Microstructure and Materials Properties of Understoichiometric TiB\textsubscript{x} Thin Films Grown by HiPIMS

Jimmy Thörnberg,\textsuperscript{a} Justinas Palisaitis,\textsuperscript{a} Niklas Hellgren,\textsuperscript{b} Fedor F. Klimashin,\textsuperscript{a} Naureen Ghafoor,\textsuperscript{a} Igor Zhirkov,\textsuperscript{a} Clio Azina,\textsuperscript{a} Jean-Luc Battaglia,\textsuperscript{c} Andrzej Kusiak,\textsuperscript{c} Maurico A. Sorica,\textsuperscript{d} J.E. Greene,\textsuperscript{a,e,f} Lars Hultman,\textsuperscript{a} Ivan Petrov,\textsuperscript{a,e,f} Per O.Å. Persson,\textsuperscript{a} and Johanna Rosen \textsuperscript{a}

\textsuperscript{a} Thin Film Physics Division, Department of Physics (IFM), Linköping University, SE-581 83 Linköping, Sweden
\textsuperscript{b} Department of Computing, Mathematics, and Physics, Messiah University, Mechanicsburg, PA 17055, USA
\textsuperscript{c} CNRS, University of Bordeaux, I2M, UMR 5295, F-33400 Talence, France
\textsuperscript{d} Department of Physics and Astronomy, Uppsala University, Box 516, SE-75120 Uppsala, Sweden
\textsuperscript{e} Frederick Seitz Materials Research Laboratory and Department of Material Science, University of Illinois, Urbana, Illinois 61801, USA
\textsuperscript{f} Materials Science and Engineering Department, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

Abstract

TiB\textsubscript{x} thin films with a B content of 1.43 ≤ \(x\) ≤ 2.70 were synthesized using high-power impulse magnetron sputtering (HiPIMS) in comparison to direct-current magnetron sputtering (DCMS). HiPIMS allows compositions ranging from understoichiometric to overstoichiometric dense TiB\textsubscript{x} thin films with a B/Ti ratio between 1.43 and 2.06, while DCMS yields overstoichiometric TiB\textsubscript{x} films with a B/Ti ratio ranging from 2.20 to 2.70. Excess B in overstoichiometric TiB\textsubscript{x} thin films from DCMS results in a hardness up to 37.7±0.8 GPa, attributed to the formation of an amorphous B-rich tissue phase separating stoichiometric TiB\textsubscript{2} columnar structures. We furthermore show that understoichiometric TiB\textsubscript{1.43} thin films synthesized by HiPIMS exhibit a superior hardness of 43.9±0.9 GPa, where the deficiency of B is found to be accommodated by Ti-enriched planar defects.
The apparent fracture toughness and thermal conductivity of HiPIMS films with a B/Ti ratio of 1.43, are 4.2±0.1 MPa\(\sqrt{\text{m}}\) and 5.1 W/(m.K), respectively, as compared to corresponding values for overstoichiometric TiB\(_{2.20}\) DCMS thin film samples of 3.2±0.1 MPa\(\sqrt{\text{m}}\) and 3.0 W/(m.K). This work increases the fundamental understanding of understoichiometric TiB\(_x\) thin films and their materials properties, and show that understoichiometric films have properties matching or going beyond those with excess B.

