SIMS Proceedings Papers

SURFACE and INTERFACE ANALYSIS

Received: 10 September 2009 Revised: 23 February 2010 Accepted: 14 March 2010 Published online in Wiley Online Library: 19 May 2010

(wileyonlinelibrary.com) DOI 10.1002/sia.3442

Sputtered molecular fluoride anions: HfF_n^- and WF_n^-

Hubert Gnaser,[a,b*] and Robin Golser[c]

The emission of negatively charged HfF_n^- ($n \leq 5$) and WF_n^- ($n \leq 7$) molecular ions sputtered from a mixed Hf–W–PbF_2 fluoride sample by a 13 keV Cs^+ ion beam was studied. The emitted ions were detected in a high-sensitivity double-focusing secondary ion mass spectrometer. In the HfF_n^- and WF_n^- series, HfF_5^- and WF_6^- are the anions formed most abundantly, with their ratio amounting to $HfF_5^-/WF_6^- \sim 6$, whereas $HfF_5^-/WF_5^- \sim 18$. In particular, the rather high yield of the HfF_5^- anion could be essential for the sensitive detection of live ^{182}Hf, a radionuclide (half-live ~9 million years) that might originate from stellar events in the vicinity of the Earth. Generally, these high ion yields appear to correspond with a high electron affinity of the respective molecule. In addition, their formation may be affected by the atomic composition at the sputtering site. Because their constituents originate from (initially) separated sources (the individual Hf, W and PbF_2 particles), the production of the HfF_n^- and WF_n^- molecular anions is envisaged to require an extensive mixing between these different reservoirs during sputtering. Furthermore, the energy distributions of these molecular anion species indicate that they are released from the surface via a collision cascade that also leads to the occurrence of fragmentation processes in the emission event. **Copyright © 2010 John Wiley & Sons, Ltd.**

Keywords: sputtering; molecular fluoride anions; abundance distributions; energy distributions

Introduction

Ion bombardment of solids results in the removal of atoms and molecules from the topmost surface layer(s), a process usually called sputtering.[1] This sputtered flux often contains an appreciable number of atomic and molecular ions. Although the mechanisms leading to ion formation in sputtering are not completely understood,[2,3] these secondary ions form the basis of powerful analytical techniques such as SIMS[4] and accelerator mass spectrometry (AMS).[5] In AMS, the production of an abundant flux of stable anions by sputtering the target with Cs^+ ions is a prerequisite for the ultrahigh sensitivity achievable. While the emission of sputtered molecular ions[6,7] is often not appreciated in mass spectrometry as they may cause problems due to mass interferences, thereby limiting the detection sensitivity, some molecular ions were found to be emitted in sputtering with (much) higher abundances than the corresponding atomic ions. This appears to be particularly prominent in the case of negatively charged ions; noteworthy is the very abundant formation of some anionic fluoride molecules from many samples[8–15] and their use for analytical purposes. (An extensive review on molecular anions can be found in Ref. [16]).

An interesting application is the detection of a specific Hf isotope (^{182}Hf) by monitoring molecular Hf–fluoride anions. ^{182}Hf is a long-lived radionuclide of particular interest for the early history of the solar system. Its half-life of 8.90 ± 0.09 million years[17] is apparently long enough to survive the time interval between production through stellar nucleosynthesis and the formation of the solar system. However, it can clearly not survive the 4.6 billion years of the solar system. Therefore, it existed as an extinct radionuclide and can be detected by an isotopic anomaly of its stable daughter product ^{182}W. This ^{182}Hf–^{182}W system forms a very powerful chronometer for the timing of the formation of various early objects of the solar system.[18]

In addition, ^{182}Hf may also complement a few other radionuclides in the million-year half-life range to trace relatively recent stellar events with high neutron fluxes in the vicinity of the Earth. This may be accomplished by finding measurable traces of live ^{182}Hf in suitable terrestrial archives. Thus, finding live ^{182}Hf on Earth today would be a strong indication for introduction of material from recent nucleosynthesis, e.g. from nearby supernovae. Generally, ^{182}Hf plays an important role for the understanding of nucleosynthesis of heavy elements in stellar environments, since both *r*- and *s*-processes can be responsible for the high abundance in the early solar system.[19] Given its high sensitivity, it should be possible to detect minute amounts of ^{182}Hf by AMS. Indeed, it has been shown[20] that the main interference for the detection, the stable isobar ^{182}W, can be significantly reduced by using HfF_5^- ions and ^{182}Hf/^{180}Hf ratios down to 10^{-11} could be measured. However, the detection limit depends on the W content in the sample material. The status of the detection of ^{182}Hf by AMS has been described recently.[21,22]

The aim of the present work was to investigate the emission of sputtered Hf and W fluoride anions, in order to provide an estimate for the possible magnitude of such a W contribution. A sample containing nominally equal amounts of Hf and W was used.

