Co-sputtered TiBx Thin Films

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Co-sputtered TiB_x thin films

Alex Sredenschek

Messiah College, Department of Mathematics, Physics, and Statistics; One College Avenue, Mechanicsburg, Pennsylvania 17055

ABSTRACT

Titanium diboride (TiB_2) is a ceramic material that has attracted considerable interest due to its distinctive set of properties, such as high melting point and hardness, good thermal and electrical conductivity, as well as excellent corrosion resistance. In some applications, thin coatings of TiB_2 may be desired, and one way to obtain such coatings is through the growth of thin films. One common growth technique is magnetron sputtering. However, when films are grown by magnetron-sputtering from a single TiB_2 target, differences in preferred ejection angles and gas-phase scattering yield B-rich TiB_x films with x typically ranging from 2.5 to 3.5. In this research, we seek to investigate a potential solution to this problem by co-sputtering TiB_x films from Ti and TiB_2 targets. By varying the Ti target power from 0 to 100 W while keeping the TiB_2 power constant at 250W, the Ti concentration could be independently controlled from x ≈ 1.4 to 2.8. X-ray diffraction shows B-rich films have (100) and (101) TiB_2 crystalline structure, and Ti-rich films are amorphous. Atomic force microscopy analysis shows smooth TiB_x films (rms roughness between 0.96 nm and 2.0 nm) with lateral surface feature size between 23 nm and 45 nm.
I. INTRODUCTION

Titanium diboride (TiB$_2$) is a ceramic that has attracted considerable interest due to its distinctive set of properties, such as high melting point (3500 K), hardness (25 GPa at 20 °C), good thermal conductivity (96 Wm$^{-1}$K$^{-1}$ at 20 °C), and excellent corrosion resistance.\textsuperscript{1,2} It has a hexagonal unit cell with space group P6/mmm as shown in Figure 1. Boron atoms are arranged in a hexagonal lattice, and titanium atoms are centered on these hexagonal structures located 1/2 the c-axis above the boron atoms. Applications of TiB$_2$ include resistant wear-coatings on cutting tools, crucibles, and corrosive-resistant coatings, due to the ceramic’s high melting point and high hardness.\textsuperscript{1,3,10,11} Recent research has also investigated TiB$_2$ for chemical applications in the reduction of aluminum.\textsuperscript{1,3} The fabrication of bulk TiB$_2$ is challenged by its strong intermolecular bonding which yields low self-diffusion rates and a strong temperature dependence of grain growth. These factors, combined with the anisotropy of the hexagonal grain structure, result in internal crystalline stresses and microcracking during cooling.\textsuperscript{1} For some applications, thin coatings of TiB$_2$ are desired. Therefore, an active area of research in materials science, physics, and chemistry is the study of thin films.

\textsuperscript{4}Figure 1a: Sketch of hexagonal lattice for TiB$_2$. The c-axis is perpendicular to the page. (b) Cross section view of TiB$_2$. Ti atoms are 1/2 the c-axis above and below the hexagonal boron network.
Thin films form a class of materials that are characterized by their thickness, which typically range from a few atomic layers to several micrometers in thickness. Owing to their thickness, thin films often exhibit different properties compared to their bulk counterparts, and as such researchers have taken the task of cataloguing these properties. Thin films are typically produced by two major classes of techniques; chemical vapor deposition (CVD) and physical vapor deposition (PVD). CVD utilizes decomposition processes of molecular precursors to grow films, while PVD processes utilize methods such as evaporation or “sputtering,” to transfer species from the solid to gas phase, whereafter they are made to condense onto a substrate to form the film.

The most common growth technique for TiB$_2$ thin films is the PVD technique direct-current (DC) magnetron sputtering, which will be discussed in more detail in the experimental section.$^{5-12}$ TiB$_2$ thin films have been reported to exhibit even higher hardness ($50$ GPa)$^8$ than their bulk counterparts ($25$ GPa)$^1$ and are of particular interest to researchers. Sputtering from a stoichiometric TiB$_2$ compound target at low Ar pressure, however, commonly results in overstoichiometric TiB$_x$ films, with $x$ between 2.5 and 3.5 $^{10-12}$, while higher pressures result in closer to stoichiometric ratios.