*Keywords: Borides; HiPIMS; Titanium; Mechanical Properties; Microstructure*

1. Introduction

Titanium diboride, TiB\(_2\), is one of the more thoroughly investigated transition-metal diborides to date. This hard ceramic has attractive properties motivating this interest,[1-3] including high thermal and electrical conductivity,[4] good thermal and chemical stability[5] as well as good oxidation and mechanical erosion resistance.[6-8] While the most common method to grow TiB\(_2\) is direct-current magnetron sputtering from compound targets, several reports show other approaches in choice of synthesis, including electroplating, arc-PVD, pulsed DCMS, RF-sputtering, and HiPIMS. [9-16] DCMS typically produce over-stoichiometric material, with a B/Ti ratio in the range of 2.4 to 3.5. Previous work has shown that the excess B in these TiB\(_2\) films move towards grain boundaries and form nanostructures, a mechanism that is well described.[17, 18] Essentially, excess B forms an amorphous B-rich tissue-phase in between the nanocolumnar morphology of TiB\(_2\). The structure, in turn, prevents propagation of dislocations across columns from occurring, which increases the hardness of the TiB\(_x\) thin film. Few reports present understoichiometric TiB\(_x\) thin films.[16, 19, 20]
An emerging method for TiB$_2$ growth is HiPIMS.[16, 19-21] In contrast to TiB$_x$ thin films grown with DCMS, reports indicate that TiB$_x$ films grown with HiPIMS realize understoichiometrical compositions. The mechanism for this behavior has not yet been addressed, with limited investigation of resulting mechanical properties. M.N. Polyakov et. al.[20] demonstrate hardness of HiPIMS-grown TiB$_x$ thin films with B/Ti ratio of 1.62 to 1.97 in the range of 39-45 GPa, and attribute this to film densification. Also, explanation is lacking in literature on how the B deficiency is accommodated in the lattice of understoichiometric TiB$_x$ films. To ameliorate this, we here investigate the effect of gas pressure on HiPIMS and DCMS ion flux, atomic structure, microstructure, and expand on the properties of over- and understoichiometric TiB$_x$ films grown with HiPIMS and compare with corresponding DCMS grown films.

2. Experimental Details

The TiB$_x$ thin films with $1.44 \leq x \leq 2.70$ are grown using HiPIMS and DCMS with a 3.0’’ x 0.125’’ (99.5% purity) TiB$_2$ target (Kurt J. Lesker Co.) in an ultrahigh vacuum (UHV) system with a base pressure of $7 \times 10^{-8}$ mTorr on sapphire (001) substrates with a TiN buffer layer. The substrates were ultrasonically cleaned in acetone and isopropanol for 10 min respectively then blow dried in N$_2$. 45 and 90 nm TiN buffer films, used for increased adhesion between the substrate and the TiB$_x$ films, were deposited using DCMS with a pure Ti target (99.995% purity) with Ar and N gas, both 99.9999% pure, introduced through mass flow controllers to partial pressures of 2.75 and 0.25 mTorr, respectively. Substrate temperature was kept at 670 °C with a floating bias and a target power fixed at 185 W during buffer layer deposition. TiB$_2$ films, approximately 1 μm thick, where grown
by HiPIMS and DCMS in pure Ar at 5 mTorr and 20 mTorr at substrate temperature of 500 °C.

In-situ mass- and energy-spectroscopy analyses of ion fluxes generated in HiPIMS and DCMS were performed using a Hiden Analytical EQP1000 instrument placed at 15 cm from the target surface. In both cases, the diagnostic was done in the time-averaged mode of the analyzer,[22] i.e. the data acquisition time window of the analyzer at each measurement point (10 ms) was set the same for both HiPIMS and DCMS.[23] For each of the studied here operational conditions, the generated plasma was characterized through mass-scans at fixed ion energy and energy-scans at fixed mass-to-charge ratio for all detected ions. The energy scans were recorded in steps of 0.5 eV/charge up to 50 eV. Each scan was recorded at least three times to ensure consistency of the data. To determine the plasma composition, total intensities of the elements were calculated as sums of intensities of corresponding ions on all steps of the measurement. All values presented are repeatable with an error of 5 %. The natural isotope distribution of the elements was taken into account in line with Ref.[24]

X-ray diffraction (XRD) 0–20 scans on the thin film samples were performed using a PANalytical X'Pert powder diffractometer, with Cu source (λ = 1.54 Å). The optics utilized for these measurements were a graded Bragg–Brentano HD with ½° divergent and ½° antiscatter slits for the incident beam side, and a 5 mm antiscatter slit together with a Soller slit for the diffracted beam side. A 5-120° continuous scan was performed on the sample using a step size of 0.016° with 10 s time per step.

