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Applications of Electron-Interaction Reference Data to the Semiconductor Industry

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Many advanced plasma diagnostic techniques and plasma models require fundamental physical data in order to make accurate measurements or predictions. Fundamental electron-interaction data are among the most critical since electron collisions are the primary source of ions, reactive radicals, and excited species present in etching, cleaning, and deposition plasmas. In this paper we present (*i*) a description of some semiconductor applications that require fundamental electron-interaction data, (*ii*) an explanation of the NIST program to provide these data, (*iii*) a summary of the available fundamental electron-interaction data for plasma processing gases, and (*iv*) a discussion of general data needs.

INTRODUCTION

As the push for smaller feature sizes and higher quality devices in the semiconductor industry has increased, so has the need for sophisticated models with predictive capabilities that can guide the technology, and for advanced diagnostics to probe the details of the plasmas used to etch features, deposit materials, or clean reactor chambers. Additionally, environmental concerns have fostered the demand for the more efficient use of global warming gases used in plasma processes. Advancement in each of these areas inherently requires detailed understanding of the physics and chemistry occurring within the discharge, which itself requires knowledge of the basic collision processes occurring between the species existing in the plasma. The most fundamental of the discharge processes are collisions between electrons and atoms or molecules. These collisions are the precursors of the ions and radicals which drive the etch, cleaning, or deposition processes.

The National Institute of Standards and Technology (NIST) started a program in 1996 to provide the semiconductor community with a concise source of complete, reliable electron-interaction reference data for plasma processing gases. To date, this program has assessed the available data for 6 major processing gases: CF_4, C_2F_6, C_3F_8, CHF_3, CCl_2F_2, and Cl_2. Details of the recommended data for these gases appear in Refs. (1–6), respectively, and downloadable tables of the recommended data are available via the World Wide Web (WWW) at *http://www.eeel.nist.gov/811/refdata*. In this paper we examine areas of the semiconductor industry that require these data for reliable operation or for continued development, along with a tutorial highlighting the industry's need for these data. Additionally, we review the present state of available electron-interaction data, and in some cases provide recently updated, and previously unpublished, data. In so doing, it is our intention to clearly inform the semiconductor community about the availability or unavailability of essential data of this type.

APPLICATIONS

Numerous applications exist in the semiconductor industry that require the use of electron-interaction data, and we briefly discuss five such applications here. They are: (*i*) plasma models designed to emulate discharge conditions and plasma processes; (*ii*) new diagnostic techniques being developed for the detection of gas-phase radicals utilizing negative ion mass spectrometry or threshold ionization mass spectrometry; (*iii*) diagnostic methods based on the detection of optical emission from the discharge; (*iv*) optimization of plasma-chamber cleaning processes utilizing global warming gases, and of post-processing emission abatement techniques; and (*v*) basic research into the identity and role of transient species in reactive plasmas.

(1) Plasma Models – Many models have been applied to simulating various aspects of reactive plasmas [see Refs. (7–10), for example]. The fundamental parameters required for the accurate modeling of reactor plasmas are electron-energy distributions, electron densities, positive ion fluxes and energies, negative ion densities, and reactive radical densities. Knowledge of these parameters is the precursor to the calculation of other more industrially-significant parameters, such as etch and deposition rates, etch profiles, and plasma uniformity. However, calculation of the fundamental parameters relies heavily on knowledge of the magnitude of electron-interaction cross sections, since virtually all physical processes in the discharge are initiated by electron motion through the gas.

Electron-energy distributions are determined by elastic and inelastic electron-scattering processes as electrons are

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accelerated through the plasma gas by the applied electric field. Determination of the energies of the electrons in the discharge is the initial calculation in models based upon Boltzmann or Monte Carlo techniques (11). These models rely primarily upon cross sections for momentum transfer and vibrational excitation for determination of these distributions.

The electron density in a plasma is primarily determined by electron-impact ionization processes (which produce free electrons), electron attachment processes (which remove electrons by creating negative ions), and by secondary electron emission from surfaces. The first two processes are described by ionization and attachment cross sections, respectively, and the third process, while important and worthy of investigation, is a surface process and is not discussed here.

