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Electron impact ionization of the $TiCl_x$ ($x = 1 - 3$) free radicals

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Abstract

Titanium tetrachloride ($TiCl_4$) is used for the plasma-assisted chemical vapor deposition of titanium nitride films. We studied the electron impact ionization of $TiCl_x$ ($x = 1 - 3$) free radicals, which are abundant constitutents in $TiCl_4$-containing processing plasmas, for electron energies from threshold to 100 eV. Absolute partial cross sections for the formation of all singly charged molecular ions were measured using the fast-beam technique. Dissociative ionization was found to be the dominant process for $TiCl_3$ whereas the formation of the respective parent ions plays a more important role for $TiCl_2$ and TiCl. Total single ionization cross sections for the three radicals could not be determined with reasonable accuracy because of problems in the determination of the cross sections for the formation of the atomic ions Ti^+ and Cl^+ for the three targets and, as a consequence, no comparison of the measured cross sections with calculated total single ionization cross sections is possible. (Int J Mass Spectrom 208 (2001) 1–5) © 2001 Elsevier Science B.V.

Keywords: Titanium tetrachloride; Electron impact ionization; Cross sections; Plasma deposition

1. Introduction

Wear and corrosion resistant coatings of TiN can be deposited by plasma-activated chemical vapor deposition at substrate temperatures around 550 °C using low-pressure, nonthermal plasmas with a mixture of $Ar/H_2/N_2/TiCl_4$ [1,2]. The plasma chemical processes are determined by the properties of the plasma, which, in turn, depend on the overlap between the electron energy distribution of the plasma electrons and the cross sections for the various electron-initiated processes (e.g. vibrational excitation, dissociative attachment, dissociation, ionization, and dissociative ionization, to name just some of the important electron-driven processes) [3]. The cross sections for the electron interactions with the neutrals in the plasma including the free radicals produced by neutral dissociation of the feed gas molecules are important for a microscopic understanding of the plasma chemical processes and for the modeling of the reactive plasma. Results for the ionization properties of $TiCl_4$ were reported recently by Basner et al. [4] who carried out a comprehensive study of the

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electron impact ionization and dissociative ionization of $TiCl_4$ using a time-of-flight mass spectrometric technique.

In this article, we report the results of measurements of absolute partial cross sections for the formation of molecular ions following electron impact on the free radicals $TiCl_x$ ($x = 1 - 3$) using the fast-neutral-beam technique for impact energies from threshold to 100 eV. These measurements complement the previous studies of the ionization of $TiCl_4$ and are a continuation of our activities in the field of measurements of electron impact ionization cross sections of molecules and radicals that are important for plasma processing [4–11].

2. Experimental apparatus

A detailed description of the fast-beam apparatus and of the experimental procedure employed in the determination of absolute partial ionization cross sections has been given in previous publications from this laboratory [12,13]. The primary ion source is a commercially available Colutron ion source. $TiCl_4$, which is a liquid at room temperature, was placed in a temperature-stabilized reservoir connected to the discharge chamber by way of a heated high precision leak valve. Since $TiCl_4$ reacts with traces of water and moisture in the reservoir/gas line resulting in the formation of HCl and TiO_2, extensive cleaning of the entire reservoir/gas handling system was carried out. Positively charged $TiCl_x^+$ ($x = 1 - 3$) primary ions are extracted from the ion source, accelerated to about 3 keV, mass selected in a Wien filter, and sent through a charge-transfer cell filled with a suitably chosen charge-transfer gas for resonant or near-resonant charge transfer of a fraction of the primary ions. The residual ions in the beam were removed from the neutral target gas beam by electrostatic deflection and most species in Rydberg states are quenched in a region of high electric field. The resulting fast-neutral-target beam is subsequently crossed at right angles by a well-characterized electron beam (5–200 eV beam energy, 0.5 eV FWHM energy spread, 0.03–0.4 mA beam current). The product ions are focused in the entrance plane of an electrostatic hemispherical analyzer, which separates ions of different charge-to-mass ratios (i.e. parent ions from fragment ions). The ions leaving the analyzer are detected by a channel electron multiplier. Absolute calibration of the relative cross sections can be achieved in two ways. The fast-beam apparatus affords the capability to measure all quantities that determine the absolute cross section directly. The target density is obtained from the energy deposited by the fast-target beam into a pyroelectric detector, which is first calibrated relative to a well-characterized ion beam [14,15]. As an alternative, the well-established Kr or Ar absolute ionization cross sections can be used to calibrate the pyroelectric crystal. The calibrated detector, in turn, is then used to determine the flux of the neutral target beam in absolute terms. The second procedure avoids the frequent and prolonged exposure of the sensitive pyroelectric crystal to fairly intense ion beams [15,16]. Both calibration methods were used here and yielded results that were consistent with one another.

