

# Electron-Driven Neutral Dissociation of Si-Containing Molecules

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## ABSTRACT

A combination of electron scattering and laser-induced fluorescence (LIF) techniques has been used in the experimental determination of the absolute cross section for the formation of Si(<sup>1</sup>S) and Si(<sup>1</sup>D) ground-state atoms following the neutral molecular dissociation of Si-containing molecules such as SiH<sub>4</sub> and SiF<sub>4</sub> by electron impact. Electron impact on Si-containing molecules produces - among other species - Si(<sup>1</sup>S) ground-state atoms which are detected by pumping the Si (3p)<sup>2</sup> <sup>1</sup>S → (3p)(4s) <sup>1</sup>P transition at 390 nm with a tunable dye laser and recording the subsequent Si (3p)(4s) <sup>1</sup>P → (3p)<sup>2</sup> <sup>1</sup>D fluorescence at 288 nm. Likewise, Si(<sup>1</sup>D) ground state atoms can be detected by interchanging the pump and probe pathways in the above reaction sequence.

## 1. Introduction

The collisional interaction of an electron (or any other projectile) with a molecule may result in the dissociation of that molecule. Molecular dissociation induced by electron impact may lead to the formation of neutral ground-state fragments (neutral molecular dissociation) or may combine with other inelastic electron scattering processes resulting in dissociative excitation, dissociative ionization, and dissociative attachment. The electron impact dissociation of a molecule is not only one of the most important fundamental collisional interactions between an electron and a molecule, but dissociation processes also play an important role in many applications including gas discharges, low-temperature processing plasmas, fusion edge plasmas, gas lasers, planetary, cometary and stellar atmospheres, and radiation chemistry [1-3]. While electron impact dissociation processes have been studied extensively since the early years of this century, the focus of most experimental studies has been on dissociative excitation, dissociative ionization, and dissociative attachment processes [1,2]. This is due to the fact that in these processes the resultant dissociation products are formed with internal energy and/or charge that can be used conveniently for their quantitative detection. By contrast, neutral molecular dissociation results in two or more neutral ground-state fragments which are very difficult to detect. Rigorous quantum mechanical descriptions of molecular dissociation processes are also very difficult because of the complexity of both the target and the process. However, first results of the application of variational methods to the electron-impact dissociation of molecules have been reported in the literature recently [4,5].

McConkey and co-workers [6,7] were the first to utilize laser-induced fluorescence (LIF) techniques in the quantitative detection of neutral ground-state dissociation products following electron impact dissociation of a molecule under single collision conditions. Recently, Abramzon et al. [8,9] introduced a variant of this LIF technique, which is conceptually similar to the approach of McConkey and co-workers and differs only in the details of the experimental realization of the technique. In a first step, Abramzon et al. used their apparatus in the determination of the absolute N<sub>2</sub><sup>+</sup>(X) ionization cross section as a function of electron energy following electron impact on N<sub>2</sub> [8,9]. Here, we report results of the extension of this technique to the electron impact dissociation of SiH<sub>4</sub> and SiF<sub>4</sub> leading to the formation of Si(<sup>1</sup>S) and Si(<sup>1</sup>D) ground-state atoms. Silane, SiH<sub>4</sub>, is a frequently used constituent of low-temperature processing plasmas employed in the fabrication of Si-based

microelectronic devices and other semi-conducting components.  $\text{SiH}_4$  plays a particularly important role in the plasma-assisted deposition of silicon and amorphous silicon-hydride (a:SiH) films [10].  $\text{SiF}_4$  is the most abundant volatile by-product of the plasma-assisted etching of Si by plasmas with F-containing molecules in the feed gas mixture.

