Towards reliable X-ray photoelectron spectroscopy: Sputter-damage effects in transition metal borides, carbides, nitrides, and oxides

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Ar⁺ sputter etching is often used prior to X-ray photoelectron spectroscopy (XPS) analyses with the intention to remove surface oxides and contaminants. Since the XPS probing depth is comparable to the thickness of the ion-beam modified layer the signal from the latter dominates the spectra. We check here the conditions for reliable XPS analysis by studying ion irradiation effects for single-phase Group IVB transition metal (IVB-TM) boride, carbide, nitride, and oxide thin film specimens. The extent of sputter damage, manifested by changes in the surface composition, binding energy shift, peak broadening, and the appearance of new spectral features, varies greatly between material systems: from subtle effects in the case of IVB-TM carbides to a complete change of spectral components for IVB-TM oxides. The determining factors are: (i) the nature of compounds that may form as a result of ion-induced mixing in the affected layer together with (ii) the final elemental composition after sputtering, and (iii) the thickness of the Ar⁺-affected layer with respect to the XPS probing depth. Our results reveal that the effects of Ar⁺ ion irradiation on XPS spectra cannot be a priori neglected and a great deal of scrutiny, if not restraint, is necessary during spectra interpretation.

1. Introduction

X-ray photoelectron spectroscopy (XPS) has experienced an unprecedented growth over the last 30 years and is today by far the most commonly used surface analysis technique with 11 000 publications in 2019 only [1], leaving other techniques like Auger Electron Spectroscopy and Secondary-Ion mass Spectrometry far behind [2]. This large popularity of XPS is to large extent caused by its ability to assess chemical state of the atoms [3,4], which is often done through advanced spectrum analysis [5,6], in addition to qualitative and quantitative elemental analysis [7]. However, there is a general concern among dedicated XPS practitioners and experts about an increasing amount of published poor-quality data, incorrect interpretation, and false conclusions [8,9]. In the recent paper Linford et al. concluded that about 30% of the XPS analyses are simply incorrect, which includes also publications in high impact factor journals [8]. Translated into absolute numbers, on average, more than 3000 articles published last year are wrong. Alarming, this situation is only apparent to the limited group of experienced XPS users and the peer-review system cannot police all submitted manuscripts. Error is consequently propagating through un-critical referencing to incorrect papers or design of experiments inspired by previous false conclusions. A reason for this state of affairs is that the training of XPS operators is lagging behind the exponential increase in the demand of the technique – a situation that was predicted to take place back in 1999 [10]. Problems often encountered with XPS reports include incorrect charge referencing [11–14], mistaken peak fitting [15,16], and/or incomplete experimental protocol often without information that is essential for spectra interpretation.

Another expression of the problem with the quality of published XPS results outlined above is the uncertainty introduced by popular in situ sample treatments such as noble ion sputter etching. As the intention is to remove surface contaminants and oxides such procedure is often referred to as “surface cleaning”. This euphemistic expression on its own creates unfounded mind sets among less experienced practitioners, who may consider data recorded from such ion-etched surfaces as being representative of the native material. It is well-known, however, that irradiation by ions with energies in the range 500–4000 eV (often encountered in XPS literature) induces overlapping collision cascades in the surface layer defined by the energy and incidence angle of ion beam. This leads to a number of added artefacts including preferential elemental sputter ejection [17–19], recoil and ion implantation [20], atomic mixing [21,22], structural disorder, amorphization [23,24],...
surface segregation [25,26], surface roughening, and perhaps the most problematic of them all, changes in the surface chemistry [27–30], which is ironic to the purpose of the method. As a much larger fraction of the incident ion energy goes into surface modification than to the sputter-etched species [31], these effects are pronounced in most of the materials systems [32]. For some materials the post-sputtering in-situ anneal has been shown to minimize or even completely eliminate the ion-beam-induced damage [33–35]. This is, however, not a remedy for all types of samples and certainly not a commonly-adopted procedure in XPS analyses published in main-stream papers.

As the thickness of the ion-beam-modified layer is comparable to the XPS probing depth (5–10 nm)[36,37] all of the above issues make compositional and chemical analyses extremely challenging [38–40], and motivate efforts towards development of non-destructive surface analysis methods [41–45]. Out of the latter ones, the Ar ion cluster guns gain in popularity [46]. Their benefits have been convincingly demonstrated for organic materials [47–49], while the reports showing significant advantage for inorganic samples are still very limited [45,50], and in some cases only limited improvement have been reported [51,52]. It should also be emphasized that spectra from oxide-free untreated surfaces are rarely published along with data from etched samples, hence, the performance of Ar cluster guns is often evaluated against that of monoatomic Ar ion guns. This prevents meaningful conclusions as to whether or not the damage is completely eliminated.

The particular details of ion-surface interactions have been attributed to the interplay of mass-dependent effects (energy and momentum transfer), strength of chemical bonds, electronic processes, and diffusion [53]. Changes in the surface composition typically manifested by the underrepresentation of elements with high sputtering yields or those that easily form gaseous compounds, are however, believed to correlate underrepresentation of elements with high sputtering yields or those that easily form gaseous compounds, are however, believed to correlate with the chemical bonding rather than masses of involved species [32,53].

Sputter damage effects have been known to the surface science community for decades [54–57]. Majority of studies published in the previous century focused on changes in the surface composition in binary alloys due to preferential sputtering effects and surface segregation [19]. More specific aspects like, e.g., the evolution of XPS core level signals and changes in the surface chemistry have been addressed more recently. Refs. [45,58–63] are just a few relevant examples of such studies, which typically focus on one specific type of material, often with high technological relevance.

Here, we aim to identify the type and the extent of spectral changes introduced by Ar⁺ ion irradiation in the entire family of compounds, namely Group IVB transition metal (IVB-TM) borides, carbides, nitrides, and oxides. Specimens in the form of thin films deposited by magnetron sputtering are tested in the same instrument and under exact same conditions. Our material selection is based on two relevance criteria: (i) large number of devoted XPS studies due to the wide application range of these materials, and (ii) high susceptibility of thin film samples to sputter damage resulting from lower surface roughness, which prevents shadowing of the incident ion beam and, hence, the effective surface area exposed to the ions is larger. The combination of these two factors makes XPS spectra recorded from IVB-TM-based compounds particularly sensitive to misinterpretation and makes them ideal candidates for the present study. Two ion gun settings are tested: “standard” 4 keV with 45° incidence angle and mild etching with 0.5 keV Ar⁺ with shallow incidence angle of 70° from the sample normal. Spectra from native surfaces obtained by a variety of methods are included as reference to detect even slight modifications introduced by Ar⁺ bombardment. The primary goal is to improve reliability of XPS data interpretation by providing reference data for the type and extent of sputter damage that is created in IVB-TM compounds.

We start by presenting results obtained from native surfaces, which serve here as reference for interpretation of the Ar⁺-induced damage (Section 3.1). After that, the effect of sputtering time on the spectra appearance is treated in Section 3.2 to establish when the steady state condition is reached. Detailed evolution of core level spectra for standard (4 keV/45°) and mild (0.5 keV/70°) etching conditions is presented in Section 3.3 for all four materials systems. In Section 4.1 we provide estimates for the fraction of atoms in the volume probed by XPS that become displaced during collision cascades induced by Ar⁺ irradiation. In the following section (Section 4.2) the relative contribution due to the signal originating from the ion beam modified layer is discussed. The effects of sputter yields on the layer composition are considered in Section 4.3. Finally, peak shifts and new spectral components are treated in Section 4.4.

2. Experimental details

Polycrystalline TM (Group IVB) borides, carbides, nitrides, and oxides thin films are grown on Si(001) substrates by magnetron sputtering techniques from rectangular 8.8 × 50 cm² elemental targets in a CC800/ 9 CemeCon AG system [64]. DC magnetron sputtering (DCMS) is used for three first classes of materials while oxides are grown by mid frequency magnetron sputtering (MFMS). The total pressure and substrate temperature are kept constant during all depositions at 3 mTorr (0.4 Pa) and 460 ± 20 °C, respectively. Target-to-substrate distance of 18 cm is used in all cases. In order to minimize the influence of venting temperatures on the surface oxide layer thickness [65], all specimens are allowed to cool down to 140–180 °C before exposure to the laboratory atmosphere.

