# LOW ENERGY ELECTRON COLLISIONS IN $SiF_4$

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## ABSTRACT

Electron drift velocities in $SiF_4$-$Ar$ mixtures have been measured using a pulsed-Townsend type drift tube. A set of momentum transfer, vibrational excitation, dissociation, attachment, and ionization cross sections of electron scattering in $SiF_4$ from $0-50$ $eV$ is presented. The cross section set has been determined by the swarm analyses of electron transport data in pure $SiF_4$, in conjunction with the data in $SiF_4 - Ar$ mixtures.

## INTRODUCTION

Electron collisional processes and transport in Group IV tetrafluorides ($CF_4$, $SiF_4$) are of considerable interest due to their wide applications in dry etching for the fabrication of microelectronic devices. The $\nu_3$ fundamental vibrational mode of $SiF_4$ is of special interest in the field of laser spectroscopy due to the possibility of achieving measurements with sub-Doppler resolution on single transitions coinciding with $CO_2$ laser lines [1]. $SiF_4$ is also of interest in laser photochemistry [2], and has been the subject of investigation in $IR$ spectroscopy [3].

While there exists considerable information on the low energy electron collision cross sections in $CF_4$ [4, 5] in the literature, the corresponding data for $SiF_4$, especially the momentum transfer and vibrational excitation cross sections are not known. Absolute cross sections for the electron impact dissociation of $SiF_4$ ($> 10$ $eV$) into neutral radicals, ionization [6] and electron attachment [7] have been measured. Electron energy loss spectra for the energy loss range of 10-30 $eV$ [8], and photoabsorption studies in $SiF_4$ in the high energy region (>10 $eV$) have also been reported [9, 10]. On the swarm frontier, electron transport data comprising of drift velocities ($w_d$), attachment ($\eta/N$), and ionization ($\alpha/N$) coefficients in $SiF_4$ have recently been measured [11]. In this paper, we report a set of low energy electron collision cross sections in $SiF_4$ derived from the swarm analyses of the electron transport data of [11]. The cross section set includes momentum transfer ($q_m$), vibrational excitation, and is extended towards high energies using the measurements of [6, 7]. For checks on the consistency of the

derived cross section data, measurements and analyses of electron drift velocities in $SiF_4$-Ar mixtures are also reported.

## EXPERIMENT AND ANALYSIS

The experimental apparatus is a classical pulsed-Townsend type drift tube described in detail in [12]. A photoelectron swarm is initiated by the laser irradiation of a gold-palladium photocathode using a 266 nm quadrupled Nd Yag laser. The laser initiated swarm ($6ns$) drifts under the influence of the uniform electric field through a drift distance of 6.455 $cm$. The charge swarm is collected at the anode with a current integrating amplifier. The averaged charge ramp (over 128 repetitions of the swarm) is analyzed for the time of maximum charge arrival and this time is designated as the arrival time of the swarm. The $w_d$ is determined from the ratio of the drift distance to the arrival time and is not corrected for the effects of diffusion, ionization or attachment.

The $w_d$ measurements were made in gas mixtures from 0.1% to 4.8% $SiF_4$ in $Ar$. The gas mixtures were made by volume mixing in the drift tube using a pre-prepared mixture of 4.8% $SiF_4$ in $Ar$ with pure $Ar$ (both Matheson Semiconductor Grade). The mixing ratios were determined by pressure measurements using 10 Torr and 1000 Torr capacitative manometers. The $w_d$ measurements have an accuracy of 2% based on the measurement uncertainties of the pressure, voltage, temperature, mixture ratio, and arrival time.

