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Synthesis and characterization of $(\text{Ti}_{1-x}\text{Al}_x)\text{B}_{2+\Delta}$ thin films from combinatorial magnetron sputtering

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Abstract

$(\text{Ti}_{1-x}\text{Al}_x)\text{B}_{2+\Delta}$ films with a lateral composition gradient of $x = [0.30 - 0.66]$ and $\Delta = [0.07 - 1.22]$ were deposited on an Al_2O_3 wafer by dual magnetron sputtering at 400 °C from sintered TiB_2 and AlB_2 targets. Composition analysis indicates that higher Ti:Al ratios favor overstoichiometry in B and a reduced incorporation of O. Transmission electron microscopy reveals distinctly different microstructures of Ti- and Al-rich compositions, with formation of characteristic conical growth features for the latter along with a lower degree of crystallinity and significantly less tissue phase from B segregation at the grain boundaries. For Al-rich films, phase separation into Ti- and Al-rich diboride nanometer-size domains is observed and interpreted as surface-initiated spinodal decomposition. The hardness of the films ranges from 14 to 28 GPa, where the higher values were obtained for the Ti-rich regions of the metal boride.

Keywords: titanium aluminium diboride, thin films, combinatorial sputtering, mechanical properties, phase decomposition

1. Introduction

Titanium diboride (TiB_2) is an extremely hard ceramic material, particularly well-studied in bulk form, which has excellent thermal and electrical conductivity, high melting point, chemical stability, and resistance to mechanical erosion [1]. TiB_2 crystallizes in a hexagonal AlB_2 -type structure, where hexagonal-close-packed $\text{Ti}(0001)$ planes are interleaved by layers of interstitial B atoms. Non-reactive magnetron sputtering has been the primary technique for synthesis of thin films of TiB_2 , see, e.g., Ref. [2-6], where overstoichiometric (0001) textured films with nanocolumnar microstructure and compressive residual stress have typically been observed [3, 4, 7, 8]. The excess B segregates to grain boundaries forming an amorphous B tissue phase [4], which together with the nanocolumnar microstructure results in superhard coatings with hardness values up to ~60 GPa [4]. TiB_2 coatings pose a high potential for improved performance in various tribological applications, e.g., reduced wear and corrosion, or as protective coatings for cutting tools. However, common industrial substrates, such as most steels, have a considerably lower elastic modulus (~200 GPa [9]) than TiB_2 (~560 GPa [9]), which, combined with high thermally induced stress, negatively affects the TiB_2 coating adhesion and results in early failure. In general, materials performance may be improved by synthesis of multicomponent systems, which allows tuning of the properties and control of the microstructure, resulting in overall enhanced functionality [10, 11]. Various ternary systems of

transition metal diborides are explored in order to obtain superior properties, e.g., $W_{1-x}Ta_xB_{2-z}$ for a combination of both mechanical strength and ductility [12, 13]. An example for hard-coating applications is $Ti_{1-x}Al_xN$, where Ti in TiN is partially replaced by Al, leading to age hardening effect through isostructural clustering, a primary reason behind its success [14]. Alloying TiB_2 with Al reduces elastic modulus to about 325 GPa for low-temperature synthesis of Ti-Al-B coatings, co-deposited from TiAl and TiB_2 targets [15, 16], and with an Al content of <10 at. % (i.e., composition close to TiB_2), thus providing a significantly better elastic moduli match between the coating and the application-relevant substrate. Furthermore, most recent theoretical calculations indicate coherent isostructural decomposition of $(Ti,Al)B_{2+\Delta}$ with a strong driving force for phase separation [17] potentially increasing the hardness. Deposition and subsequent heat treatment of corresponding thin films resulted in improved mechanical properties in terms of hardness and elastic modulus [18]. It is thus important to systematically map out the composition-structure window for the Ti-Al-B system. In this study, a combinatorial approach is employed to examine the dependence of microstructure and mechanical properties in terms of elastic modulus and hardness on the composition of magnetron sputtered $(Ti_{1-x}Al_x)B_{2+\Delta}$ thin films. Emphasis is also put on investigating the correlation between degree of overstoichiometry and the Ti:Al ratio.