* Correspondence to: Hubert Gnaser, Department of Physics and OPTIMAS, University of Kaiserslautern, D-67663 Kaiserslautern, Germany. E-mail: gnaser@rhrk.uni-kl.de

a Department of Physics and OPTIMAS, University of Kaiserslautern, D-67663 Kaiserslautern, Germany

b Institute for Surface and Thin-Film Analysis IFOS, D-67663 Kaiserslautern, Germany

c VERA Laboratory, Department of Physics, University of Vienna, A-1090 Vienna, Austria

 Copyright © 2010 John Wiley & Sons, Ltd.

Bombardment was carried out by a Cs^+ ion beam. Generally, this leads to the incorporation of cesium into the near-surface region due to implantation and concurrent erosion. Previous work[23] has shown that this presence of Cs causes a pronounced lowering of the work function within the irradiated area. This work-function reduction results in a strongly enhanced production of negatively charged ions[2] and is, therefore, favorable for the detection of molecular anions with high sensitivity.

Experimental

The experiments were performed in a SIMS instrument (Cameca IMS-4f.[24]). Sputtering was done with a Cs^+ ion beam produced in a surface-ionization source. With the source at a potential of +10 kV with respect to ground and the sample at −3 kV, the primary impact energy was 13 keV and the incidence angle ∼30° relative to the surface normal. The Cs^+ ion current ranged from 50 to 100 nA, and the beam was raster-scanned across an area of about (150 µm^2). Sputtered negative ions were collected from a somewhat smaller, circular area centered within that raster.

The sample (at a potential of −3 kV) faces a grounded (extraction) electrode; this electric field effects an acceleration of the sputtered (negative) ions. The field strength in this acceleration region is ∼7 kV/cm. Upon passing the extraction electrode, the negative ion beam is focused by electrostatic lenses onto the entrance slit of the mass spectrometer. The instrument incorporates a double-focusing mass spectrometer consisting of an electrostatic sector followed by a magnetic sector field, both with a 90° deflection angle. The present results were obtained at a low mass resolution of $M/\Delta M \sim 300-600$, but a much higher resolution can be achieved[25] by narrowing the entrance and exit slits of the spectrometer.

Energy spectra are recorded by scanning the target potential (by ±130 V around its nominal value of −3 kV) and keeping the other optical elements of the secondary ion beam line unchanged. Reducing the width of the energy slit (which is located between the two sectors), only ions whose kinetic (emission) energy and the actual sample potential add up to 3 keV can pass the slit and then be detected.

Detection of secondary ions is done either by a discrete-dynode electron multiplier or, for count rates in excess of 1 MHz, by a Faraday cup, with the efficiencies of both devices carefully matched. Usually, the most abundant isotope of an element was employed for the determination of the yield data, but the correctness of the isotopic patterns was checked, if possible.

The specimen studied (Hf–W–PbF_2) was a mixture of Hf, W and PbF_2 powders with a ratio of 1 : 1 : 8. For the analysis, the mixed powder was pressed into an In foil of high purity (99.9999%). The dispersion of the powders was such that parts of the In foil were still visible between the more densely packed areas. To minimize charge build-up during ion irradiation all specimens were coated with an Au layer (∼50 nm thick). In addition, a low-energy electron beam could be directed onto the surface in order to reduce the accumulation of positive charge if needed.

Results and Discussion

The goal of this work was the investigation of sputtered molecular fluoride anions of Hf and W and the determination of their (relative) abundance distributions. These data may provide a guideline for the efficient detection of Hf by AMS. In addition, the distributions may then be correlated with parameters relevant for the stability and the ionization of these molecules such as dissociation energies and electron affinities, if such information becomes available.