Film compositional and structural analysis was done with a scanning electron microscope (SEM) LEO 1550 Gemini equipped with an Oxford Instruments energy-dispersive X-ray (EDX) detector operating with an acceleration voltage between 5-15 keV, time-of-flight
elastic recoil detection analysis (ToF-ERDA), with a 36 MeV $^{127}$I$^{+8}$ beam incident at 67.5° to the sample normal with a recoil angle of 45°, and Rutherford backscattering spectrometry (RBS) with a 2 MeV $^4$He$^+$ beam incident at 5° with a scattering angle of 170°.[13-15] The two latter analyses were carried out at the Tandem Laboratory at Uppsala University.

High-resolution scanning transmission electron microscopy (HRSTEM) imaging and selective area electron diffraction (SAED) was used to determine the atomic structure, and to further verify the composition and crystallographic relations of the film. Microscopy was performed using the Linköping double corrected FEI Titan™ 60-300 equipped operated at 300 kV. STEM high angle annular dark field (STEM-HAADF) imaging was performed by using a 21.5 mrad convergence semi-angle, which provided sub-Ångstrom resolution probes with ~ 60 pA beam current and using an angular detection range of 46-200 mrad.

Mechanical properties of the films were studied with the aid of a Hysitron TI 950 nanoindenter system and an ultra-micro indentation system (UMIS). To investigate the indentation hardness, $H$, and combined elastic modulus of the contacting bodies, $E^*$, every sample was subjected to 90 indentations with a Berkovich diamond tip within the load range of 0.1–13 mN. The $H$ and $E^*$ values were obtained by evaluating the load–displacement curves by means of the Oliver and Pharr method.[25] Subsequently, the elastic modulus of the films, $E$, was calculated assuming a Poisson’s ratio, $\nu$, of 0.15.[26, 27] Given the impact of the stoichiometry on the elastic constants of TiB$_x$, the upper and lower limits of $E$ were calculated for a Poisson’s ratios of 0.1 and 0.3, respectively.[28, 29] After plotting $H$ and $E$ values as a function of penetration depth, only $H$ values from a fully developed plastic zone and yet unaffected by the substrate were considered film-
only hardness, while a smooth curve was fitted to the $E$ values and subsequently extrapolated back to zero depth to obtain film-only elastic modulus.[30]

A qualitative analysis of the fracture behavior of the system film/substrate was carried out by means of nanoindentation utilising UMIS equipped with a cube-corner indenter tip. The applied load, $P$, was varied within the range 5–300 mN, incremented in steps 10 mN within the load range 10–50 mN and in steps 50 mN within the load range 50–300 mN. By examining the imprints with the aid of an SEM and measuring the average crack length, $c$, – for an applied load – the apparent fracture toughness of the system film/substrate, $K_C$, can be evaluated as follows:

$$ K_C = \alpha \cdot \sqrt{\frac{E}{H}} \cdot \frac{P}{c^{3/2}}, $$

(1)

where $\alpha$ is an empirical calibration constant taken for 0.036.[31] To achieve a statistical distribution of $K_C$, five indents were made at every load. After plotting $K_C$ values as a function of penetration depth, a linear fit to the data points was extrapolated back to 1/10 of the film thickness to minimise any substrate effect.[32]

The electrical resistivities of the TiB$_x$ samples, with the TiN buffer layer, were obtained by measuring the sheet resistance with a four-point probe (Jandel RM3000). The effective resistivity of the TiB$_x$ layer was obtained using the following equation[33]:

$$ \rho_{\text{eff}} = (e_{TiN} + e_{TiBx}) \frac{\rho_{TiN} \rho_{TiBx}}{e_{TiN} \rho_{TiBx} + e_{TiBx} \rho_{TiN}} $$

(2)

The electrical resistivity of a TiN film of 45 nm deposited on Al$_2$O$_3$ was also measured for reference.