2. Experimental Details

Combinatorial deposition of Ti-Al-B on a 3" diameter $Al_2O_3(0001)$ wafer was performed by non-reactive dual dc magnetron sputtering using 3" sintered TiB_2 (99.5 % purity) and AlB_2 (99.9 % purity) targets, each positioned at an angle of 39° from the substrate normal, with an orthogonal distance of 15 cm. Sapphire substrate was chosen due to a good lattice match and good film adherence. Prior to deposition the substrate was degassed in the vacuum chamber at the growth temperature of 400 °C for 30 min. The vacuum chamber, which had a base pressure of $4.5 \cdot 10^{-6}$ Pa, was fed with 10.4 sccm Ar introduced up to a partial pressure of $1.3 \cdot 10^{-1}$ Pa. The deposition was carried out for 2 h in power-controlled mode with 100 W (2.19 W/cm^2) on the TiB_2 and 100 W (2.19 W/cm^2) on the AlB_2 targets, and with a substrate bias of -50 V. The wafer orientation with respect to the targets is shown in the inset in Fig. 1. Hereafter, the wafer areas closer to the TiB_2 target and the AlB_2 target are referred to as the TiB_2 -side and the AlB_2 -side, respectively. The layers were grown to a thickness of 200 to 250 nm.

The structural properties of the films were investigated by X-ray diffraction (XRD) using a Panalytical Empyrean MRD system equipped with a Cu $K\alpha$ source ($\lambda = 1.54 \text{ \AA}$). Symmetric θ - 2θ scans were performed with X-rays in point focus using a hybrid mirror optics on the incident side and an X-ray lens on the diffracted side. The diffractograms were acquired in a 5×5 array (see inset in Fig. 1) with a distance of 13.5 mm between each spot.

The nanoindentation hardness (H) and reduced Young's modulus (E_r) were investigated by a Triboindenter TI950 instrument from Hysitron. The nanoindentations were conducted with a Berkovich diamond probe, which has been calibrated prior to the analysis using a fused silica reference. H and E_r were calculated by the method of Oliver and Pharr using the unloading elastic part of the load-displacement curve [19]. A mapping of the mechanical properties was performed by recording loading-unloading curves in load-controlled mode at 25 different area spots arranged in a $5 \times 5 \text{ cm}^2$ grid, corresponding to the same positions as for the XRD measurements. An array of twelve indents separated by 10 μm and with a penetration depth of 50 nm was recorded at each area spot, the mean value and the standard deviation of H and E_r for these 12 indents in each area is reported. The maps were generated by the software Origin Pro 8.5 using an increase factor of 200 points and a smoothing parameter of 0.1. **In a recent**

paper, the influence of the substrate on the measured film mechanical properties has been discussed [20]. The work shows how Buckle's rule of the 10 % film-thickness indentation depth limit is not valid all the time. That rule is not stringent enough for hard coatings on a very soft substrate, and inversely, the rule is too strict for coatings on a harder substrate. As it is discussed by Broitman [20], in our case the low tip penetration, in combination with the supporting sapphire substrate (hardness 30 GPa [21]), assures that the substrate does not influence the measured H and E_r values.

Elemental composition was determined using a Kratos Analytical Ultra^{DLD} X-ray photoelectron spectroscopy (XPS) system with monochromatic Al $K\alpha$ radiation. The measurements were performed at selected positions on the 5 x 5 grid (see schematics in Table 1) along the expected composition gradient through the wafer center as well as along a parallel line on either side. Prior to analysis, 3 x 3 mm² surface area was sputter-etched for 3 min using 500 eV Ar⁺ ions at an incident beam angle of 25° relative to the surface plane. Quantification was performed after the background contributions were removed using a Shirley function. The difference in the photoemission cross-section was compensated through relative sensitivity factors obtained from the Vision Processing software package provided by Kratos Analytical. The relative sensitivity factors used were 2.001 for Ti 2p, 0.193 for Al 2p, 0.159 for B 1s, 0.780 for O 1s, 0.278 for C 1s, and 0.477 for N 1s.