Neidhardt et al. explained the mechanisms leading to Ti-rich TiB$_x$ films; due to the large mass difference among Ar$^+$ ions and the TiB$_2$ target species, B is ejected preferentially along the target normal while Ti atoms angular ejection extends toward larger angles. Increasing the sputtering pressure and/or the target-to-substrate distance reduces the Ti deficiency due to higher gas-phase scattering of lighter B atoms.$^{11}$ Petrov et al. demonstrated a method to increase the Ti-incorporation in sputtered TiB$_x$ thin films; Ti atoms are selectively ionized due to their lower ionization potential, and the Ti$^+$ ions are steered to the growing film via a tunable external
Helmholtz coil, which provide control of the B/Ti ratio.\textsuperscript{10} To successfully tune this B/Ti ratio through changes in plasma characteristics, Petrov and Neidhart both grew TiB\textsubscript{x} films from a single TiB\textsubscript{2} target; co-sputtering has not been investigated as a solution to the Ti deficiency.

In this research, we investigate an alternative approach to tune the B/Ti ratio in TiB\textsubscript{x} films via DC magnetron co-sputtering from Ti and TiB\textsubscript{2} targets. We keep the TiB\textsubscript{2} target power constant at 250 W, and vary the Ti power from 0 W to 100 W in 25 W increments, to control the B/Ti ratio and study the effects of these parameters on film composition and properties.

\section{EXPERIMENTAL DETAILS}

\subsection{Magnetron sputtering}

Magnetron sputtering is a common physical vapor deposition (PVD) process used to produce thin films. A schematic diagram of the sputtering system is shown in Figure 2. In this technique, a vacuum chamber (a) is evacuated to high- or ultrahigh-vacuum, after which a process gas (in this case, Ar) is introduced to a typical process pressure in the range 1 to 50 mTorr (e). A disk (“target”) of the desired deposition material (c) is attached to a “magnetron” (b); a negative potential (typically -300 to -600 V, depending on process gas and pressure) is applied to the target (d); the electric field ionizes the process gas, and, due to strong permanent magnets in the magnetron, secondary electrons are trapped in a circular path and a sustained glow-discharge plasma is formed over the target (f). The negative target potential accelerates Ar\textsuperscript{+} ions towards the target and breaks, or “sputters”, target atoms away (g), ejecting them towards the substrate (h) where they condense to form the film (i). To promote dense films, a negative bias potential (j) may be applied to the substrate to attract positively-charged ions to the substrate. To promote the
growth of crystalline films, a heater (k) can be used to heat the substrate; thermal energy allows for higher diffusion rates of Ti and B on the growth surface.

![Figure 2: Schematic of a DC magnetron co-sputtering system. Ti and TiB₂ targets are shown on magnetrons. An argon plasma forms over the targets and produces vaporized target species that condense on the substrate to](image)

Tunable parameters in magnetron sputtering include process gas type and pressure, applied target power, substrate temperature and bias voltage, magnetic field configuration, and system geometry (e.g., substrate-target distance and magnetron position).

An increase in target power increases sputtered-target-atom flux and may increase deposition rate. Applying a substrate bias has a similar effect, but rather than controlling the energy by gas-phase collisions, a negative substrate bias will accelerate positive Ar⁺ ions as well as sputtered target ions towards the substrate and thereby densify the film. Similarly, a positive bias will repel target ions from the substrate, yielding rough and porous films.

The process gas pressure and target-substrate distance affect deposition rates and film density. Films grown under a high pressure and a large target-to-substrate distance tend to be more porous, since the deposition species arrive at the substrate with low energies due to excessive gas
scattering. On the other hand, low pressures and short target-substrate distances result in high energy collisions between target species and the substrate which promotes the growth of dense films. However, the risk is that the high-energy ion bombardment results in more crystallographic defects in the film.

Increased substrate temperature promotes crystalline structure evolution in films. Elevated thermal energy enables incident sputtered atoms to migrate along the growth surface to find lower-energy, crystalline states and will promote homogenous crystalline or polycrystalline phase formation, as opposed to amorphous films.