We established that all molecular fragment ions produced by dissociative ionization of $TiCl_x^+$ with an excess kinetic energy of less than 3 eV per fragment ion are collected and detected with 100% efficiency using a combination of in situ experimental studies and ion trajectory modeling calculations [12]. The absolute cross sections reported here were determined with uncertainties of ±15% for the parent ionization cross section and ±18% for the dissociative ionization cross section. These error margins, which are similar to what we quoted previously for ionization cross sections measured for other free radicals in the same apparatus [12,13], include statistical uncertainties and all known sources of systematic uncertainties.

3. Results and discussions

We limit the results reported in this article to the measured molecular ionization cross sections only, that is to the $TiCl_x^+$ cross sections ($x = 1 - 3$) from $TiCl_3$, the $TiCl_2^+$ and $TiCl^+$ cross sections from $TiCl_2$, and the $TiCl^+$ cross section from TiCl. Although we saw ion signals attributable to the formation of the atomic fragment ions Ti^+ and Cl^+ for all three $TiCl_x$ radicals, we were not able to extract reliable absolute partial cross sections from the recorded ion signals in these cases. This was largely due to the fact that the atomic fragment ion signals were much more spread out spatially compared to the molecular ion signals at the position of the channeltron detector. This may have been caused by, among other factors, a broad distribution of kinetic excess energies of the atomic product ions. As a consequence, the atomic product ion signals could not be focused down to sufficiently well-defined beams that could be quantified by sweeping the ion beam across the entrance cone of the channeltron detector as is usually done in order to ensure that the entire ion signal for a given product ion is collected and a reliable cross-section value can be extracted from the collected ion signal [12,13]. Although cross sections for the formation of atomic fragment ions in molecular dissociative ionization processes are typically very small for most polyatomic molecules [4–11,19], this was not the case for the $TiCl_4$ molecule [4] and may also not be true for the $TiCl_x$ free radicals. Thus, in the absence of measured absolute partial atomic fragment ionization cross sections for Ti^+ and Cl^+, we are not able to determine reliable experimental total single ionization cross sections for the three radicals, which are the only ionization cross sections that can be compared to calculated ionization cross sections [17,18].

We focused our cross-section measurements to the electron energy range below 100 eV. As was observed before for $TiCl_4$ [4], most of the partial ionization cross sections for the $TiCl_x$ radicals rise rapidly from threshold to a maximum at comparatively low impact energies which may be indicative of the presence of indirect ionization processes (see the following discussion).

Fig. 1 shows the measured absolute partial cross sections for the formation of the molecular ions $TiCl_x^+$ ($x = 1 - 3$) produced by electron impact on $TiCl_3$ for electron energies up to 100 eV. The three curves represent the result of single data runs. The shapes of the relative cross-section curves were reproducible to better than ±5% (except in the near-threshold region). The formation of the $TiCl_2^+$ fragment ions is the dominant channel with a peak cross section of about 4.3×10^{-16} cm^2 at 25 eV. The $TiCl^+$ cross section reaches a maximum value of 2.7×10^{-16} cm^2 at 30 eV, whereas the $TiCl_3^+$ parent ionization cross-section peaks at a value of only 1.6×10^{-16} cm^2 at about 20 eV. We note that the cross-section shapes for all three partial ionization cross sections rise rapidly from threshold and reach their respective maxima at relatively low impact energies, approximately twice the corresponding threshold energies and decline only gradually with increasing impact energy. In fact, the $TiCl_2^+$ cross section remains essentially flat between 25 and 100 eV. Similar cross-section shapes were reported by Basner et al. [4] for some partial ionization cross sections of $TiCl_4$ [4]. Such a cross-section shape is rather unusual for most molecules and atoms whose ionization cross sections tend to peak at energies that correspond to four or five times the threshold energy [19]. Basner et al. [4] suggested that these rapidly rising cross-section shapes may be due to the presence of indirect ionization processes which are characterized by cross sections that peak at very low impact energies [19]. The measured appearance energies for the three $TiCl_x^+$ ($x = 1 - 3$) ions from $TiCl_3$ are consistent with known $TiCl_3$ ionization energy and the minimum energies for the formation of the $TiCl_2^+$ and $TiCl^+$ fragment ions based on available thermochemical data for these species [20–23] within the margin of uncertainty of our appearance energy