Samples for transmission electron microscopy (TEM) analysis were obtained from the wafer at positions D and H along the Ti-Al gradient. Plan-view TEM samples were prepared by focused ion beam (FIB) technique employing a Carl Zeiss Cross-Beam 1540 EsB system following a procedure described elsewhere [20]. Cross-sectional TEM samples were prepared by the traditional "sandwich" approach which includes sample cutting, gluing, and polishing followed by Ar⁺ ion milling at 5 keV and 5° angle from both sides in a Gatan precision ion polishing system (PIPS). A final low energy milling step was applied at 2 keV in order to reduce the surface damage. Scanning TEM high angle annular dark field (STEM-HAADF) imaging, STEM energy-dispersive X-ray spectroscopy (STEM-EDX), and STEM electron energy-loss spectroscopy (STEM-EELS) were performed using the double-corrected Linköping FEI Titan³ 60–300, operated at 300 kV. High-resolution STEM-HAADF images were acquired by using a 21.5 mrad probe convergence angle for sub-Ångstrom imaging with ~80 pA current. STEM-EDX and STEM-EELS spectrum imaging (SI) were performed using ~0.3 nA beam current. STEM-EDX spectrum images of 252 x 252 pixels were acquired for 3 min employing the high sensitivity Super-X EDX detector. STEM-EELS spectrum images of 50 x 50 pixels were acquired for 5 min using a 0.25 eV/channel energy dispersion, 0.2 s dwell time for each pixel and employing a Gatan GIF Quantum ERS post-column imaging filter [22].

3. Results and Discussion

Figure 1 shows XRD θ - 2θ scans acquired at different spots on the wafer. In all scans peaks at ~27.3° and 56.3° are present, which can be attributed to the (0001) and (0002) planes of the expected AlB₂-type crystal structure [23]. The incident X-ray beam has not been filtered entirely from the Cu $K\beta$ radiation, and thus the β peak from the Al₂O₃ substrate is also present at 37.6°. The inset in Fig. 1 shows a close-up on the (0001) film peak. The scans fall in five distinct groups (five scans in each), depending on distance to the targets. For these groups, the (0001) peak position shifts from 27.26° to 27.48° ($\Delta 2\theta = +0.22^\circ$) as well as the intensity is reduced by 60 % from the initial value when measured from the AlB₂-side to TiB₂-side of the wafer along the expected Al-Ti composition gradient. The previously reported (0001) peak positions for isostructural AlB₂ and TiB₂ phases are at 27.30° [24] and 27.54° [4], respectively.

No peak shift or intensity change is observed in between the measurements performed in the direction perpendicular to the plane intersecting the two targets.

Table 1 presents elemental composition and corresponding stoichiometry determined by XPS at selected positions on the wafer. The Ti:Al ratio changes uniformly from 0.70:0.30 on the TiB₂-side to 0.35:0.65 on the AlB₂-side. The Ti:Al ratio at the wafer center is 0.53:0.47, which is close to the expected 0.50:0.50 ratio based on equal powers applied to the TiB₂ and AlB₂ targets in combination with similar TiB₂ and AlB₂ growth rates. The Ti:Al ratio is constant perpendicular to the line joining TiB₂- and AlB₂-sides. The B content, although overall overstoichiometric, tends to be slightly higher on the right side of the wafer. This effect could be explained by an asymmetric experimental setup with minor unintentional sputtering from an unused B target mounted closer to the right side of the wafer. Higher accommodation of B is obtained for higher Ti:Al ratios. This is consistent with the previously established overstoichiometry in magnetron sputtered TiB₂ thin films [25, 26]. On the other hand, lower Ti:Al ratio, i.e., more Al, correlates with an increased incorporation of O. It can, to the most part, be ascribed to post-deposition O incorporation, evident from O primarily located along the grain boundaries as revealed in Fig. 2e.

