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Electron interactions with FEBID precursor tungsten hexachloride (WCl₆)

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RATIONALE

Secondary electrons with an energy distribution below 100 eV are formed when high-energy particles interact with matter. In the focused electron beam induced deposition, high energetic beams are used to decompose organometallic compounds on surfaces. We investigated electron ionisation of WCl₆ and dissociative electron attachment to WCl₆ in the gas phase in order to better understand the decomposition mechanism driven by secondary electrons.

METHODS

A double focusing mass spectrometer coupled with a Nier-type ion source apparatus was used to perform the present studies. The electron ionisation studies have been performed with an electron energy of 70 eV and dissociative electron attachment studies in an energy range of 0 – 14 eV.

RESULTS

Tungsten hexachloride rapidly oxidises, leading to the formation of a mixture of pure WCl₆ and WCl₄O together with WCl₂O₂ species. The fragmentation of the three chlorinated compounds is effective, although electron impact to WCl₆ leads to W⁺ in contrast with WCl₂O₂ and WCl₄O leading to WO₂⁺ and WO⁺, respectively, as lighter fragments. With regards to electron attachment, the decomposition of the precursor molecules is observed, however W⁻ was not detected within the detection limit of the apparatus.

CONCLUSIONS

Electron ionisation and dissociative electron attachment (DEA) to WCl₆ (WCl₄O and WCl₂O₂) lead to strong fragmentation. In electron ionisation, the loss of all chlorine ligands is observed as well as in the oxidised WCl₆, the fragmentation by losing the chlorine atoms is also detected. DEA results have shown the dissociation by the cleavage of chlorine atoms as well as by the scission of an oxygen atom. The formation of chlorine and oxygen anions was detected indicating the formation of a neutral counterpart containing the metal atom, free to be attacked by the next electron.

Introduction

Focused Electron Beam Induced Deposition (FEBID) is used^[1] as a powerful tool for creating nanostructures on a surface with a large variety of industrial applications. Nanotechnology is an area of interest, mainly in mask repair^[2], fabrication of sub- μm Hall devices^[3], growth of nanowires^[4] and tips for emission field microscopy^[5], among others. In brief, FEBID consists of a focused high-energy electron beam, operating at incident energies from 1 to 30 keV^[1,6,7], reacting with organometallic precursor molecules in a continuous stream. Precursor molecules used are typically compounds with a central metal atom and organic ligands. Upon high-energy interaction with organometallic precursor, the metal is deposited on the surface and the organic ligands are pumped away. FEBID is an alternative technique to chemical vapour deposition (CVD). However in the FEBID process the reaction is driven by the incident electron, and CVD is a primary thermal driven process. FEBID has been proved as a clean and precise tool for manipulating and controlling matter at nano scale. However, in FEBID the spatial resolution and purity of the metal deposit still challenging the technique.^[6]

When the high-energy electron beam irradiates the sample, many events are initiated. Consequently, secondary electrons (<50 eV) (SE) and back-scattered electrons (>50 eV) (BSE)^[6] are produced in unavoidable secondary reactions, contributing to the loss of resolution. Experimental and theoretical demonstrations have shown that those electrons peak at energies below 15 eV, and the subsequent processes are far to be negligible, since they influence the fragmentation pathways.^[1] Dissociative electron attachment (DEA) processes are open at this low energy regime, since they are driven by SE's. DEA is a resonance process where the electron is initially captured in a low-lying unoccupied molecular orbital forming a transient negative ion (TNI) in a vibrationally or electronically excited state. The formed unstable TNI will further decay via dissociation (see equation I) or by free electron reemission (autodetachment) (see equation II).^[8]