Thermal characterization of the TiB$_2$ films was performed using a modulated photothermal radiometry (MPTR) setup, used and previously reported in Refs. [34, 35].
The laser beam was modulated in frequency in the 0.7 to 5 kHz range and was focused at the surface of the films by an appropriate optical path. The films are capped with a platinum layer of approximately 100 nm which acts as the optical-to-thermal transducer. The infrared (IR) radiation from the heated surface is collected by two parabolic mirrors and focused at the sensitive element of an IR detector. The phase between the reference excitation and the measured signal from the detector is measured using a lock-in amplifier. The equivalent thermal conductivity accounting for the TiB_x film and the film-substrate interface is then identified by minimizing the quadratic gap between the measured phase and that calculated from the model that describes the heat diffusion within the sample in the experimental configuration. The heat diffusion model is based on the heat diffusion within the layer and the substrate, assuming isotropic properties for both materials. The model requires knowing the heat capacity per unit volume of the layer and the thermal properties of the substrate. The minimization is achieved by using the Levenberg-Marquardt algorithm.

3. Results and Discussion

The elemental composition of the films determined by ToF-ERDA is given in Tab. 1; the composition is henceforth used for sample notation. The residual gas contamination for the DCMS and HiPIMS thin films were also measured displaying similar impurity of roughly 0.5±0.1% for N, O and C. The composition of the thin films deposited with DCMS was TiB_{2.70} and TiB_{2.20} for a deposition pressure of 5 mTorr, and 20 mTorr, respectively. This overstoichiometry is consistent with previous reports on TiB_x thin films from DCMS.[17, 18] Furthermore, the reduced B content with increasing pressure is in line with previous work,[36] suggesting B transported preferentially along the target
normal and Ti having a wider distribution angle at lower pressure, and with an increased B scattering with increased pressure reducing the overstoichiometry.[36]

The films deposited with HiPIMS have composition TiB$_{1.43}$ and TiB$_{2.06}$ for a pressure of 5 mTorr and 20 mTorr, respectively. The reasons for this drastic reduction in B content compared to DCMS are discussed in Ref.[19]; While in DC mode the deposition flux is mostly neutral, in HIPIIMS the ionization of the sputtered flux is higher and strongly affects the gas phase transport. Ti has a lower ionization potential of 6.82 eV compared to B, 8.30 eV, and is thus ionized to larger fraction, leading to a reduced B/Ti ratio in the HIPIIMS deposited films; The Ti ions which leave the target area are steered towards the substrate by the plasma focusing action of the stray magnetic field of the outer magnetic pole. The B content in the HIPIIMS films increases with increasing pressure, which is the opposite trend compared to DCMS. This is consistent with plasma characterization and the integrated ion flux, showing that as the pressure increases, both the Ti and B ion flux decrease, though the Ti flux at a faster rate. The total deposition flux of Ti and B is also reduced for HiPIMS, compared to DCMS,[19] see Tab. 2. Going from DCMS to HiPIMS is also accompanied by an increase in film density, measured using areal density from RBS and film thickness from cross-sectional SEM, from 3.5-3.7 to 4.3-4.5 g/cm$^3$, where the latter is close to the TiB$_2$ bulk density of 4.5 g/cm$^3$.[4] This suggests that 1) more energy is provided in the HiPIMS depositions, facilitating film densification and 2) the Ti is separated from the diboride phase in some form and therefore, density is increased.

All films studied here are approximately of the same thickness, around 1 µm, as measured with cross-sectional SEM.

Previous reports on understoichiometric TiB$_x$ thin films from HiPIMS claim compositions in the range of $x = 1.4$-2.4, $x = 1.83$-2.08 and $x = 1.62$-1.97 as measured by
Hellgren et. al.,[19] Bakhit et. al.,[16] and M.N. Polyakov et. al.,[20] respectively. Those findings are comparable to our films, where we find compositions ranging from under-stoichiometric TiB$_{1.43}$, to stoichiometric TiB$_{2.06}$.