Positive ion bombardment is one of the main drivers of plasma surface reactions, and the ion flux is a direct result of electron-impact ionization. Although the final identity and magnitude of the positive ion flux may be dependent upon secondary reactions, such as ion-molecule reactions occurring as the ion travels through the discharge, the initial ion-formation process is driven by electron-impact processes. Partial ionization cross sections are required to determine the identity and quantity of the initial ions created in the plasma.

Negative ion production and the resulting densities are determined by direct electron attachment and dissociative attachment processes. Dissociative attachment processes can be a very effective way to produce both negative ions and radicals due to the large cross sections at low electron energies exhibited by some molecules.

Reactive radicals are produced by three basic processes: electron-impact dissociative ionization, where a positive ion and a radical are produced; electron-impact dissociative attachment, where a negative ion and a radical are produced; and neutral dissociation, where two neutral fragments are produced by electron impact. Knowledge of the cross sections related to these reactions is necessary for calculating the density of these highly reactive species that are critical to etching and deposition processes.

Electron transport parameters and rate coefficients are often the first parameters calculated by plasma models. Accurate measurements of these values are essential to validate the model calculations. The transport parameters commonly calculated in some models include: electron drift velocity, transverse electron diffusion coefficient to electron mobility ratio, density reduced ionization coefficient, density reduced electron attachment coefficient, and total electron attachment rate constant.

(2) Mass Spectrometric Diagnostics – The need to measure the identity and density of gas-phase plasma products, including reactive radicals, in industrial plasmas has led to the development of two mass spectrometric-based diagnostics: negative ion mass spectrometry and threshold ion mass spectrometry. Negative ion mass spectrometry detects gas-phase plasma products by monitoring negative ions formed by electron attachment to radicals, excited species, and molecules formed by reactions in the plasma (12,13). Cross sections for electron attachment and dissociative attachment are required for the feed gas and for the species to be detected in order for this technique to be effective.

Threshold ionization mass spectrometry detects radicals by monitoring positive ions generated by collisions of radicals with electrons whose kinetic energy is above the ionization threshold of the radical, but below the ionization threshold of the feed gas (14–16). This allows detection of radicals even when the mass spectra of the radicals are similar to those of the feed gas. This technique, too, requires detailed electron-impact ionization cross sections for the feed gas and the radicals at energies near threshold. This same technique can be used to detect excited species.

(3) Optical Emission Diagnostics – The light emission from a processing plasma is often used to monitor plasma uniformity, excited species densities, and electron-energy distributions. The later two applications require electron-impact excitation cross sections for the feed gas and for the gas-phase products produced in the discharge.

(4) Environmental Applications – Environmental concerns over the use of fluorinated compounds, that are often global warming gases, have prompted significant interest in increasing the efficiency of plasma-assisted cleaning techniques (17), and in the development of post-processing emission abatement techniques (i.e., the destruction or conversion of any remaining feed gas being exhausted from the reactor). Both of these processes, cleaning and abatement, require the dissociation of the feed gas into reactive radicals, which is nearly entirely dependent upon electron-impact ionization and dissociative collisions. Knowledge of the cross sections for these collisions is necessary to optimize such industrial processes.

(5) Basic Research – Fundamental electron-interaction data are applicable to a wide range of basic research being preformed in support of the semiconductor industry. Even a cursory discussion of all of these areas is obviously beyond the scope of this article. However, research into the detection and role of transient species in a plasma is of particular interest and importance.

As mentioned previously, the detection of transient species, such as radicals and excited species (vibrationally and electronically excited), often requires knowledge of the electron-interaction cross sections with these species. Many of these cross sections are currently unknown. Of perhaps greater importance, is the determination of the effect that these species have on the plasma itself. Early data indicate that electron interactions with transient species often have cross sections that are orders of magnitude greater than for similar interactions with the feed gas.

