INTRODUCTION

In a low-pressure, nonequilibrium plasma in a fluorocarbon gas such as that used in a processing reactor in semiconductor device fabrication, the active chemical species are all fragments of the feed gas. The fluorocarbon feed gas is itself chemically benign and the parent ions are unstable and do not persist for a sufficient time to contribute to plasma chemistry. The active fragments are produced by electron impact in the 5 to 30 eV energy range typical of the electron-energy distribution in the plasma. In general, electron-molecule collisions leading to dissociation include dissociative ionization, neutral dissociation, dissociative electron attachment, and dipolar dissociation. For fluorocarbons, only the first two are important. Dissociative attachment must be initiated by the resonant attachment of an electron to yield a negative ion that is sufficiently long-lived for dissociation to compete with autodetachment of the electron. Resonant electron attachment is not a significant feature of electron-fluorocarbon interactions. Dipolar dissociation proceeds through very high-lying electronic states. The cross sections are generally small, especially for electrons with energies less than about 30 eV. Although not a mathematical certainty, it is generally observed that the neutral fragments from both dissociative ionization and neutral dissociation are odd-electron species; they are radicals. Chemically they are very reactive. In addition, in comparison to ions, these species have relatively low sticking probabilities at surfaces. As a consequence radicals may persist in the plasma for a much longer time than ions. The concentration of radicals in a plasma can exceed the concentration of ions by as much as four orders of magnitude.

Measurements of cross sections for the production of radicals in low energy electron-molecule collisions are clearly needed to understand plasma chemistry in general, and to model and optimize the operation of particular plasma reactors. To measure a dissociation cross section one must detect one or the other of the fragments.
Experimentally it is much easier to detect a charged species so, if the choice exists, a charged fragment of a dissociation is detected rather than a neutral fragment. This is obvious from the literature describing radical production from electron-impact on fluorocarbons; there are many more reports of measurements of cross sections for dissociative ionization \( (e^- + AB \rightarrow A^+ + \cdot B + 2e^-) \) than for neutral dissociation \( (e^- + AB \rightarrow \cdot A + \cdot B + e^-) \) since a measurement of a neutral dissociation cross section requires the detection of one or the other of the neutral products.\(^1\)

Mass spectrometric and optical techniques are the obvious choices for the detection of radicals, but it must be borne in mind that cross section measurements should be carried out under single-collision conditions requiring essentially single-radical sensitivity. Optical methods can be very sensitive in the detection of atoms, however these methods are usually not sufficiently sensitive for the detection of molecular radicals where the absorption and emission probability is spread over many transitions. In addition, optical techniques, such as laser-induced fluorescence, suffer a lack of generality--one must know in detail the spectrum of each species to be detected. On the other hand, a mass spectrometer can be employed to detect almost any volatile species at concentrations below \(10^2 \text{ cm}^{-3}\) owing to the fact that the typical electron-impact-ionization source ionizes all species with approximately the same high efficiency; however, this lack of specificity may be either a blessing or a curse. To measure a cross section for radical production, a beam of electrons is passed through a target gas at such low densities that only a small fraction of the target is dissociated. The problem that arises with mass spectrometric detection is that ionization of both the radicals and the target gas give the same ionic species. For example, the \(69 \text{ amu} \ CF_3^+\) peak is the most prominent feature in the mass spectrum of both \( CF_4 \) and \( CF_3 \). Some degree of specificity has been achieved by adjusting the ionizer electron energy to the threshold for the species of interest.\(^2,3\)

Our approach to the specific and nearly-universal detection of radicals involves the method by which radicals in the gas phase were first identified. In these experiments a stream of dissociated gas was exposed to a mirror of lead or tellurium.\(^4-6\) The disappearance of the mirror along with the subsequent isolation of various volatile lead and tellurium compounds in the effluent confirmed the existence of radicals as a distinct chemical entity. In our case we have the advantage of very sensitive mass spectrometric analysis to detect the volatile products of radical-metal reactions.

THE EXPERIMENT

In our apparatus a beam of electrons passes through a target gas in a collision cell that has a tellurium mirror on its inner surface. With a mass spectrometer we measure a signal that is proportional to the partial pressure of a diradical telluride (e.g., Te(CF₃)₂) from the reaction of the tellurium with radicals produced by electron impact on the target gas. The telluride partial pressure is proportional to the radical production rate that is in turn proportional to a cross section. The virtue of this technique is that the tellurium surface does not react with the target gas. In addition, the portion of the mass spectrum under observation is displaced by more than 128 amu (the nominal tellurium mass) from the region displaying peaks characteristic of the parent gas.