IVB-TM borides are grown from compound TiB₂, ZrB₂, and HfB₂ targets in Ar atmosphere with the average power Pavg = 2 kW. IVB-TM carbides are grown in Ar atmosphere employing the co-sputtering geometry with one graphite target serving as a source of carbon and one elemental target of respective transition metal, both tilted toward the substrate by 21°. The average power to the metal target is 1 kW, while the power to the graphite target is optimized, depending on TM reactivity towards C, from 2 kW for Ti and Zr, to 3 kW for Hf. More details concerning these films are given in Ref. [17]. IVB-TM nitrides are grown in Ar/N₂ gas mixtures with Pavg = 2 kW and the N₂-to-Ár flow ratio of 0.20 ± 0.02 optimized to obtain stoichiometric layers. Corresponding details are reported in Ref. [18]. IVB-TM oxides are grown in Ar/O₂ gas mixtures with the O₂-to-Ár flow ratio of 0.13. The MF power is 1 kW (50 kHz, 50% duty cycle). For the growth of IVB-TM borides, carbides, and nitrides a DC substrate bias of ~60 V is employed. In the case of IVB-TM-TM derived 100 V MF bias (200 kHz, 500 ns reverse time) is used.

Phase content and preferred crystallite orientation of all specimens is determined from θ-2θ x-ray diffractometry (XRD) carried out using a Philips X’Pert MRD system operated with point-focus Cu Kα radiation. All XPS experiments are performed in an Axis Ultra DLD instrument from Kratos Analytical (UK) with the base pressure during spectra acquisition better than 1.1 × 10⁻⁹ Torr (1.5 × 10⁻⁷ Pa), achieved by a combination of turbomolecular and ion pumps. Monochromatic Al Kα radiation (hv = 1486.6 eV) is employed with the anode power set to 150 W. All spectra are collected at normal emission angle. To avoid referencing to the C 1s signal from adventitious carbon, which can not be considered a well-defined compound [11,12,66], all spectra, except for oxides, are referenced to the Fermi level (FL) cut off, which defines the “0” eV on the binding energy (BE) scale. Spectra from oxides do not exhibit FL cut off due to their insulating character and are, hence, shown as recorded. The latter prevents that absolute BE values are extracted so we focus instead on relative spectral changes.

The analyzer pass energy is set to 20 eV, which yields the full width at half maximum of 0.55 eV for the Ag 3d₅/₂ peak. No charge compensation is used during analyses. To allow spectra acquisition from TM oxide samples they were intentionally grown relatively thin, 20–50 nm, so that electrons originating from the substrate could provide sufficient charge compensation. Sputter-etching is performed under two different conditions. In the first case, the intention is to minimize the destructive effects of ion beam by using low-energy Eₜₐ₉ = 0.5 keV Ar⁺ ions incident at an shallow angle of α = 70° with respect to the sample normal. The
average ion current density \( j \) is estimated as 22.2 \( \mu \text{A/cm}^2 \) corresponding to the ion flux \( \Phi = 1.4 \times 10^{14} \text{ cm}^{-2} \text{s}^{-1} \) (assuming singly-ionized \( \text{Ar}^+ \)). For the second set of experiments, “typical” etching conditions are used with \( E_{\text{Ar}} = 4 \text{ keV} \) and \( \alpha = 45^\circ \). With these settings \( j = 83.0 \mu\text{A/cm}^2\) and \( \Phi = 5.2 \times 10^{14} \text{ cm}^{-2} \text{s}^{-1} \). In both cases, the ion beam is rastered over a 3 x 3 mm\(^2\) area, while the area analyzed by XPS is 0.3 x 0.7 mm\(^2\) and centered in the middle of the ion-etched crater. The sputtering rates obtained using the reference TiN sample are 0.8 and 10.0 nm/min. for the low- and high-energy etching conditions, respectively. New sample pieces are used for each set of sputtering conditions. Spectra deconvolution and quantification is performed using CasaXPS software package and sensitivity factors supplied by the instrument manufacturer [67].

3. Results

3.1. Native samples

Before going into the effects of sputter etching, we start data presentation with a summary of core level peak positions recorded from native samples, to serve as a reference. It is noted though, that due to the nature of the employed sample preparation technique (magnetron sputtering), a certain degree of an inherent ion-induced damage is present even in this case, in the form of point defects, grain refinement, and interstitials [68].

Fig. 1 shows the BE shifts \( \Delta \text{BE} \) (relative to peak positions in metallic samples) measured for primary metal peaks Ti 2p\(_{3/2}\), Zr 3d\(_{5/2}\), and Hf 4f\(_{7/2}\) from all compounds. The all-positive values of \( \Delta \text{BE} \) indicates shift towards higher BE for each compound. For all three metal lines, a shift towards higher BE is observed during compound formation with respect to the metallic sample, with the magnitude that scales with the element electronegativity \( \chi \) (Pauling scale [69]), i.e., increasing in the order: B (\( \chi = 2.04 \)), C (\( \chi = 2.55 \)), N (\( \chi = 3.04 \)), and O (\( \chi = 3.44 \)). The relationship, however, is far from linear; metal line BE = \( n \cdot \chi \) with \( n \) ranging from 0.8 eV for borides, 0.4 eV for nitrides and 2.8 eV for oxides. For each compound class, there is consistency between shifts in metal peak positions and the corresponding A 1s signals (shown in Figs. 7–10). For example, the metal lines from borides exhibit \( \Delta \text{BE} \) that is largest for Ti 2p\(_{3/2}\) at 0.8 eV, followed by 0.5 eV for Zr 3d\(_{5/2}\), and 0.4 eV for Hf 4f\(_{7/2}\).

The corresponding B 1s peak position varies from 187.9 eV for TiB\(_2\), to 188.1 eV for ZrB\(_2\), and 188.3 eV for HfB\(_2\), all values being significantly lower than that of the B-B sample with B 1s peak at 189.4 eV [70]. Hence, the larger the metal line shift towards higher BE the lower the BE of the corresponding B 1s peak. This correlation indicates that the negative charge transfer from Me to B atoms taking place upon Me-B bond formation is largest for TiB\(_2\) and smallest for HfB\(_2\). The effect is, however, rather small, which may be intuitively explained by the fact that physical properties typically associated with bond strength like enthalpy of formation or melting point are rather similar for all three diborides (see Table 1) [71].

While carbides show similar behavior to borides, BE shifts for nitrides go in the opposite direction, i.e., \( \Delta \text{BE} \) is smallest for Ti 2p\(_{3/2}\) at 1.3 eV, and increases to 1.4 eV for Zr 3d\(_{5/2}\), and 1.6 eV for Hf 4f\(_{7/2}\). This is accompanied by the N 1s shift from 397.4 eV for TiN, to 397.3 eV for ZrN, and 397.2 eV for HfN. Hence, in contrast to borides and carbides, the negative charge density on the A element (and, thus, the charge transfer upon A-Me bond formation) increases with increasing TM atomic number, which agrees with the increasing heat of formation. Oxides are the only group that does not show consistent trend.