XRD θ-2θ diffractograms are shown in Fig. 1. All curves display TiB$_2$ peaks with the addition of the TiN(111) buffer and Al$_2$O$_3$ substrate peaks. No competing Ti-B phases such as Ti$_2$B$_3$, TiB or pure Ti are visible. Diffraction from TiB$_2$(001) and (002) peaks can be seen in all films, very pronounced in the DCMS deposited samples, in particular for TiB$_{2.20}$ (20 mTorr). The DCMS TiB$_{2.70}$ film (5 mTorr) also shows (100) and (101) peaks, indicating mixed texture at lower pressure. The HiPIMS films, TiB$_{1.43}$ (5 mTorr) and TiB$_{2.06}$ (20 mTorr), show the opposite trend with the TiB$_{1.43}$ film exhibiting strong (001) texture.

The XRD results are compared to cross section view through SEM, Fig. 2. All films show signs of columnar structure extending throughout the film thickness. The column size increases as pressure increases in DCMS, a)-b), and in HiPIMS, c)-d). A change in microstructure might be due to growth conditions, possibly including a change in composition. TiB$_2$ is a line compound and as such favors formation of stoichiometric TiB$_2$. When the B content significantly exceeds the B/Ti > 2 the TiB$_x$ film develops a nanocolumnar structure encapsulated in excess B so as to form a B tissue phase.[17, 18]

The DCMS films both exhibit a columnar structure with the largest ones for TiB$_{2.20}$. In the HiPIMS thin films, TiB$_{1.43}$ and TiB$_{2.06}$, the foremost shows a dense structure of TiB$_2$ phase, whilst the latter displays a coarser columnar structure, see Fig. 2. The two thin films closer to stoichiometry have larger columns size, while the strongly over- and understoichiometric have finer columns. For the understoichiometric films, the XRD data
show no indication of secondary phase precipitation like Ti crystallites to balance the stoichiometry. The whereabouts of the Ti-enrichment thus requires more detailed analysis, here specifically HRSTEM imaging, as presented below.

The two thin films grown by HiPIMS, TiB\textsubscript{1.43} and TiB\textsubscript{2.06}, were investigated by plan-view STEM, and the results are shown in Fig. 3 a)-c) and d)-e), respectively. From the overview images, it is clear that both thin films exhibit a similar structure with column widths of the order of ~50 nm. The local increased contrast originates from grains, which are oriented with their (001) zone axis along the electron beam. Under such condition the electron probe channels very strongly along the atomic columns, which together with thermal diffused scattering results in increased intensity at the annular detector, overwhelming the atomic number contrast imaging.[37-39] The grains deviating from the zone axis appear dark. At higher magnifications apparent differences can be found between two samples. The most striking difference is the presence of a tissue phase between the dendritic/fractal-like columns in the TiB\textsubscript{2.06} thin film, while the structure is dense and free from any tissue phase for the TiB\textsubscript{1.43} thin film. The latter on the other hand unveil cloud-like striations inside the columns, which at high magnification appear to be a high density of stacking faults, see Fig. 3 c). These striations were further investigated by HR-STEM methods on a TiB\textsubscript{1.44} thin film deposited using the same experimental setup though with an elevated temperature, HiPIMS at 900 °C at 20 mTorr, owing to a higher crystalline quality with fewer stacking faults causing image distortions. The results are shown in Fig. 4 and with a more detailed investigation of the stacking faults presented in Ref. [40]. The STEM image in Fig. 4 presents the core of a column, viewed on-axis, e.g., parallel to the <001> direction. The structure clearly exhibits a hexagonal appearance, however, stacking faults on the prismatic planes are visible throughout the grain. The
stacking faults make up an intricate pattern, but remains fixed to the (1-100) prismatic planes of the TiB₂ crystal structure. Further, it was found that stacking faults are deficient in B and rich in Ti, as judged from the elemental contrast in Fig. 4. The presence of such stacking faults thus serves to accommodate B deficiency in the bulk of the crystals. The inset in Fig. 3 a) and Fig. 4 shows an SAED and Fast Fourier Transform (FFT) patterns, respectively, from the TiB₁.₄₃ and TiB₁.₄₄ (900 °C) thin films, which indicates the predominantly polycrystalline with <001> texture, in agreement with XRD, Fig. 1. SAED from the TiB₂.₀₆ thin film, see inset Fig. 3 d), shows additional rings indicating off c-axis contributions to the coatings texture in agreement with XRD, see Fig. 1.

