through a 1st. order rate process, leading to SiF_2 and SiF_4 . The process is spontaneous and can occur even in the absence of the plasma. There is some apparent disagreement between the chemical character of the interaction of Si and SiO_2 surfaces with fluorine and the results in the ionic regime found by Lee *et al.* (ref. 27).² In this last case an enhancing ionic effect was found for low pressure discharges fed with $\text{CF}_4\text{-O}_2\text{-Ar}$ mixtures, where F atom was the assumed etchant. However, ion enhancing effects could be due to either an induced dissociation of radicals absorbed on the surface or to their desorption. This could exclude an ionic bombardment activation of the spontaneous etching process by fluorine atoms. On the other hand, under the experimental conditions of ref. 27, the concentration of radicals can still be high enough to cause their significative absorption. From these considerations it can be stressed that, up to date, there are not unambiguous demonstrations of an enhancing effect induced by ions in the chemical spontaneous process of Si-etching with F atoms. Similar considerations can be applied to SiO_2 , which can be etched anisotropically in feeds containing large excess of radicals (such as freons in mixture with H_2 or C_2F_4) and not in $\text{CF}_4\text{-O}_2$ plasmas. It can be concluded, as a general rule, that the more is the F atom density in plasma media, the less is the degree of anisotropy. Obviously, different considerations can be done when milder etchants, as chlorine or bromine, are utilized instead of fluorine.

The effect of oxygen addition. Addition of O_2 to freon plasmas causes large changes in both etching character and in product distribution. Oxygen, in fact, reacts with radicals through the following reactions (ref. 28):

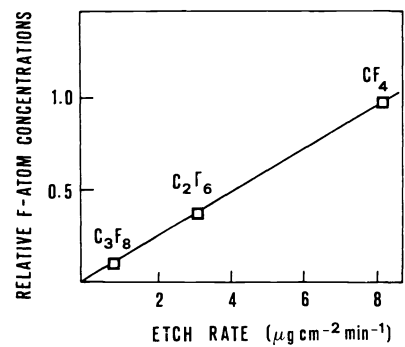


Fig. 2- Si-etch rates *vs.* relative $[\text{F}]$ in discharges fed with C_3F_8 , C_2F_6 , CF_4 .

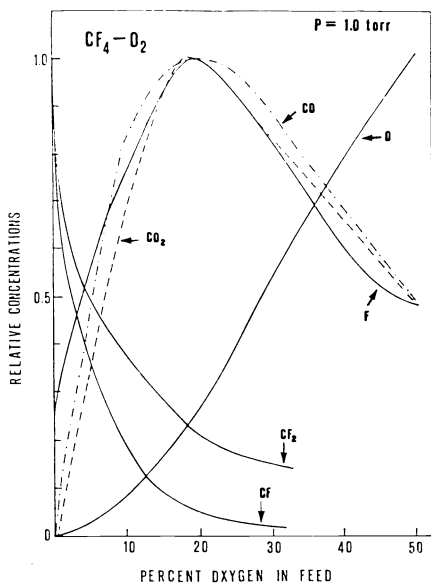
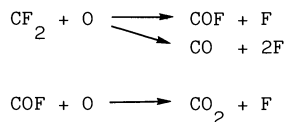


Fig. 3- Relative concentrations of some emitting species in $\text{CF}_4\text{-O}_2$ discharges (1 torr, 50 W, 30 sccm).



Reactions 4, as well as those involving other CF_x radicals, contribute to rise F atom concentration either directly and by decreasing their recombination with radicals. These effects are shown in Fig. 3, where the trends of CF, CF_2 , F, CO, CO_2 and O are reported as a function of oxygen percentage in $\text{CF}_4\text{-O}_2$ discharges operated at pressure = 1 torr, power = 50 W and a total gas flow rate of 30 sccm (discharge volume 13 cm³). It is evident the decrease of the radicals and the increase of CO, CO_2 and F, as expected on the basis of reactions 4. These species, however, follow composition dependences through maxima, which are due to the combination of three effects with increasing % O_2 : (a) increased production of C-O-F compounds; (b) dilution increase; (c) electron density₂ decrease. The last point has been deduced on the basis of the actinometric emission results for $\text{CF}_4\text{-O}_2$ discharges.