An example of this is shown in Fig. 1, where it can be seen that the cross section for electron scattering from metastable argon is significantly greater than from ground state argon (18,19). Similar results have been observed for molecules (20,21). This implies that the presence of these species may exert significant influence on the behavior of electrons in a plasma. The data for argon in Fig. 1 are especially noteworthy because argon is used as a buffer gas in many plasma reactors.

DATA ANALYSIS

The goal of the NIST effort in this area is to provide complete and accurate fundamental information on low-energy electron-molecule interactions with plasma processing gases used in the semiconductor industry. These data include electron-collision cross sections, and electron transport and rate coefficients. The gases currently being investigated include etching and cleaning gases (CF_4, CHF_3, C_2F_6, C_3F_8, Cl_2, NF_3, HBr, and SF_6), buffer gases (Ar and He), and common impurities or additives to plasma reactors (O_2, H_2O, and N_2). This list is modified and expanded as the needs of the industry change.

Data for each gas are accumulated, assessed, and evaluated, and then a NIST-recommended set of data is derived and placed in a database on the World Wide Web. The method for data review, assessment, and dissemination is as follows:

- perform thorough literature searches,
- review and assess available data,
- determine most reliable data,
- derive "recommended" data set,
- determine gaps in available data,
- perform measurement or calculation of needed data at NIST if possible,
- encourage the performance of required measurements or calculations elsewhere,
- write comprehensive archival paper, and
- present recommended data on the WWW (*http://www.eeel.nist.gov/811/refdata*).

The website allows easy access to the data for users in industry, academia, and government laboratories, including direct downloading of data. The site is maintained with the most up-to-date data available.

The assessment process is illustrated in Fig. 2 for the momentum transfer cross section of CF_4. A thorough evaluation of the literature reveals momentum transfer cross section data that differ by more than two orders of magnitude. However, assessment of the data allows the determination of the reliable cross section shown by the solid black line.

To date, analyses of the plasma processing gases CF_4, C_2F_6, and CHF_3 have been published (1,2,4), and the data for C_3F_8 have been accepted for publication (3). The assessment of electron-interaction data is nearly complete for Cl_2 (6). A similar analysis has been performed for CCl_2F_2, due to its importance in atmospheric chemistry and ozone depletion (5).

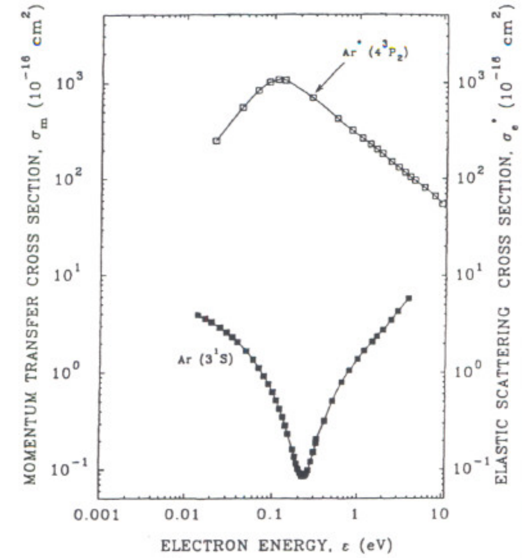

FIGURE 1. Momentum transfer cross section from ground state argon and elastic scattering cross section from metastable argon from Refs. (18) and (19), respectively.

REFERENCE DATA

In this section we review the completed NIST assessments of electron-interactions with the gases of greatest interest to the semiconductor industry: CF_4, CHF_3, C_2F_6, and C_3F_8. The data presented here reflect the most current data available,