Fig. 5 shows an evaluation of the mechanical properties. The hardness, \( H \), of TiB₁.₄₃ is highest at 43.₉±₀.₉ GPa followed by TiB₂.₀₆ at 40.₇±₁.₅ GPa, both deposited using HiPIMS. This is on par with the highest reported hardness of understoichiometric TiBₓ thin films.[20] The DCMS films TiB₂.₂₀ and TiB₂.₇₀ decrease from 37.₇±₀.₈ GPa to 22.₃±₀.₆ GPa, respectively. The increase in \( H \) for TiB₁.₄₃ can be attributed to smaller grain size, as seen in Fig. 2, high mass density, and the high concentration of Ti stacking faults acting like barriers for dislocation glide. The \( H \) for the TiB₁.₄₄ sample deposited at 900 °C, only used for TEM analysis, was measured at 38.₇±₀.₉ GPa.

The elastic modulus, \( E \), of respective film can be seen in Fig. 5 a). The trend shows a slight increase in \( E \) going from understoichiometric, TiB₁.₄₃ at 5₁₁±₁₀ GPa, to stoichiometric, TiB₂.₀₆ at 5₄₁±₁₈ GPa, followed by a steady decrease of \( E \) as B content rises to TiB₂.₂₀ at 5₀₈±₆ GPa and TiB₂.₇₀ at 3₉₃±₅ GPa. Evidently \( E \) adheres to the same trend as \( H \), suggesting that the growing volume fraction of the B tissue phase around the TiB₂ grains could be one of the reasons for reduced mechanical properties in overstoichiometric TiBₓ films.
The TiB\textsubscript{1.43} and TiB\textsubscript{2.06} films exhibit the highest resistance to crack propagation with the apparent fracture toughness, $K_C$, calculated to be 4.2±0.1 MPa√m and 3.2±0.1 MPa√m, respectively, shortly followed by TiB\textsubscript{2.20} at 3.2±0.1 MPa√m, see Fig. 5 a). Each clearly outperform the TiB\textsubscript{2.70} film showing $K_C$ of 2.0±0.1 MPa√m. The dependence of the apparent fracture toughness, that is, resistance to crack propagation, on the stoichiometry of the TiB\textsubscript{x} films is visually emphasized by the SEM top-view images of the residual imprints in the corresponding samples, see Fig. 5 b). The images show well-defined indents with pile-up for all samples, except for the DCMS TiB\textsubscript{2.70} sample in which there is material collapse in a brittle manner. Cracks are seen generated at the triangle corners, extensively so for the two DCMS films and least for the HiPIMS TiB\textsubscript{1.43} case. Pile-up behavior attest plastic deformation operating. The very limited cracking and the clear plastic appearance of indents in the understoichiometric HiPIMS films, is thus evidence of toughness quality.