The electron kinetics in the swarm analyses was obtained by conventional "two-term" solution of the collisional Boltzmann transport equation (BTE) [13]. A set of *trial* cross sections was constructed as the input to the numerical solution of the BTE. The *trial* cross section set was constructed with the inelastic threshold information (table 1), and a judicious estimate (based on comparisons with $CF_4$) of the magnitude, and the shape of the cross sections, near and above their thresholds.

| Process | Threshold (eV) | Label |
|---|---|---|
| Vibration $\nu_1$ | 0.099 | $\sigma_{\nu 1}$ |
| Vibration $\nu_2$ | 0.032 | $\sigma_{\nu 2}$ |
| Vibration $\nu_3$ | 0.126 | $\sigma_{\nu 3}$ |
| Vibration $\nu_4$ | 0.052 | $\sigma_{\nu 4}$ |
| $e + SiF_4 \rightarrow SiF_3 + F + e$ | 10.8 | $\sigma_{d1}$ |
| $e + SiF_4 \rightarrow SiF_2 + F_2 + e$ | 13.9 | $\sigma_{d2}$ |
| $e + SiF_4 \rightarrow SiF_3^- + F$ | 10.1 | $\sigma_a$ |
| $e + SiF_4 \rightarrow SiF_3^+ + F + 2e$ | 16.0 | $\sigma_i$ |

Table 1: Inelastic processes and their thresholds considered for $SiF_4$

The $w_d$ were then calculated from the following expression.

$$w_d = -\frac{1}{3}\left(\frac{2e}{m_e}\right)^{1/2}\left(\frac{E}{N}\right)\int_0^\infty \frac{1}{\sum_s \delta_s \sigma_T^s(\epsilon)}\frac{df_0(\epsilon)}{d\epsilon}\epsilon d\epsilon \qquad (1)$$

where $e$ is the electronic charge, $m_e$ is the electronic mass, $\delta_s$ is the fractional concentration of species $s$ in the gas mixture, $\sigma_T^s$ is the total scattering cross section of species $s$, $\epsilon$ is the electron energy, and $f_0$ is the isotropic component of the electron energy distribution function (EEDF). The calculated $w_d$ were then compared with the experimental data. If the difference between the experimental and calculated $w_d$ was greater than the experimental error margins, then the cross sections were modified in the appropriate energy range. The comparison and modification of the cross sections were repeated till a satisfactory agreement between the calculated and the experimental data was achieved. The collision cross sections of $Ar$ were taken from [14], and were fixed throughout this study.

## RESULTS AND DISCUSSION

Figure 1 presents the comparisons between the experimental and the calculated $w_d$ in $Ar$, pure $SiF_4$, and $\%SiF_4$-$Ar$ mixtures from the converged cross set of $SiF_4$ in the unfolding procedure. Since the elastic scattering in the highly dilute mixture is essentially controlled by $Ar$, the initial estimates of the vibrational excitation cross sections of $SiF_4$ were made from the $w_d$ data of 0.1% mixture. From beyond 1% mixture composition, the $q_m$ of $SiF_4$ also have to be included in the swarm analyses. The $w_d$ data in gas mixtures are dominated by the well known phenomenon of Negative Differential Conductivity [15]. This feature also shows up at higher E/N in pure $SiF_4$. Further, at low E/N, the $w_d$ data in mixtures show a large increase over corresponding data of either constituent gas (figure 1). The demanding requirement to achieve agreement with the experimental $w_d$-E/N-concentration *surface* enhances uniqueness in the derived cross sections.

Once the low energy momentum transfer and vibrational excitation cross sections were determined, the data base was extended towards higher electron energies to include attachment, dissociation and ionization. It is to be noted that since the errors in the swarm analysis are correlated at different energies, the accuracy in the swarm analysis towards high electron energies is very sensitive to the magnitude of the electron scattering at low energies. Figure 2 presents the comparisons between the experimental and the calculated $\eta/N$, $\alpha/N$ coefficients [11]. These coefficients were calculated by the following expression.