where OM is an organometallic molecule. The SE produced in the FEBID process, will drive DEA processes that will play an important role in the FEBID mechanism due to the high DEA cross sections. For tungsten, iron and platinum deposits, $\text{W}(\text{CO})_6$ ^[9,10], FeCO_5 ^[11] and MeCpPtMe_3 ^[12], respectively, are widely used as precursors. As so, several experimental DEA studies have been already performed with a variety of precursor molecules. Not only the mentioned precursors have attracted the attention in those studies, but also $\text{Pt}(\text{PF}_3)_4$ ^[13,14], $\text{Co}(\text{CO})_3\text{NO}$ ^[15] $\text{Cu}(\text{hfac})_2$ and $\text{Pd}(\text{hfac})_2$ ^[16] for Pt, Co, Cu and Pd metal deposition. In the DEA studies performed by Wnorowski *et al.*^[9], the complete dissociation by the interactions of low energy electrons with $\text{W}(\text{CO})_6$, i.e. the formation of the bare metal anion, was not observed. In the early 70's Preiss^[17] has published an electron ionisation study of halides of some transition elements. In the Preiss study, fragmentation processes, charge distributions as well as relative stabilities of fragment cations and doubly charged ions were discussed.

In this communication we report electron ionisation as well as low energy electron interactions studies to the WCl_6 molecule. Tungsten hexachloride rapidly hydrolysed, leading to the formation of a mixture of pure WCl_6 and WCl_4O together with WCl_2O_2 species.^[18] This reaction can occur within the sample preparation and in the surfaces of the ion source chamber, before electron interaction.

Methods

The present measurements were obtained with a double-focusing mass spectrometer (VG-ZAB-2SE) from former VG ANALYTICAL (UK). The mass spectrometer consists out of a Nier-

type ion source and a mass analyser. The later, a two sector field instrument in reversed Nier-Johnson geometry, was utilized at an ion acceleration voltage of about 6 kV. The measurements were obtained with a mass resolution of ~ 1500 (FWHM). A channeltron-type secondary electron multiplier was used to detect the ion signal. A more detailed description can be found in reference 18. The sample container was located outside the ion source chamber. To provide an appropriate working pressure of about 5×10^{-7} mbar in the ion source, the sample was heated up to ~ 70 °C. The target molecules were directed into the ion block where they interacted with the electron beam. The anions were produced via electron attachment using an electron current of 10 μ A with a resolution of about 1 eV (FWHM). The same electron current was applied for the electron ionisation studies. To avoid coating, the ion block was heated up. For the present measurements two different ion block temperatures were used, namely 140 °C and 240 °C. A second gas inlet into the ion source chamber enabled us the calibration for the electron energy via the 0 eV resonance of SF_6^- and the resonances of its fragment anion F^- .^[19] The investigated tungsten hexachloride (purity $\geq 99.9\%$) was purchased from Sigma Aldrich (Vienna, Austria).

Results

WCl_6 strongly reacts with water, leading to the production of WCl_4O and WCl_2O_2 , W(VI) hydrolysed species. Before entering in the vacuum chamber, the sample was handled under argon atmosphere. Although this procedure was followed, the WCl_6 hydrolysis reaction took place on surfaces in the ion source chamber. We can attribute this fact to the residual presence of water, driving the following reactions:

The electron ionisation and DEA studies were performed on the assumption that a mixture of WCl_6 , WCl_4O and WCl_2O_2 , was in the chamber. As such, the results presented in this communication will draw electron interactions with these three tungsten compounds. We note that the relative abundance of these precursor compounds was also depending on the temperature of the ion source. At an elevated ion source temperature the ion yields from WCl_6 and WCl_2O_2 increased relative to the ion yields formed via WCl_4O . The decrease of the yields was only verified for the ions formed from WCl_4O . We can conclude that temperature mostly affects WCl_6 and WCl_2O_2 .