The electrical resistivities of the TiB\textsubscript{x} thin films are given in Tab. 3. The electrical resistivity of the TiN adhesion layer was 31.5±0.4 μΩ·cm, a typical value for PVD films, yet higher than bulk and single-crystal films at ~20 μΩ·cm.[41] The TiB\textsubscript{x} thin film values obtained, 367±7 and 309±4 μΩ·cm for TiB\textsubscript{1.43} and TiB\textsubscript{2.70} respectively, are also higher than those encountered for single crystal bulk samples (~15 μΩ·cm),[42] however they are in the same range as the values reported for e-beam evaporation and RF sputtered thin films (267 and 230 – 330 μΩ·cm, respectively).[43, 44] The stoichiometric TiB\textsubscript{2.06} film has the lowest resistivity which can be attributed to the lack of amorphous B-rich tissue phase, which is also in accordance with Shutou et al.[44] The resistivity is more than 2.3 times larger for both the over-stoichiometric and under-stoichiometric films. The densities of each films were deduced through RBS and cross-sectional SEM and were
multiplied by the specific heat of stoichiometric TiB$_2$ (617 J/g.K), taken from the literature.[4]

The phase of the thermal IR response obtained for the TiB$_x$ films are given as a function of frequency for the different B/Ti ratios and are shown in Fig. 6. The equivalent thermal conductivity of each film is identified from the measured phase and are reported in Tab. 3, 2.43±0.23 and 4.60±0.22 W/(m.K) for TiB$_{1.43}$ and TiB$_{2.70}$ respectively. The thermal conductivities of the films are fairly similar and in the same range of magnitude. The lowest thermal conductivity is obtained for TiB$_{1.43}$. Although this film exhibits the highest density, the stacking faults observed may cause high mass defect scattering, which directly affects the thermal conductivity of the film. On the other hand, TiB$_{2.06}$ has the highest thermal conductivity, which can be related to the near-stoichiometric composition of the film. Finally, the thermal conductivities of TiB$_{2.20}$ and TiB$_{2.70}$ samples (both DCMS ones) are slightly lower than TiB$_{2.06}$ which is mostly related to their lower density and microstructure.

4. Conclusions

High-power impulse magnetron sputtering (HiPIMS) paves the way for a control of the stoichiometry of TiB$_x$ thin films. TiB$_x$ thin films with a B content of 1.43 ≤ x ≤ 2.70 were synthesized using HiPIMS and DCMS. HiPIMS yields dense films with a B/Ti ratio between 1.43 and 2.06, while DCMS yields overstoichiometric TiB$_x$ with a B/Ti ratio ranging from 2.20 to 2.70. For both methods and pressures used, 5 and 20 mTorr, the TiB$_x$ thin films showed a nanocolumnar TiB$_2$ structure. The excess B in the overstoichiometric TiB$_x$ thin films was located the grain boundaries as a B-rich tissue phase, while the only understoichiometric films, deposited with HiPIMS at 5 mTorr, show
no visible boundary phases. Instead we identified tightly packed TiB$_2$ nanocolumnar structures with planar defects of Ti-enriched stacking faults, accommodating the B deficiency. The understoichiometric TiB$_{1.43}$ thin film showed a hardness of 43.9±0.9 GPa, an elastic modulus of 511±10 GPa, a fracture toughness of 4.2±0.1 MPa$\sqrt{m}$, electrical resistivity of 367±7 $\mu\Omega\cdot$cm and a thermal conductivity of 5.1 W/(m.K), all values exceeding those obtained for the overstoichiometric thin films.

5. Conflicts of interest

There are no conflicts to declare.

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8. Images:

Table 1 – Samples used with their respective notation, method, pressure, growth temperature, B/Ti ratio (from ERDA), and density (areal density from ERDA and film thickness from cross-view SEM). *TiB$_{1.44}$ was only used for the on-axis HRTEM.