The chemical evolution of the B/Ti ratio on the wafer can be attributed to a combination of different kinetic energy of the atoms emitted from the target and their angular distribution. This, in turn, may be influenced by gas-phase scattering, where Ti has a shorter mean-free-path compared to B at the same pressure, based on mass and radius of the colliding atoms [26]. An increase in pressure and/or distance, as well as an increase in off-axis angle used for deposition, has previously been shown to reduce the B/Ti ratio, at least in part, explained by gas-phase scattering [26]. Furthermore, it has been suggested that use of a high bias for deposition of a metal boride can cause preferential resputtering of B [27], to what extent depending on sputtering angle, ion kinetic energy, etc. Hence, resputtering also needs to be considered for evaluation of the wafer composition.

The deviation from chemical purity and exact diboride stoichiometry in our samples motivates that the comparison with the theoretical results of Alling *et al.* [17] is made with some care. However, as we conclude that the main part of the overstoichiometry in B is accommodated in the tissue phase, the local composition in the AlB₂-structure phase is closer to the ideal case than what would be assumed from the total global composition. Therefore, a comparison of the present findings with the prediction of Alling *et al.* [17] is still valuable.

A detailed STEM study was performed for the Ti-Al-B films obtained from wafer positions D and H, corresponding to Ti- and Al-rich specimens of (Ti_{0.70}Al_{0.30})B_{3.22} and (Ti_{0.34}Al_{0.66})B_{2.07}. The Al-rich composition was chosen motivated by the theoretically predicted maximum mixing enthalpy (i.e., strongest driving force for phase separation) for $x = 0.625$ [17], with the opposite Ti:Al ratio chosen for reference.

Figures 2a and b show the STEM-HAADF images from the Al-rich (Ti_{0.34}Al_{0.66})B_{2.07} film, in plan-view and cross section, respectively, revealing a dense columnar structure. The ~230 nm thick film exhibits conical columns, emerging at the interface to the substrate and competing for growth along the substrate normal direction with an internal fine structure that is crystallographically aligned along [0001]. Cross-sectional STEM-HAADF images (Fig. 2b) revealed pronounced bright line at the substrate/film interface which was attributed to the enhanced Ti content at the beginning of the film growth which was confirmed by EDX analysis (not shown). Also, cross-sectional HRTEM showed that very first atomic layers of grown

material exhibit an amorphous nature meaning that no considerable strain is introduced through lattice mismatch (not shown).

The majority of the columns exhibit a rounded surface truncation and homogenous STEM-HAADF contrast with a column width in the range of 20-30 nm (Fig. 2a), which run parallel to the film growth direction with constant width throughout the film (Fig. 2b). However, a significant number of larger column-like features, locally increasing the film roughness, was observed in plan-view exhibiting elliptic shapes with widths in the range of 50-80 nm (Fig. 2a). Cross-sectional imaging revealed that these column-like features observed in plan-view relate to columns of conical shape with their width gradually increasing throughout the thickness of the film.

Interestingly, the conical-growth features exhibit partitioning of Al and Ti, as revealed from atomic number sensitive STEM-HAADF imaging and STEM-EDX elemental mapping as shown in Fig. 2c-e. The STEM-HAADF images display darker and brighter contrast in areas that correspond to enrichment in Al and Ti, respectively. From the elemental maps it is also apparent that tissue phase enclosing the conical defects enriched in oxygen. Al-rich and Ti-rich parts are asymmetric, where the Al-rich one is always smaller in volume which is most likely related to self-shadowing effects of the opposite incoming Ti and Al fluxes, given the surface height modulation of the emerging cones. STEM-EELS elemental mapping further revealed the boron and oxygen distribution in the conical defects, where B is found to peak at the edge of the Al-rich Ti-Al-B part and is significantly reduced in the adjacent areas that instead are enriched in oxygen. Larger area STEM-EELS maps revealed the slight enrichment of B at grain boundaries, which are considered as amorphous tissue phase, while for more pronounced boundaries between columns a significant amount of O is observed (see Fig. 3). Background-subtracted and deconvoluted core-loss EELS spectra displaying strong B-K absorption edges and their characteristic shapes obtained from indicated regions of the Al-rich ($\text{Ti}_{0.34}\text{Al}_{0.66}\text{B}_{2.07}$) film are shown in Fig. 4. The individual spectra were extracted from the EELS map (Fig. 3). and vertically shifted with respect to each other. The spectra reveal significant differences in the fine structures suggesting different B chemical environments. The overall B edge fine structure contains a shoulder at ~190 eV and two apparent features at ~195 eV and ~204 eV energy loss. The most pronounced features at ~195 eV were observed for B edge obtained from at the tissue phase enclosing the conical defect (spectrum “1” in Fig. 4), which is also enriched in oxygen (Fig. 3e). Previously such sharp features were matched and attributed as the signature of B-O bonding in MoB_{2-x} film tissue phase [28].