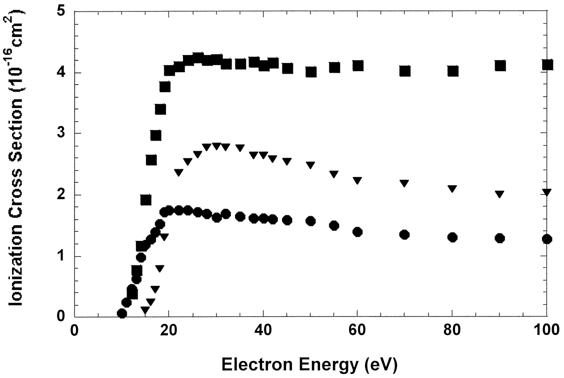

Fig. 1. Absolute partial cross sections for the formation of $TiCl_3^+$ ions (solid circles), $TiCl_2^+$ ions (solid squares), and $TiCl^+$ ions (solid inverted triangles) following electron impact on $TiCl_3$ from threshold to 100 eV.

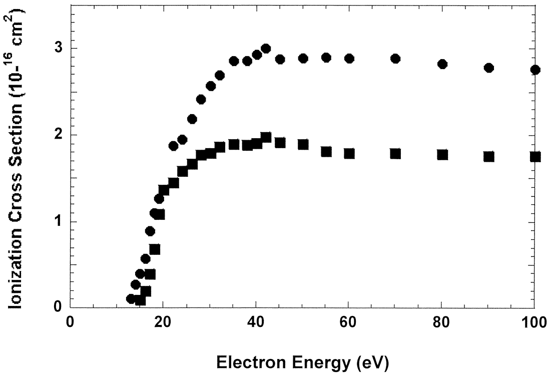

Fig. 2. Absolute partial cross sections for the formation of $TiCl_2^+$ ions (solid circles) and $TiCl^+$ ions (solid squares) following electron impact on $TiCl_2$ from threshold to 100 eV.

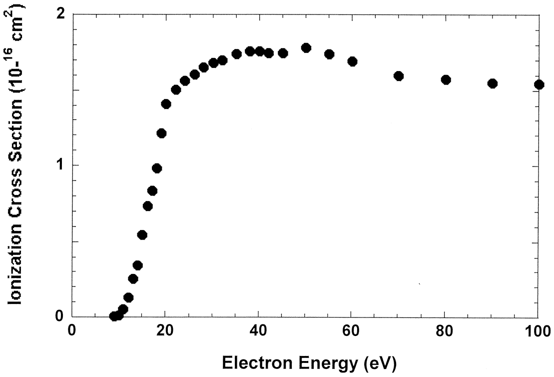

Fig. 3. Absolute partial cross sections for the formation of $TiCl^+$ ions (solid circles) following electron impact on TiCl from threshold to 100 eV.

determination (about ±1.0 eV) and within the accuracy of the energy of our electron beam which was calibrated to within ±0.5 eV relative to the well-known ionization energy of Xe [20]. Specifically, we measured the following appearance energies, $TiCl_3^+$/$TiCl_3$: 10 ± 1.5 eV, $TiCl_2^+$/$TiCl_3$: 12.5 ± 1.8 eV, and $TiCl^+$/$TiCl_3$: 14 ± 1.8 eV.

Fig. 2 shows the measured absolute partial cross sections for the formation of the molecular ions $TiCl_x^+$ ($x = 1,2$) produced by electron impact on $TiCl_2$ for electron energies up to 100 eV. In contrast to $TiCl_3$, the ionization of $TiCl_2$ is dominated by the formation of $TiCl_2^+$ parent ions with a peak cross section of about 3×10^{-16} cm^2 at 40 eV. The maximum value of the $TiCl^+$ fragment ionization cross section is about 2×10^{-16} cm^2 at about the same energy of 40 eV. Compared to $TiCl_3$, the two partial ionization cross-section curves for $TiCl_2$ rise somewhat more gradually and reach a maximum at an energy that corresponds to about three times the threshold energy. This may indicate that indirect ionization processes are less prominent in this case. As was the case for $TiCl_3$, the measured appearance energies for the two $TiCl_x^+$ ($x = 1,2$) ions from $TiCl_2$ are also consistent with known $TiCl_2$ ionization energy and the minimum energy for the formation of $TiCl^+$ based on available thermochemical data [20–23], $TiCl_2^+$/$TiCl_2$: 12 ± 1.5 eV, $TiCl^+$/TiCl: 14.5 ± 1.8 eV. Last, for TiCl we only report a measurement of the $TiCl^+$ parent ionization cross section (see Fig. 3) which reaches a maximum of 1.8×10^{-16} cm^2 at 40 eV. The measured $TiCl^+$ cross-section shape is similar to the cross-section shapes for $TiCl_2$ (see Fig. 2). The measured ionization energy for TiCl of 9.5 ± 1.5 eV is consistent with the known ionization energy of this radical [20–23].

