



# On the electron impact ionization of silicon and metal containing organic molecules



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## ABSTRACT

Calculation of electron impact total inelastic cross sections for three silicon containing organic molecules (Trimethylsilane, Tetraethoxysilane and Hexamethyldisiloxane) and three organometallic complexes (Cyclopentadienyltrimethyl-platinum, Bismethylcyclopentadienyl-ferrum and Bismethylcyclopentadienyl-ruthenium) were performed employing spherical complex optical potential formalism. The complex scattering potential ionization contribution method was then used to derive total ionization cross sections from inelastic cross sections for these targets. The results presented here are for the incident electron energy ranging from ionization threshold to 2000 eV. The comparison with existing measurement shows promising results.

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## 1. Introduction

Electron induced chemistry plays crucial role in many technological processes such as plasma assisted thin film deposition, plasma etching, surface treatment and cleaning and modelling of fusion edge plasmas [1,2]. With the advent of low temperature plasma and its introduction to these industries [1], the study of electron impact collision processes is now inescapable. The use of silicon and metal containing organic complexes for technological plasma has already been realized. The unstable silicon containing organic compound like Trimethylsilane (TMS)  $[\text{SiH}(\text{CH}_3)_3]$  is used for plasma assisted chemical vapour deposition of semiconducting and insulative films. Hexamethyldisiloxane (HMDSO)  $[(\text{CH}_3)_3\text{-Si-O-Si-(CH}_3)_3]$  based polymer films are quite useful in corrosion protection [3] due to their unique optical properties [4]. For the deposition of polymer layers on various substrates, HMDSO is extensively used in chemical industry [5,6]. Hence, electron scattering studies on its monomer become essential for understanding its behaviour during collision in a non-equilibrium environment of low-temperature plasma used in the deposition techniques. Tetraethoxysilane (TEOS)  $[\text{Si}(\text{O-CH}_2\text{-CH}_3)_4]$  is useful for the production of  $\text{SiO}_2$  layers in semiconductor chip manufacturing [7]. The organometallic compounds like Cyclopentadienyltrimethyl-platinum

( $\text{CpPtMe}_3$ ), Bismethylcyclopentadienyl-ferrum ( $\text{MeCpFe}$ ) and Bismethylcyclopentadienyl-ruthenium ( $\text{MeCpRu}$ ) are suitable for decorative coatings and for hardening the surfaces in different plasma enhanced processes. This class of precursor molecules are especially employed in electron beam induced deposition (EBID) [8], which is a high energy electron scattering process. However, the spatial resolution and purity of deposition is not only dependent on the primary electron collisions, but also due to the processes of secondary electron generated by the primary electron beam on the substrate. Hence, different thermochemistry data and knowledge of electron impact ionization cross section in metal-organic compounds becomes necessary during the plasma assisted chemical vapour deposition [9]. Since electron impact ionization on plasma is one of the dominant ion-information processes, knowledge of electron impact ionization cross section is necessary in the understanding and the modelling of the plasma-enhanced deposition techniques.

However, the literature survey shows a fragmented study of electron collision and ionization by the silicon and metal containing organic molecules chosen here. The lone measurement for electron impact ionization cross-section for TMS was performed by Jiao et al. [10] using Fourier transform mass spectrometry over the energy range from ionization threshold to 70 eV. Basner et al. [11] measured total ionization cross section for HMDSO up to 70 eV using mass spectrometric technique. Electron impact experimental partial ionization cross section for HMDSO is reported by Seefeldt et al. [12] from ionization threshold to 50 eV. The experimental electron impact ionization using a double-focusing mass spectrometer of

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TEOS is reported by Basner et al. [13] over the energy range from threshold to 70 eV. Holtgarve et al. [14] measured the partial ionization cross sections for e-TEOS for most intensive fragment ions up to 50 eV using Fourier transform mass spectrometry. Basner et al. [15] measured the electron impact ionization cross section of all the present metallic organic compounds studied here from threshold to 90 eV. A double-focusing mass spectrometer with an improved ion extraction system was used in their measurements.

In the theoretical front, Probst et al. [16] reported electron impact ionization cross section for TEOS and HMDSO from ionization threshold to 2000 eV using Deutsche-Mark (DM) formalism. Deutsch et al. [17] and Deutsch and Schmidt [18] employed modified additivity rule (MAR) to calculate the electron impact ionization cross section for all the metal-organic complexes from threshold to 90 eV. There is also a single ionization cross section data point at 70 eV reported in Basner et al. [15] using additivity rule through statistical approach given by Fitch and Sauter [19].

In the present work our main aim is to calculate electron impact total ionization cross sections for various silicon and metal organic molecules (Fig. 1) from ionization threshold to 2000 eV. Towards this goal a quantum mechanical approach called spherical complex optical potential (SCOP) formalism [20–22] is employed initially to calculate total inelastic cross sections. Then the total ionization cross sections are derived from inelastic cross sections employing the semi-empirical methodology, complex scattering potential ionization contribution (CSP-ic) formalism [23–26]. The salient features of these theoretical methodologies are discussed in the next section.