The decrease of electron density with % O_2 does not influence directly Si or SiO_2 etch rates, because they do not depend appreciably on the flow and energy of the charged particles bombarding the substrates, when F is the etching species.

The trend of F atoms reported in Fig. 3 very closely follows that of SiO_2 etch rate. This indicates that oxide etch rate, E_{SiO_2} , in close analogy with Si etching₂, depends linearly on F atom density:

$$E_{\text{SiO}_2} = k_{\text{SiO}_2} [\text{F}] \quad (5)$$

as unambiguously shown in Fig. 4. Again, this is a purely chemical etch law, as confirmed by Flamm and coworkers (ref. 30). They have determined also the values of k_{SiO_2} as a function of the substrate temperature. Eventhough the presence of oxygen atoms does not influence directly SiO_2 etch rates, nevertheless it plays a major role during silicon etching. When high levels of O are attained in the discharge, equation 3 does not hold in describing the functional dependence of E_{Si} on [F]. The rate equation, in fact, must take into account a competition of O atoms in the chemisorption over Si-surface sites. This competition causes Si etch rates to be retarded: this effect increases with O atoms and with dilution in $\text{CF}_4\text{-O}_2$ discharges (refs. 20,31). The pure chemical nature of the O/F competition has been demonstrated in ref. 32, where similar effects have been found in $\text{SF}_6\text{-O}_2$ discharge, although very different densities of atoms, radicals and ions are present. In Fig. 5 it is shown a hysteresis effect of Si etch rate vs. [F], due to the increasing retarding action which increases with O_2 in both $\text{SF}_6\text{-O}_2$ and in $\text{CF}_4\text{-O}_2$ mixtures.

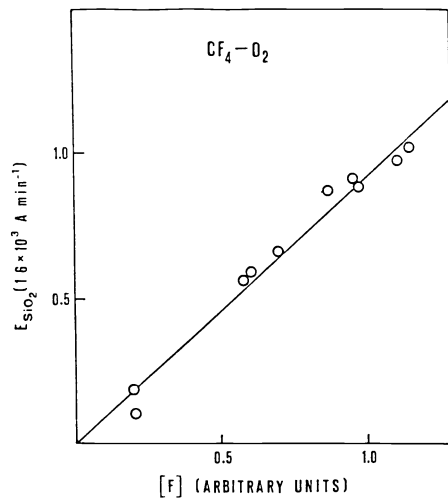


Fig. 4- SiO_2 etch rate vs. [F]. Conditions as in figure 3.

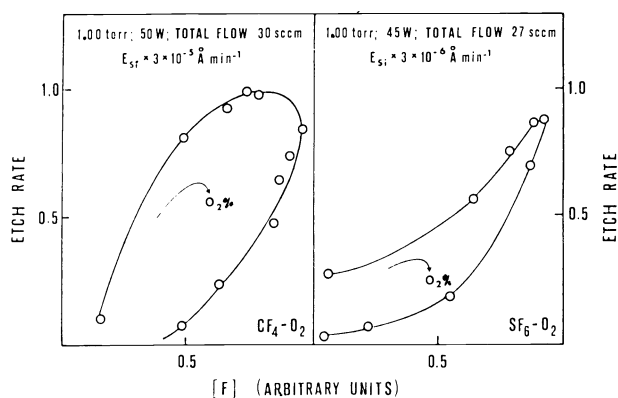


Fig. 5- Si-etch rate vs. $[F]$ at various $O_2\%$ in CF_4-O_2 and SF_6-O_2 discharges.

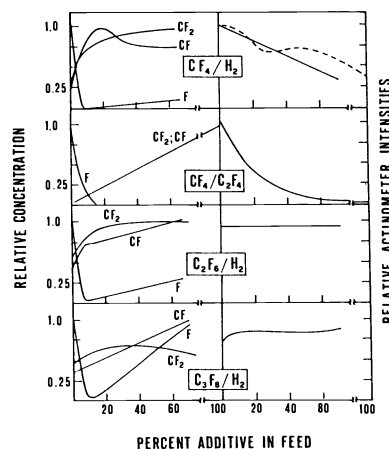


Fig. 6- Trends of atoms and radicals (left side) and emissions of actinometers (proportional to fast electron density) (right side). Dashed curve is for probe measurements of ref.7. (0.5 torr, 50 W, 50 sccm).