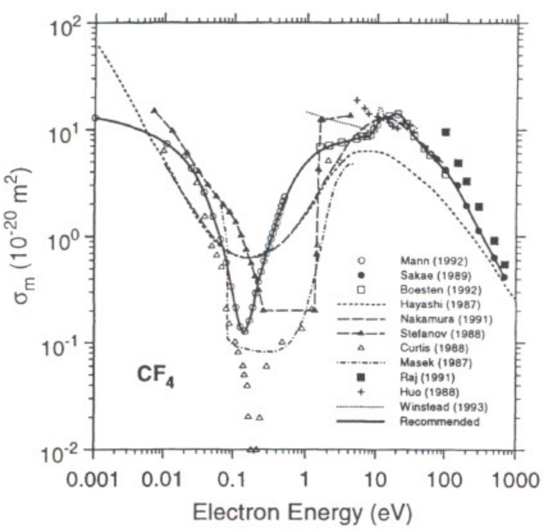

FIGURE 2. Momentum transfer cross sections for CF_4 from the archival literature. The solid line is the NIST recommended cross section. Details of the method to determine the recommended cross section, and of the references for the data shown in this figure may be found in Ref. (1).

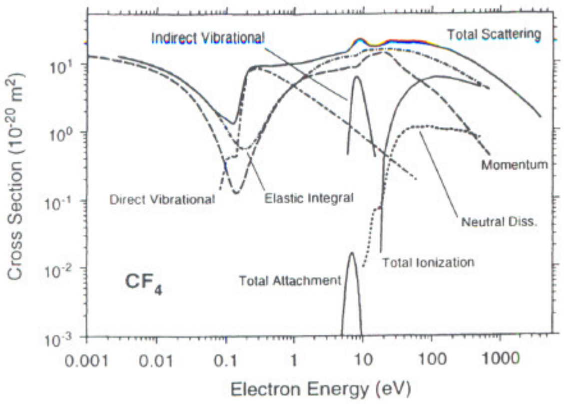

FIGURE 3. Electron-interaction cross sections for CF_4 (1).

and in some cases represent an update of the recommended cross section sets published previously.

Carbon Tetrafluoride (CF_4) – The data on electron-scattering cross sections, and attachment, ionization, and transport coefficients are reasonably complete for CF_4 (1). Figure 3 shows the independently assessed electron-interaction cross sections. The sum of the elastic, vibrational, ionization, attachment, and neutral dissociation cross sections has been shown to agree well with the recommended total electron-scattering cross section (1), thus demonstrating the overall consistency of the data.

The cross section for dissociation into neutrals shown here in Fig. 3 is updated from our previously published recommended set (1). Our previous set of recommended values for dissociation into neutrals was based upon the only directly-measured experimental data existing at the time (22). However, new direct measurements over a limited range of electron energies (23) confirm our earlier concern that the previous experimental measurements (22) of this cross section were too low. The new values presented here for dissociation into neutrals are based upon the recent measurements of Motlagh and Moore (24). Confirmation of this cross section over an extended range of electron energies is a significant data need for CF_4.

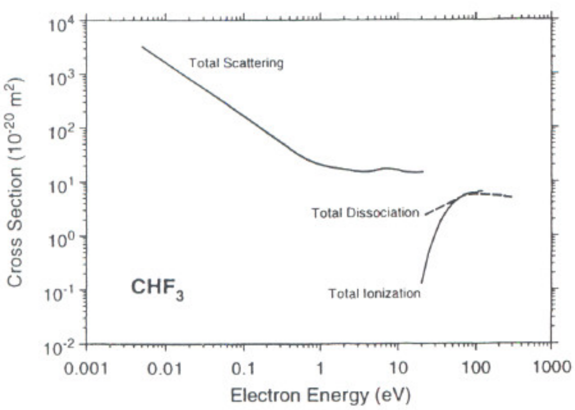

FIGURE 4. Electron-interaction cross sections for CHF_3 (4).

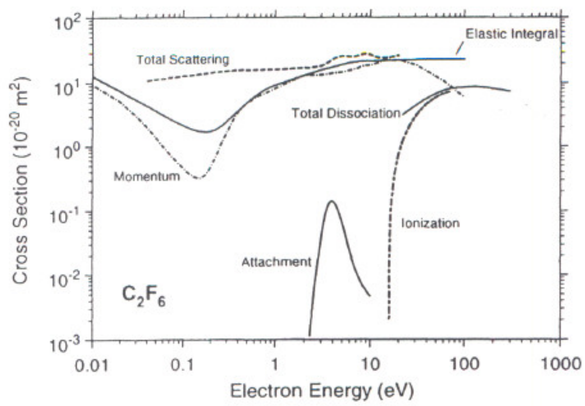

FIGURE 5. Electron-interaction cross sections for C_2F_6 (2).