4. Conclusions

We measured absolute partial electron impact ionization cross sections for the formation of molecular ions from the $TiCl_x$ ($x = 1 – 3$) free radicals. Dissociative ionization was found to be the dominant process for $TiCl_3$, whereas the formation of the respective parent ions plays a more important role for $TiCl_2$ and TiCl. Total single ionization cross sections for the three radicals could not be determined with reasonable accuracy because of problems in the determination of the cross sections for the formation of the atomic ions Ti^+ and Cl^+ for the three targets and, as a consequence, no comparison of the measured cross sections with calculated total single ionization cross sections is possible. The shape of the partial ionization cross sections indicates the presence of indirect as well as direct ionization processes with a dominance of the indirect processes at lower electron energies. The absolute cross-section values measured here are indispensable for a microscopic understanding and a detailed modeling of the plasma chemical processes in $TiCl_4$-containing plasmas as well as for the critical evaluation of mass spectrometric plasma diagnostics data obtained in these plasmas.

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References

[1] J. Patscheider, L. Shizhi, S. Veprek, Plasma Chem. Plasma Processes 13 (1996) 567.

[2] M. Eckel, P. Hardt, M. Schmidt, Surf. Coat. Technol. 11 (1999) 1037.

[3] K. Becker, Elementary Collision Processes in Plasmas, in Lectures on Plasma Physics Plasma Technology, R. Hippler, S. Pfau, M. Schmidt, K.H. Schoenbach (Eds.), VHG Chemie Verlag, Weinheim, 2001.

[4] R. Basner, M. Schmidt, K. Becker, V. Tarnovsky, H. Deutsch, Thin Solid Films 374 (2000) 291.

[5] V. Tarnovsky, A. Levin, K. Becker, R. Basner, M. Schmidt, Int. J. Mass Spectrom. Ion Processes 133 (1994) 175.

[6] R. Basner, M. Schmidt, H. Deutsch, V. Tarnovsky, A. Levin, K. Becker, J. Chem. Phys. 103 (1995) 211.

[7] R. Basner, M. Schmidt, H. Deutsch, Contrib. Plasma Phys. 35 (1995) 375.

[8] R. Basner, R. Foest, M. Schmidt, F. Sigeneger, P. Kurunczi, K. Becker, H. Deutsch, Int. J. Mass Spectrom. Ion Processes 153 (1996) 65.

[9] R. Basner, M. Schmidt, V. Tarnovsky, K. Becker, Int. J. Mass Spectrom. Ion Processes 171 (1997) 83.

[10] R. Basner, R. Foest, M. Schmidt, K. Becker, H.Deutsch, Int. J. Mass Spectrom. Ion Processes 176 (1998) 245.

[11] R. Basner, M. Schmidt, K. Becker, H. Deutsch, Electron Impact Ionization of Organic Silicon Compounds, Advances in Atomic, Molecular, and Optical Physics Vol. 43, M. Inokuti, K. Becker (Eds.), Academic, New York, 2000, pp. 147–185.

[12] V. Tarnovsky, P. Kurunczi, D. Rogozhnikov,, K. Becker, Int. J. Mass Spectrom. Ion Processes 128 (1993) 181.

[13] V. Tarnovsky, K. Becker, J. Chem. Phys. 98 (1993) 7868.

[14] R.C. Wetzel, F.A. Biaocchi, T.R. Hayes, R.S. Freund, Phys. Rev. A 35 (1987) 559.

[15] V. Tarnovsky, K. Becker, Z. Phys. D 22 (1992) 603.

[16] R.S. Freund, R.C. Wetzel, R.J. Shul,, T.R. Hayes, Phys. Rev. A 41 (1990) 3575.

[17] Y.-K. Kim, W. Hwang, N.M. Weinberger, M.A. Ali, M. E. Rudd, J. Chem. Phys. 106 (1997) 1026.

[18] H. Deutsch, K. Becker, S. Matt, T.D. Märk, Int. J. Mass Spectrom. 197 (2000) 37.

[19] Electron Impact Ionization, T.D. Märk, G.H. Dunn (Eds.), Springer, Wien 1985.

[20] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levine, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) 1.

[21] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Chuney, R.L. Nutall, J. Phys. Chem. Ref. Data 11 (1982) 1.

[22] M.W. Chase Jr., K.A. Davis, J.R. Downey, D.J. Frurip, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Ref. Data 14 (1985) 1.

[23] The Handbook of Chemistry and Physics, 65th ed., R.C. Weast, M.J. Astle, W.H. Beyer (Eds.), CRC Press, Boca Raton, FL, 1985.