3.2. Spectral changes vs sputter time

As many previous studies reported a gradual change in the surface composition as a function of sputtering time [26,27,29,32] we have performed initial tests to establish how long sputtering is required in the case of IVB-TM-based borides, carbides, nitrides, and oxides in order to reach steady state. Fig. 2 shows the A/Me elemental ratio (A = B, C, N, O, and Me = Ti or Hf) extracted from the respective core level spectra plotted as a function of sputtering time for the case of 0.5 keV / 70° Ar\(^+\). The latter sputtering conditions are expected to result in longer time required to reach steady state. There are clear differences between material systems studied here. For example, the B/Ti ratio in the case of TiB\(_2\) sample shows a gradual increase during the first 10 min, while C/Ti or O/Hf ratios reach the steady state values already after 2 min. In the latter case the initially high A/Me ratios are due to the presence of adventitious carbon at the surface [12]. Interestingly, the N/Ti ratio remains essentially unchanged during the whole experiment. The latter result is, however, rather coincidence as revealed by pronounced Ti 2p and N 1s spectral changes plotted in Fig. 3, in which evolution of the core level spectra with sputtering time is shown for the most characteristic cases of TiB\(_2\), TiC, TiN, and TiO\(_2\). For all samples except the last one, the native surface oxide is essentially removed after 2 min of sputtering as evidenced by the loss of metal-oxide peaks. This, however, does not imply that the steady state condition has been established for all films. For instance, both Ti 2p and B 1s spectra exhibit a gradual intensity change that does not saturate before the total sputtering time adds up to 10 min. In contrast, C 1s and Ti 2p spectra obtained from TiC specimen show no dependence on sputtering time after the first 2 min. Thus, based on these tests, all results presented in the remaining part of this paper are obtained after the sputtering time of 10 min to ensure that the steady state conditions are compared. Inspection of C 1s and O 1s spectra reveals that this amount of Ar\(^+\) bombardment is sufficient to remove surface hydrocarbon contaminations and oxides.

3.3. Changes induced by sputtering

BE shifts of the main metal and A element (A = B, C, N, O) peaks are compiled in Figs. 4 and 5, respectively, and changes in the A/Me elemental ratios (relative to that of native surface) resulting from sputtering are plotted in Fig. 6. The latter data are normalized to the XPS-derived stoichiometry obtained from native surfaces (see Table 1 and Sections 3.3.1-3.3.4 for details) in order to compare relative changes induced by Ar ion bombardment between different materials systems. Results shown in Figs. 4-6 are discussed compound-wise in Sections 3.3.1–3.3.4 together with corresponding core level spectra (Figs. 7–10). To facilitate spectra comparison, primary metal signals are normalized to the total area under the spectra. Subsequently, all A 1s spectra (A = B, C, N, O) are normalized by the area under corresponding metal peak, to highlight changes in film stoichiometry.

3.3.1. IVB-TM borides

Core level spectra recorded from TiB\(_2\), ZrB\(_2\), and HfB\(_2\) surfaces

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**Table 1**

| Compound type | Ti 2p\(_{3/2}\) | Zr 3d\(_{5/2}\) | Hf 4f\(_{7/2}\) |
|---------------|----------------|----------------|----------------|
| TiB\(_2\)     | 454.0 eV       | 187.9 eV       | 188.3 eV       |
| ZrB\(_2\)     | 454.1 eV       | 188.1 eV       | 188.3 eV       |
| HfB\(_2\)     | 454.2 eV       | 188.4 eV       | 188.3 eV       |

**Fig. 1.** Summary of binding energy shifts \( \Delta \text{BE} \) for main metal core level peaks, Ti 2p\(_{3/2}\), Zr 3d\(_{5/2}\), and Hf 4f\(_{7/2}\), obtained from analyses of IVB-TM boride, carbide, nitride, and oxide thin film samples. Shifts are given relative to peak positions in metallic samples and the positive value of \( \Delta \text{BE} \) indicates shift towards higher BE.
Table 1

| IVB-TM compound | Major crystal phase | Preferred orientation | Melting point [°C] | $\Delta H_f^{\text{iso}}$ [eV/atom] | A/Me (native) | A/Me (500 eV Ar$^+$) | A/Me (4 keV Ar$^+$) |
|-----------------|---------------------|-----------------------|-------------------|--------------------------------------|--------------|-----------------------|----------------------|
| TiB$_2$         | h-TiB$_2$           | 001                   | 3225              | −3.4                                 | 3.44 ± 0.17  | 2.52 ± 0.13           | 2.15 ± 0.11          |
| ZrB$_2$         | h-ZrB$_2$           | 001                   | 3245              | −3.4                                 | 2.41 ± 0.12  | 1.87 ± 0.09           | 1.78 ± 0.09          |
| HfB$_2$         | h-HfB$_2$           | 001                   | 3380              | −3.5                                 | 1.60 ± 0.08  | 1.76 ± 0.09           | 1.23 ± 0.06          |
| TiC             | c-TiC               | 111                   | 3100              | −1.9                                 | 0.87 ± 0.04  | 0.99 ± 0.05           | 0.95 ± 0.05          |
| ZrC             | c-ZrC               | 111                   | 3400              | −2.0                                 | 0.74 ± 0.04  | 0.77 ± 0.04           | 0.75 ± 0.04          |
| HfC             | c-HfC               | 002                   | 3900              | −2.3                                 | 0.78 ± 0.04  | 0.79 ± 0.04           | 0.79 ± 0.04          |
| TiN             | c-TiN               | 111                   | 2930              | −3.5                                 | 0.97 ± 0.05  | 0.78 ± 0.04           | 0.68 ± 0.03          |
| ZrN             | c-ZrN               | 002                   | 2980              | −3.8                                 | 1.11 ± 0.06  | 0.64 ± 0.03           | 0.52 ± 0.03          |
| HfN             | c-HfN               | 002                   | 3305              | −3.8                                 | 1.22 ± 0.06  | 0.72 ± 0.04           | 0.55 ± 0.03          |
| TiO$_2$         | tetragonal (rutile) | –                     | 1843              | −9.8                                 | 2.27 ± 0.11  | 1.73 ± 0.09           | 1.89 ± 0.09          |
| ZrO$_2$         | monoclinic          | –                     | 2715              | −11.4                                | 2.43 ± 0.12  | 1.90 ± 0.10           | 1.87 ± 0.09          |
| HfO$_2$         | monoclinic          | –                     | 2758              | −11.4                                | 2.77 ± 0.14  | 1.85 ± 0.09           | 1.80 ± 0.09          |

Fig. 2. A/Me elemental ratio (A = B, C, N and Me = Ti or Hf) extracted from the corresponding core level spectra and plotted as a function of sputtering time. The Ar$^+$ energy is 0.5 keV and the ion incidence angle from the surface normal is 70°. In the case of carbide samples the initially high A/Me values are due to the surface contamination.

etched with $E_{Ar^+} = 0.5$ keV and $\alpha = 70°$ or $E_{Ar^+} = 4$ keV and $\alpha = 45°$ are shown in Fig. 7(a)–(f). B 1s signals together with primary metal lines – Ti 2p, Zr 3d, and Hf 4f - are included. The reference spectra corresponding to native borides are obtained from samples that are in-situ capped with 3-nm thick dense Al layers immediately after the film growth to prevent oxidation during air-exposure necessary to transfer samples into the XPS instrument. It has been shown earlier that the Al capping layers as thin as 1.5 nm provide effective protection against surface oxidation of polycrystalline TiN/Si(001) thin films up to at least two months air storage time and, hence, allow for nondestructive acquisition of high-resolution core-level spectra, which are identical to that of films grown and analyzed in-situ [41]. Moreover, such approach allows to obtain surface stoichiometry free from Ar ion bombardment induced artefacts. All metal line signals obtained from Al-capped IVB-TM boride films presented in Fig. 7 are clearly free of oxide components, which indicates that the capping approach works well also in this case. This is predominantly due to the fact that the AlB$_2$ enthalpy of formation ($\Delta H_f^{\text{AlB}_2} = −1.6$ eV/atom) is lower than that of diborides included in this study ($\Delta H_f^{\text{TiB}_2} = −3.4$ eV/atom, $\Delta H_f^{\text{ZrB}_2} = −3.3$ eV/atom, $\Delta H_f^{\text{HfB}_2} = −3.5$ eV/atom) [71], which eliminates the risk of interfacial reactions.

