

The Role of Electron Impact Ionization Cross Sections in Low-Temperature Plasmas

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1 Introduction

The use of non-equilibrium, low-temperature plasmas for materials processing is the key to the advancement of many rapidly developing technologies. The selective and highly anisotropic etching of materials and the controlled deposition of thin films in the fabrication of microelectronic structures is one important area of plasma-assisted material processing. Plasma polymerization and plasma-assisted surface modification are other areas of great technological importance. Plasma-based processes are used in about 35% of the steps involved in the manufacture of semiconductor chips and “the more sophisticated the chip, the larger the number of steps relying on plasma technology” [1]. The past five years have seen an increased level of activity in efforts to provide a more scientific underpinning of low-temperature plasma processing, a development stimulated by the 1991 National Research Council (NRC) report on “Plasma Processing of Materials: Scientific Opportunities and Technological Challenges” [1] and several related reports. Despite these efforts, low-temperature plasma technology (LTPT) today remains a discipline where technological advances routinely outpace the fundamental understanding of the key processes at a microscopic level. Even though process and reactor modeling and plasma diagnostics techniques made very promising advances, a serious lack of sufficient and sufficiently reliable collisional and spectroscopic data often prevents the exploitation of the full potential of modeling codes, CAD tools, and plasma diagnostics techniques. This has been noted in a recent follow-up NRC report on “Modeling, Simulation, and database Needs in Plasma Processing” [2]. The report cites three main reasons for the poorly developed status of the database, (i) the continued comparatively low level of research efforts in this area, (ii) little coordination between the activities of the few groups working in this field, particularly poor coordination between experimental efforts and theoretical calculations, and (iii) a very serious lack of communication between the community that generates the data and the community that uses the data.

2 Background

A low-temperature plasma is a system far from thermodynamical equilibrium. The electron temperature is much higher than the gas temperature (which is often close to the ambient temperature) and can drive “high temperature” chemistry without the adverse effects of high ambient temperatures on the processed materials. The reactive species in a processing plasma, primarily chemically active neutral and ionic radicals and molecules and atomic ions, result from the collisionally induced break-up of the parent feedstock molecules. A quantitative and detailed understanding of the processes leading to the formation of the reactive plasma constituents and of

their structure is important for three reasons, (i) to determine the composition of the plasma and thus the plasma properties and the key plasma chemical reaction pathways, (ii) to determine the flux of reactive plasma species to the wafer or substrate and thus the utility of a particular plasma for a specific processing application, and (iii) to provide the basis for optical and mass spectrometric diagnostics of the relevant gas phase and surface processes as well as for state-of-the-art computer simulations and CAD tools for process modeling and reactor design.

Electron and photon interactions with reactive plasma constituents under single collision conditions are a versatile probe of the structure and dynamics of the parent plasma constituents as well as of the dominant secondary plasma species such as chemically reactive radicals which are produced by collision-induced dissociation and ionization of the parent molecules. With average electron energies of 0.5 eV to 5 eV for typical technological low-temperature plasmas, the high energy tail of the electron energy distribution function (eedf) extends well into the impact energy regime above the thresholds of the cross sections for the electron-impact dissociation and ionization of the parent plasma constituents. The overlap of the eedf and the near-threshold regions of these cross sections determines the efficiency of the formation of the various neutral and ionic plasma species. The experimental determination of electron-impact cross sections for the dissociation and ionization of the parent molecules, particularly the low-energy, near-threshold regions of the cross sections and measurements of all types of cross sections for electron collisions with chemically reactive neutral and ionic plasma radicals are of crucial importance in any effort to understand, describe, model, and characterize the properties of a particular processing plasma. The gas phase processes, in turn, determine the flux of ions and neutrals to the wafer or substrate and, therefore, indirectly determine the surface processes as well.

3 Current Activities

Our group at the City College of New York, which has recently been relocated to the Stevens Institute of Technology in Hoboken, NJ, in collaboration with the group of Prof. Märk in Innsbruck, Austria and Prof. Deutsch in Greifswald, Germany has been engaged for several years in a comprehensive effort aimed at the experimental and theoretical study of elementary processes and the generation of basic collisional and spectroscopic data relevant to low-temperature processing plasmas

3.1 Experimental Activities

The main focus of the experimental part of the research project is the study of the collisionally induced ionization, dissociation and dissociative ionization of selected molecules and free radicals. The choice of target molecules to be investigated is based on two considerations which are given roughly equal weight, (1) the relevance of the particular species in low-temperature plasmas and (2) common features among the targets from a more basic collision physics viewpoint (e.g. interesting and/or similar molecular or electronic structure, members of a particular molecular/radical sequence, etc.). The project up to now has studied primarily molecular and radical targets of the form AB_x with $A = C, N, Si$, $B = F, H$, and $x = 1 - 4$ (see tables below). The work for the fluorine-containing targets has been completed except for SiF_4 which will be studied in the near future employing a mass spectrometric technique (see below). All other experiments

were carried out in our well-characterized fast-beam apparatus [3,4]. Comparisons between the ionization behavior of the various targets have been made from several viewpoints:

1. along each row in the above table
2. along each column in the above table
3. between the various rows in the above table
4. between the various columns in the above table

Table 1: Fluorine-containing Species

CF_4 ¹⁾	CF_3	CF_2	CF
---	NF_3	NF_2	NF
SiF_4 ²⁾	SiF_3	SiF_2	SiF

¹⁾This molecule was studied by several other groups, but not as part of this project

²⁾This molecule will be investigated in the near future

It was the objective to correlate the ionization properties (magnitude of total and partial ionization cross sections, peak ionization cross section values, cross section shapes, ratio of parent to fragment ionization cross sections, mechanisms of fragment ion formation, etc.) with the molecular and electronic structure

of the targets. We subsequently investigated the corresponding hydrides.

