ELECTRON ATTACHMENT TO SF_6 AND SO_2

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INTRODUCTION

SF_6 is a favorable gas for use in the plasma etching of microelectronic devices. However, SF_6 plasmas are complex because of the large number of secondary products that are formed by reactions with oxygen and trace amounts of water. Under some etching conditions the mole fraction of stable decomposition products in an SF_6/O_2 plasma can exceed 20% of the neutral species.[1] A full understanding of the physical processes occurring in SF_6 discharges requires a detailed knowledge of the interaction of low energy electrons with SF_6 and its electrical discharge by-products. We have measured absolute cross sections for electron scattering and for negative ion formation through electron attachment to SF_6 and to several by-products (SO_2, SOF_2, SO_2F_2, SOF_4, and SF_4) produced by electrical discharges in SF_6 . Due to space limitations only the results for SF_6 and SO_2 are presented in this abstract. Preliminary results of these measurements were presented previously[2] and are now superseded by the cross sections presented here.

EXPERIMENT

An electron transmission spectrometer employing a trochoidal monochromator[3] forms the basis of these experiments. This instrument consists of a thermionic electron source followed by the trochoidal monochromator, an accelerating lens, a gas cell, and a retarding lens which permits only unscattered electrons to be transmitted to an electron collector. The instrument is immersed in a uniform magnetic field of about 7 mT. The electron energy resolution is about 100 meV and the temperature within the collision region is maintained at 328 K. Total electron scattering cross sections are obtained by measuring the attenuation of the transmitted current due to the introduction of a sample into the gas cell.[4] Cross sections for electron attachment (lifetimes $> 10\ \mu s$) and dissociative attachment processes are determined from a measurement of the product negative ion flux to the walls of the gas cell.[5] The cross sections reported are believed to be accurate to within $\pm 15\%$ for electron energies above 1 eV. Below this energy, the uncertainty increases to as much as $\pm 50\%$ at the lowest energies (≤ 0.2 eV). The limit of sensitivity in the dissociative attachment cross section measurements is about 2×10^{-18} cm^2.

EXPERIMENTAL RESULTS AND DISCUSSION

SF_6

The total cross sections for electron scattering by SF_6 determined in the present experiment are not shown here but agree with previously reported values[6,7] to within the uncertainties discussed above.

Negative ion formation from SF_6 by electron attachment and dissociative attachment has received considerable study. However, only two experimental determinations of the dissociative attachment cross sections for SF_6 have been previously published.[8,9] Absolute cross sections for electron attachment and dissociative attachment to SF_6 as measured by the present experiment are presented in Figure 1 for electron energies from 0.2 eV to > 1.0 eV. Attachment and dissociative attachment cross sections measured by Kline *et al.*[8] and calculated by Hunter *et al.*[9] from swarm data are shown for comparison.

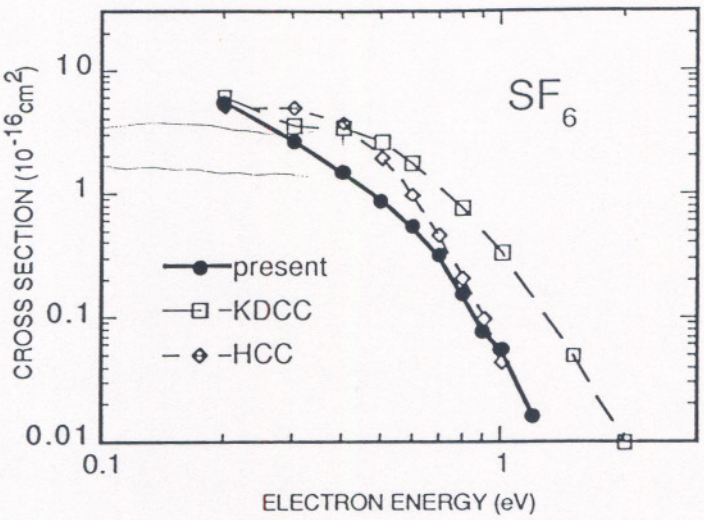

Figure 1. Cross sections for electron attachment and dissociative attachment to SF_6 from 0.2 to 2 eV. Previous data from references 8 (KDCC) and 9 (HCC) are presented for comparison.

The cross sections in Figure 1 for Kline *et al.* and for Hunter *et al.* are the sum of their cross sections for SF_6^- and SF_5^- production. Note that our cross section values agree with both previous measurements at 0.2 eV and then fall below both measurements until again agreeing with Hunter *et al.* near 1 eV. The fact that the present measurements consistently fall below those reported by Kline and coworkers[8] is in general agreement with other analyses[9–11] of swarm data for which the experimentally determined electron collision cross sections were adjusted downward in order to derive accurate transport, ionization, attachment, and dissociation coefficients of SF_6.

SO_2

To date three conflicting experimental measurements of the total cross section for electron scattering by SO_2 have been published.[12–14] These three sets of data are shown by the upper curves in Figure 2 along with the measurements from the present experiment. Our results are in closest agreement with the recent results of Szmytkowski and Maciag,[14] although discrepancies exceeding 20% are observed, especially at lower energies. Broad maxima observed near 2.5 eV and 5 eV in the cross sections measured here and in those of Szmytkowski and Maciag[14] correspond to the resonances observed by Sanche and Schulz[15] in derivative electron transmission spectra.

