Kinetics of electron attachment to fluorocarbon radicals

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The literature contains almost no experimental data on electron attachment to transient species, such as most radicals. We have recently developed a novel flowing afterglow technique to measure several types of otherwise difficult to study plasma processes, including thermal attachment to radicals.[1] Variable electron and neutral density attachment mass spectrometry (VENDAMS) exploits dissociative electron attachment in a weakly ionized plasma as a radical source. Here, we apply VENDAMS to a series of halocarbon precursors in order to study the kinetics of electron attachment to fluorocarbon radicals. These reactions are of interest as it is known that fluorocarbon radical concentrations affect the efficiency of plasma etching of semiconductor materials, an important industrial process for fabricating microelectronics;[2] however, the kinetics of these processes are entirely undetermined. Thermal electron attachment rate coefficients are measured for CF_2, CF_3, C_2F_5, 1-C_3F_7, 2-C_3F_7, 1-C_3F_5, 2-C_3F_5, and 3-C_3F_5 from 300 to 600 K. The magnitude and temperature dependence of the rate coefficients varies significantly from species to species, as is expected for electron attachment processes, which are highly sensitive to the specifics of the potential surface; however, across all species and conditions, attachment never exceeds 5% of the calculated collisional rate coefficient. The C_2 and C_3 species all attach purely dissociatively to form F^-. CF_2 does not attach electrons to form stable anions. CF_3 attaches both dissociatively and associatively, and rate coefficients for the individual product channels are measured as both a function of temperature and of pressure. The results are fit using a kinetic modeling approach, in which electron attachment is separated as fully as possible into discrete steps and each individual step treated using statistical theory.[3] The modeling reproduces the experimental data exceptionally well, and is used to extrapolate from the results to temperature and pressure conditions inaccessible by the experiment, including to non-thermal plasmas most relevant to plasma processing.

References

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