Changes to the core level spectra of (TM)B$_2$ films induced by sputtering include: (i) loss of area under the B 1s peak, (ii) shift of all signals to lower BE values, (iii) broadening of both B 1s and metal lines, and (iv) appearance of new contributions on the lower BE side of the original B 1s peak. Although all effects are more pronounced for higher Ar$^+$ energy they are definitely present even after the mild etching case with 0.5 keV Ar$^+$ incident at shallow angle. These examples illustrate the severeness of risks associated with extracting the chemical information from previously “sputter cleaned” surfaces. The XPS-derived film stoichiometry deviates from the nominal value obtained from non-sputtered Al-capped samples showing the B-deficiency that increases with $E_{Ar^+}$ for all compounds (see Fig. 6) such that the relative change in the B/Me ratio with respect to the value obtained for native samples is in the range 0.51–0.77 after the 4 keV Ar$^+$ treatment. Peak shifts observed after sputtering introduce another risk of misinterpretation, especially if one attempts to extract the absolute BE values from the spectra and perform peak assignment by comparing those numbers to data in public XPS data bases. As illustrated in Figs. 4 and 5 peak shifts are in the range 0.1–0.5 eV for both metal and A element signals. All metal peaks shift towards metallic positions as the surfaces become B-deficient. Hf 4f$_{7/2}$ from HfB$_2$ after 4 keV Ar$^+$ etch appears at 14.2 eV, which is identical to that of metallic sample. Zr 3d$_{3/2}$ is at 178.9 eV only 0.3 eV higher BE than that of metallic sample. The Ti 2p$_{3/2}$ moves least among all IVB-TM and after 4 keV etch is at 454.4 eV, which is still 0.5 eV higher than metal sample. Peaks after sputter etch are, however, much broader than those from metallic samples – likely due to convolution of signal contributions from the etch-affected surface layer and deeper lying unaffected regions. The situation is further complicated by apparent spectral broadening and emergence of features resulting from sputter damage. Here, the best illustration is the new component in the B 1s spectra that appears on the lower BE side of the main line (see Fig. 7), shifted by ca. 1 eV, with an intensity that scales with both $E_{Ar^+}$ and TM atomic number.

Thus, for all IVB-TM borides tested here, only in the case of TiB$_2$ etched with low ion energy and shallow ion incidence angle the resulting spectra are similar to those obtained from native surfaces. In all other cases, spectral changes induced by ion irradiation are too extensive to conclude anything about surface chemistry of non-treated samples.

3.3.2. IVB-TM carbides

TM and C 1s core level spectra recorded from TiC, ZrC, and HfC surfaces etched either with $E_{Ar^+} = 0.5$ keV and $\alpha = 70°$ or $E_{Ar^+} = 4$ keV and $\alpha = 45°$ are shown in Fig. 8(a)–(f). The reference spectra corresponding to native carbides are obtained from samples that are UHV- annealed with e-beam heater (between 2 and 10 h at 600–1000°C, depending on the sample), which results in an oxygen-free surface [17,43].

In contrast to borides, nitrides, and oxides, the core level spectra of IVB-TM carbides are relatively little affected by Ar$^+$ irradiation. No preferential sputtering of C is observed as illustrated by essentially unmodified C 1s spectra. For ZrC, the C/Zr ratio actually increases as a result of the sputter etch (cf. Fig. 6). When it comes to new spectral features, there are just subtle changes in the C 1s spectra of TiC and ZrC with a slight asymmetry on the high BE side of the main lines (cf. Fig. 8(a) and (c)). Binding energies of all C 1s peaks do not show any changes as a result of Ar$^+$ irradiation (see Fig. 5), while Ti 2p$_{3/2}$, Zr 3d$_{3/2}$, and Hf 4f$_{7/2}$ peaks shift slightly by −0.1 eV to lower BE. Likewise, no
broadening of C 1s or metal lines is observed after Ar ion bombardment. This result is in agreement with earlier reports which show little sputter damage in the case of TiC sputtered by Ar⁺ with energy in the range 150–4000 eV [17,28]. We suggest that the preserved sample stoichiometry is the main reason responsible for the fact that core level spectra of IVB-TM carbides are unchanged after Ar⁺ irradiation. The ion-surface interactions responsible for the retained composition in the carbide system are discussed below.

Hence, carbides seem to be the most forgiving material class for XPS practitioner by means of resistance, for which spectral changes induced by severe sputtering are very subtle and, thus, the risk of spectral misinterpretation is small. This does not imply, however, that the original material is not affected by the Ar irradiation. It is possible that some bond types detected in the XPS analysis are reinstated (reformed in the same configuration) ones following splitting of the same native bond by the impacting Ar ions.

3.3.3. IVB-TM nitrides

Core level spectra acquired from TiN, ZrN, and HfN surfaces etched either with $E_{Ar^+} = 0.5$ keV and $\alpha = 70^\circ$ or $E_{Ar^+} = 4$ keV and $\alpha = 45^\circ$ are shown in Fig. 3(a)-(h). The reference spectra corresponding to native nitrides are obtained from samples that are in-situ capped with ~2.5-nm thick Cr layers [18,41]. The CrN enthalpy of formation ($\Delta H^0_{\text{CrN}} = -1.2$ eV/atom) is significantly lower than that of all Group IVB-TM nitrides.

![Graphs showing the evolution of core level spectra as a function of sputtering time for TiB₂, TiC, TiN, and TiO₂.](image-url)
Fig. 4. Summary of binding energy shifts of main metal peaks, Ti 2p, Zr 3d, Hf 4f, after sputtering with (i) Ar⁺ energy $E_{Ar^+}$ of 0.5 keV and the ion incidence angle from the surface normal $\alpha = 70^\circ$ (gentle etch), (ii) $E_{Ar^+} = 4.0$ keV and $\alpha = 45^\circ$ (standard etch). All shifts are relative to peak positions in metallic samples.

Fig. 5. Summary of A 1s binding energy shifts ($A = B, C, N, O$) in etch conditions with (i) Ar⁺ energy $E_{Ar^+}$ of 0.5 keV and the ion incidence angle from the surface normal $\alpha = 70^\circ$ (gentle etch), (ii) $E_{Ar^+} = 4.0$ keV and $\alpha = 45^\circ$ (standard etch).

Fig. 6. Changes in the A/Me elemental ratios ($A = B, C, N, O$ and Me = Ti, Zr, Hf) relative to the values obtained from native surfaces.

$(\Delta E_{TiN}^H = -3.5$ eV/atom, $\Delta E_{ZrN}^H = -3.8$ eV/atom, $\Delta E_{HfN}^H = -3.8$ eV/atom) [72], which excludes the interfacial reactions that could affect spectra appearance.

Similar to borides, nitrides are also sensitive to the Ar⁺ irradiation even if the low energy is used. Changes observed in the core level spectra include: (i) the area loss under the N 1s peak, (ii) shift of N 1s signals to higher BE values, (iii) shift of metal spectra towards lower BE’s, (iv) broadening of both N 1s and metal lines, (v) new contributions in the N 1s peak, and (vi) loss of the satellite peaks.

Data summarized in Fig. 6 reveal that loss of N resulting from preferential resputtering takes place and the effect increases with increasing $E_{Ar^+}$ for all compounds. The relative decrease in the N/Me ratio with respect to the value obtained for native samples is smallest for TiN – 0.80 after the 0.5 keV etch - and 0.70 after the 4 keV Ar⁺ treatment. The N deficiency is more pronounced for higher mass IVB-TM nitrides: 0.58 following the 0.5 keV etch for both ZrN and HfN, which decreases further to only 0.52 and 0.45, respectively after 4 keV Ar⁺ irradiation. Except for TiN, this pronounced N loss is accompanied by the shift of the N 1s spectra towards higher BE, ~0.2 eV for ZrN and ~0.6 eV for HfN, while corresponding metal peaks shift in the opposite direction by 0.3 eV and 0.7 eV, respectively. Such behavior indicates a presence of a reduced (N-deficient phase) with BE lower than that of a stoichiometric nitride, in accordance with the quantitative analyses that reveal severe N loss. The resulting spectrum is, thus, a superposition of two doublets: one due to the deeper-lying unaffected IVB-TM nitride and one due to the substoichiometric nitride at the surface. Both metal and N 1s lines become broader as a result of Ar⁺ bombardment. In the N 1s spectra of ZrN and HfN multiple components are observed.