The effect of H_2 or C_2F_4 addition. Addition to freons of either H_2 or of unsaturates, as C_2F_4 , leads to media characterized by large densities of radicals, since F atoms do not recombine radicals because they form HF and C_2F_6 (ref.12,25). The effect of these additions is shown in Fig. 6, where profiles of F, CF_x and fast (>11 eV) electrons are plotted. Similar results can be obtained by adding C_2H_2 , C_2H_4 or with severe loading conditions.

In general, introduction of either H_2 or of C_2F_4 in the freon feed allows an increasing substitution of F atoms with CF_x radicals. The reported two-fold role of these radicals (see Table I) gives these discharges a character of both selective etching media for SiO_2 and Si_3N_4 (ref. 29) and of polymerizing systems. This last effect is evidenced in Fig. 7, where polymerization rates on silicon substrates, r_p , are also plotted as a function of the additive percentage in CF_4-H_2 or C_2F_4 mixtures. In this figure it is also shown that experimental results are well fitted by the equation:

$$r_p = k f(n_e) [CF_x] \quad (6)$$

where $f(n_e)$ is a parameter proportional to the density of fast (≥ 11 eV) electrons. It should be considered, however, that $f(n_e)$ can also be correlated to the ion density in the discharge and can be seen as an overall parameter, since contributions of ions and electrons cannot be separated. Equation 6 has been derived by assuming an activation growth model (ref. 25) based on CF_x radical addition on polymer activated sites, which can be summarized as follows:



In this scheme process (7) consists of parallel reactions, in which branch a accounts for product formation through radical recombinations, and branch b represents the direct addition of CF_x radicals on activated surface sites of the growing polymer, $(POL)_n^*$. Reaction (8) accounts for polymer activation through charged particle bombardment, and reaction (9) represents the termination stage. It is worthy to consider that recent experiments, performed by superimposing a low energy ion bombardment to a fluoropolymer deposition in a glow discharge, have confirmed the presence of a surface activation

stimulated by low energy ions (<50 eV) (ref. 33).

Some experiments with $C_2F_6-H_2$ mixtures have been also performed at various substrates temperatures for discharge operated at 0.3 torr and high voltages ref. 34). Results are shown in Fig. 8 in the form of Arrhenius plot. The figure shows that, at higher temperatures, deposition rates do not display an Arrhenius type behaviour; namely there is a negative apparent activation energy. At lower temperatures, apparent activation energies are close to zero.

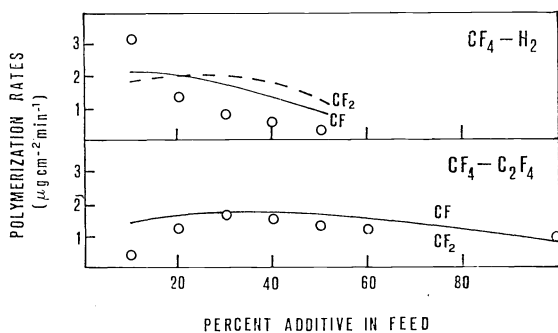


Fig. 7- Experimental and calculated deposition rate in CF_4-H_2 or C_2F_4 discharges. The curves are calculated assuming either CF_2 or CF radicals as building blocks for polymerization.

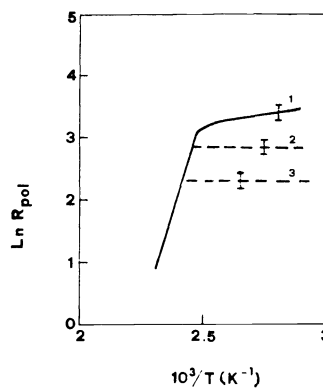


Fig. 8- Arrhenius plot of polymer deposition rates in $C_2F_6-H_2$ discharges. (1) 50% H_2 , 1200 V; (2) 50% H_2 , 850 V; (3) 20% H_2 , 1200 V. (0.3 torr, 25 sccm, 40 W).