Structural evolution in thin films is determined by surface energetics and kinetics of adatoms—adsorbed species on the substrate and underlying film layers. Figure 3a illustrates a typical evolution of a polycrystalline thin film. As sputtered species condense on the substrate, they will nucleate and begin to form clusters of atoms called islands. Often, the islands have different crystallographic orientations or structures, and grain boundaries for between them as they grow. The grain boundaries may shift during and after island formation which is driven by energetics at island boundaries and island surfaces. Islands with lower energy per atom will dominate as the system seeks to minimize the surface energy. Coarsening—grain boundary-driven recrystallization—drives formation of preferential orientation and typically yields planes the densest planes: (0002) for hexagonal closest packed (hcp), (111) for face-centered cubic (fcc), and (110) for body-centered cubic (bcc). The ratio of substrate temperature to bulk melting point
(T/T_m) is an important parameter that influences island formation and film growth. Low temperature ratios and large island sizes promote grain boundary-driven coalescence of islands.\footnote{14}

Thornton\footnote{15} developed a “Standard Zone Model” (SZM) diagram (Fig 3b) where different film morphologies are identified as a function of process pressure, ion flux, and T/T_m ratios. One SZM is shown in Figure 3b where we see Zones 1, T, 2, and 3 plotted against Ar process pressure and T/T_m.

We focus here on Zone 1 which is dominant at low process pressures and low T/T_m ratios; we operate at Ar pressures of 2 mTorr and T/T_m \approx 0.2. Zone 1 is characterized by void defects which result from atomic shadowing; the flux of sputtered species is higher for islands with higher thicknesses. Films grown in this regime are characterized by under-dense, fiber-like structures which often exhibit amorphous character. An increase in T/T_m promotes surface adatom diffusion and dense films. Moreover, lower T/T_m ratios are more attractive for applications as they allow for processing at lower temperatures.\footnote{15}
B. TiB\textsubscript{x} Growth

In this work, TiB\textsubscript{x} films were grown by DC magnetron co-sputtering from a TiB\textsubscript{2} and a Ti target. A BOC Edwards Auto500 Sputter-Coater, with a base process pressure of \( \lesssim 1 \times 10^{-7} \) Torr, was used for film deposition. The process gas was Ar at 2.2 mTorr. Advanced Energy MDX 500 and MDX 1K DC power supplies were connected to the Ti target, and TiB\textsubscript{2} targets, respectively. The TiB\textsubscript{2} target power was fixed at 250 W, and the Ti target power was incremented from 0 to 100 W in 25 W intervals. All films were grown at a substrate temperature of 450 °C, and substrate bias of -100 V, in order to promote growth of dense, crystalline films. Substrates were single-side polished 1 cm x 1 cm Si(100) wafers coated with ~50 nm of Ti to promote substrate-bias effects on film growth, and the target-substrate distance was held fixed at 10 cm. Table 1 shows the six films grown with their growth parameters.

Table 1: Films grown with deposition parameters. Ti (W) and TiB\textsubscript{2} (W) refer to the applied Ti and TiB\textsubscript{2} target powers, respectively.

<table>
<thead>
<tr>
<th>Film</th>
<th>Ti (W)</th>
<th>TiB\textsubscript{2} (W)</th>
<th>Ar Pressure (mTorr)</th>
<th>Substrate Bias (V)</th>
<th>Substrate Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB-0</td>
<td>0</td>
<td>250</td>
<td>2</td>
<td>-100</td>
<td>450</td>
</tr>
<tr>
<td>TiB-25</td>
<td>25</td>
<td>250</td>
<td>2</td>
<td>-100</td>
<td>450</td>
</tr>
<tr>
<td>TiB-50</td>
<td>50</td>
<td>250</td>
<td>2</td>
<td>-100</td>
<td>450</td>
</tr>
<tr>
<td>TiB-75</td>
<td>75</td>
<td>250</td>
<td>2</td>
<td>-100</td>
<td>450</td>
</tr>
<tr>
<td>TiB-100</td>
<td>100</td>
<td>250</td>
<td>2</td>
<td>-100</td>
<td>450</td>
</tr>
<tr>
<td>Ti</td>
<td>250</td>
<td>0</td>
<td>2</td>
<td>-100</td>
<td>450</td>
</tr>
</tbody>
</table>

The key difference in our growth technique compared to the literature is the use of co-sputtering. Rather than just using a TiB\textsubscript{2} target, which tends to yield B-rich films, we grow films using both TiB\textsubscript{2} and a Ti target, in order to independently tune the Ti concentration in the films.
C. Film Characterization

We characterized the crystalline structure, chemical structure, and film morphology using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

1. X-ray Diffraction (XRD)

X-ray diffraction is a technique used to probe the crystalline structure of materials. X-rays are produced by radiation emitted from collisions between high-energy electrons and a metal target. These X-rays are collimated and sent into a sample at a series of angles, and those X-rays that obey the relationship known as Bragg’s Law will yield constructive interference;

\[ 2d \sin(\theta) = n\lambda, \quad n \in \mathbb{N} \quad \text{(eq. 1)} \]

Here, \( d \) is the interatomic spacing of the atoms, \( \theta \) is the angle at which the x-rays enter the material, \( n \) is an integer indicating the order of diffraction, and \( \lambda \) is the wavelength of the incident X-rays. A schematic diagram of this process and the measurement device is shown in Figure 4.