Group IVB-TM nitrides differ from other types of samples included in this study in that their core level spectra of metal lines possess peculiar satellite peaks that appear on the high BE side of the primary lines (marked with “S” in Fig. 9(b), (d), and (f)). These satellites have been thoroughly studied in the case of TiN, however, no consensus has been reached as to their origin. Initially they were connected to the presence of oxygen on the TiN surface, and assigned either to Ti oxide [73] or TiO₂Nₓ [74]. However, these explanations were disproved first by the study of Burrow et al. [75] who concluded, that the intensity of these extra peaks does not scale with the bulk O/Ti ratios and later by the work of Haasch et al. [42] which revealed that the satellites are present even in the Ti 2p spectrum of the in situ grown single-crystal TiN sample.
obtained under extremely clean conditions and without any oxygen present. Remaining plausible explanations include shake-up effects due to intraband transitions between filled and partially filled valence electron energy levels near the Fermi energy [76], decrease in the screening ability of the conduction electrons [77,78], or structural effects [79]. Satellites in the Zr 3d spectrum of ZrN and Hf 4f spectrum of HfN are less pronounced, in agreement with previous reports [18,80,81]. The relatively low energy spread between the spin-split effects [79] is shown to reproduce the correct spin-split ratios, 3d_{5/2}/3d_{3/2} = 3/2 and 4f_{5/2}/4f_{3/2} = 4/3, for Zr 3d and Hf 4f spectra of IVB-TM nitrides, respectively [18]. What makes ZrN and HfN further different is the correlation between the intensity of extra peaks and N/Me ratio [77].

In summary, TiN etched with low ion energy and shallow ion incidence angle is the only case among TM nitrides where the resulting spectra are similar to those obtained from native surfaces. In all other cases, spectral changes induced by ion irradiation are too extensive to conclude anything about surface chemistry of non-treated samples.

### 3.3.4. IVB-TM oxides

Metal and O 1s core level spectra acquired from TiO_2, ZrO_2, and HfO_2 surfaces etched either with E_{Ar+} = 0.5 keV and α = 70° or E_{Ar+} = 4 keV and α = 45° are shown in Fig. 10(a)-(f). Spectra denoted “native” are obtained from films that have been exposed to air for less than 10 min necessary to transfer specimens from the growth chamber to the load lock system of the XPS instrument. For this material class, the most severe risk of atmosphere exposure, i.e., surface oxidation is naturally eliminated, hence the only artefact can be a minor hydrocarbon contamination (adventitious carbon), which does not affect the core levels of interest.

Only a first glance at the presented spectra reveals that changes induced by Ar+ irradiation in the core level spectra of IVB-TM oxides are most severe of all compound classes, in particular for metal core level lines, and include: (i) the area loss under the O 1s peak, (ii) shift of O 1s spectra to higher BE’s, (iii) shifts of metal peaks, (iv) severe broadening of metal satellite features, and (v) shifts of metal satellite features.

### 3.3.5. IVB-TM carbonitrides

Metal and C 1s core level spectra recorded from TiC, ZrC, and HfC surfaces etched with either E_{Ar+} = 0.5 keV and α = 70° or E_{Ar+} = 4 keV and α = 45° are shown in Fig. 11(a)-(f). The reference spectra corresponding to native carbides in black) are obtained from samples that are UVH-annealed with e-beam heater (between 2 and 10 h at 600–1000 °C, depending on the sample), which results in oxygen-free surface. Metal signals are normalized to the total area under the spectra, while all C 1s spectra are normalized by the area under the corresponding metal spectra to better reflect changes in film stoichiometry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In summary, the C 1s core level spectra of IVB-TM carbonitrides persist even after the E_{Ar+} = 4 keV Ar+ irradiation, however, they clearly decrease in intensity. The overall decrease in the satellite peak intensities after sputtering can be explained by the severe N-deficiency due to preferential resputtering, as previous studies demonstrated clear correlation between the intensity of extra peaks and N/Me ratio [77].

### 3.3.6. IVB-TM metallophanes

Metal and O 1s core level spectra acquired from TiOCl, ZrOCl, and HfOCl surfaces etched either with E_{Ar+} = 0.5 keV and α = 70° or E_{Ar+} = 4 keV and α = 45° are shown in Fig. 12(a)-(f). Spectra denoted “native” are obtained from films that have been exposed to air for less than 10 min necessary to transfer specimens from the growth chamber to the load lock system of the XPS instrument. For this material class, the most severe risk of atmosphere exposure, i.e., surface oxidation is naturally eliminated, hence the only artefact can be a minor hydrocarbon contamination (adventitious carbon), which does not affect the core levels of interest.

Only a first glance at the presented spectra reveals that changes induced by Ar+ irradiation in the core level spectra of IVB-TM metallophanes are most severe of all compound classes, in particular for metal core level lines, and include: (i) the area loss under the O 1s peak, (ii) shift of O 1s spectra to higher BE’s, (iii) shifts of metal peaks, (iv) severe broadening of metal satellite features, and (v) shifts of metal satellite features.

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**Fig. 8.** Primary metal and C 1s core level spectra recorded from (a-b) TiC, (c-d) ZrC, and (e-f) HfC surfaces sputtered with either E_{Ar+} = 0.5 keV and α = 70° (in red) or E_{Ar+} = 4 keV and α = 45° (in green). The reference spectra corresponding to native carbides (in black) are obtained from samples that are UVH-annealed with e-beam heater (between 2 and 10 h at 600–1000 °C, depending on the sample), which results in oxygen-free surface. Metal signals are normalized to the total area under the spectra, while all C 1s spectra are normalized by the area under the corresponding metal spectra to better reflect changes in film stoichiometry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 9.** Primary metal and N 1s core level spectra recorded from (a-b) TiN, (c-d) ZrN, and (e-f) HfN surfaces sputtered with either E_{Ar+} = 0.5 keV and α = 70° (in red) or E_{Ar+} = 4 keV and α = 45° (in green). The reference spectra corresponding to native nitrides (in black) are obtained from samples that are in-situ capped with ~2.5-nm thick Cr capping layers immediately after the film growth to prevent oxidation during air-exposure. Metal signals are normalized to the total area under the spectra, while all N 1s spectra are normalized by the area under the corresponding metal spectra to better reflect changes in film stoichiometry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
main lines. The latter in the case of the 4f_{7/2} peak extends down to 14.3 eV, which is characteristic of metallic Hf.

Hence, for oxides, in contrast to other systems, changes are most severe for the oxide of the lightest IVB-TM – TiO$_2$. The overall spectral evolution is also very dramatic in each case to the extent that prevents most conclusions as to the chemical state of non-treated surfaces.

4. Discussion

The results presented in Figs. 7–10 reveal that the influence of Ar ion sputter etch on the XPS core level spectra of TM (Group IVB) borides, carbides, nitrides, and oxides thin films is, in general, severe and should always be considered while extracting chemical information. In addition, for all materials systems, Ar sputter damage increases with increasing ion energy. The extent of the sputter damage detectable by XPS varies, however, between systems from minor effects in the case of IVB-TM carbides to a complete change of spectral appearance noted for IVB-TM oxides. IVB-TM borides and nitrides constitute intermediate cases with changes in core level spectra increasing with TM mass.

It is well-established that the bombardment with noble gas ions with energy in the range from several hundred to few thousands eV results in a wide variety of destructive effects. Preferential resputtering of lighter atoms likely results in an increased metallic character of the ion-beam modified surface layer with consequences for BE’s of all XPS peaks. Mobility and reactivity of all species that are created by ion impact, their ability to form gaseous products, and diffusion rates of such products to the surface, along with the existence of substoichiometric phases and the potential to form metastable phases determine the final composition of top most layers and, hence, the appearance of the XPS spectra.