Electron ionisation

In Figure 1 a positive mass spectrum is presented. For a better visualisation it is split into two mass ranges. The mass region of the doubly charged species is shown in Figure 1a, while the singly charged species are shown in Figure 1b. In both cases, different series of fragment cations are identified. The heaviest cation identified in the mass spectrum is the tungsten penta chlorine, WCl_5^+ that is formed by the dissociative interaction of an electron with WCl_6 . This fragment cation is formed by a single cleavage of a W–Cl bond. Further scission of chlorine atoms leads to formation of WCl_4^+ , WCl_3^+ , WCl_2^+ , WCl^+ and formation of the bare tungsten cation, W^+ . In the previous study from Priess^[17], the complete single ionised series was observed, from WCl_6^+ to W^+ . Although, Priess has observed WCl_6^+ , the intensity is 1000 times less than the most intense cation (WCl_4^+). The sensitivity of the actual experiment does not allow to identify WCl_6^+ . From WCl_4O another series is present which includes scission of Cl atoms, i.e. formation of WCl_4O^+ , WCl_3O^+ , WCl_2O^+ , WClO^+ and WO^+ . The third series is formed by the ionisation of WCl_2O_2 resulting in WCl_2O_2^+ , WClO_2^+ and WO_2^+ .

Moreover, doubly ionised species are evident in the mass spectrum. Two series are identified in the case of the doubly charged species, presented in figure 1a. The heaviest mass identified corresponds to WCl_4^{2+} with formation of lighter doubly charged ions by Cl secession, WCl_3^{2+} , WCl_2^{2+} , WCl^{2+} having as the lighter fragment cation the W^{2+} species. These doubly charged species were, as well identified by Preiss.^[17] The second series of the doubly charged species from WCl_4O leads to WO^{2+} , together with WClO^{2+} , $\text{WCl}_2\text{O}^{2+}$ and $\text{WCl}_3\text{O}^{2+}$ by splitting-off a Cl atom. By the single and double charged ion series, the bond selectivity in the scission of Cl atom against O, is evident. This can be explained by the double bond character of W-O. Additionally, there was the formation of Cl^+ and HCl^+ in small amounts observable, not shown in the mass range of the presented mass spectrum in figure 1. The formation of Cl^+ indicates the cleavage of the W-Cl bond, leaving back a neutral metal counter part. The presence of HCl^+ is an evidence of hydrolysed WCl_6 . This fact supports the formation of WCl_4O and WCl_2O_2 precursors, following the (III) and (IV) reactions with formation of HCl .

Dissociative electron attachment

As referred to the section before, the oxidation of WCl_6 leads to a mixture of three different compounds in the sample. Due to this observation, this section is discussed in terms of DEA to WCl_6 , WCl_2O_2 and WCl_4O . Figure 2 summarises the dissociation reactions (from 1 to 14) upon electron attachment to WCl_6 , WCl_2O_2 and WCl_4O for the observed fragments and possible neutral counter products.

Three anionic fragments are formed upon electron capture from WCl_6 . The most intense fragment anion formed is WCl_4^- . This reaction (1) implies the cleavage of two Cl-W bonds with formation of Cl_2 or two Cl atoms. The formation of this anionic fragment has a threshold around 3.5 eV and is centred at 5.3 eV, additionally there is a weak resonance observable at 8.0 eV (see figure 3b). The abstraction of two Cl atoms can be accomplished by Cl_2 formation. Indeed, the Cl_2 bond formation reaction is exothermic by 2.51 eV^[20] favouring the WCl_4^- formation. The abstraction of three Cl atoms, with formation of WCl_3^- , is associated with reaction channel (2). The threshold for this reaction is ~1.3 eV, three resonances at 2.9, 6.7 and 9.5 eV can be identified from the DEA ion yield curve (Fig. 3 d)). A third reaction pathway is identified by Cl^- formation (3). In this pathway the electron is captured in an unoccupied orbital via two shape resonances with thresholds at 0.0 and 2.0 eV. The formation of WCl_3^- is driven by a single core excited resonance centred at 6.7 eV, with a threshold close to 5.0 eV. The appearance energies for these fragments can be used to estimate the electron affinities of the WCl_4 and WCl_3 fragments. The bond dissociation energy for a W-Cl bond is estimated to be 4.4 eV.^[21] The electron affinity as function of DEA thermochemical threshold, is given by equation (V):

$$\text{EA}(\text{WCl}_X) = (6-X) \cdot \text{BDE}(\text{W-Cl}) - E_{\text{Th}}(\text{WCl}_X^-) \quad (\text{V})$$

where $X = 3, 4$; EA is the electron affinity, E_{Th} threshold energy and BDE the bond dissociation energy for W-Cl. Using equation (V) the electron affinities for WCl_4 and WCl_3 are $\text{EA}(\text{WCl}_4) \leq 5.3$ eV and $\text{EA}(\text{WCl}_3) \leq 12.2$ eV, respectively. The high values obtained for the EA of these species are just rough estimations. These can be explained because the low threshold energies should be diminished by the exothermic parallel reactions, such as Cl_2 formation. This fact is not considered in the present EA estimation.