$$\frac{\eta}{N} = \frac{k_a}{w_d} \quad and \quad \frac{\alpha}{N} = \frac{k_i}{w_d} \tag{2}$$

where $k_a$ and $k_i$ are the rate coefficients for electron impact attachment and ionization processes respectively. The converged cross section set of $SiF_4$ is shown in figure 3. We note that whereas minor adjustments to the measured attachment cross sections [7] were required to fit the $\eta/N$ data, the measured cross sections for dissociation and ionization [6] required significant modifications in the $\alpha/N$ calculations. The reason for this is that the calculations of $k_i$ are very sensitive to the magnitudes of $\sigma_{d1}$ and $\sigma_{d2}$. Further, since the errors in the absolute cross sections of [7] may be as high as 100%, the agreement between the the measurements of [7] and figure 3 is considered fair.

Finally, we would like to add a comment of caution for the cross sections presented in figure 3. Since these cross sections have been essentially derived from "two-term" calculations of the Boltzmann equation, they will always be consistent as long as the electron kinetics are obtained from the "two-term" approximation. The large magnitudes of $\sigma_\nu$ as compared to those of $\sigma_m$ indicate that in the proximity of the electron energies where vibrational excitation is the dominant inelastic process, the "two-term" approximation is no longer valid for the description of electron collisional kinetics [16] (the EEDF is highly anisotropic). The discrepancies between the "two-term" and the "multi-term" or "Monte-Carlo" calculated transport coefficients can be quite large at the E/N values where vibrational excitation dominates [16, 13]. A "Monte-Carlo" analysis of the electron transport and subsequent improvements to the cross sections (particularly to $\sigma_m$) are currently in progress.

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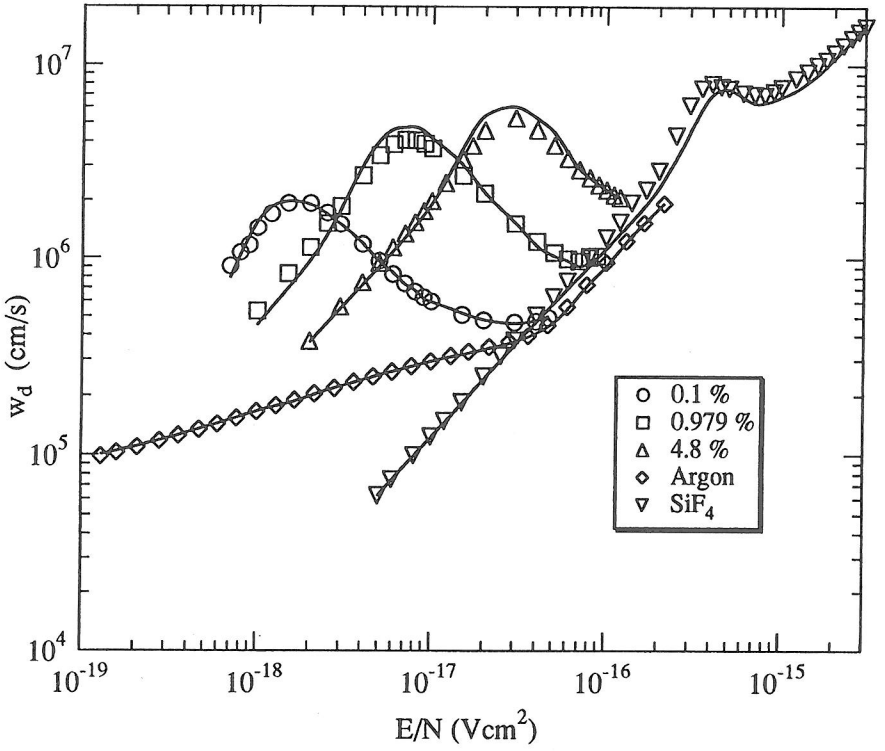


Figure 1: Electron drift velocities in $Ar$, $SiF_4$, and $SiF_4 - Ar$ mixtures. Points represent experimental data. Lines represent calculations using the converged cross sections derived from the swarm analyses.