In addition, the secondary effect like surface roughening, amorphization, and Ar implantation cannot be neglected. Previous studies reported correlation between the magnitude of spectral changes upon Ar$^+$ irradiation and the enthalpy of formation. For example, Lewin et al. found that the destabilization of TiC by alloying with poor carbide forming elements such as Ni, Al, Fe, or Cu increases the susceptibility for sputter damage [28]. Our results obtained for the thermodynamically stable materials show the opposite trend: the spectral changes increase with increasing enthalpy of formation (cf. data in Table 1). $\Delta H^+$ is in the range $-1.9$ to $-2.3$ eV/atom for carbides, which are essentially not affected by Ar$^+$ etch, while $\Delta H^+$ is much higher for heavily-affected oxides (from $-9.8$ to $-11.4$ eV/atom). Borides and nitrides constitute intermediate cases both when it comes to spectral changes as well as $\Delta H^+$ values. We see this trend rather as accidental as, in fact, no correlation of sputter damage to $\Delta H^+$ is expected. The incident ion energy, even in the case of low energy sputtering, is $\sim 40$ to $\sim 260$ times larger than the involved bond energies. In addition, TRIM simulations of ion-induced collision cascades indicate that up to 60% of the initial Ar$^+$ energy can be transferred to the primary recoils (as opposite to giving rise to multiple low-energy recoils). What we instead consider to be the more relevant factor for the appearance of XPS spectra from Ar$^+$-sputtered surfaces is (i) the nature of compounds that may form as a result of ion-induced mixing in the affected layer together with (ii) the final elemental composition. In addition, to quantify the potential visibility of the sputter damage in the actual core level spectra one has to compare the thickness of the affected layer to the XPS probing depth. We discuss these aspects below.

4.1. Fraction of Ar$^+$-affected atoms in the specimen volume probed by XPS

For the XPS practitioner, it is essential to realize the influence of the experimental parameters such as the choice of inert gas, incident ion flux, ion energy, and ion incidence angle on the resulting sputter damage in the surface region. In particular, what fraction of atoms in the volume probed by XPS becomes displaced during collision cascades? Even though a
significant fraction of recoiled atoms might end up in the same bonding configuration as in the as-deposited state, with no evident effect on the spectrum, the answer to the above question gives a better notion for what material is actually being analyzed. This is an essential action, which should always precede the spectra analysis and interpretation in terms of chemical bonding, to minimize the risk of erroneous conclusions. Below we discuss these issues for the case of severe and gentle Ar$^+$ sputtering.

The average Ar$^+$ ion flux $\phi$ for the two sputtering conditions tested in this paper, $E_{\text{Ar}}^0 = 4.0$ keV/\(\alpha = 45^\circ\) and $E_{\text{Ar}}^0 = 0.5$ keV/\(\alpha = 70^\circ\), is $5.2 \times 10^{14}$ cm$^{-2}$ s$^{-1}$ and $1.4 \times 10^{14}$ cm$^{-2}$ s$^{-1}$, respectively. Let us consider first the high energy case. The details of collision cascade events induced by ion irradiation obtained from Monte Carlo type Transport of Ions in Matter (TRIM) simulations reveal that, on average, each incident ion gives rise to 60 $\pm$ 10 atom displacements, while the number of sputtered atoms per incident ion (the sputtering yield $\gamma$) is approximately an order of magnitude lower and varies from 1.5 to 7.6, depending on the particular element and material system under consideration (see Section 4.2 for more details). This difference is essential as it implies that at any instant of time majority of displaced atoms remains at the surface (as opposed to the "ideal case" scenario for XPS, in which all affected atoms are sputtered away). Moreover, TRIM simulations show that the affected volume extends to $\approx 80$ Å, which is quite material-independent (see Fig. 12 and Section 4.2 for more detailed treatment). The atom displacement rate in this volume is, thus, $3.9 \times 10^{22}$ cm$^{-3}$ s$^{-1}$, or, in other words, the number of displacements during 2.5 s equals the total number of atoms in the affected volume. If we further take into account that with the sputter rate of 0.52$\gamma$ Å/s time necessary to remove 80 Å is $154/\gamma$ s, hence, in the range 20 to 102 s, it becomes evident that each atom within the volume where collision cascades take place is displaced several times before it is eventually sputtered away. The same conclusion holds even for more gentle sputtering conditions $E_{\text{Ar}}^0 = 0.5$ keV/\(\alpha = 70^\circ\). In the latter case the atom displacement rate is lower at $7.0 \times 10^{21}$ cm$^{-3}$ s$^{-1}$, but the affected volume extends to only 20 Å (see Section 4.2), which together with a lower sputter rate of 0.14$\gamma$ Å/s and lower sputter yields, 0.5 $\leq$ $\gamma$ $\leq$ 3.2 (see Section 4.3), implies that the time necessary to remove 20 Å is 3 to 20 times longer than that required to displace all atoms within the affected volume. These estimates demonstrate that the chances to find a non-affectted surface within the volume defined by the extend of collision cascades are close to zero, irrespective of whether severe or gentle sputter etch is applied. It needs to be emphasized though, that not all of the affected atoms give rise to spectral changes as the latter requires that recoils end up in a different chemical environment. Not only is the total number of created recoils (per incident Ar$^+$ ion) more than seven times higher in the former case, but also the recoil penetration depth increases by a factor of four with respect to the low energy/shallow incidence angle sputtering. In the latter case $\gamma$ $\approx$ 20 Å, while after high energy Ar$^+$ sputtering it increases to $\approx$ 90 Å. Very similar trends are also observed in simulations performed for other materials systems included in this study. Due to space limitations only data for Ti compounds are shown in Fig. 12. It can be observed that all A-element recoils produced after the $E_{\text{Ar}}$ = 4 keV/\(\alpha = 45^\circ\) sputter etch indicate $\xi$ in the range from 80 to 95 Å.

What is essential for XPS best practice is to take into consideration that the length scales mentioned above are in the same range as XPS probing depths $\gamma$ with commonly used excitation sources. $\gamma$ is defined as the thickness of the top surface layer, which accounts for 95% of the total signal intensity. Since, in the absence of elastic scattering of the photoelectrons, one assumes an exponential decay of signal intensity $I$ with depth $d$ such that $I \propto \exp(-d/\lambda)$, in which $\lambda$ is the inelastic electron mean free path, it follows that for electrons emitted along the surface normal $\gamma$ $\approx$ 3 $\times$ $\lambda$. With Al K$\alpha$ ($h\nu$ = 1486.6 eV) or Mg K$\alpha$ ($h\nu$ = 1253.6 eV) radiation core level electrons have kinetic energies in the range 100–1200 eV, which results in $\lambda$ of the order of 10–25 Å and 30 $\leq$ $\gamma$ $\leq$ 75 Å [37,84,85]. Hence, the choice of Ar$^+$ etch conditions (energy and incidence angle) becomes detrimental for what fraction of the measured XPS signal originates from the specimen volume not affected by the ion beam.

This point is illustrated in Fig. 13, in which the fraction of the B 1s signal intensity $\beta$ originating from the Ar$^+$-affected surface layer of thickness $\xi$ given by $\beta = [1 - \exp(-\xi/\lambda)]$ is plotted in the form of a 2D contour map as a function of ion energy $E_{\text{Ar}}$ and the ion incidence angle $\alpha$ for the case of Ar$^+$ impinging onto the TiB$_2$ surface. $\xi$ values are simulated by TRIM for 0.25 $\leq$ $E_{\text{Ar}}$ $\leq$ 4 keV and 0 $\leq$ $\alpha$ $\leq$ 80°, while $\lambda$ is taken directly from Ref. [36] for the case of 1300 eV electrons (B is}