A non-Arrhenius behaviour can be indicative of a competition between an absorption equilibrium of radicals on the surface and the subsequent chemical interaction of the radicals with the activated surface sites. By increasing the substrate temperature, the absorption equilibrium, which has a negative enthalpy variation, becomes the bottleneck for the overall kinetics of deposition.

Inorganic fluorine containing feeds. Also inorganic fluorinated gases, such as NF_3 and SF_6 , are suitable for Si and SiO_2 etching, as they are source of large concentrations of F atoms (see Table I). The chemistry of SF_6 (ref. 32) is similar to that of freons, in fact sulphur containing deposits can be obtained with either H_2 admission or under loading conditions. NF_3 , as a feed for etching, has the considerable advantage of not giving rise to solid residues, even under loading conditions. It should also be considered, for clarity sake, that F_2 can also spontaneously etch both Si and SiO_2 (ref. 26); however, the rate of the process is much lower than that with F atoms.

XeF_2 has also been studied as a feed for Si etching (ref. 35). It can also be utilized as a plasma-less etching gas which allows infinite selectivity of Si-etching with respect to SiO_2 . In this case the Arrhenius plot of Si-etch rate shows two different values of apparent activation energy. This variation is indicative of two kinetic regions. At low temperatures it is absorption, with its negative ΔH , to regulate plasma-solid interactions, while at higher temperatures the direct reaction with the surface can explain the "regular" behaviour and the positive apparent activation energy.

Chlorine containing gases. Many chlorine and bromine containing mixtures can be utilized for plasma etching of various materials, as some refractories, III-V compounds, Si and its compounds and various metals, as it is shown in Table I. Utilization of chlorine and bromine containing feeds is a must for materials which form non-volatile fluorides, such as GaAs, Al, InP and Cr. In this case etchant active species can be either atoms or molecules, depending on the substrate. When appropriate ion fluxes impinging substrates are ensured, anisotropic etching can be obtained, since chlorine and bromine are milder etchants and their interaction with solids can be affected by an ion induced damage of the surface (ref. 30). A noticeable exception is aluminum; in this case it has been shown that a clean surface can be spontaneously etched by Cl_2 molecules and no enhancement has been observed

with ion bombardment or plasma ignition (ref. 36). However, very high etch rates are obtained (in the range of $\mu\text{m min}^{-1}$) with aluminum, so Cl_2 can not be considered a mild etchant for Al etching. Addition of CCl_4 (or BCl_3) in the feed for Al-etching processes has some advantageous features, due to the presence of CCl_x and BCl_x radicals in the discharge; these radicals can, in fact:

1. scavenge H_2O and O_2 , which otherwise generate AlO_x on the substrate;
2. Selectively etch AlO_x layers, allowing a reproducible reduction of the induction time prior to Al-etching;
3. absorb preferentially on sidewalls, where they can not be desorbed by vertically impinging ions, allowing a recombinant mechanism of anisotropy.

Gas phase density of radicals is a function of the percentage of added CCl_4 , as it is shown in Fig. 9 for CCl_4 - Cl_2 mixtures (ref. 21). From the figure it appears that it is possible to control $[\text{Cl}]/[\text{CCl}_2]^2$ ratio, as found for freons when oxygen is added, and hence etching and polymerizing character of the discharge. During Al etching it is necessary to have radicals in gas phase for the reasons examined in points 1-3; however, this causes some effects due to polymerization on substrates and reactor walls, in particular at low temperature. In Fig. 10 are plotted the emissions of some species and of the actinometers during aluminum etching in 20% CCl_4 - Cl_2 mixtures as a function of the discharge duration (ref. 34). The reactor utilized is a parallel plate one, with thermoregulated electrodes. Substrates lie on ground electrode and temperature for data of Fig. 10 is kept at 20°C . Important features of the figure are:

- (1) actinometer emissions do not vary with discharge duration; (2) Al and AlCl emissions have the same profile, which should represent that of AlCl_3 in gas phase; (3) Cl_2 emission slightly decreases with discharge duration, while Al and AlCl emissions have a steeper profile. This is evidenced by the ratio of Cl_2 to Al emissions, which increases with discharge duration; (4) induction time is lower than 5 min, and is evidenced with the arrow in the figure.