Previous measurements[16–19] of the cross sections for dissociative attachment to SO_2 differ in magnitude by as much as 70%. Figure 2 shows the measured dissociative attachment cross sections from the present experiment and from Refs. 16–19. Qualitative agreement between these measurements is good with each experiment showing peaks near 4.7 eV and 7.2 eV. Mass spectrometric studies[18] have shown that the peak near 4.7 eV is composed primarily of O^- and SO^- while the peak near 7.2 eV is almost solely O^-. The peak near 4.7 eV corresponds to the broad maximum in the total cross section data near 5 eV. The present data are clearly in better agreement with the dissociative attachment cross sections reported previously in Refs. 16–18 than those reported in Ref. 19.

This work was supported by NSF Grant No. CHE-87-21744 and the U. S. Department of Energy.

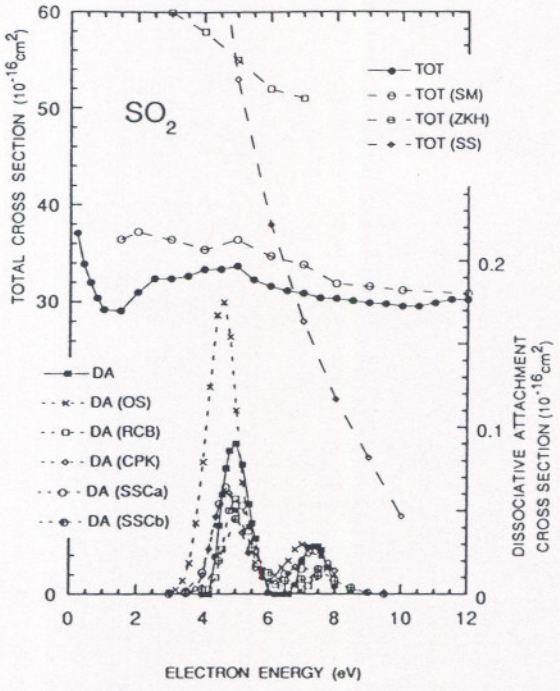

Figure 2. Total electron scattering cross sections and dissociative attachment cross sections for SO_2. Previously published total cross sections from references 12 (ZKH), 13 (SS), and 14 (SM), and previously published dissociative attachment data from references 16 (RCB), 17 (CPK), 19 (OS), and 18 (SSCa and SScb) are shown for comparison.

REFERENCES

1. G. Turban and M. Rapeaux, *J. Electrochem. Soc.* **130**, 2231 (1983).
2. J. K. Olthoff, R. J. Van Brunt, H.-X. Wan, J. H. Moore, and J. A. Tossell, in *Gaseous Dielectrics VI* (L. G. Christophorou and I. Sauers, Eds.), Plenum Press, New York, in press.
3. A. Stamatovic and G. J. Schulz, *Rev. Sci. Instrum.* **41**, 423 (1970); M. R. McMillan and J. H. Moore, *ibid.* **51**, 944 (1980); G. J. Schulz, *Phys. Rev. A* **5**, 1672 (1972).
4. H.-X. Wan, J. H. Moore, and J. A. Tossell, *J. Chem. Phys.* **91**, 7340 (1989).
5. H.-X. Wan, J. H. Moore, and J. A. Tossell, *J. Chem. Phys.* **94**, 1868 (1991).
6. R. E. Kennerly, R. A. Bonham, and M. McMillan, *J. Chem. Phys.* **70**, 2039 (1979).
7. M. S. Dababneh, Y. -F. Hsieh, W. E. Kaupilla, C. K. Kwan, S. J. Smith, T. S. Stein, and M. N. Uddin, *Phys. Rev.* **A38**, 1207 (1988).
8. L. E. Kline, D. K. Davis, C. L. Chen, and P. J. Chantry, *J. Appl. Phys.* **50**, 6789 (1979).
9. S. R. Hunter, J. G. Carter, and L. G. Christophorou, *J. Chem. Phys.* **90**, 4879 (1989).
10. A. V. Phelps and R. J. Van Brunt, *J. Appl. Phys.* **64**, 4269 (1988).
11. J. P. Novak and M. F. Fréchette, *J. Appl. Phys.* **55**, 107 (1984).
12. M. Zubek, S. Kadifachi and J. B. Hasted, in *Book of Abstracts of the European Conference on Atomic Physics*, eds. J. Kowalski, G. zu Putlitz and H. G. Weber (Heidelberg, 1981) p. 763.
13. Cz. Szmytkowski, in *Book of Abstracts of the 2nd European Conference on Atomic and Molecular Physics*, eds. A. E. de Vries and M. J. van der Wiel (Amsterdam, 1985) p. 66.
14. C. Szmytkowski and K. Maciag, *Chem. Phys. Lett.* **124**, 463 (1986).
15. L. Sanche and G. J. Schulz, *J. Chem. Phys.* **58**, 79 (1973).
16. J. Rademacher, L. G. Christophorou, and R. P. Blaunstein, *J. Chem. Soc. Faraday Trans. II*, **71**, 1212 (1975).
17. I. M. Čadež, V. M. Pejčev, and M. V. Kurepa, *J. Phys. D: Appl. Phys.* **16**, 305 (1983).
18. S. M. Spyrou, I. Sauers, and L. G. Christophorou, *J. Chem. Phys.* **84**, 239 (1986).
19. O. J. Orient and S. K. Srivastava, *J. Chem. Phys.* **78**, 2949 (1983).