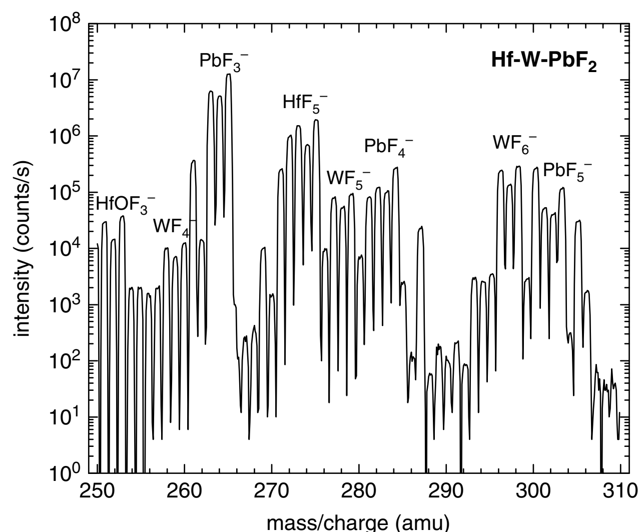

Figure 1. Mass spectrum of negative ions sputtered from a mixed Hf–W–PbF_2 sample by 13 keV Cs^+ ions. Several of the HfF_n^-, WF_n^-, and PbF_n^- mass peaks are labeled.

Generally, mass spectra of fluoride samples demonstrate the presence of a rather large variety of atomic and molecular anions in the sputtered flux.[10–15] This observation is also corroborated by the mass spectra obtained from the mixed Hf–W–PbF_2 specimen. Figure 1 depicts part of such a spectrum in the region of the larger fluoride species. Apart from the Hf and W fluoride anions (HfF_n^- and WF_n^-) that are of primary interest here, abundant mass peaks of PbF_n^- are observed. Similar to previous work,[11] also $HfOF_n^-$ molecules are detected.

The abundance distributions (i.e. the intensities as a function of the number of F atoms in the molecule, n) of the molecular anions HfF_n^- ($n \leq 5$) and WF_n^- ($n \leq 7$), sputtered from Hf–W–PbF_2 are shown in Fig. 2. To facilitate a comparison, the data are normalized to the intensities of the most abundant anions (HfF_5^- and WF_6^-, respectively). Some of the HfF_n^- molecules could not be identified unambiguously; in these cases, the intensity data are specified as an upper limit of the abundance of the respective anion. The ratio of the anions formed most abundantly (HfF_5^- and WF_6^-) amounts to ∼6, whereas the ratio HfF_5^-/WF_5^- ∼18.

In addition, Fig. 2(a) depicts relative intensities of HfF_n^- species sputtered from a HfF_4 sample, obtained previously by SIMS[11] and by AMS.[26] Clearly, the HfF_n^- abundance distributions from the two different specimens are rather different, whereas they are essentially identical for the HfF_4 specimen when using either SIMS or AMS. This finding indicates that the emission of fluoride anions is not influenced by the largely different sputtering geometries and bombardment conditions employed in these two techniques. By contrast, the emission of HfF_n^- molecules with $n \leq 4$ is strongly reduced for Hf–W–PbF_2 (or, if normalization is done using one of these molecules, HfF_5^- would be much enhanced as compared to HfF_4). The intensities of the HfF_5^- ions sputtered from the two samples (Hf–W–PbF_2 and HfF_4) are rather similar (Fig. 1 and Ref. [11]), but an absolute comparison is not feasible because of the different sample properties and compositions.

Copyright © 2010 John Wiley & Sons, Ltd. View this article online at wileyonlinelibrary.com