Plan-view high-resolution STEM-HAADF images acquired from a conical growth feature and corresponding fast Fourier transform (FFT) patterns show that the Ti- and Al-rich counterparts exhibit the same crystallographic nature and identical relationship to the substrate. A *c*-axis fiber texture is, however, present as reflected in the selected area electron diffraction (SAED) pattern with arch-like single-crystal diffraction peaks shown in the insets of Fig. 2a-b, consistent with XRD results. The fiber texture is interpreted here as semi-coherent domains evolving in a fan-like manner from [0001].

According to Alling *et al.* [17], the driving force for phase separation is highest at $x = 0.625$, which is close to our analyzed samples with $x = 0.66$. The STEM-EDX finding in Fig. 2c-e about the formation of Ti- and Al-rich diboride domains can thus be interpreted as phase separation during film deposition of supersaturated (Ti,Al) B_2 solid-solutions. The different domains should form semi-coherent interfaces by virtue of the difference in lattice parameter as a function of metal ratio. The phase separation is, however, not complete and would exclude

a nucleation and growth process for TiB_2 and AlB_2 , since no splitting of the (0001) peak parallel to the film surface is present (c f. Fig. 1). The observed transformation can be better interpreted as spinodal decomposition towards TiB_2 and AlB_2 . The process is surface-initiated, because the partitioning of elements would experience less diffusion barrier in comparison to bulk, as reported for the TiAlN thin film system [29]. Thus, the composition gradient would be strongest across planes most inclined to the surface, which, however, could not be sampled with the present θ - 2θ scans due to the exclusive crystallographic texture. Future investigations should probe the $\{10\cdot10\}$ and $\{11\cdot20\}$ planes for peak broadening and/or shoulder formation effects.

We propose that the different diboride domains evolve in the observed fan-like manner because of the lattice misfit dislocation formation in combination with concurrent local B segregation to the growth surface, that hinders coherent growth of either phase. A corresponding microstructure evolution was reported for the TiSiN thin film system [30]. This growth mode is most characteristic for our high-Al-content diboride films, as the Ti-rich films exhibit weaker metal segregation, as expected from the theoretical predictions [17].

Figure 5 shows STEM-HAADF images from Ti-rich $(\text{Ti}_{0.70}\text{Al}_{0.30})\text{B}_{3.22}$ revealing a dense columnar structure of the film and the film thickness of around 240 nm. The grains in plan-view projection are preferentially elongated along the $[1\cdot100]$ direction with their characteristic width of 10-20 nm perpendicular to the grain elongation and 40-50 nm parallel. In cross-section the film exhibits a dense columnar microstructure, where the grains are inclined $\sim 20^\circ$ with respect to the surface normal (in $[11\cdot20]$) (see Fig. 5b), which accounts for plan-view observations of grain elongation.

We have observed a deviation of the lattice plane orientation from the ideal c -axis orientation towards the film surface (see Fig. 5c-d). The c -axis of the same grain is deviating by $\sim 5^\circ$ from its ideal $[0001]$ orientation close to the film surface as compared to the film-substrate interface. SAED patterns shown in the insets of Fig. 5 reveal the fiber texture of the grown film with c -axis preferential growth orientation, which starts to deviate towards the film surface. $(\text{Ti}_{0.70}\text{Al}_{0.30})\text{B}_{3.22}$ contains conical domains similar in nature to ones observed in $(\text{Ti}_{0.34}\text{Al}_{0.66})\text{B}_{2.07}$. However, the density of such domains is low; only one conical domain was observed in plan-view, where the Al-rich counterpart was significantly smaller in volume compared to the Ti-rich one. STEM-EDX/EELS mapping revealed that Ti and Al are homogeneously distributed within the grains while the grain boundaries are B-enriched which is attributed to the formation of a B tissue phase. No preferential O incorporation in the tissue phase was observed in this case.