## 2. Theoretical methodology

The spherical complex optical potential formalism is an effective technique to calculate intermediate to high energy (~10 eV to 2000 eV) electron impact integral scattering cross sections. This methodology has been successfully applied for diatomic molecules, dimers and polyatomic systems previously [23–26]. As the name suggest, a complex potential is developed initially to represent the electron-target scattering system. Using this potential a solution for the asymptotic wave function from Schrödinger's equation is obtained [27]. Here the total potential of the system representing the electron-target interaction is called an optical potential. This is a function of radial distance,  $r$  and incident electron energy,  $E_i$  represented by,

$$V_{opt}(r, E_i) = V_R(r, E_i) + iV_I(r, E_i). \quad (1)$$

where the real part consists of,

$$V_R(r, E_i) = V_{st}(r) + V_{ex}(r, E_i) + V_p(r, E_i) \quad (2)$$

here  $V_{st}$ ,  $V_{ex}$  and  $V_p$  stands for static, exchange and polarization potential respectively. The parameterized Hartree Fock wavefunction of Cox and Bonham [28] and Salvat et al. [29] were employed to obtain the charge densities and static potentials for atoms with  $Z \leq 54$  and  $Z > 54$  respectively. The spherically averaged molecular charge density,  $\rho(r)$  is determined from these atomic charge densities using simple additivity method. This is justified as these molecules are very large with individual atoms of respective molecule widely placed. Also, formulating charge density and static potential for such complex system is not feasible. Here the atomic charge densities are added together for each constituting groups and then normalized taking into account the covalent bonding and electron number [30]. The exchange potential for the systems studied here are developed from the Hara's parameter free and energy dependent 'free electron gas exchange model' [31]. The polarization potential is derived from the parameter free model of correlation-polarization potential given by Zhang et al. [32]. Since

the non-spherical channels like vibrational and rotational excitation have their thresholds occurring at low energy region (<10 eV), such processes are neglected in the present study. The energy range of present interest is from ionization threshold of the target to 2000 eV.

The imaginary part of the complex potential, also called the absorption potential ( $V_{abs}$ ), is responsible for the total loss of flux scattered through the allowed electronic excitation or ionization channels. To account for this, we have employed the quasi-free and Pauli-blocking model potential of Staszewska et al. [33] given by:

$$V_{abs}(r, E_i) = -\rho(r) \sqrt{\frac{T_{loc}}{2}} \left( \frac{8\pi}{10k_F^3 E_i} \right) \theta(p^2 - k_F^2 - 2\Delta) \times (A_1 + A_2 + A_3) \quad (3)$$

The parameters  $A_1$ ,  $A_2$  and  $A_3$  depend differently on target charge density, incident energy and energy parameter  $\Delta$ .  $\Delta$  is the factor that decides the effect of inelastic processes and is assumed to be ionization potential of the target by Staszewska et al. [33] in their original model. However, this will restrict the inelastic process to occur below the ionization threshold of the target, which is not true since electronic excitations can happen below that energy. Considering this, the minimum value of  $\Delta$  is usually chosen to be the first excitation energy of the target molecule. However, the first excitation energy of the molecules studied here are not available from literature. Hence, a minimum value 0.8I is chosen for  $\Delta$ . Then it is assumed to take an energy dependent functional form,

$$\Delta(E_i) = 0.8I + \beta(E_i - I) \quad (4)$$

Here  $\beta$  is obtained from the initial condition that  $\Delta = I$  (eV) at  $E_i = E_p$ , the value of incident energy at which present  $Q_{inel}$  reaches its peak. Beyond that  $\Delta$  is kept constant and is equal  $I$ . This form for  $\Delta$  is significant because it will allow inelastic channel to open below  $I$ .

In Eq. (3) the local kinetic energy of the incident electron can be written as:

$$T_{loc} = E_i - (V_{st} + V_{ex} + V_p) \quad (5)$$

The momentum and Fermi wave vector of the electron is given by  $p = (2E_i)^{1/2}$  and  $[3\pi^2\rho(r)]^{1/3}$  respectively and  $\theta(X)$  is called the Heaviside unit step-function.

Once the total potential as mentioned in Eq. (1) is developed, the Schrödinger's equation is solved through partial wave analysis to get phase shifts as output. These phase shifts carries the complete representation of scattering when an electron is impinging on a molecular target. By employing these phase shifts the elastic and inelastic cross sections at different incident energies can be derived [27].

Since the inelastic cross section contains only the spherical terms (electronic excitation and ionization), it can be written as:

$$Q_{inel}(E_i) = Q_{ex}(E_i) + Q_{ion}(E_i) \quad (6)$$

The total inelastic cross section is not directly measurable while excitation and ionization can be determined experimentally. In Eq. (6) the first term signifies the sum of excitation cross section for all the electronic channels. This term arises from the low lying dipole allowed transitions for which the cross section decreases rapidly at higher energies. The second term represents integral ionization cross section. Since the threshold of excitation usually falls below ionization,  $Q_{ex}$  decreases while  $Q_{ion}$  increases quite rapidly as the energy increases above ionization threshold with inelastic cross section as the upper limit, i.e.,

$$Q_{inel}(E_i) \geq Q_{ion}(E_i) \quad (7)$$

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