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Ion chemistry of tetramethyl sil ane (TMS) by el ectron impact

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ABSTRACT: We studied electron impact ionization of tetramethylsilane (TMS), Si(CH₃)₄, which is utilized in plasma polymerization applications, using a semi empirical Jain-Khare theoretical technique. Absolute partial cross sections for the formation of all fragment ions were measured by Jain-Khare method from threshold up to 120 eV. We obtained the following sixteen ions: CH₃⁺, Si⁺, SiH⁺, SiCH₂⁺, SiCH₃⁺, HSiCH₃⁺, HSiCH₃⁺, SiC₂H⁺, SiC₂H₃⁺, SiC₂H₅⁺, Si(CH₃)₂⁺, HSi(CH₃)₂⁺, Si(CH₃)₃⁺, HSi(CH₃)₃⁺, HSi(CH₃)₃⁺, HSi(CH₃)₄⁺. The agreement between our measured absolute partial ionization cross-sections & R.Basner et al data sets obtained by experimental technique are generally good for the silicon-containing fragment ions. The earlier work done is for 90 eV & here we have extended it up to from threshold to 120 eV.

KEYWORDS: Ionization Cross Section, Electron impact ionization

I.INTRODUCTION

Tetramethylsilane (TMS),Si[CH₃]₄, is a highly volatile compound with several important technological applications, being for instance routinely employed as an etchant gas in microelectronics.TMS is also commonly used as a monomer for low temperature plasma technology. Tetramethylsilane is a sensible precursor for the production of silicon carbide films by plasma enhanced chemical vapor deposition. It is also employed as a calibrant in NMR spectroscopy, the volatile liquid's simple molecular structure and available high purity can be exploited in the gas phase as well. The most widely used compounds include tetraethoxysilane[1-2]Hexamethyldisilanzane [3] and tetramethylsilane (TMS) [4-5] which is the simplest organosilicon compound. The electron impact ionization of the monomer is one of the most fundamental collision processes in a non equilibrium, low temperature plasma used in plasma polymerization applications. The detailed understanding and modeling of the plasma-enhanced deposition process require a knowledge of the total and partial electron impact ionization cross-sections. In any plasma one must generate positive ions and electrons to maintain electrical conductivity. This typically involves electron impact ionization, but when molecular species are present the ionization can be dissociative. Fragments formed by dissociative ionization are charged free radicals which, when neutralized, remain coordinatively unsaturated. Electron impact ionization cross-sections of tetramethylsilane have been measured previously by R.Basner *et al* [6] using high resolution double focusing sector field mass spectrometer and McGinnis *et al* [7] using Fourier transform mass spectrometry.This Present work results are based on semi-empirical Jain-Khare[10-13] theoretical technique.

II.THEORETICAL METHODOLOGY

Ionization process are described (e, 2e) or (e, 3e.) or Multi-electron coincidences corresponding to the removal of one, two and multi-electrons. These processes may be followed by single step, double step processes. Even on the theoretical side several more methods are available to compute the cross sections over a wide range of atoms and molecules. For example, there is no explanation for direct dissociate, total, single and double ionization cross section. The present calculations are carried out using semi-empirical formalism developed by Jain and Khare [10-13].This formula is also applicable to calculate partial, photo, integral ionization cross Golden Research Thoughts ISSN 2231-5063 Volume-3, Issue-3, Sept-2013

sections of atoms and molecules. The formula is useful for finding the rate coefficient of any atoms and molecules. This is a theoretical approach. In brief, the single differential cross sections in the complete solid angle ($\Omega = 4\Pi = \int 2\pi \sin \theta d\theta$) as a function of secondary electron energy ε corresponding to the production of i^{th} type of ion in the ionization of a molecule by incident electron of energy E is given by equation 1:

$$Q_{i}(E,W,\theta) = \frac{a_{0}^{2}R^{2}}{E} \left[\int_{k\to0}^{E-I_{i}} \left\{ \frac{E-W}{E-I_{i}} \frac{1}{W} df_{i}(W,K,\theta) \times \ln\left[1+C_{i}(E-I_{i})\right] + \frac{1}{E(\varepsilon_{0}^{3}+\varepsilon^{3})} \times S_{i}\left(\varepsilon - \frac{\varepsilon^{2}}{E-\varepsilon} + \frac{\varepsilon^{2}}{(E-\varepsilon)^{2}}\right) \right\} \right] 2\pi \sin\theta d\theta \dots (1)$$

where, $W (=\varepsilon + I_i)$ is defined as energy loss suffered by the incident electron.