The output of this technique yields a plot of X-ray intensity versus the scattering angle \( 2\theta \). Peaks are indicative of crystalline structure and are mapped to reference values. Results are
reported via Miller indices \((h, k, l)\), indicating crystallographic orientation of crystalline planes. An absence of peaks on the intensity plot this indicates the presence of an amorphous film (no long-range structure). It is common for sputtered films to exhibit a variety of crystalline phases because film growth is highly sensitive to deposition parameters. A Rigaku Model Rigaku Miniflex II XRD system was used in this research which uses Cu K-alpha X-rays \((\lambda = 1.5406 \text{ Å})\).

2. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy for chemical analysis, ESCA) is a technique to analyze chemical composition of materials. The technique exploits the photoelectric effect—the emission of electrons from electromagnetic radiation. In the XPS system, X-rays are produced from a source and sent into the sample, and ejected electron energies are measured. Using these energies, we can back-calculate using computer software to find the characteristic binding energy of the ejected electrons as peak positions of an intensity (counts per second) versus incident X-ray energy plot. The kinetic energy of the electrons is,

\[
E_k = hf - E_b - \phi \tag{eq. 2}
\]

where \(E_k\) is the kinetic energy of the electrons, \(hf\) is the X-ray energy, \(E_b\) is the binding energy of the electron, and \(\phi\) is the work function of the measurement system (known).\(^{16,17}\) Figure 5a shows an energy-level diagram illustrating the photoelectric effect. A sample is irradiated by X-rays of known energy, and electrons are ejected from atomic energy levels. The chemical environment of a sample will shift binding energies of elements and appear in XPS output as shifted peaks. Moreover, elemental quantification can be performed through analysis on peak intensities which are proportional to percent elemental composition. XPS serves as a useful characterization tool to analyze a sample’s chemical environment and elemental composition.
The intensity of ejected electrons depends on the orbital from which it was ejected. To correct for this, a scaling factor known as the relative sensitivity factor (RSF) is introduced. This is a dimensionless number which is unique to the instrument and is calibrated in advance. Here, we obtained RSF values from the XPS analysis software (Casa XPS) and the instrument used from the University of Maryland, shown in Table 2. To calculate the B/Ti ratio, we take the ratio of the corrected areas, shown in Eq. 3, where \( A_B \) and \( A_{Ti} \) are the raw areas of the B 1s and Ti 2p peaks, respectively, and \( RSF_B \) and \( RSF_{Ti} \) are the RSF values for the B 1s and Ti 2p peaks, respectively.

\[
\frac{B}{Ti} = \frac{A_B / RSF_B}{A_{Ti} / RSF_{Ti}} \quad \text{(eq. 3)}
\]

<table>
<thead>
<tr>
<th></th>
<th>B 1s</th>
<th>Ti 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casa</td>
<td>0.4866</td>
<td>7.81</td>
</tr>
<tr>
<td>UMD</td>
<td>0.159</td>
<td>2.001</td>
</tr>
</tbody>
</table>

A competing process with the photoelectric effect is Auger electron emission, illustrated in Fig 5b. As photoelectrons are ejected, lower energy states become vacant. Higher energy electrons relax and emit photons which may eject electrons from other energy levels. These secondary electrons, called Auger electrons, are denoted using a three-letter string of letters from the \( n = 1, 2, 3 \ldots \) shells, labelled as K, L, M, and so forth, respectively. The first letter represents the energy level of the initial hole, the second letter represents the energy level from which the excited core electron relaxes, and the third letter represents the energy level from which the Auger electron was emitted. Much like the photoelectrons ejected due to the photoelectric effect, computer software can match peak positions of Auger electrons with tabulated values allowing for elemental and chemical composition identification.
Ti and B form stable oxides at standard conditions (TiO$_2$ and B$_2$O$_3$, respectively), and will always be present on air-exposed samples. Since XPS is a very surface sensitive technique, those surface oxides, as well as adventitious water and hydrocarbons, need to be removed for the most accurate determination of the film bulk composition. This is done by a sputter etch using Ar$^+$ ions. However, the large mass difference between Ti and B may result in preferential sputtering of one species over another and skew the B/Ti ratio data. This can be mitigated by using low ion energies.