## II. Experimental Apparatus and Procedure

The apparatus consists of an electron-beam and a gas-beam intersecting at right angles inside a vacuum chamber in conjunction with a tunable laser beam which propagates either parallel or antiparallel to the electron beam in order to maximize the overlap of the three beams. Optical detection of the LIF signal from the interaction region is made perpendicular to both the electron beam and the gas beam. The energy of the electron beam can be varied between 5 eV and 400 eV with typical beam currents of 3  $\mu\text{A}$  at 25 eV and 20  $\mu\text{A}$  at 100 eV and an energy resolution of about 0.5 eV (FWHM). The electron beam is collected in a Faraday cup which consists of three electrically insulated elements which enables us to measure the beam current as well as the beam divergence. The gas beam is an effusive beam emanating from a multi-capillary array of rectangular shape which is positioned about 8 mm above the electron beam axis. Roughly 50% of the total gas throughput passes through a rectangle of the size of the nozzle array in the interaction region. The pushing pressure behind the nozzle is continuously monitored by a capacitance manometer. The laser system consists of a pulsed Lumonics EX-520 excimer laser operating at 308 nm (XeCl) which is used to pump a Lumonics HD-500 dye laser using Exalite 392A as the dye of choice in the pump wavelength region around 390 nm. The laser system produces 0.0015 ns wide pulses of less than 10 ns duration of up to 3 mJ energy per pulse in the wavelength range from 375-397 nm. The laser beam enters and exists the vacuum chamber through Brewster-angle windows and the beam intensity passing through the vacuum chamber is monitored by a laser pulse energy meter. The fluorescence from the interaction region is imaged onto the cathode of a cooled Hamamatsu R1104 photomultiplier tube (PMT). Spectral isolation is achieved by a narrow-band interference filter. The output pulses of the PMT are processed by a gated photon counter whose output, in turn, is directed into a personal computer for data storage and further analysis. A different dye and a frequency doubler are employed for the measurements in the pump wavelength region around 288 nm.

The LIF measurements were carried out as follows. After the end of the laser pulse and after suitable delay had elapsed to allow scattered laser light to decay, a first gate (gate A) of the gated photon counter was opened for a period  $T$  corresponding to about 5 times the radiative lifetime of the radiating state. The data in gate A contain the LIF signal, any residual background and/or noise, and fluorescence produced by the continuous electron beam. At time  $T$ , gate A was closed and a second gate (gate B) was opened for the same period  $T$ . Since after a period of 5 lifetimes any residual LIF signal is negligible, the data in gate B contain only any residual background/noise and fluorescence produced by the continuous electron beam. The LIF signal was then obtained as the difference between the accumulated counts in gate A and gate B.

In Si, we employed the following LIF and detection scheme. Si atoms in the  $^1\text{S}$  state of the ground-state  $(1s)^2(2s)^2(3s)^2(3p)^2$  electron configuration resulting from the electron impact dissociation of  $\text{SiH}_4$  were detected by pumping the  $(3p)^2\ ^1\text{S} \rightarrow (3p)(4s)\ ^1\text{P}$  transition around 390 nm and recording the subsequent  $(3p)(4s)\ ^1\text{P} \rightarrow (3p)^2\ ^1\text{D}$  fluorescence at 288 nm. The pump and detection pathways were interchanged for the detection of  $\text{Si}(^1\text{D})$  atoms. LIF spectra in Si were recorded for impact energies from 20 eV to 120 eV. The properly normalized LIF spectra recorded at different electron energy yield the absolute cross section for the formation of  $\text{Si}(^1\text{S})$  following neutral dissociation of  $\text{SiH}_4$  as a function of energy.