Point 1 ensures that electrical conditions are not varying with discharge duration and that actinometry is applicable, so emission intensity are proportional to ground state concentrations. The slight decrease of Cl_2 is probably due to the increasing degree of coverage with $(\text{CCl}_x)_n$ polymer of inner walls when discharge duration increases. The steeper decrease of Al and AlCl signals is due to the presence of a glow-polymer: this is, in fact, an increasing diffusion barrier, partially preventing either in-diffusion of Cl_2 active species or out-diffusion of etch product AlCl_3 . The increase of the ratio of Cl_2 to Al emissions implies that etch rate (proportional to I_{Al} or I_{AlCl}) decreases with duration, even in the case of constant Cl_2 concentrations. It is worth to notice that, by increasing substrate temperature, diffusion limitations reduce their importance, because polymerization rate decreases with temperature. In fact, at temperatures 70°C , I_{Al} , I_{AlCl} and $I_{\text{Cl}_2}/I_{\text{Al}}$ variations are strongly reduced.

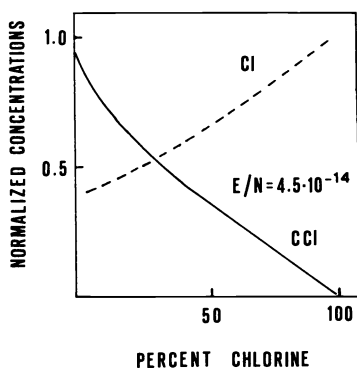


Fig. 9- Trends of CCl and Cl vs. $\text{Cl}_2\%$ in CCl_4 - Cl_2 discharges. (0.3 torr, 70 watt, 25 sccm, 27 MHz, tubular reactor, disch. vol. 13 cm^3).

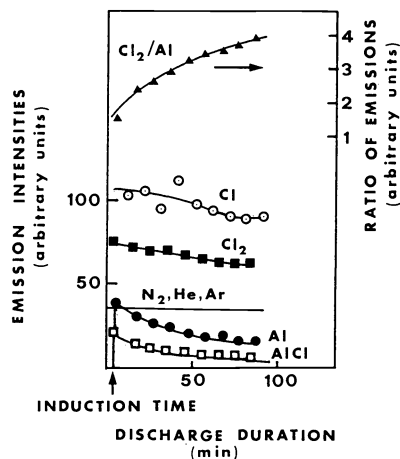


Fig. 10- Trends of Cl , Cl_2 , Al, AlCl and actinometers (N_2 , He, Ar) emissions, and of Cl_2/Al vs. discharge duration in 20% CCl_4 - Cl_2 during Al etching. (0.3 torr, 300 watt, 25 sccm, 27 MHz, parallel plate reactor of 1200 cm^3 , substrate temp. 20°C).