 I_i = the ionization threshold for the production of i^{th} type of ion,

 a_0 = the Bohr radius,

 ε_{θ} = energy parameter,

 C_i = collision parameter,

- S_i = number of ionizable electrons,
- R = Rydberg constant and
- Θ = the scattering angle respectively.

In the present formulation, the dipole oscillator strengths df_i / dw are the key parameters. The oscillator strength is directly proportional to the photo ionization cross section [10-15]. Summation of PDDCS (Partial double differential cross section) over the system gives the total (DDCS) (Double differential cross section)

$$Q_{i}^{t}(E,W,\theta) = \sum_{i} Q_{i}(E,W,\theta).$$

Here it is interesting to note that $Q_i(E,W,\theta)$ is isotropic and hence the material property of molecule, i.e., the oscillator strength must be isotropic in nature. Here $df_i(W, K, \theta)$, the differential generalized oscillator strength (DGOS) in the optical limit $(K \rightarrow 0)$ has been used. From Lassettre's Theorem [8-9] the DGOS in the Bethe regime is reduced to the cosine distribution form of the linear optical oscillator strengths $df_i(W,0)/dW$, i.e.

 $df_i(W, K, \theta) \rightarrow (1/4\pi) [1 + \beta P_2(\cos\theta)] \times df_i(W, 0)/dW,$

where β is the asymmetric parameter and $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ is the second order Legendre

polynomial. In the present treatment, β is chosen as the probability of ionizing electrons in the ionization processes however, it depends on the ejected electron energy. The oscillator strengths are directly proportional to the photo ionization cross sections. Further integration of Equation (1) with respect to the scattering angle θ (from 0 to 2π) gives the PSDCS (Partial single differential cross section)

$$Q_{i}(E,W) = \int Q_{i}(E,W,\theta) d\Omega,$$

where differential solid angle $d\Omega$ is $2\pi \sin\theta d\theta$ Similarly, SDCS (Single differential cross section) are given as

$$Q_{i}^{T}(E,W) = \sum_{i} Q_{i}(E,W).$$

Further integration of PSDCS with respect to W from I to W_{max} (= E) results in PICS (Partial integral cross section), i.e.

$$Q_i(E) = \int Q_i(E, W) dW$$

The present formulation requires the major input data of the photo ionization cross-sections in terms of the optical oscillator strengths.

III. RESULTS AND DISCUSSION

Cross sections for the ionization of tetramethylsilane are shown in figures 1 to 4 with fitting parameters in Table 1 to 4. The predominant ion at all energies is the trimethylsilyl cation, $(CH_3)_3Si^+$. The next most abundant species is dihydromethylsilyl cation, $CH_3SiH_2^+$.

120

1.589

Table 1

Partial c	ross-sectio	on values for	electron in	pact ionization	of TMS				
Electron Energy	n Parti	Partial ionization-cross section (10^{-16} cm^2)							
(eV)	Frag	mented ions							
	$\mathrm{CH_3}^+$	Si ⁺	SiH^+	SiH ₃ ⁺					
10	0.001				2.0				
19 24	0.001	0.062	0 184		1.8-				
30	0.002	0.002	0.184	0 496					
32	0.242	0.330 0.472	0.505	0.598					
34	0.463	0.588	0.617	0.709					
36	0.568	0.699	0.726	0.820					
38	0.668	0.803	0.828	0.927					
40	0.760	0.900	0.922	1.027					
45	0.960	1.105	1.121	1.242					
50	1.119	1.265	1.276	1.409	° 0.0 − ** *				
55	1.242	1.388	1.395	1.535	-0.2				
60	1.339	1.481	1.485	1.629	$\begin{array}{c} 20 & 40 & 60 \\ \textbf{Electron Energy (eV)} \\ (-\bullet -/CH^{+} - \star -/Si^{+} - \star -/SiH^{+} \text{ and } - \star -/SiH^{+}) \text{ the present results} \end{array}$				
70	1.469	1.604	1.602	1.748	(• IGH_3^* , * IGH_3^* , * IGH_3^*) and • IGH_3^* are present results. (• ICH_3^* , * ISI^* , × $ISIH^*$ and × $ISIH_3^*$) R.Basner et al results.				
80	1.542	1.668	1.664	1.806					
90	1.581	1.697	1.691	1.828					
100	1.596	1.705	1.697	1.827	Figure 1. Shows partial ionization cross section				

Figure 1. Shows partial ionization cross section of the CH_3^+ , Si^+ , SiH^+ and SiH_3^+ of TMS molecule.