These observations point towards challenges of producing stoichiometric, single-phase high structural quality $(\text{Ti}_{1-x}\text{Al}_x)\text{B}_2$ films without a tissue phase during sputtering from diboride targets. Despite the very close to ideal B:metal ratio of 2:1 in position H, the relatively high Al content promotes formation of the conical domains. On the other hand, increasing the Ti content tends to result in B excess.

Figures 6a and b present hardness and reduced elastic modulus maps, respectively. A continuous hardness increase from 14 GPa closest to the AlB_2 target to 28 GPa at the TiB_2 -side is observed, although the increase is more pronounced on the left side of the wafer. A similar behavior is observed for the reduced elastic modulus, which is increasing from 106 GPa to 278 GPa when going from the side closest to the AlB_2 target to the TiB_2 -side. It has been shown, that AlB_2 exhibits lower hardness and reduced elastic modulus compared to TiB_2 in thin film

form [4, 9, 31] as well as in *ab initio* calculations for bulk crystals [32], and thus the observed decrease in the values correlates with a decreasing Ti:Al ratio.

Mechanical properties are also affected by formation of conical domains, along with a varying width of the tissue phase in between the grains. A large disparity is seen between the left and right side of the wafer with higher elastic modulus values for the latter side, which might be related to the more pronounced B excess and would thus have an effect on the film microstructure.

Figures 6c and d present standard deviation of the measured hardness and reduced elastic modulus values, respectively. The H data dispersion is small in all areas at the upper part of the wafer, i.e., up to $x = 0.5$, while the data is increasingly more dispersed with higher Al content. Larger H data dispersion in each analyzed area most likely originates from the formation of conical domains observed in TEM (Fig. 2 and 3). These surface defects are randomly distributed and will affect the H values according to the number of cones that are affected in one indentation. On the other hand, the E_r dispersion is less than 7 % in areas where H dispersion climbs to 17 %. The elastic modulus represents the elastic behavior of the material calculated from the unloading part of the load-displacement nanoindentation curve (after the plastic deformation took place), and therefore is not affected by the plastic deformation of the cones. Thus, H dispersion on nanoindentation data can be used in our case to visualize the inhomogeneities of the microstructure (Fig. 6c). It also indicates that formation of the domains is promoted as soon as the Al content is higher than Ti, i.e., $x > 0.5$.

It is well known that surface roughness influences nanoindentation data [20, 33]. Evidently, the formation of the cones increases the roughness in some areas of our sample, but we can dismiss the possibility that the measured high dispersion on H is produced only by an increase of roughness: in that case, both H and E_r should be affected in a similar way (see [33] and references therein).

4. Conclusions

We have performed combinatorial thin film synthesis of $(\text{Ti}_{1-x}\text{Al}_x)\text{B}_{2+\Delta}$ with $x = [0.3 - 0.66]$ and $\Delta = [0.07 - 1.22]$ using dual magnetron sputtering. Structural and compositional analyses show columnar microstructure with conical features for the Al-rich compositions. Surface-initiated spinodal decomposition towards TiB_2 and AlB_2 nanometer-size semicoherent domains is demonstrated for Al-rich diboride compositions. Ti-rich films, however, exhibit no metal segregations in line with recent theoretical predictions of lower driving force for separation of those compositions of the pseudo-binary alloys. A hardness increase from 14 GPa to 28 GPa is observed with increasing Ti to Al ratio. Apart from a known higher hardness of TiB_2 compared to AlB_2 , the mechanical properties are likely affected by the observed formation of conical domains, along with a varying width of the tissue phase at the column or domain boundaries.