![Fig. 11. TRIM-simulated B recoil concentration profiles for Ar$^+$ ions incident on IVB-TM boride surfaces: TiB$_2$, ZrB$_2$, and HfB$_2$. Two conditions are considered: (i) $E_{\text{Ar}}$ = 4 keV/\(\alpha = 45^\circ\), and (ii) $E_{\text{Ar}}$ = 0.5 keV/\(\alpha = 70^\circ\). The effect of ion energy and incidence angle on the thickness of the affected layer $\xi$ is striking, independently of the TM mass. Not only is the total number of created recoils (per incident Ar$^+$ ion) more than seven times higher in the former case, but also the recoil penetration depth increases by a factor of four with respect to the low energy/shallow incidence angle sputtering. In the latter case $\xi$ $\approx$ 20 Å, while after high energy Ar$^+$ sputtering it increases to $\approx$ 90 Å. Very similar trends are also observed in simulations performed for other materials systems included in this study. Due to space limitations only data for Ti compounds are shown in Fig. 12. It can be observed that all A-element recoils produced after the $E_{\text{Ar}}$ = 4 keV/\(\alpha = 45^\circ\) sputter etch indicate $\xi$ in the range from 80 to 95 Å. What is essential for XPS best practice is to take into consideration that the length scales mentioned above are in the same range as XPS probing depths $\gamma$ with commonly used excitation sources. $\gamma$ is defined as the thickness of the top surface layer, which accounts for 95% of the total signal intensity. Since, in the absence of elastic scattering of the photoelectrons, one assumes an exponential decay of signal intensity $I$ with depth $d$ such that $I \propto \exp(-d/\lambda)$, in which $\lambda$ is the inelastic electron mean free path, it follows that for electrons emitted along the surface normal $\gamma$ $\approx$ 3 $\times$ $\lambda$. With Al K$\alpha$ ($h\nu$ = 1486.6 eV) or Mg K$\alpha$ ($h\nu$ = 1253.6 eV) radiation core level electrons have kinetic energies in the range 100–1200 eV, which results in $\lambda$ of the order of 10–25 Å and 30 $\leq$ $\gamma$ $\leq$ 75 Å [37,84,85]. Hence, the choice of Ar$^+$ etch conditions (energy and incidence angle) becomes detrimental for what fraction of the measured XPS signal originates from the specimen volume not affected by the ion beam.

This point is illustrated in Fig. 13, in which the fraction of the B 1s signal intensity $\beta$ originating from the Ar$^+$-affected surface layer of thickness $\xi$ given by $\beta = [1 - \exp(-\xi/\lambda)]$ is plotted in the form of a 2D contour map as a function of ion energy $E_{\text{Ar}}$ and the ion incidence angle $\alpha$ for the case of Ar$^+$ impinging onto the TiB$_2$ surface. $\xi$ values are simulated by TRIM for 0.25 $\leq$ $E_{\text{Ar}}$ $\leq$ 4 keV and 0 $\leq$ $\alpha$ $\leq$ 80°, while $\lambda$ is taken directly from Ref. [36] for the case of 1300 eV electrons (B is}
excited with Al Kα photons) in Ti (no values for TiB2 are available). A first glance at the 2D contour map reveals that with the exception of the upper left corner, corresponding to the lowest ion energy and the highest incidence angle from the surface normal, the B 1s signal is dominated by contribution from the Ar+-affected layer (β > 0.5). Even for the gentle set of conditions, that is the lowest ion energy (0.25 keV) and the highest incidence angle (80° from surface normal), about 45% of the B 1s signal intensity originates from the layer affected by Ar+. This number increases fairly quickly with increasing $E_{Ar^+}$ and decreases with incidence angle from the surface normal, the B 1s signal is dominated by preferential resputtering of lighter components (with the apparent exception of C). This can explain the fact that spectral changes observed in IVB-TM carbides are relatively small (cf. Fig. 8), as well as, that no preferential sputtering of C is observed (see Fig. 6) or, in some case, like ZrC the C/Zr ratio actually increases as a result of the sputter etch.

4.3. Sputter yield effects

One of the detrimental effects of the Ar+ bombardment is the preferential resputtering of lighter atoms. This effect is clearly visible in Figs. 7-10 as the loss of area under the A element core level spectra with respect to that of a corresponding TM. The critical parameters that can help to quantify these effects are IVB-TM and A element sputtering yields, $\gamma_M$ and $\gamma_A$, respectively. Both can be obtained from TRIM simulations for the specific set of sputtering conditions. Fig. 14 shows the $\gamma_A$ vs. $\gamma_M$ plots for (a) $E_{Ar^+} = 4.0$ keV/α = 45° and (b) $E_{Ar^+} = 0.5$ keV/α = 70°. $\gamma_A$ > $\gamma_M$ for borides, nitrides and oxides, which agrees well with the common perception that lighter elements are preferentially resputtered. This effect accounts for changes in core level spectra (cf. Figs. 7, 9, and 10), as well as for variation in the A/Me ratio upon sputtering (cf. Fig. 6).

Interestingly, carbides exhibit the opposite behavior, i.e., in this case $\gamma_A$ < $\gamma_M$ for $E_{Ar^+} = 4.0$ keV/α = 45° and $\gamma_A$ < $\gamma_M$ for $E_{Ar^+} = 0.5$ keV/α = 70°. This can explain the fact that spectral changes observed in IVB-TM carbides are relatively small (cf. Fig. 8), as well as, that no preferential sputtering of C is observed (see Fig. 6) or, in some case, like ZrC the C/Zr ratio actually increases as a result of the sputter etch.

4.4. Peak shifts and new spectral components

Another aspect of spectral changes induced by sputtering clearly visible in Figs. 7-10 are binding energy shifts of the primary metal and A (A = B, C, N, and O) element peaks summarized in Figs. 4 and 5, and the appearance of new spectral contributions. The primary reason for peak shifts in XPS is a change in the chemical bonding state. Preferential resputtering of lighter components (with the apparent exception of carbon - see Fig. 6) likely results in an increased metallic character of the ion-beam modified surface layer and peak shifts towards metallic positions (i.e. towards lower BE). The fraction of atoms that is not sputtered away is subject to a complete rearrangement during collision cascades and likely ends up in a new bonding configuration (hence with modified distribution of valence charge) in a disordered surface layer. Concurrently, reforming of bonds indistinguishable from those originally formed during materials synthesis make take place. The existence of substoichiometric stable phases and/or possibility to form metastable phases due to ion-induced mobility is decisive for which becomes the dominant mechanism. The potential influence of surface roughening, amorphization, and Ar implantation cannot be neglected. All above factors can give rise to Be shifts. In addition, as XPS is highly sensitive to surface electrical potential, peak shifts can also result as a consequence of modified electrical properties in the Ar beam affected layer. In such case purely spectroscopic effects like different charging state and/or modified screening properties become essential. Additional complication in spectral interpretation is that the overall spectrum apart from the Fermi edge plot for (a) $E_{Ar^+} = 4.0$ keV/α = 45° and (b) $E_{Ar^+} = 0.5$ keV/α = 70° A

![Fig. 13. 2D contour map of the fraction of the B 1s signal intensity $\beta$ originating from the Ar+-affected surface layer of thickness $\xi$ plotted as a function of ion energy $E_{Ar^+}$ and the ion incidence angle $\alpha$ for the case of Ar+ impinging onto the TiB2 surface.](image-url)

![Fig. 14. TRIM-simulated A element sputter yield $\gamma_A$ (A = B, C, N, O) plotted for Group IVB TM borides, carbides, nitrides, and oxides as a function of metal sputter yield $\gamma_M$. Two sputtering conditions are considered: (i) $E_{Ar^+} = 0.5$ keV and $\alpha = 70°$ (gentle etch), and (ii) $E_{Ar^+} = 4.0$ keV and $\alpha = 45°$ (standard etch).](image-url)
also present on the low BE side of primary lines. This overall shift of all core level lines to lower BE cannot be explained in terms of Me-B bond cleavage in MeB2 followed by formation of B-understoichiometric phases (e.g., Ti3B4 or Ti2B), as any change in the distribution of valence charge should result in B 1s and metal peaks shifting in the opposite directions (cf. the case for IVB-TM oxides discussed below). However, in addition to chemical modifications, the Ar⁺ irradiation causes preferential B resputtering (cf. Fig. 6), which leads to an enhanced metallic character of the Ar⁺ affected surface layer, that in turn results in better screening of core holes after photoionization and, thus, lower apparent BE of all electrons originating from this layer (both metal as well as B 1s). The shift of B 1s peaks towards lower BE caused by metallic character of the affected layer overcompensates any potential shifts in the opposite direction caused by atomic rearrangement and possible formation of metastable substoichiometric phases. This is because the latter effect is expected to be relatively small due to the fact that B has the lowest electronegativity of all A elements included in this study resulting in the smallest charge transfer involved in the bond formation. BE shifts are more pronounced for higher Ar⁺ energy due to (i) the significantly higher intermixing rate (cf. Section 4.1), and (ii) higher signal fraction originating from the modified layer (as depicted in Fig. 13 for B 1s the ion beam modified layer accounts for 56 and 94% of the total intensity for 0.5 keV/α = 70° and 4.0 keV/α = 45°, respectively). Based on the 4.0 keV/α = 45° results, which are essentially representative of the ion beam modified layer, it becomes evident that BE shifts and spectral changes increase from TiB2 to HfB2, what agrees very well with an increasing B deficiency (B/Me ratio decreases from 0.73 for TiB2 to only 0.51 for HfB2, see Fig. 6). The latter explains why BE of Hf 4f peaks of HfB2 following the 4.0 keV/α = 45° etching is essentially the same as that recorded for metallic Hf specimen (Hf 4f/2 at 14.2 eV), while Ti 2p peaks from sputtered TiB2 sample appear at 0.4 eV higher BE than in the case of metallic Ti. The nature of the new B 1s peaks that appear on the low BE side of the original lines is not clear.