We collaborated with Dr. Karen Gaskell from the University of Maryland at College Park to perform XPS analysis using using a Kratos AXIS 165 instrument (Kratos Analytical, UK), equipped with a monochromatic Al K$_\alpha$ source ($h\nu = 1486.6$ eV). Prior to data collection, the air-exposed surfaces were sputter-cleaned for 2 minutes using a 4 keV Ar$^+$ ion beam incident at an angle 70° relative to the surface normal, followed by 5 minutes at 0.5 keV. All spectra were collected at normal emission angle. High resolution spectra were obtained using an analyzer pass energy of 20 eV. TiB$_x$ film data were corrected for sample charging using the B 1s peak at 188.2 eV while Ti film data was charge corrected about the Ti 2p$_{3/2}$ peak (454.4 eV).

Figure 5a: Schematic of photoelectron ejection in a XPS system. X-Rays are sent into a sample and excite an electron from an orbital to vacuum. The ejected electron’s kinetic energy is measured by a detector, and the binding energy of that electron is calculated. (b) Schematic diagram of the Auger electron emission process. In 1, an electron from the n = 2 (L) shell relaxes to fill the vacancy in the n = 1 (K) shell. This relaxation releases a photon in 2 which excites the electron in the L shell and ejects it in 3. This Auger electron would be a KLL electron.
3. Atomic Force Microscopy

Atomic force microscopy is a surface-sensitive technique that can be used to determine surface roughness as well as a topographic map of a sample. A sharp tip, supported by a cantilever, is scanned across the sample. The cantilever has a well-known spring constant (usually around 0.1~1 N/m) that obeys Hooke’s Law. Also, on top of the cantilever is a mirror, and a laser is directed towards this mirror and into a photodetector. As the probe interacts with the sample, the cantilever will move, and the laser will strike the photodetector at different spots. Computer software then takes this information and generates a topographic image of the sample. Figure 6 below shows a basic schematic of an AFM device. The AFM in this research was used in tapping mode.

Rms (root mean square) roughness $R$ was determined using the following expression,

$$ R = \sqrt{\frac{1}{N} \sum_i (Z_i - \bar{Z})^2} \quad (eq. 3) $$

where $N$ is the number of data measurements, $Z_i$ is the height of a given peak, and $\bar{Z}$ is the average height of the measured peaks. We used a Digital Instrument Multimode AFM instrument operating with a Nanoscope III controller in tapping mode.

![Figure 6: Sketch of AFM device. The probe taps across the sample at a normal driving frequency. As the probe interacts with the sample via electrostatic interaction, the cantilever will move. This causes the laser to reflect off of the sample at different angles into the detector.](image)
ImageJ software was used to compute the effective lateral area of peaks, and the number of peaks was counted by hand using topographical AFM images. Assuming each of the \( n \) islands is circular in shape in its horizontal cross section with radius \( r \), we can write the average area \( \langle A \rangle \) as 
\[
\langle A \rangle = n\pi r^2.
\]

III. RESULTS AND DISCUSSION

A. Composition

XPS survey spectra of select Ar-sputter-cleaned films are shown in Fig. 7. All films show residual O, N, and C signals, as well as Ar due to the Ar\(^+\) etching. Atomic composition was calculated using these survey spectra and is shown in Table 3. Carbon, nitrogen, and argon content is small in all films (less than 3.4% C, 5.9% N, and 3.2% Ar). Oxygen content is higher in all films, but TiB-50 and TiB-75 have higher oxygen content (44.39% and 46.23%, respectively) than TiB-0, TiB-25, TiB-100, and Ti (< 20%). Moreover, the Ti content does not strictly decrease (nor does B content increase) as Ti target power increases. This can be attributed to a failure to remove thick surface oxides (TiO\(_2\) and B\(_2\)O\(_3\)) from an insufficient etch time. The calculation of the B/Ti ratio from TiB-50 and TiB-75 high resolution spectra will be slightly inaccurate because this data includes oxide contributions and does not give as accurate of a picture as the bulk film; however,

*Figure 7: XPS survey spectra for TiB-100, TiB-0, and Ti films.*
surface and bulk composition of TiB\textsubscript{x} should be nearly identical. For TiB-0, TiB-25, TiB-100, and Ti, Ti content increases and B content decreases with increasing Ti target power as expected.