A substantial number of fragment anions are formed by the DEA to WCl_4O and WCl_2O_2 . From DEA to WCl_4O six different fragments have been identified. The parent anion, WCl_4O^- is formed throughout a resonance at about 0 eV and another weak resonance centred at 3.3 eV

(see reaction (4) in figure 2). Due to the low signal intensity for this anion, it is not possible to accurately identify a third structure at high energy, centred at ~ 5.0 eV. We ascribe both resonances at higher energy rather to an impurity than molecular anion formation.

The electron capture will induce dissociation of one or two Cl atoms leading to the formation of WCl_3O^- and WCl_2O^- , reactions (5) and (6), respectively. The cleavage of a W–Cl bond is driven by a resonance centred at ~ 2.7 eV and the two W–Cl bond cleavages are led by a resonance centred at ~ 6.5 eV, tentatively assigned as a core excited. The energy dependence of the DEA cross sections for the formation of these individual fragment anions are presented in figure 3 c) and e), respectively. The fragmentation pattern is characterized by the parent anion formation and the loss of one or two chlorine atoms. Another dissociative pathway by the cleavage of a W–O bond leads to WCl_4^- , reaction (7). The threshold for this anion formation is placed at 3.5 eV, in a broad resonance centred at 5.5 eV (Fig. 3b)). This is a competitive process with DEA to WCl_6 leading also to WCl_4^- , reaction (1). Reaction (8) describes the formation of WCl_3^- from WCl_4O . This reaction is driven by two core excited resonances above the threshold energy of 5.0 eV and with maxima at 6.9 and 9.6 eV (Fig. 3d)).

The cleavage of a W–O bond and W–Cl bond lead to Cl^- and O^- formation, reactions (9) and (10), respectively. These reactions, as for Cl^-/WCl_6 , will leave the neutral metallic compound in the surface, ready for the next incoming electron to attack with formation of an anionic leaving atom. In the case of Cl^- the formation occurs via a threshold peak at about ~ 0 eV due to the positive electron affinity of chlorine and via another resonance centred at ~ 3.5 eV. In contrast, the O^- formation is due to core excited resonances peaking at 6.4 eV and 9.1 eV, (Fig 3g) and h)).

The third DEA process is done to the WCl_2O_2 species. This process leads to the formation of 4 anionic fragments. The cleavage of a W–Cl bond leads to the formation of WClO_2^- species through a core excited resonance peaking at ~ 4.7 eV, reaction (11). DEA energy profile is shown in the figure 3 f). We can observe this anion only at the ion block temperature of 240°C within the detection limit of the apparatus.

WCl_2O^- is formed by the loss of oxygen atom, reaction (12). The formation of this anionic species occurs at 140° and 240°C ion block temperatures. The DEA energy profiles are presented in Figure 4 b) for these two temperatures. For the lower temperature the formation is driven in the most abundant resonance peaking at ~ 6.6 eV with a threshold close to 4.6 eV. However, at higher temperatures the resonance centred at 4. eV, with a threshold at 2.0 eV, becomes dominante, which we ascribe, as mentioned above to DEA to WCl_4O . Another two fragmentation channels lead to Cl^- and O^- formation, reactions (13) and (14), respectively, as well as for WCl_4O . As described above, the Cl^- is formed via shape resonance and O^- via core excited resonance.