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Table	2
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1.789

Partial cross-section values for electron impact ionization of TMS

1.673

1.682

Electron Energy	Partial	ionization	cross sectio	n $(10^{-16} \mathrm{cm}^2)$	
(eV)	Fragme	ented ions			
	SiCH ₂ ⁺	SiCH ₃ ⁺	HSiCH ₃ ⁺	H ₂ SiCH ₃ ⁺	
14	0.005				
21	0.011	0.564			22-
24	0.013				
25	0.043	0.886			ų 1.6-
26	0.084	0.951			
40	0.822	1.011	1.237	1.582	
45	1.019	1.212	1.440	1.771	ğ 1.0-1 → × V
50	1.174	1.366	1.594	1.920	ğ 0.8-]
55	1.294	1.483	1.708	2.029	5 ^{0.6}
60	1.386	1.570	1.791	2.106	
70	1.509	1.681	1.891	2.189	δ 0.2
80	1.578	1.736	1.932	2.212	
90	1.609	1.757	1.940	2.201	

100	1.623	1.757	1.927	2.171	
120	1.608	1.725	1.872	2.083	

Table 3

Partial cross-section values for electron impact ionization of TMS										
Electron Energy	Partial	Partial ionization-cross section (10^{-16} cm^2)								
(eV)	Fragme	ented ions								
	SiC_2H^+	SiC ₂ H ₃ ⁺	SiC ₂ H ₅ ⁺	Si(CH ₃) ₂ ⁺						
18	0.007	0.007								
19	0.022	0.022			2.0 -					
20	0.073	0.073			- 1.8 - - 1.8 -	* * * *				
21	0.137	0.137			°€ 1.6 – ⊈ 1	× · · · · · · · · · · · · · · · · · · ·				
22	0.210	0.210			E 1.4-	A A A A A A A A A A A A A A A A A A A				
23	0.288	0.288			L 1.2 –	<i>▼ ↓ •</i>				

19	0.022	0.022		
20	0.073	0.073		
21	0.137	0.137		
22	0.210	0.210		
23	0.288	0.288		
28	0.335	0.582	0.624	
29	0.399	0.646	0.691	
40	0.620	0.885	1.193	1.245
45	0.824	1.082	1.372	1.416
50	0.989	1.245	1.523	1.554
55	1.121	1.375	1.641	1.660
60	1.226	1.476	1.732	1.741
70	1.371	1.611	1.846	1.840
80	1.458	1.684	1.900	1.885
90	1.507	1.719	1.918	1.897
100	1.532	1.730	1.913	1.889
120	1.538	1.711	1.867	1.840

Selected results of the ionization crosssection measurements for TMS are presented in figures 1- 4. Figures 1 and 2 show the cross-sections for formation of the fragment ions corresponding to (CH_3^+) , (Si^+) , (SiH^+) , (SiH_3^+) , $(SiCH_2^+)$, $(SiCH_3^+)$, $(H_2SiCH_3^+)$, $(HSiCH_3^+)$ from threshold to 120 eV.

Maximum cross-section of $1.75 \times 10^{-16} \text{ cm}^2$ is found for SiCH₃⁺ ion at 100 eV, Maximum crosssection of 2.21×10^{-16} cm² is found for H₂SiCH₃⁺ ion at 80eV. The maximum cross-section for the methyl ion (CH₃⁺) reaches a value of about 1.5×10^{-16} cm² at about 100 eV. The maximum ionization cross section in figure 1 is of SiH_3^+ ion which is $1.828 \times 10^{-16} \text{ cm}^2$ at an energy range of 90 eV and for figure 2 is of $H_2SiCH_3^+$ ion which is 2.20×10^{-16} cm² at the same electron energy range. All other maximum crosssection values shown in figures 1 and 2 are below 2.20×10^{-16} cm². Figure 3 shows ionization cross section of SiC_2H^+ , $SiC_2H_3^+$, $SiC_2H_5^+$ and $Si(CH_3)_2^+$. Both TMS and its hydride analog silane have triply degenerate highest occupied molecular orbitals. Removal of an electron from these orbitals produces



Figure 3. Shows partial ionization cross section of the SiC_2H^+ , $SiC_2H_3^+$, $SiC_2H_5^+$ and $Si(CH_3)_2^+$ of TMS molecule.

an ion whose geometry, according to the Jahn-Teller theorems [6], must distort to lift the orbital degeneracy.

We note that the measured CH_3^+ crosssection represents a lower limit, since these fragment ions are formed with a wide distribution of excess kinetic energies and thus the quantitative detection of CH_3^+ fragment ions is likely to be affected. It is noteworthy that the parent ionization cross-section $Si(CH_3)_4^+$ is small with maximum peak value of 01.89×10^{-16} cm². By far the largest ionization crosssection with a peak value of 2.55×10^{-16} cm² is measured for $Si(CH_3)_3^+$ which corresponds to $Si(CH_3)_3^+$ fragment ion. This finding is very similar to what was observed before in ionization studies of TMS by R.Basner et al [6]. This cross-section is shown in Figure 4 together with the partial ionization cross-section of TMS and the results of R.Basner et al [6] cross-section calculations. The values of all sixteen ionization cross-sections measured in this work are summarized in tabulated form for easier quantitative reference in Table 1-4.