| Sample  | Method | Pressure [mTorr] | Temperature [$^\circ$C] | B/Ti ratio (from ERDA) | Density [g/cm$^3$] |
|---------|--------|-----------------|-------------------------|------------------------|-------------------|
| TiB$_{2.70}$ | DCMS | 5 | 500 | 2.70 | 3.7 |
| TiB$_{2.20}$ | DCMS | 20 | 500 | 2.20 | 3.5 |
| TiB$_{1.43}$ | HiPIMS | 5 | 500 | 1.43 | 4.5 |
| TiB$_{2.06}$ | HiPIMS | 20 | 500 | 2.06 | 4.3 |
| TiB$_{1.44}$* | HiPIMS | 20 | 900 | 1.44 | - |

Table 2 – In-situ mass- and energy-spectroscopy analyses of Ti, Ar and B ion fluxes generated in HiPIMS and DCMS at 3 and 20 mTorr.

| Mode | Pressure [mTorr] | Ar counts $[10^7]$ | Ti counts $[10^7]$ | B counts $[10^7]$ | B/Ti [%] |
|------|-----------------|--------------------|-------------------|-----------------|---------|
| DCMS | 3               | 3.40               | 0.31              | 0.037           | 10.6    |
|      | 20              | 1.74               | 0.27              | 0.024           | 8.0     |
| HiPIMS | 3               | 3.20               | 1.90              | 0.470           | 19.8    |
|      | 20              | 4.70               | 1.00              | 0.270           | 21.5    |
Figure 1 – Full range θ-2θ XRD pattern of four TiB, films grown with HiPIMS and DCMS at varying pressures, deposited on Al₂O₃ substrates with 90 nm TiN buffer layer grown with DCMS with Ar and N pressures of 2.75 and 0.25 mTorr, respectively. Substrate and TiN peaks are denoted in the legend.

Figure 2 – Cross-sectional SEM images acquired from a) TiB₂.₇₀ (DCMS 5mTorr), b) TiB₂.₂₀ (DCMS 20mTorr), c) TiB₁.₄₃ (HiPIMS 5mTorr) and d) TiB₂.₀₆ (HiPIMS 20mTorr). Showing larger columnar structures for the 20 mTorr thin films.
Figure 3 – Plan-view STEM images acquired from TiB\text{1.43} (5 mTorr) and TiB\text{2.06} (20 mTorr) thin films grown with HiPIMS, showing a)-c) a densely columnar structure and d)-f) columnar structure with B-tissue phase boundaries, presented as darker regions between grains, respectively. Insets in a) and d) shows corresponding SAED patterns from the films.
Figure 4 – Plan-view HRSTEM images acquired from TiB$_{1.44}$ (HiPIMS 900 °C in 20 mTorr), revealing Ti-enriched stacking planar faults in the core of the columns. The inset shows the corresponding FFT pattern from a larger area.

Figure 5 – a) Hardness, H, Elasticity, E, and apparent fracture toughness, $K_c$, as a function of the B/Ti ratio with b) top-view SEM images of the residual imprints after an indentation with a cube-corner indenter tip at $P = 10$ mN (resulted in penetration depths of 190–270 nm). Arrows indicate end-points for cracks generated by the indentation.
Table 3 – Electrical resistivity measured using the four-point probe Jandel RM3000 and thermal conductivities identified using the phase measured by MPTR of the TiBₓ thin films.

| Ti/B ratio (ERDA) | Density (g/cm³) | Electrical resistivity (μΩ·cm) | ρCp (J/cm³·K) | Equivalent thermal conductivity (W/m.K) 2D model |
|------------------|----------------|-------------------------------|---------------|------------------------------------------|
| TiB₁.₄₃          | 4.5            | 367±7                         | 2.9616        | 2.43±0.23                                |
| TiB₂.₀₆          | 4.3            | 133±7                         | 2.6531        | 5.49±0.61                                |
| TiB₂.₂₀          | 3.5            | 309±4                         | 2.1595        | 3.23±0.41                                |
| TiB₂.₇₀          | 3.7            | 413±8                         | 2.2829        | 4.60±0.22                                |

Figure 6 – Phase lag of the thermal response of the TiBₓ films with respect to the different B/Ti ratios.