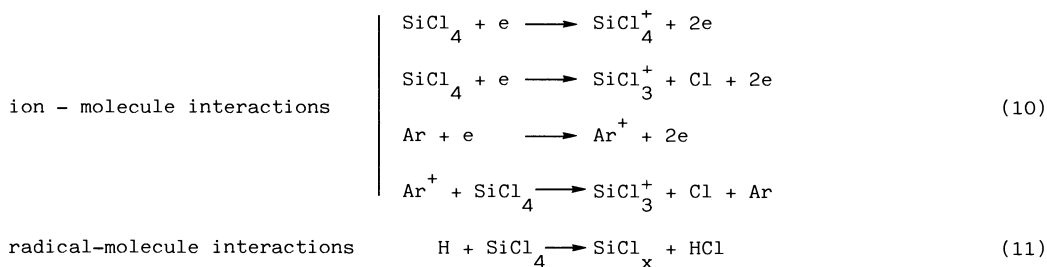
Silicon halides

Volatile halogenated silicon compounds SiX_4 (SiF_4 , SiCl_4 , ...) are a class of chemical reactants widely utilized in plasmachemical processes. They can provide both halogen atoms, $\text{X}(\text{F}, \text{Cl})$, for etching purpose and silicon containing radicals, SiX_n , for deposition of various silicon alloys (a-Si:H,X ; SiO_2 ; Si_3N_4 ; Si:C ; ...). The great importance that silicon based alloys are assuming in material science has addressed the utilization of plasma reactors fed with silicon halides mostly towards deposition, rather than etching. In particular, SiF_4 fed plasmas, firstly utilized as F atom source for material etching (see Table I), have been recently employed as source of active SiF_x species for the deposition of hydrogenated and fluorinated silicon films (a-Si:H,F) (Ref. 37). This material has revealed to be a valid alternative with respect to that obtained by SiH_4 glow discharges (a-Si:H), for applications in electrophotography, image pickup systems, field effect transistors (FET) and, mainly, in low-cost photovoltaic device manufacturing. More recently, SiCl_4 glow discharges have been utilized (Ref. 38-41) to deposit hydrogenated and chlorinated silicon films (a-Si:H,Cl) and, besides the material characterization, a considerable effort has been devoted to the study of the involved plasmachemical processes. The deposition-etching duality, characterizing SiF_4 and SiCl_4 glow discharges, can be resolved by adding the proper additive to the feed, according to the arguments reported in the "General Picture" section. In particular, it has been found that these plasmas cannot give deposition, until some halogen scavengers (mainly H_2) are added to the feed. The presence of additives can affect either the production of active species in the gas phase, either the growth mechanism, through surface reactive processes.

In the following, experimental evidences will be discussed on the different roles played by homogeneous and heterogeneous processes occurring in SiCl_4 and SiF_4 glow discharges.

Silicon tetrachloride. A glow discharge fed with SiCl_4 -Ar mixture with and without H_2 has been studied from a mechanistic point of view by Mayo et al. (ref. 42). They have utilized a mass spectrometer to sample stable and unstable species from the reactor as a function of the residence time.

Two different dissociation channels of SiCl_4 have been reported to occur, according to the utilized mixture:



Processes (10) have been found to prevail in absence of H_2 , while processes (11) have to be added when H_2 is present; this explains the experimental observed increase of SiCl_4 dissociation with H_2 addition. More recently, Bruno et al. (ref. 43) have observed a decrease of SiCl_4 dissociation, when H_2 is added to SiCl_4 -Ar plasma. In this study AOEES has been utilized to detect unstable emitting species. The observed spectra from SiCl_4 - H_2 -Ar plasma contain emission lines of Cl, H, Ar, Si, the bands of SiCl and also a strong continuum centered at $\lambda = 330$ nm, which has been assigned to SiCl_2 transition to a repulsive state ($\text{SiCl} + \text{Cl}$). Figure 11 shows the effect of the progressive substitution of H_2 with Ar on the relative densities of the above mentioned species. In the figure it is reported the ratio of the emission intensity of each species with respect to that of Ar, according to the actinometric technique (ref. 21). In the same figure, the deposition (r_D) and etch (r_E) rates, measured "in situ" by laser interferometry technique (ref. 44), have been reported. The strong decrease of SiCl_x density when few percentages of H_2 are added to SiCl_4 -Ar mixture can be attributed to a decrease of SiCl_4 dissociation. Since a decrease of electron concentration is expected when a molecular gas (H_2) is added to an Ar plasma (ref. 45), the electron impact process of eqs. 1 is therefore the main dissociation channel. The deposition-etching transition observed at $x_{\text{Ar}} = 0,9$ is associated with the appearance of a significant amount of Cl atoms in the gas phase, which are effective for silicon etching (ref. 36). The dependence of the etch rate of Si:H,Cl films on Cl atom concentration is shown in Fig. 12, where the deposition zone is also shown.