**Table 3: Atomic compositions for films obtained from XPS survey spectra.**

<table>
<thead>
<tr>
<th>Film</th>
<th>O 1s (%)</th>
<th>C 1s (%)</th>
<th>N 1s (%)</th>
<th>Ar 2p (%)</th>
<th>Ti 2p (%)</th>
<th>B 1s (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB-0</td>
<td>10.7</td>
<td>2.1</td>
<td>1.6</td>
<td>2.2</td>
<td>19.7</td>
<td>63.7</td>
</tr>
<tr>
<td>TiB-25</td>
<td>8.1</td>
<td>1.0</td>
<td>5.8</td>
<td>2.1</td>
<td>20.2</td>
<td>62.8</td>
</tr>
<tr>
<td>TiB-50</td>
<td>44.4</td>
<td>2.4</td>
<td>1.1</td>
<td>1.4</td>
<td>15.0</td>
<td>35.7</td>
</tr>
<tr>
<td>TiB-75</td>
<td>46.2</td>
<td>2.2</td>
<td>0.7</td>
<td>1.4</td>
<td>17.6</td>
<td>31.8</td>
</tr>
<tr>
<td>TiB-100</td>
<td>20.9</td>
<td>3.4</td>
<td>0.5</td>
<td>3.4</td>
<td>28.3</td>
<td>43.7</td>
</tr>
<tr>
<td>Ti</td>
<td>16.1</td>
<td>2.1</td>
<td>4.4</td>
<td>4.0</td>
<td>73.3</td>
<td>——</td>
</tr>
</tbody>
</table>

The B/Ti ratio was calculated using the B 1s and Ti 2p peak areas corrected using each of these sets of RSF values (Table 2) and was plotted against applied Ti target power (Fig. 8). The B/Ti ratio shows a strictly decreasing relationship with Ti target power as expected with increased Ti flux in the growth process. However, independent verification of B/Ti ratios with a technique not requiring instrument-specific sensitivity factors, such as Rutherford Backscattering (RBS) or Elastic Recoil Reflection Analysis (ERDA), is necessary to narrow the range for the B/Ti ratio as a function of Ti target power. We expect the B/Ti vs. Ti target power curve to be closer to the RSF values as reported in Casa because the literature shows TiB\textsubscript{2} film growth yielding B/Ti around 3.0.
In either case, we are confident the B/Ti ratio lies within this range, and we have successfully tuned the B/Ti ratio to be overstoichiometric and substoichiometric.

**B. Bonding Structure**

High resolution spectra of Ti 2p spectra are shown in Figure 9. Ti-Ti peaks are fit according to the Ti film for reference, and Ti-B peaks are fit using asymmetric peaks. The Ti-Ti peaks are ~0.4 eV lower in binding energy than the Ti-B peaks, and components must be fit for each of these bonding states to obtain an accurate picture of the chemical nature of the films. Peak intensity is proportional to elemental concentration and can be used to quantify the amount of each bonding state. TiB-100 shows a higher concentration of the Ti-Ti bonding state than the Ti-B state, while TiB-0 shows the opposite trend. Peak positions for fitted curves for TiB-0, TiB-100, and Ti are shown in Table 4. There is little variation in Ti-Ti peak positions across samples (less than 0.2 eV) and Ti-B peak positions across samples (less than 0.1 eV). Ti-O peak positions show greater differences (~0.3 eV), but these peaks had small (~1 %) concentration contributions to the total area of the Ti 2p peaks.