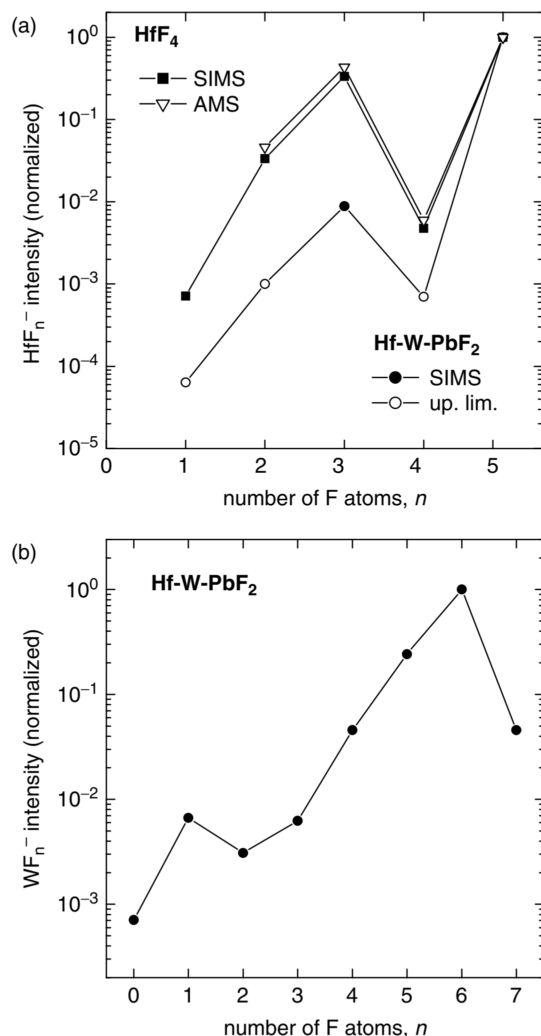

Figure 2. Normalized intensities of HfF_n^- (a) and WF_n^- (b) anions sputtered from the Hf–W–PbF_2 sample as a function of the number of fluorine atoms n in the respective molecules. If a molecular species could not be identified unambiguously, only an upper limit as to its relative ion intensity is specified (open circles, labeled 'up. lim.'). In (a) relative intensities of HfF_n^- species sputtered from an HfF_4 sample are depicted, obtained previously by SIMS[11] and by AMS.[26]

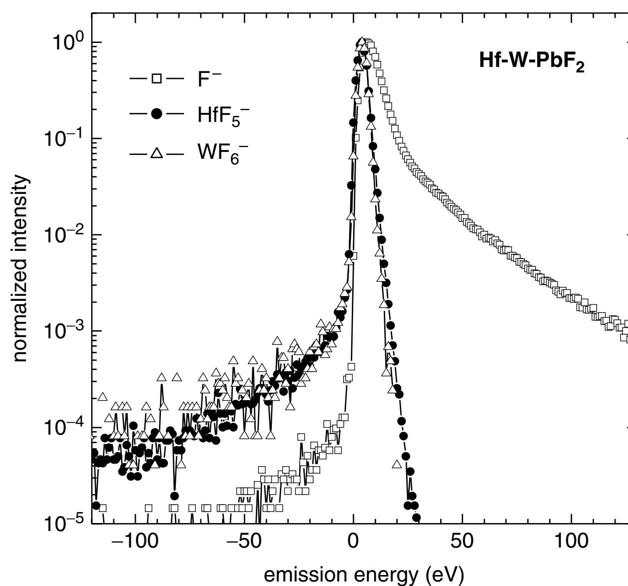

Figure 3. Normalized energy spectra of F^-, HfF_5^- and WF_6^- anions sputtered from an Hf–W–PbF_2 sample. The tails at 'negative' energies are due to fragmentation processes (see text).

The abundance distribution of WF_n^- is shown in Fig. 2(b). The WF_6^- species has the highest intensity, but WF_n^- molecules are clearly observed for $1 \leq n \leq 7$. A similar WF_n^- pattern is reported in Ref. [15]. The emission of molecular WF_n^- anions is of considerable interest because electron affinities A have been computed recently for WF_n molecules ($n \leq 6$).[27] The theoretical results show that WF_6 features the highest electron affinity ($A \sim 3.4$ eV), in agreement with the experimental finding of WF_6^- being the most abundant anion. In fact, the measured WF_n^- intensities were found recently[14] to correlate exponentially with the theoretical electron affinities. This finding is in agreement with theoretical models of sputtered ion formation that predict an exponential dependence of the ionization probability of *atomic* anions, P^-, on their electron affinity[2]

$$P^- \propto \exp[-(\Phi - A)/\varepsilon] \tag{1}$$

Here Φ is the surface work function of the specimen, A is the electron affinity, and ε may depend (slightly) on the perpendicular component of the ion's emission velocity.[2] Φ will change (decrease) initially due to Cs incorporation, but should be constant for steady-state irradiations. Such an exponential scaling has been verified for atomic ions,[2] but is possibly valid also for molecular ions. It appears reasonable, hence, to assume that the intensity variations of the molecular ions shown in Fig. 2 reflect, to some extent, the different electron affinities of these molecules.