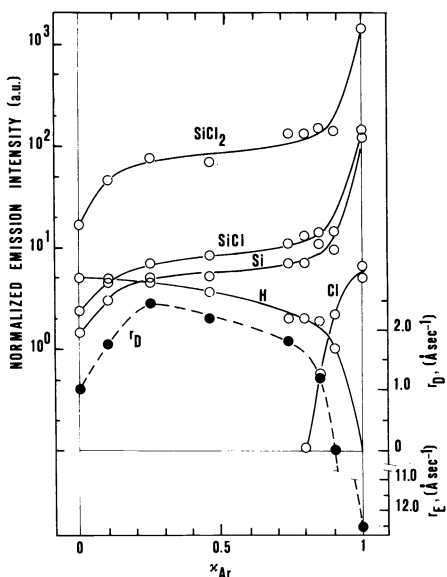


Fig. 11- Intensity of emitting species (O) normalized to Ar peak vs. H_2 -Ar mixture composition, x_{Ar} . Values of deposition, r_D , and etch rate, r_E , (●) refer to the right hand side scale. (1.0 torr, 60 sccm, 10.W, $\Phi_{SiCl_4}/\Phi_T=0.05$, substrate temp. 300°C).

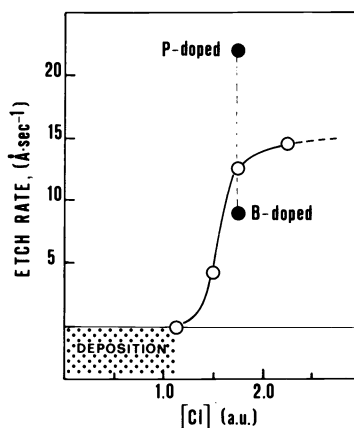
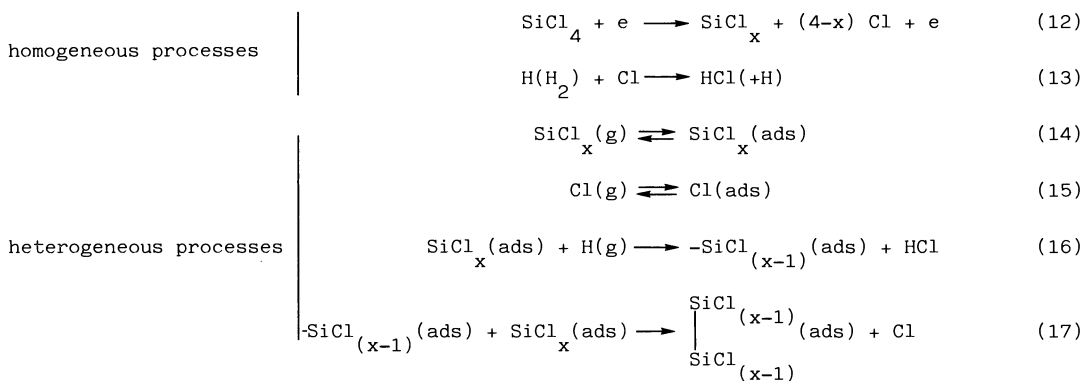


Fig. 12- Etch rate of Si:H,Cl films vs. Cl atom density, [Cl]. Full circles refer to rate of P and B-doped samples. Dotted area indicates deposition zone. (Discharge mixture: $SiCl_4$ -Ar; for other parameters see caption of Fig. 11).

The saturation of r_E value shown by the "plateau", as well as the remarkable dopant effect (full points), are indicative of the presence of Cl atom chemisorption processes in the etching mechanism. The same dopant effect has been also found in deposition experiments of ref. 46, and has been attributed to $SiCl_x$ chemisorption. These results provide some indications on homogeneous and heterogeneous x reactions occurring in $SiCl_4$ glow discharges:



where eq. (17) accounts for the competition between deposition and etching processes. It can also be seen that the feed additive H_2 has a twofold role: (a) to scavenge Cl atoms in the gas phase so affecting the $[Cl]/[SiCl_x]$ ratio and (b) to abstract chlorine from the absorbed $SiCl_x$, so producing free-bond silicon species ($-SiCl_{(x-1)}$) for the material growth. From this mechanism the kinetic expression $r_D \propto [H][SiCl_x]$ has been derived and experimental data confirm this relationship, at least in the deposition region where Cl atoms are absent (see Fig. 11).