In sharp contrast to all other materials systems included in this study Group IVB-TM carbides are least affected by Ar⁺ etching. This applies also to BE shifts that are very subtle and do not exceed 0.1 eV, which is of the order of measurement accuracy. The fact that C is not preferentially removed during sputtering (see Fig. 6) accounts for the unchanged electrical properties of the surface layer and, hence, explains the lack of BE shifts of the type observed for borides. Even in the hypothetical case of local C understoichiometry (XPS-derived compositions are not sensitive to local variations) no chemical shifts are expected as NaCl-structure IVB-TM-based carbides are well-known for their ability to accommodate significant C vacancy on the anion lattice. Severe C deficiency (C/Me < 0.67) is required for precipitation of metallic phase [86,87]. The second, and perhaps even more critical factor, for the observed insensitivity to sputter damage is the lack of stable substoichiometric carbon compounds that could potentially form as a result of ion-induced mixing in the surface region. This makes Group IVB-TM carbides unique among all material classes included in this study (oxides being on the other extreme). The above is further supported by the fact that XPS spectra acquired from Group VB and VIB-TM carbides which are known to form substoichiometric phases [88,89], show pronounced changes after the same Ar⁺ ion etching [17].

The nature of peak shifts observed for IVB-TM nitrides (cf. Fig. 9) depends on the involved metals. In general, spectral changes increase with increasing TM mass. In the case of TiN BE’s are essentially unaffected by sputtering (the only measurable shift is 0.3 eV detected for the Ti 2p2/3 peak after 4.0 keV/α = 45° etching), which is rather surprising taking into account large N deficiency (N/Me = 0.47 after high energy sputtering) and the fact that BE shifts involved in Ti-N bond formation are significantly larger than for borides due to significantly higher N electronegativity. For both ZrN and HfN, the N 1s peaks exhibit shifts toward higher BE while corresponding metal lines move towards lower BE, which reveals, on average, less ionic character of N and TM bonds in the Ar⁺ modified layer. The results suggest possible formation of metastable substoichiometric phases like Zr2N or Hf2N.

All IVB-TM oxides exhibit similar evolution of core level peaks after Ar⁺ sputtering: O 1s peaks move towards higher BE while IVB-TM peaks possess several new contributions at significantly lower BE than the original signals (see Fig. 10). The latter appear with reduced intensity and shifted to the higher BE’s. The presence of low BE peaks in all metal core level spectra indicates reduction of original oxides to several lower oxidation states (primarily TiO and TiO₂) including even purely metallic state (lowest BE features match the positions of metallic lines), in agreement with earlier reports [50,90–92]. The shifts of original metal peaks to higher BE likely result from differential charging due to modified electrical properties in the Ar⁺ affected layer. The same effect is also responsible for the observed shifts of all O 1s peaks towards higher BE.

Hence, the largest spectral changes observed for IVB-TM oxides are attributed to the fact that several stable oxides exists (2⁺ and 3⁺ being the most common) with the oxidation number lower than the starting compound (4⁺). Under the conditions of high mobility induced by ion mixing and oxygen loss due to preferential resputtering formation of lower oxidation states is a very likely scenario.

5. Summary and conclusions

We performed systematic studies of the effect of sputter etching with Ar⁺ ions prior to XPS analyses, on the appearance of core level spectra recorded from polycrystalline Group IVB transition metal boride, boride, nitride, and oxide thin film specimens. The aim is to enhance the reliability of XPS spectra interpretation by (i) illustrating the problems, and (ii) providing general guidelines. IVB-TM compounds are well-suited for this study due to: (i) a large number of devoted XPS papers resulting from the wide application range of these materials, and (ii) relatively high susceptibility of thin film samples to sputter damage. All samples are tested in the same instrument under the exact same conditions for two ion gun settings: “standard” 4 keV with 45° incidence angle and mild etching with 0.5 keV Ar⁺ with shallow incidence angle of 70° from sample normal. The spectra obtained from native surfaces are included for comparison.

We conclude that the influence of Ar⁺ etch on the core level spectra varies greatly between materials systems from very subtle effects in the case of Group IVB-TM carbides to a complete change of spectral appearance for IVB-TM oxides. IVB-TM borides and nitrides constitute intermediate cases with changes in core level spectra increasing with TM mass. Details are summarized in Table 2. In general, except for carbides and low-energy etch on TiN and TiB2, spectra recorded after Ar⁺ irradiation are not representative of native surfaces. Both, metal and A element core level lines experience BE shifts, broadening, new spectral components, and variations in the A/Me ratio. Unfortunately, this is also the case for the mildest set of sputtering conditions in the form of low ion energy and shallow incidence angle.

There are three primary factors that determine the extent of spectral changes. First, the existence and/or the nature of compounds that may form as a result of ion-induced mixing in the surface layer. For example, the formation of several stable oxides with lower oxidation state than the original IVB-TM dioxides accounts for large spectral changes observed in this class of materials. This is in contrast to IVB-TM carbides, for which no substoichiometric phases exist and, consequently, essentially no spectral changes are observed (further supporting evidence comes from earlier experiments with VB and VIB-TM carbides, which are able to form substoichiometric phases and do show spectral changes upon sputtering). Second factor is the resulting elemental composition, i.e., the magnitude of preferential sputtering effects. This is the driving force which, if present, greatly facilitates formation of compounds with lowered A/Me ratio. This is exactly the case for IVB-TM oxides, where severe O loss contributes to the formation of compounds with lower oxidation state. IVB-TM carbides again exhibit entirely different behavior with preserved C/Me ratio. In addition, the preferential
resputtering of lighter component results in more metallic character of the modified layer, which leads to purely spectroscopic effects such as (i) peak shifts to lower BE (both metal and A element lines) due to better screening of core holes, and/or (ii) a modified charging state also affecting peaks positions. Finally, the relative spectral contribution from the unaffected deeper-lying sample regions may to some extent counteract the damage caused by Ar etching in the top layers. An important thing is that, in contrast to the two first factors, the instrument user can to some extent influence the result by a proper selection of experimental parameters such as the sputtering ion energy, the ion incidence angle, and the excitation source together with the choice of core levels for analysis (both affecting the XPS probing depth).

Our results, even though limited to IVB-TM compounds, should serve as a warning for spectra overinterpretation, and, at the same time, emphasize the importance to develop methods for non-destructive XPS techniques. Common referring to Ar etch as "surface cleaning" is misleading and should be avoided in publications as it creates a lax mind set. With the overall application-driven trend of developing yet more complex compounds, the analysis problems outlined above for already relatively simple binary compounds become even more motivated to address.

**CRediT authorship contribution statement**

**G. Greczynski:** Conceptualization, Investigation, Funding acquisition, Writing - original draft. **L. Hultman:**: Writing - review & editing.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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