Conclusions

In the present communication we have presented electron interaction studies, covering negative and positive ion formation, with precursor FEBID WCl_6 . Due to the high oxidative ability of WCl_6 , electron interactions with mixtures of WCl_6 , WCl_4O and WCl_2O_2 were observed. Electron ionisation studies have been performed at 70 eV electron energy. The scission of chlorine atoms from WCl_6 , WCl_4O and WCl_2O_2 is assigned. We have attributed the formation of W^+ from electron ionisation to WCl_6 and WO_2^+ from electron ionisation to WCl_2O_2 and WO^+ from electron ionisation to WCl_4O . The electron impact is very efficient in cleaving the W–Cl bond. The DEA measurements were performed in an energy range of ~ 0 to 14 eV. The interactions of those low energy electrons open different fragmentation pathways, not only by chlorine scission, but also oxygen scission. Interesting to note is the formation of chlorine and oxygen anions, which leads to the formation of neutral metal containing counter parts.

Regarding to the role of low energy (<100 eV) electron interactions with FEBID precursor molecules such as WCl_6 , the contrast between ionisation and electron attachment is clear. It is evident for the formation of bare metal cation species but not for the corresponding anion. The electron attachment to WCl_6 is effective to cleave three W–Cl bonds, leading to the lighter metal containing fragment with chlorine ligands. Chlorine anions were detected indicating the formation of neutral metal containing fragments available for following low-energy electron attack.

Previously, it was observed^[22] that WF_6 leads to tungsten deposits with higher purity than W(CO)_6 which was ascribed to less carbon incorporation and the higher vapour pressure of WF_6 . We note that for the present molecule the formation of a ligand anion and a neutral metallic fragment reduced by one ligand is a very efficient process in contrast to other organometallic molecules used in FEBID (e.g. like W(CO)_6). Hence, in FEBID using halogenated (e. g. WCl_6 or WF_6) molecules a neutral fragment is left as deposit on the surface available for an electron attack by the next electron. We believe that this effect also contributes to cleaner tungsten deposits.