*Figure 9: XPS fine resolution spectra of Ti 2p peaks. Ti 2p peaks for each particular binding states are separated by 6 eV, and the Ti-Ti and Ti-B peaks are 0.5 eV apart.*
**Table 4: Peak positions for Ti bonding states present in films.**

<table>
<thead>
<tr>
<th>Film</th>
<th>Ti-Ti 3/2 (eV)</th>
<th>Ti-Ti 1/2 (eV)</th>
<th>Ti-B 3/2 (eV)</th>
<th>Ti-B 1/2 (eV)</th>
<th>Ti-O 3/2 (eV)</th>
<th>Ti-O 1/2 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB-0</td>
<td>454.60</td>
<td>460.40</td>
<td>454.88</td>
<td>460.91</td>
<td>457.60</td>
<td>463.60</td>
</tr>
<tr>
<td>TiB-100</td>
<td>454.57</td>
<td>460.37</td>
<td>454.94</td>
<td>461.01</td>
<td>457.29</td>
<td>463.29</td>
</tr>
<tr>
<td>Ti</td>
<td>454.74</td>
<td>460.59</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**C. Crystalline Structure**

Figure 10 shows XRD 0-2θ scans of TiBₓ films grown at 0, 25, 50, 75, and 100 W Ti target powers with constant 250 W TiB₂ target power, in addition to a pure Ti film grown at 250 W Ti target power. XRD analysis shows the presence of two textures in TiBₓ films: TiB₂ (100) at 2θ = 34° and TiB₂ (101) at 44°. As the Ti power decreases, we see that these peak intensities increase. This can be explained by the lower Ti content of low-power Ti films. High Ti-power films appear to be amorphous in texture. B-rich films (TiB-0, TiB-25, and TiB-50) show strong TiB₂ texture. Ti-rich films, however, show amorphous structure, evidenced by the broad shoulders in XRD data. TiBₓ films would show Ti texture if they shared peaks corresponding to Ti(1000), Ti(0002), and Ti(1011) at $2\theta = 35.4°, 38.6°, 40.5°$, respectively. The transition from nanocrystalline to amorphous texture with increasing Ti target power is accompanied with the B/Ti ratio gradient shown by XPS analysis.

*Figure 10: XRD spectra for TiBₓ films grown at 0, 25, 50, 75, and 100 W Ti target powers.*
D. Film Topography

AFM in tapping mode was performed on films to study film topography. 1μm x 1μm scans of films were taken (Figure 11). All TiBₓ films show similar topographical structures with rms roughness between 0.96 nm and 2.02 nm and small surface features (Table 5). There are significant differences in Ti film and TiBₓ film topology, evidenced by differences in rms roughness and surface feature size. This can be explained by the significant differences in crystalline structure given by XRD analysis. The minimization of average feature size for near-stoichiometric films (TiB-50 and TiB-75) can be explained by denser films formed by a more stable compound formed by the proper stoichiometric ratio in TiBₓ.

Figure 11: AFM images (1μm x 1μm, scale = 10 nm for TiBₓ films and 50 nm for Ti film) of TiBₓ films labelled by applied Ti target power. Pure Ti films were also grown at 250 W applied Ti power.

<table>
<thead>
<tr>
<th>Film</th>
<th>Rₚ / nm</th>
<th>⟨r⟩ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB-0</td>
<td>1.0</td>
<td>31</td>
</tr>
<tr>
<td>TiB-25</td>
<td>1.5</td>
<td>45</td>
</tr>
<tr>
<td>TiB-50</td>
<td>0.9</td>
<td>25</td>
</tr>
<tr>
<td>TiB-75</td>
<td>2.0</td>
<td>23</td>
</tr>
<tr>
<td>TiB-100</td>
<td>1.4</td>
<td>31</td>
</tr>
<tr>
<td>Ti</td>
<td>11.1</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 5: Summary of TiBₓ film and Ti film root mean square (rms) roughness and average feature size. TiBₓ films show evident differences from the Ti film, and near-stoichiometric films show the lowest average feature size.
IV. SUMMARY AND CONCLUSIONS

We successfully tuned the B/Ti ratio in TiB\textsubscript{x} thin films using dc magnetron co-sputtering with x between 1.4 and 2.8. Ti-rich films show amorphous structure, and B-rich films show (100) and (101) TiB\textsubscript{2} texture with a mixture of amorphous and TiB\textsubscript{2} texture for near-stoichiometric films. Rms roughness varies between 0.9 nm and 2.0 nm for TiB\textsubscript{x} thin films, and surface feature size varies between 23 and 45 nm for TiB\textsubscript{x} films. Future studies will include investigation of electronic and mechanical properties of films; verification of the B/Ti ratio using RBS and ERDA analysis; and film morphology with scanning electron microscopy and transmission electron microscopy. Additionally, films will be annealed and have their crystalline structure re-analyzed to investigate the possibility of altering film texture post-deposition.

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References