Additional data needs include experimental determination of direct and indirect vibrational excitation (the values shown here are derived from theoretical calculations), and resolution of some discrepancies in measurements of the total ionization and elastic integral cross sections.

Trifluoromethane (CHF_3) – Figure 4 shows the meager electron-scattering cross section data for this important plasma processing gas (4). This data set serves as an illuminating contrast to the much more complete set of data available for CF_4. Basic measurements and calculations are needed for virtually all elastic and inelastic electron scattering processes, including momentum transfer, vibrational excitation, elastic scattering, differential scattering, and electron transport, attachment and ionization coefficients. Confirmation is required of the measured cross sections for total electron scattering and for total ionization. The previously recommended data for dissociation into neutrals are not shown here since these data are expected to suffer from the same shortcomings as those for CF_4 discussed above.

Perfluoroethane (C_2F_6) – Figure 5 shows the moderately complete cross section set for C_2F_6 (2). Many of the data are still preliminary (e.g., the cross section for momentum transfer at low energies). New cross section data are needed, especially for dissociation into neutrals, and vibrational and electronic excitation. Additional data are needed for momentum transfer, elastic integral, total ionization, and total scattering cross sections, in order to confirm existing data. There exist reasonably accurate data on attachment, ionization and transport coefficients.

Perfluoropropane (C_3F_8) – Figure 6 shows the presently available electron-scattering cross sections for C_3F_8 (3). Like C_2F_6, many of these data are preliminary and previously unpublished. The total electron-scattering cross section data are recent unpublished measurements, and the momentum transfer and elastic integral cross sections are from unpublished data derived from differential scattering cross

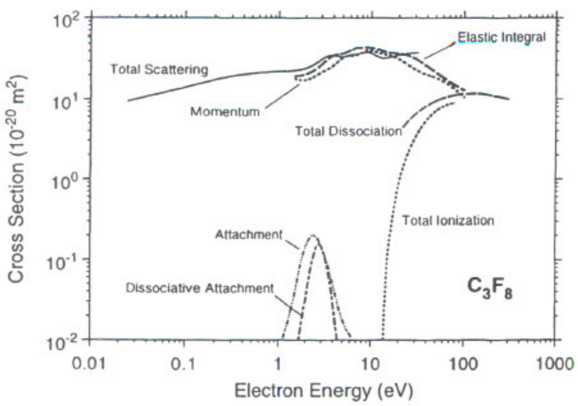

FIGURE 6. Electron-interaction cross sections with C_3F_8 (3).

section measurements. The preliminary values for elastic integral and momentum transfer cross sections exceed the measured total scattering cross section near 10 eV, but they are not incompatible within the combined estimated uncertainties. The total ionization, dissociative attachment (T≅300 K), and total dissociation cross sections are assessments based on the published experimental data in the literature. No measurements exist for electron-impact dissociation into neutral fragments and vibrational and electronic excitation. Much work is needed for virtually all cross sections and the electron transport coefficients for this molecule.

DATA NEEDS

At this time a reasonably complete set of electron-interaction cross sections exists only for CF_4. The other gases assessed in this project all have significant gaps in the known cross sections. Two nearly universal needs for these plasma processing gases are experimentally derived cross sections for vibrational excitation and for dissociation into neutrals. Both of these processes play critical roles in industrial plasmas, and a minimal amount of data are currently available for CF_4, with no data available for the other gases.

More generally, electron-interaction cross sections are needed for radicals and excited species commonly produced in industrial plasmas. Electron-impact ionization cross sections have been measured for some radicals produced in CF_4 plasmas (25), but no measurements are available for any other electron-collision interaction or any other plasma processing gases.

Existing data for electron transport and rate coefficients are reliable for most of the plasma processing gases, with a few major exceptions. No transport data are available for CHF_3, except for some recent measurements of drift velocity (26).

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