The distinct divergence in the distributions of the HfF_n^- species obtained from the two different specimens (Fig. 2(a)) indicates that, apart from the ionization process, other factors may influence the abundance distribution of sputtered molecules. Atomistic computer simulations[28] and energy spectra of sputtered molecules[29] demonstrate rather convincingly that the emission of molecular species is governed by a concerted energy transfer to the nascent molecule from a collision cascade at the surface; it eventually may lead to the molecule's release from the surface. This has at least two consequences: First, the sputtered flux is proportional to the target (surface) composition, and the probability to form a molecule with a specific composition will depend on the composition of the specimen. In other words, to form a molecule with a given number of F atoms necessitates that a sufficient number of F atoms are present at the molecule's emission site on the surface. Second, in such a sputtering event a considerable amount of energy might be imparted onto the departing molecules (i.e. they are ejected 'hot'); they may cool by the evaporation of atoms or (small) fragment species[6,7] Therefore, the relative stability of a molecular species against such a fragmentation reaction may influence the observed distributions in Fig. 2.

The occurrence of fragmentation is also seen clearly in the energy spectra of sputtered fluoride molecular anions. Figure 3 depicts such spectra for HfF_5^- and WF_6^- ions. The spectra are seen to extend to apparent 'negative' emission energies. These negative tails are due to the decay of cluster species during their passage through the accelerating field of the mass spectrometer: the resulting daughter ions carry only a fraction of the full accelerating energy as compared to the intact species that experience the full acceleration[30,31] On the other hand, the energy spectra of these

Copyright © 2010 John Wiley & Sons, Ltd.

molecules fall off rather steeply with increasing (positive) emission energy. By contrast, the energy distributions of atomic ions (F^- in Fig. 3) extend to large emission energies, as is typical for sputtered atomic species.[29] All distributions exhibit a low-energy peak (at ~4 eV for HfF_5^- and WF_6^-, and ~6 eV for F^-) which constitutes a strong indication that those ion species are formed in a collision cascade at the surface.

In a recent study of fluoride anion emission in sputtering[15] it was proposed that PbF_2 acts as a particularly effective fluorine donor in near-surface chemical reactions. Thereby, the abundant flux of sputtered molecular fluoride anions can be rationalized. There is, however, another aspect of great importance for the formation of these molecular species. For the HfF_n^- and WF_n^- molecules monitored in the present work, the atomic constituents originate from (initially) different sources, i.e. the Hf and W atoms from the respective Hf and W powders and the F atom(s) from the PbF_2. In order to form such molecules, these distinct reservoirs have to be mixed thoroughly during ion irradiation, so that at the emission site the various species are present in a sufficient quantity. Different possibilities can be envisaged as to how this may happen (see the corresponding discussion in Ref. [14]). Eventually, all these processes will result in a stationary state in terms of the relative elemental coverage on the surface. Hence, the degree of mixing may influence the abundance of the emitted molecules; if there are, for example, not enough F atoms present at the sputtering site, the formation of molecules with a large number of F constituents will have a low probability.

Conclusion

The emission of negative molecular ions from a Hf-W-PbF_2 specimen due to sputtering has been studied and the flux of HfF_n^- and WF_n^- anions was monitored. In these series, HfF_5^- and WF_6^- are the anions formed most abundantly. In that sample, their ratio amounts to ~6, whereas the ratio HfF_5^-/WF_5^- ~18. To form these molecular anions, their constituents have to undergo an extensive mixing between the different reservoirs (the individual Hf, W and PbF_2 particles) during sputtering. The energy distributions of these molecular anions indicate the presence of fragmentation in the emission process.

Acknowledgements

The authors are grateful to Oliver Forstner for providing the Hf–W–PbF_2 sample.