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	Ti	Al	B	O	C	N	
A	15.0	6.9	61.4	12.7	3.4	0.6	<div><div><div>TiB₂ target</div><div>(Ti_{0.69}Al_{0.31})B_{2.80} A</div><div>(Ti_{0.70}Al_{0.30})B_{3.22} D</div><div>(Ti_{0.70}Al_{0.30})B_{3.08} I</div><div>(Ti_{0.61}Al_{0.39})B_{2.90} E</div><div>(Ti_{0.53}Al_{0.47})B_{2.51} B</div><div>(Ti_{0.53}Al_{0.47})B_{2.64} F</div><div>(Ti_{0.53}Al_{0.47})B_{2.62} J</div><div>(Ti_{0.45}Al_{0.55})B_{2.42} G</div><div>(Ti_{0.35}Al_{0.65})B_{2.11} C</div><div>(Ti_{0.34}Al_{0.66})B_{2.07} H</div><div>(Ti_{0.35}Al_{0.65})B_{2.13} K</div><div>AlB₂ target</div></div></div>
B	12.5	10.9	58.7	13.9	3.4	0.6	
C	8.6	15.9	51.8	17.6	5.4	0.7	
D	15.1	6.4	69.2	7.1	1.8	0.5	
E	13.8	8.7	65.2	10.1	1.7	0.5	
F	12.8	11.4	63.9	10.1	1.4	0.5	
G	11.5	14.0	61.7	10.5	1.8	0.5	
H	8.1	15.9	49.6	18.4	7.6	0.4	
I	15.4	6.6	67.8	7.4	2.3	0.5	
J	12.6	11.2	62.3	11.7	1.7	0.5	
K	8.9	16.4	53.8	16.7	3.7	0.5	

Table Captions

Table 1 Elemental composition [at. %] and corresponding stoichiometry determined by XPS at selected positions. The estimated error is ± 0.5 at. %.

Figure Captions

Fig. 1 XRD θ - 2θ scans acquired as 5 x 5 array on the wafer showing peaks related to the AlB_2 -type structure. The top-right inset shows the (0001) peak at higher magnification revealing higher 2θ angles and lower intensities for the TiB_2 -side of the wafer. The wafer orientation with respect to the targets along with the XRD and nanoindentation (■ and ✕), XPS (✕), and TEM (bold letters) analysis points are also shown.

Fig. 2 (a) Plan-view and (b) cross-sectional STEM-HAADF images together with corresponding electron diffraction patterns showing the microstructure of $(\text{Ti}_{0.34}\text{Al}_{0.66})\text{B}_{2.07}$ film (position H). Plan-view EDX maps displaying elemental (c) Ti, (d) Al, and (e) O distributions.

Fig. 3 (a) Plan-view STEM-HAADF images together with corresponding EELS maps displaying elemental (b) Al, (c) B, (d) Ti, and (e) O distributions.

Fig. 4 EELS B-K edge spectra recorded from various regions in the plan-view from $\text{Ti}_{0.34}\text{Al}_{0.66}\text{B}_{2.07}$ film. (1): B tissue phase surrounding a conical defect and containing O, (2): grain in the film, (3): tissue in the film, (4): Ti-rich side of the conical defect, (5): Al-rich side of the conical defect, and (6): edge of the Al-rich side of the conical defect (B edge integrated intensity is the highest in this point (see Fig. 3c)).

Fig. 5 (a) Plan-view and (b) cross-sectional STEM-HAADF images together with corresponding electron diffraction patterns showing the microstructure of $(\text{Ti}_{0.70}\text{Al}_{0.30})\text{B}_{3.22}$ film (position D). Cross-sectional high-resolution STEM-HAADF images together with selective area electron diffraction patterns showing the lattice plane orientation in the $(\text{Ti}_{0.70}\text{Al}_{0.30})\text{B}_{3.22}$ film close to film-substrate interface (c) and near the film top surface (d).

Fig. 6 Nanoindentation maps of the variation in (a) hardness and (b) reduced elastic modulus across the Ti-Al-B coating deposited on an Al_2O_3 wafer; (c) and (d) visualize the data dispersion for the hardness and elastic modulus values, respectively, in each analyzed area. Larger data dispersion on H most likely originates from the formation of conical domains observed in TEM (see Fig. 2a and 3). The position of the TiB_2 and AlB_2 targets relative to the wafer during the deposition as well as the mapped area are indicated in the inset in Fig. 1.