Table	4
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Partial cross-section values for electron impact ionization of TMS									
Electron Energy		Partial ionization-cross section (10^{-16} cm^2)							
(eV)		Fragmented ions							
	HSi(CH ₃)	02 ⁺ Si(CH ₃)3 ⁺	HSi(CH ₃)	$)_3^+$ Si(CH ₃) ₄ ⁺					
10 11	0.005 0.044	0.002 0.029	0.059						
12 13	0.084 0.239	0.068 0.202	0.12 0.221		12				
14 15	$0.404 \\ 0.569$	0.353 0.508	0.346 0.493		10 - ****				
16 17	0.73 0.882	0.662 0.809	0.647 0.799		10. ¹⁶ cm ¹				
18 19	1.025	0.949	0.945						
20 34	1.28	1.2	1.212	2 16	s = * S 2 4 - *				
36	1.323	2.192	2.100	2.10					
38 40	1.501 1.73	2.266 2.328	2.211 2.264	2.293 2.344					
45 50	1.715 1.813	2.443 2.511	2.36 2.415	2.433 2.483	0 20 ⁴⁰ Electron Energy (eV) (• (USI(CH)) + (SU(CH))				
55 60	1.879 1.922	2.547 2.559	2.442 2.45	2.505 2.507	$(\bullet /HSi(CH_3)_2, * \mathscr{A} /Si(CH_3)_3, * \mathcal{A} /Si(CH_3)_3 and * \mathcal{A} /Si(CH_3)_4) ine present results.$				
70	1.961	2.54	2.426	2.476	Figure 4. Shows partial ionization cross section of the $HSi(CH_3)_2^+$, $Si(CH_3)_3^+$, $HSi(CH_3)_3^+$ and $Si(CH_3)_4^+$				
90 100	1.962	2.489 2.422 2.35	2.370	2.349	of TMS molecule.				
100	1.91	2.33	2.243	2.270					

The appearance energies of all the sixteen ions of silane is taken from R.Basner et al [6] paper.

2.125

IV. CONCLUSION

120 1.83

We measured partial ionization cross sections for electron impact ionization of the simplest organosilicon molecule TMS using semi-empirical formalism developed by Jain and Khare. We observed that the predominant ion at all energies is the trimethylsilyl cation, $(CH_3)_3Si^+$. A detailed comparison of our TMS ionization cross-sections with the values reported by R.Basner *et al* [6] reveals good agreement in terms of the cross-section shapes, but does not reveal good agreement in terms of the absolute cross-section values for some of the most intense ion peaks.

2.204

2.106

REFERENCES

- [1] A.W.Luft, Appl.Phys.Commun.8(1988)1.
- [2] D.A Gougherty and A.Gallagher, J.Appl. Phys.67 (1990)139.
- [3] A.M.Wrobel, *J.Macromol.Sci.Chem.A.*201 (1983) 583.
- [4] I.Tajama and M.Yamamoto, J.Polym. Sci:Part A Polym. Chem. 25(1987)1737.
- [5] P.Favia, Plasma Sources Sci. Technol., 1(1992)59.
- [6] R. Basner, R.foest, M.Schmidt, F.Sigeneger, P.Kurunczi, K.Becker, H.Deutsch, Int. J.Mass

Spectrometry and Ion Processes 153(1996)65-78. [7]S.McGinnis, Chem. Phys. Lett. 232(1996)99.

- [8]T.W. Shyn, W.E. Sharp, *Phys. Rev. A* 20(1979) 2332.
- [9] E N Lassettre, A Skerbele and A D Michael, J. *Chem. Phys.* (1967) 46, 4536.
- [10] S.P. Khare, Planet. Space Sci. 17 (1969) 1257.
- [11] S.P. Khare, W.J. Meath, J. Phys. B 20 (1987)

Available online at www.aygrt.isrj.net

2101.

- [12] P. Bhatt, S.Pal, J. Electron Spectro. Related Phenomenon 129(2003)35-41.
- [13] P. Bhatt, S.Pal, J. of Mass Spectrometry 229(3)(2003)151-156.
- [14] Satyendra Pal, J. Phys.: Conf. Ser. (2009)163, 012030.
- [15] Satyendra Pal, J. Phys. Scr. (2011) 6.