PLASMA POLYMERIZATION AND ETCHING MECHANISMS IN FLUOROCARBON SYSTEMS

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The renewed impetus to studying fluorocarbon discharges is clearly driven by the needs of the rapidly emerging etching and polymerization technologies which require on the one hand the ability to selectively remove material from a surface with ever increasing directional resolution and on the other hand to deposit polymeric material with unique properties uniformly over large surface areas.

It is important to recognize that unique differences should be anticipated in the plasma chemistry of fluorocarbons from that of hydrocarbons. This can be attributed in part to the strong C-F bond and relatively weak F-F bond. Thus while elimination of H_2 and HF is a favorable process in the case of hydrocarbons and fluorohydrocarbons, for fluorocarbons C-C bond cleavage is more likely.

Recent in-situ plasma diagnostic studies involving halocarbon discharges have helped considerably in delineating some of the physical and chemical processes which control the etching and polymerization processes. It is clear that most of the important plasma gas phase excitation, ionization and fragmentation processes in the 10^{-1} - 10^{-4} Torr pressure regime are primarily controlled by collisions of the gaseous species with electrons,[(1)] whereas the collisional partners which lead to subsequent loss processes of active gaseous species are manifold.[(2)] It is self evident therefore that control over electron energy and density in various regions of the plasma will afford considerable control over the production of highly active species which are thought in part to be responsible for some of the unique reactions encountered in plasmas.

Emphasis in this paper will be placed on approaches which lead to the removal of reactive species from the gas phase as well as the special role of energetic positive ions in plasma-surface interactions. Controlled scavenging of critical species from the gas phase and/or at specific surfaces and the degree of positive ion bombardment at a given surface can in fact result in simultaneous polymerization at one surface and etching at another within the same apparatus.[3,4]

Attention will also be drawn to the significance of the residence time of active species in the plasma region of interest. It will become evident that the flow rate and pressure as well as the consumption of active species per unit area of active surface can alter the resultant chemistry dramatically.[5,6,7,8] Clearly one should expect both the etching and polymerization process to be different depending on where the polymerizing or etching surface of interest is located with respect to the plasma region. One would expect and finds that, for example, the polymerization process will approach conventional polymerization mechanisms and resultant structures the further removed the polymerizing surface of interest is from the plasma region.[9,10] Whereas many discharge configurations are being explored in this general context, the r.f. capacitively coupled, planar diode systems appear to be emerging as the most reliable and flexible to meet a variety of technological needs.

Another key point that will be stressed is the fact that in r.f. driven diode configurations, as commonly used, all surfaces including the grounded surfaces are at a negative potential with respect to the plasma potential and are therefore subject to positive ion bombardment.[11,12] The relative surface area of the grounded surfaces to that of the excitation electrode, in part, dictates the energy with which positive ions arrive at grounded surfaces. Certainly at the negatively biased excitation electrode negative charge carriers bombardment is insignificant and at all other surfaces only those negative charge carriers (electrons and negative ions) which have sufficient energy to overcome the sheath potential at such surfaces can ultimately arrive. Sheath potentials at grounded surfaces in commonly used r.f. diode configurations can vary from a few tens to several hundred electron volts depending on the particular geometry. Consequently, the role of negative charge carriers in the surface plasma etching and surface polymerization process is considered secondary. The role of negative ion gas phase collisions may however be quite significant but definitive evidence as to their role has not been established so far in this context.

As we shall see, the particular surface chemistry which ultimately dominates at a particular surface in a given experiment will be greatly influenced by the flux and energy of positive charge carriers that arrive at that surface simultaneously with ground state and excited state neutral species as well as the chemical nature of the surface.

A brief description of the key plasma diagnostic techniques which have been especially useful in delineating the gas phase processes and gas surface interactions in fluorocarbon plasmas will be given followed by a more extensive discussion of the relationship of plasma etching and polymerization mechanisms.

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