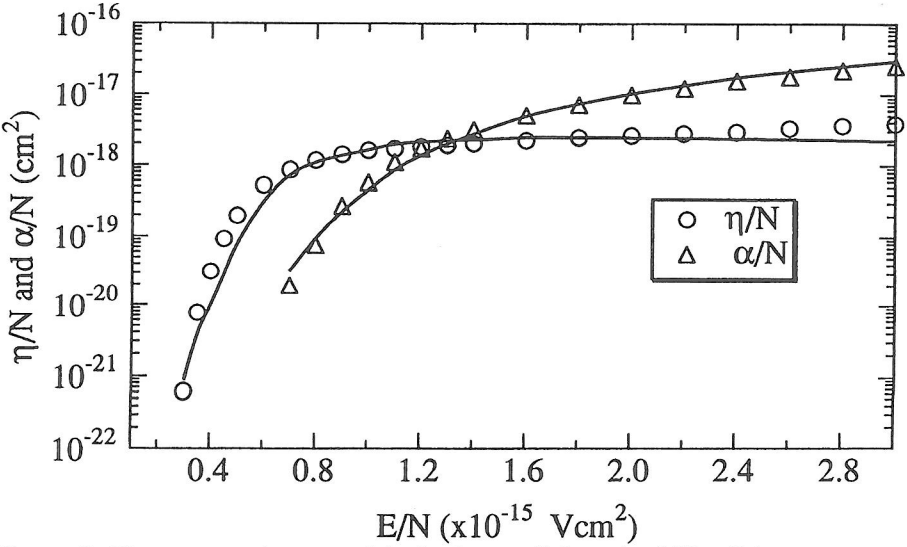


Figure 2: Electron attachment and ionization coefficients in $SiF_4$. Points represent experimental data [11]. Lines represent calculations using the converged cross sections derived from the swarm analyses.

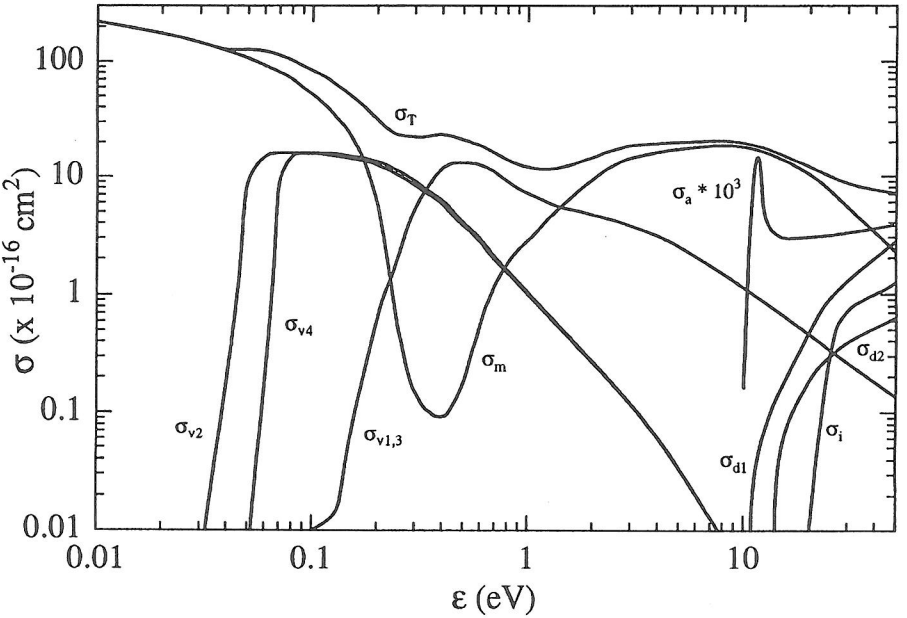


Figure 3: Swarm derived electron collision cross section set of $SiF_4$. Refer to table 1 for denoted symbols.