Table 2: Hydrogen-containing Species

CH_4	CH_3	CH_2	CH
---	NH_3	NH_2	NH
SiH_4	SiH_3	SiH_2	SiH

(For reasons of experimental convenience we frequently substituted the deuterated compounds in our experiments. This is of no consequence for the results and their interpretation, since ionization cross sections are insensitive to isotope effects to a very high degree of approximation.)

By replacing the F atoms by the lighter H atoms, we essentially go from a multi-center to a quasi single-center molecule. Furthermore, by replacing the very electronegative fluorine atoms by hydrogen, the molecular and electronic properties of the targets were modified significantly.

The most recent experimental work focused on ND_x ($x=1-3$) and silane, SiH_4 . There are some notable similarities between the ND_x ionization data and the previously obtained SiD_x and CD_x data. Similar to the case of SiD_x and CD_x , the ionization of the ND_x targets is dominated by the formation of the respective parent ions and the parent ionization cross section has essentially the same value for all three targets. Furthermore, dissociative ionization, although a less important process, is, in turn, dominated by a single channel, viz. the removal of a single D atom for all three targets. Lastly, all fragment ions (except for D^+) are formed with little excess kinetic energy. There is also two notable differences between the CD_x and ND_x data on one side and the SiD_x data on the other side. For one, the SiD_x ionization cross sections are significantly larger (more than a

factor of 2) than the ND_x and CD_x ionization cross sections, which, in turn, are of very similar magnitude. Secondly, in the case of SiD_x , the cross section for the dominant dissociative ionization channel had the same value for all three SiD_x species, while there is a systematic decrease in the dominant dissociative ionization cross section for ND_x and CD_x with decreasing value of x , i.e. the ND^+/ND_2 and CD^+/CD_2 cross sections are smaller than the $\text{ND}_2^+/\text{ND}_3$ and $\text{CD}_2^+/\text{CD}_3$ cross sections, while the N^+/ND and C^+/CD cross sections are the smallest.

Silane, SiH_4 , is in the same class of molecule as e.g. SiF_4 and CF_4 in the sense that it does have a stable parent ion. As a consequence, the fast-beam method is not suitable to study SiH_4 . A mass spectrometric technique had to be employed (in collaboration with the group of Dr. M. Schmidt at the INP Greifswald, Germany) to investigate this molecule. There had been three earlier studies of the ionization of silane carried out by three different groups using three different techniques, but the agreement was very poor (more than a factor 3 difference in some partial and in the total ionization cross section). Great care was exercised in the characterization of our mass spectrometer and in the analysis and minimization of possible sources of systematic errors. As a result, we believe that the apparatus is capable of measuring absolute molecular ionization cross sections at the 15-20% level of accuracy. As expected, our experiments revealed that dissociative ionization processes are the dominant ion formation mechanisms and all molecular fragment ions (except for H_2^+) are formed with little excess kinetic energy. By contrast, the H^+ fragment ion is formed with a broad distribution of kinetic energies peaking at several electronvolts per fragment ion.

3.2 Cross Section Calculations

We have also developed and refined various semi-empirical and semi-classical methods for the calculation of total single ionization cross sections of molecules and radicals. The main effort is on the development and refinement of a modified additivity rule which allows predictions of total single ionization cross sections of complex molecules for which more rigorous calculations are difficult. This model expresses the molecular ionization cross section in terms of the ionization cross sections of the constituent atoms and empirically determined weighting factors which account for molecular bonding. Up to now, our efforts focused on refining the additivity concept for molecules of the form AB_n . We are also working on the extension of this concept to more complex molecules of the form $\text{A}_x\text{B}_y\text{C}_z$.

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References

- [1] "Plasma Processing of Materials: Scientific Opportunities and Technological Challenges", *National Academy Press* 1991
- [2] "Modeling, Simulation, and Database Needs in Plasma Processing", *National Academy Press* 1996
- [3] R. C. Wetzel, F. A. Biaocchi, T. R. Hayes, and R. S. Freund, *Phys. Rev. A* **35** 559 (1987); R. S. Freund, R. C. Wetzel, R. S. Shul, and T. R. Hayes, *Phys. Rev. A* **41** 3575 (1990)
- [4] V. Tarnovsky and K. Becker, *Z. Phys. D* **22** 603 (1992); V. Tarnovsky, P. Kurunczi, D. Rogoshnikov, and K. Becker, *Int. J. Mass Spectrom. Ion Proc.* **128** 181 (1993)