References

[1] P. Sigmund, ed., *Fundamental Processes in Sputtering of Atoms and Molecules*, *K. Dan. Vidensk. Selsk. Mat. Fys. Medd.* 43 **1993**.
[2] M. L. Yu, in *Sputtering by Particle Bombardment III*, eds., R. Behrisch, K. Wittmaack (Springer: Berlin **1991)**, p. 91.
[3] H. Gnaser, *Low-Energy Ion Irradiation of Solid Surfaces* (Springer: Berlin, **1999**).
[4] A. Benninghoven, F. G. Rüdenauer, H. W. Werner, *Secondary Ion Mass Spectrometry* (Wiley: New York, **1987**).
[5] C. Tuniz, J. R. Bird, D. Fink, G. F. Herzog, *Accelerator Mass Spectrometry* (CRC Press: Boca Raton, **1998**).
[6] B. U. R. Sundqvist, in *Sputtering by Particle Bombardment III*, eds., R. Behrisch, K. Wittmaack (Springer: Berlin, **1991)**, p. 257.
[7] H. M. Urbassek, W. O. Hofer, K. Dan. *Vidensk. Selsk. Mat. Fys. Medd.* **1993**, *43*, 97.
[8] H. Gnaser, H. Oechsner, *Nucl. Instrum. Methods B* **1993**, *82*, 518.
[9] M. J. Van Stipdonk, R. D. Harris, E. A. Schweikert, *Rap. Commun. Mass Spectrom.* **1997**, *11*, 1794.
[10] R. Middleton, J. Klein, *Phys. Rev. A* **1999**, *60*, 3515.
[11] H. Gnaser, *Nucl. Instrum. Methods B* **2002**, *197*, 49.
[12] X.-L. Zhao, A. E. Litherland, J. P. Doupe, W. E. Kieser, *Nucl. Instrum. Methods B* **2004**, *223–224*, 199.
[13] X.-L. Zhao, A. E. Litherland, *Nucl. Instrum. Methods B* **2007**, *259*, 224.
[14] H. Gnaser, *Nucl. Instrum. Methods B* **2009**, *267*, 3519.
[15] X.-L. Zhao, A. E. Litherland, J. Eliades, W. E. Kieser, Q. Liu, *Nucl. Instrum. Methods B* **2010**, *268*, 807.
[16] J. Simons, *J. Phys. Chem. A* **2008**, *112*, 6401.
[17] C. Vockenhuber, F. Oberli, M. Bichler, I. Ahmad, G. Quitté, M. Meier, A. N. Halliday, D.-C. Lee, W. Kutschera, P. Steier, R. J. Gehrke, R. G. Helmer, *Phys. Rev. Lett.* **2004**, *93*, 0172501.
[18] A. N. Halliday, D.-C. Lee, *Geochim. Cosmochim. Acta* **1999**, *63*, 4157.
[19] C. Vockenhuber, R. Golser, W. Kutschera, A. Priller, P. Steier, A. Wallner, M. Bichler, *Nucl. Phys. A* **2005**, *758*, 340c.
[20] C. Vockenhuber, M. Bichler, R. Golser, W. Kutschera, A. Priller, P. Steier, S. Winkler, *Nucl. Instrum. Methods B* **2004**, *223–224*, 823.
[21] C. Vockenhuber, A. Bergmaier, T. Faestermann, K. Knie, G. Korschinek, W. Kutschera, G. Rugel, P. Steier, K. Vorderwinkler, A. Wallner, *Nucl. Instrum. Methods B* **2007**, *259*, 250.
[22] S. Winkler, L. K. Fifield, S. G. Tims, C. R. Morton, *Nucl. Instrum. Methods B* **2007**, *259*, 256.
[23] H. Gnaser, *Phys. Rev. B* **1996**, *54*, 16456.
[24] H. N. Migeon, C. Le Pipec, J. J. Le Goux, in *Secondary Ion Mass Spectrometry SIMS V*, eds., A. Benninghoven, R. J. Colton, D. S. Simons, H. W. Werner, (Springer: Berlin, **1986)**, p. 155.
[25] H. Gnaser, *Phys. Rev. A* **1997**, *56*, R2518.
[26] C. Vockenhuber, Doctoral thesis, University of Vienna **2004**.
[27] K. G. Dyall, *J. Phys. Chem. A* **2000**, *104*, 4077.
[28] B. J. Garrison, A. Delcorte, K. D. Krantzman, *Acc. Chem. Res.* **2000**, *33*, 69.
[29] H. Gnaser, in *Sputtering by Particle Bombardment*, eds., R. Behrisch, W. Eckstein, *Top. Appl. Phys.* Vol. 110 (Springer: Berlin, **2007)**, pp 231.
[30] H. Gnaser, *Nucl. Instrum. Methods B* **1999**, *149*, 38.
[31] H. Gnaser, *Nucl. Instrum. Methods B* **2000**, *164–165*, 705.

 Copyright © 2010 John Wiley & Sons, Ltd.