### III. Results and Discussion

The absolute cross section for the  $N_2(X) \rightarrow N_2^+(X)$  is known [8,9]. Thus, its value at 45 eV of  $40 \times 10^{-18} \text{ cm}^2$  can be used to put the  $Si(^1S)$  cross section on an absolute scale in a straightforward fashion. We determined a value of  $30 \times 10^{-18} \text{ cm}^2$  at 45 eV. The error margin of our absolute cross section measurement is estimated to be 25%. The measured cross section (shown in fig. 1 below) rises rapidly from threshold to a plateau around 30 eV and peaks in the energy range from 50 - 70 eV with a maximum value of about  $4 \times 10^{-17} \text{ cm}^2$ . The cross section declines fairly rapidly with increasing impact energy. The two data points at 40 eV were obtained under very different experimental conditions and thus demonstrate the reliability of the experimental technique. The shape of the cross section is rather similar to the shapes of various photoemission cross sections of Si and  $SiH_4$  reported by Perrin and Aarts [11] which all displayed a prominent structure in the low-energy regime around 30 eV followed by a maximum around 60 eV and rapid decline towards higher impact energies. The shape of our cross section is rather similar to the shapes of various photoemission cross sections of Si and  $SiH_4$  reported by Perrin and Aarts [11] which all displayed a prominent structure in the low-energy regime around 30 eV followed by a maximum around 60 eV and a rapid decline towards higher impact energies. It is interesting to note that the total  $SiH_4$  ionization cross section has a maximum value of  $5.4 \times 10^{-16} \text{ cm}^2$  at 70 eV [12] which is roughly half the magnitude of the total  $SiH_4$  neutral dissociation cross section obtained by Perrin et al. [13]. Basner et al. [12] also observed that the ionization of  $SiH_4$  by electron impact is entirely dominated by dissociative processes resulting in the formation of various singly and doubly charged fragment ions.

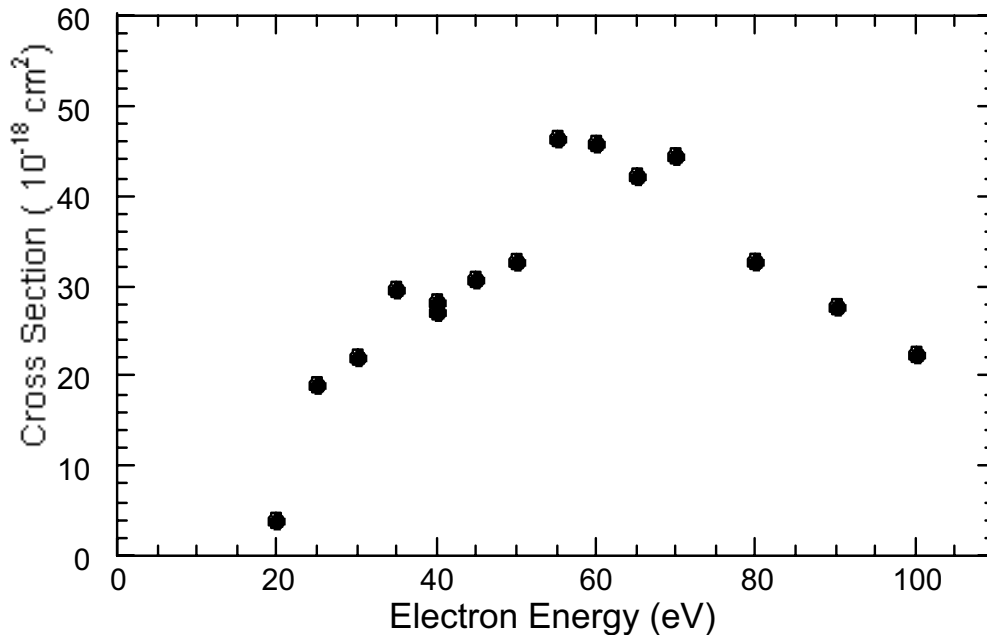


Fig. 1: Absolute cross section for the formation of  $Si(^1S)$  atoms following electron-impact induced neutral dissociation of  $SiH_4$  as a function of electron energy.

Measurements of the cross section or formation of  $Si(^1S)$  atoms following electron-driven neutral molecular dissociation of  $SiF_4$  are currently underway as are measurements of absolute cross sections for the formation of  $Si(^1D)$  atoms following electron-impact dissociation of both molecules. Earlier attempts to measure cross sections for  $Si(^1S)$

formation from Si-organic compounds such as TMS, TEOS, and HMDSO were unsuccessful, but allowed us to establish upper limits on these cross sections that were on the order of  $10^{-20}$  cm<sup>2</sup> at 70 eV

## Acknowledgments

We wish to acknowledge financial support of this work Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. We further acknowledge the use of equipment funded under NASA grants NAG5-4978 and NAG5-8971. One of us (KM) is also grateful for partial support from the above NASA grants.

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