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References

- [1] I. Utke, P. Hoffmann, J. Melngailis. Gas-Assisted Focused Electron Beam and Ion Beam Processing and Fabrication. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **2008**, 26, 1197.
- [2] T. Liang, E. Frendberg, B. Lieberman, A. Stivers. Advanced photolithographic mask repair using electron beams. *J. Vac. Sci. Technol. B* **2005**, 23, 5.
- [3] G. Boero, I. Utke, T. Bret, N. Quack, M. Todorova, S. Mouaziz, P. Kejik, J. Brugger, R. S. Popovic, P. Hoffmann. Submicrometer Hall devices fabricated by focused electron-beam-induced deposition. *Appl. Phys. Lett.* **2005**, 86, 042503.
- [4] A. Fernández-Pacheco, J. M. De Teresa, R. Córdoba, M. R. Ibarra. Magnetotransport properties of high-quality cobalt nanowires grown by focused-electron-beam-induced deposition. *J. Phys. D: Appl. Phys.* **2009**, 42, 055005.
- [5] H. W. P. Koops, C. Schössler, A. Kaya, M. Weber. Conductive Dots, Wires, and Supertips for Field Electron Emitters Produced by Electron-Beam Induced Deposition on Samples Having Increased Temperature. *J. Vac. Sci. Technol. B* **1996**, 14, 4105.
- [6] W. F. van Dorp, C. W. Hagen. A critical literature review of focused electron beam induced deposition. *J. Appl. Phys.* **2008**, 104, 081301.
- [7] M. Huth, F. Porrtati, C. Schwalb, M. Winhold, R. Sachser, M. Dukic, J. Adams, G. Fantner. Focused electron beam induced deposition: A perspective. *Beilstein J. Nanotechnol.* **2012**, 3, 597.
- [8] R. M. Thorman, R. Kumar T. P., D. H. Fairbrother, O. Ingólfsson. The role of low-energy electrons in focused electron beam induced deposition: four case studies of representative precursors. *Beilstein J. Nanotechnol.* **2015**, 6, 1904.
- [9] K. Wnorowski, M. Stano, C. Matias, S. Denifl, W. Barszczewska, Š. Matejčík. Low-energy electron interactions with tungsten hexacarbonyl--W(CO)₆. *Rapid Commun. Mass Spectrom.* **2012**, 26, 2093.
- [10] K. Wnorowski, M. Stano, W. Barzczewska, A. Jówko, Š. Matejčík. Electron impact ionization of W(CO)₆: appearance energies. *Int. J. Mass Spectrom.* **2012**, 314, 42.
- [11] M. Lacko, P. Papp, K. Wnorowski, Š. Matejčík. Electron-induced ionization and dissociative ionization of iron pentacarbonyl molecules. *Eur. Phys. J. D* **2015**, 69, 1.
- [12] S. Engmann, M. Stano, Š. Matejčík, O. Ingólfsson. Gas phase low energy electron induced decomposition of the focused electron beam induced deposition (FEBID) precursor trimethyl (methylcyclopentadienyl) platinum(IV) (MeCpPtMe₃). *Phys. Chem. Chem. Phys.* **2012**, 14, 14611.
- [13] M. Allan. Electron scattering in Pt(PF₃)₄: elastic scattering, vibrational, and electronic excitation. *J. Chem. Phys.* **2011**, 134, 204309.
- [14] O. May, D. Kubala, M. Allan. Dissociative electron attachment to Pt(PF₃)₄-a precursor for focused electron beam induced processing (FEBIP). *Phys. Chem. Chem. Phys.* **2012**, 14, 2979.
- [15] S. Engmann, M. Stano, P. Papp, M. J. Brunger, Š. Matejčík, O. Ingólfsson. Absolute cross sections for dissociative electron attachment and dissociative ionization of cobalt tricarbonyl nitrosyl in the energy range from 0 eV to 140 eV. *J. Chem. Phys.* **2013**, 138, 044305; 1.
- [16] S. Engmann, B. Omarsson, M. Lacko, M. Stano, S. Matejcik, O. Ingolfsson. Dissociative electron attachment to hexafluoroacetylacetone and its bidentate metal complexes M(hfac)₂; M = Cu, Pd. *J. Chem. Phys.* **2013**, 138, 1.
- [17] V. H. Preiss. Massenspektrometrische Untersuchungen an einigen Hafogeniden der 5. Haupt- und Nebengruppe. *Z. anorg. allg. Chem.* **1972**, 292, 280.
- [18] L. F. Audrieth. *Inorganic Syntheses*. McGraw-Hill Book Company, **2007**.
- [19] E. Illenberger, J. Momigny. *Gaseous Molecular Ions: An Introduction to Elementary*

- Processes Induced By Ionization*. Springer-Verlag, New York, **1992**.
- [20] Properties of atoms, radicals and bonds. can be found under <https://labs.chem.ucsb.edu/zakarian/armen/11---bonddissociationenergy.pdf>, accessed 06-01-2016
- [21] M. Schadel, D. Shaughnessy. *The Chemistry of Superheavy Elements*. Springer, London, **2003**.
- [22] S. J. Randolph, J. D. Fowlkes, P. D. Rack. Focused, Nanoscale Electron-Beam-Induced Deposition and Etching. *Crit. Rev. Solid State Mater. Sci.* **2006**, 31, 55.

Figures

Figure 1 – Ionisation mass spectrum of the sample containing WCl_6 , WCl_4O and WCl_2O_2 obtained by electron ionisation with an electron energy of 70 eV. For better visualisation it is separated into doubly charged cations (a) and singly charged cations (b). The arrows in (b) indicate the main isotope of the overlapping fragment pattern.

Figure 2 – Proposed fragmentation pathways upon electron attachment to WCl_6 , WCl_4O and WCl_2O_2 .

Figure 3 – Energy scans of all detectable fragment anions. All measurements were done at the ion block temperature of 140 °C except panel f) which was obtained at the ion block temperature of 240 °C (see text). In the panels a-f) the possible neutral precursors are given.

Figure 4 – Comparison of the energy scans of WCl_3^- (a) and WCl_2O^- (b) obtained at two different ion block temperatures, 140 °C and 240 °C, respectively.

Figure 1

Figure 2

Figure 3

Figure 4