Silicon tetrafluoride. Plasma of SiF_4 , SiF_4-O_2 , SiF_4-H_2 and SiF_4-SiF_2 have been studied either for etching or for deposition purposes (refs. 37,47,48).⁴ Also in this case, the additives play the role of changing the ratio $[F]/[SiF_x]$. Oxygen addition strongly increases fluorine atom concentration and, therefore, the etch rate of silicon based materials (see Table I). On the contrary, deposition of silicon films occurs when H_2 and SiF_2 are added to the feed, just as H_2 does when added to $SiCl_4$ plasma. Few studies on the deposition

mechanism occurring in SiF_4 plasmas are available, despite the wide characterization on the deposited material and its recent utilization in solar cell production (ECD-Sharp). Matsuda et al. (ref. 49) suggested a simplified deposition model of a-Si:H,F films, which successfully explains the reason why no deposition occurs until H_2 is added to pure SiF_4 . They stressed in the model the importance of F abstraction from the surface by H atoms, in analogy with the process of eq. 16 involving Cl atoms. Similar conclusions on the role of H atoms have been reported by Matsukura et al. (ref. 50), who found that the process $\text{SiF}_x + y\text{H} \rightarrow \text{SiH}_n$ (or SiHF_m) + zHF occurs also in the gas phase, since spectroscopic measurements evidenced SiHF_m emission. Furtherly, the authors attributed to electron impact the main dissociation channel. Silicon difluoride, SiF_2 , is the only example of additive different from H_2 in inducing the deposition from SiF_4 plasma (ref. 48). The effect of SiF_2 addition can be considered equivalent to what unsaturates (C_2F_4) do, when added to a CF_4 plasma (ref. 25).

TABLE I. Summary of principal halogen containing mixtures and of active species for etching and deposition. Principal materials which can be etched or deposited are also listed (refs. 12, 17, 30, 36-38, 51, 52).

| MIXTURES | ETCH. SPECIES | POLYM. SPECIES | ETCHED OR DEPOSITED MATERIALS |
|---|-------------------------------------|-----------------|---|
| CF_n CF_n - O_2 CF_n CF_n - O_2 | F, F_2 | | Si, SiO_2 , Si_3N_4 , resists, Mo, Nb, Ta, Ti, V, W |
| CF_n CF_n - H_2 ; CF_n CF_n - CF_4 | CF_x | CF_x | SiO_2 , Si_3N_4 (CF_x) CF_x |
| SF_6 ; SF_6 - O_2 ; SF_6 - H_2 | F, F_2 | SF_x | Si, SiO_2 , Si_3N_4 , resists, Mo, Nb, Ta, Ti, V, W sulphur |
| CCl_4 ; CCl_4 - Cl_2 ; CCl_4 - O_2 ; CCl_2F_2 | Cl, Cl_2 CCl_x | CCl_x | Si, SiO_2 , Si_3N_4 , Al, GaAs, InP, Au, Cr, Ti Al_2O_3 (CCl_x) CCl_x |
| BCl_3 ; BCl_3 - Cl_2 | Cl, Cl_2 BCl_x | BCl_x | Si, SiO_2 , Si_3N_4 , Al, GaAs, InP, Au, Cr, Ti Al_2O_3 B_2O_3 (with H_2O , O_2 in discharge) |
| SiF_4 ; SiF_4 - H_2 ; SiF_4 - O_2 | F, F_2 | SiF_x | Si, SiO_2 , Si_3N_4 , resists, Mo, Nb, Ta, Ti, V, W a-Si:H,F; SiO_2 (with H_2O , O_2 in discharge) |
| SiCl_4 ; SiCl_4 - H_2 ; SiCl_4 - O_2 | Cl, Cl_2 | SiCl_x | Si, SiO_2 , Si_3N_4 , Al, GaAs, InP, Au, Cr, Ti a-Si:H,Cl; SiO_2 (with H_2O , O_2 in discharge) |
| XeF_2 | F, F_2 XeF_2 | | Si, SiO_2 , Si_3N_4 , resists, Mo, Nb, Ta, Ti, V, W Si |
| Br_2 | Br, Br_2 | | GaAs, InP, Si, Ti |

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