Nanomechanical and nanotribological behavior of hafnium boride thin films

Shahla Chowdhury^{1,4}, Kyriaki Polychronopoulou^{1,2}, Andrew Cloud³, John R. Abelson³,

Andreas A. Polycarpou^{1,4}

¹Department of Mechanical Science and Engineering, University of Illinois at Urbana

Champaign, 1206 W Green Street, Urbana, IL-61801, USA

²Mechanical Engineering Department, Khalifa University of Science Technology & Research,

P.O Box 127788, Abu Dhabi, UAE

³Department of Materials Science and Engineering, University of Illinois at Urbana

Champaign, 1304 W Green Street, Urbana, IL-61801, USA

⁴Department of Mechanical Engineering, Texas A&M University, 3123 TAMU, College

Station, TX, USA

Email addresses of the authors

chowdhury.s@tamu.edu

kpolychronopoulou@gmail.com

andrewncloud@gmail.com

abelson@illinois.edu

apolycarpou@tamu.edu

Abstract

Nanocrystalline HfB₂, HfBN and multilayer HfB₂/HfBN films were deposited using chemical vapor deposition. Half of the amorphous as-deposited films were subjected to annealing at 700°C to obtain their annealed equivalent samples. Nanoindentation and nanoscratch experiments were performed to measure their mechanical properties, friction and scratch/wear behavior. The annealed films showed higher hardness values compared to the as-deposited films, with the HfB₂ film exhibiting the highest hardness. All three films exhibited similar shear strength around 3 GPa for as-deposited and 5.5 GPa for annealed films, implying reduced delamination propensity for the annealed samples. The annealed HfBN and multilayer HfB₂/HfBN films exhibited lower friction and wear, compared to the rest of the films. Specifically, the annealed multilayer HfB₂/HfBN films, exhibited an order of magnitude lower wear, compared to the HfB₂ films, making them excellent candidates for low friction and low wear hard coating applications.

Keywords: Hafnium Boride; nanocoating; nanomechanics; nanowear; XPS; SEM

Abbreviations: Atomic Force Microscope (AFM); Auger Spectroscopy (AES); Chemical Vapor Deposition (CVD); Coefficient of Friction (COF); High Resolution Transmission Electron Microscopy (HRTEM); Physical Vapor Deposition (PVD); Root-mean-square (rms); Scanning Electron Microscopy (SEM); Transmission Electron Microscopy (TEM); X-ray Diffraction (XRD); X-ray Photoelectron Spectroscopy (XPS)

1. Introduction

Advanced hard protective coatings are required in application fields such as air-conditioning and refrigeration compressors, microelectromechanical systems, magnetic storage devices, drawing dies and punches (used in metal cutting and forming). In general, these coatings are expected to be used under unlubricated (extreme) conditions and still possess low friction, low wear and high corrosion resistance [1-4]. In the case of miniaturized applications, where the size of the components and the amount of load needs to be very small, scratch resistance and wear behavior is of great importance. Among the candidates for wear resistant coatings are metal borides, and particularly hafnium diboride (HfB_2), which has a high melting point, a bulk hardness of 29 GPa and good corrosion resistance. Despite the promising candidacy of metal diborides for such applications, limited number of studies have been reported on these materials, compared to metal nitride and carbide systems [5-7]. Deposition methods, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques are used, where the deposition conditions tailor the stoichiometry and subsequently the mechanical properties, friction and wear performance of the films [8,9].

Goncharov [10] reported on how the deposition conditions of HfB_2 affect the mechanical properties: A bias potential of ± 50 V and a substrate temperature of $\sim 500^\circ\text{C}$ leads to the formation of super stoichiometric highly textured films with a hardness of 44 GPa and an elastic modulus of 396 GPa. The films were a combination of amorphous-crystalline phases ($\text{HfB}_2 + \text{BN}$), where grains of the HfB_2 nanocrystalline phase were dispersed within the amorphous phase of graphite-like BN phase. In a comparative study of nanoindentation on HfB_2 single crystal and $\text{HfB}_{2.7}$ nanocrystalline thin films, deposited on a steel substrate by magnetron sputtering, it was shown that the boron super stoichiometry and small grain size can lead to a significant increase in hardness and decrease of elastic modulus of the $\text{HfB}_{2.7}$

composition (in comparison to the bulk single crystal). The high value of 87% elastic recovery in the HfB_{2.7} implies a promising wear-resistant coating [11].

In coating applications, it is also important to understand the substrate effects in measuring mechanical properties of the coatings [12]. Previously, properties such as wear resistance, high critical delamination load and low cohesive force, as well as high hardness were reported for PVD grown titanium-boride and titanium-boron-nitride films [13-17]. Heck *et al.* [13] found that TiB is the best candidate material for transforming and machining aluminum, whereas TiAlB(N) is a promising coating material to transform brass. TiAl(N)-coatings were also found to be good candidates for transforming steel. In another study, Rebholz *et al.* [15] could not find any correlation between BN content and friction in TiAlBN films. Experimental nanoindentation and nanoscratch techniques have been employed to measure hardness, reduced modulus and friction of HfB₂ films [18]. Wear depth after scratch was also measured for investigating elastic recovery of the coatings.

The nanoscratch technique is also a useful tool for measuring adhesion properties of films on a substrate. A sharp diamond tip is used to initiate the delamination of the coating with the combination of tip movement in the vertical and horizontal directions along the surface. Various models have been developed to determine the shear strength as well as the energy release rate at the interface from scratch experiments. The applicability of these models depends on the failure mode observed. Benjamin and Weaver [19] and Ashcroft and Derby [20] analyzed the interfacial shear strength produced at the coating-substrate interface for coating removal, given by the following equation

$$\tau_c = \left(\frac{HP_c}{\pi(r^2 - (P_c/\pi H))} \right)^{1/2}$$

Where τ_c is the shear force per unit area (shear strength) to delaminate the coating and is

given in terms of the substrate hardness H , the critical applied load P_c and the radius of the indenter tip r . This analysis is applicable when the substrate deforms plastically.

In the present study, single layered (thickness ~100 nm) and multilayered (thickness ~680 nm) HfB₂ as-deposited coatings at 400°C and following annealing at 700°C were studied in terms of their nanomechanical and nanotribological properties. In this work annealing does not increase the hardness and modulus values. With annealing microstructural changes take place in the film, and these changes include the formation of soft or hard phases. Also, annealing can lead to the formation of denser films, which could give rise to hardness increase. This can be due to recovery effects, such as dislocation annihilation [21, 22]. Torrents *et al.* [23] reported a temperature region dependence of Ni hardness, where the hardness can increase or decrease depending on phenomena such as annealing twins formation or grain growth. Characterization tools, such as scanning electron microscopy (SEM), Auger Spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) were used to measure the thickness and the chemical composition of the coatings.

2. Experimental procedure

2.1. Film deposition and growth

Thin HfB₂ films were deposited by thermal CVD of Hf(BH₄)₄ precursor in an ultra-high vacuum chamber [24]. The addition of nitrogen atoms (8-20%) was incorporated using a remote plasma source, as described by Jayaraman *et al.* [25]. The multilayer HfBN/HfB₂ films were deposited by incorporating N using a co-flux of ammonia. Flow was controlled via a needle valve. CVD can produce stoichiometric thin films of HfB₂ in a batch process that is conducive to industry. Hard tool coating is one possible application for this growth

method. The CVD HfB₂ films grown in this work, were under different conditions from those investigated by Jayaraman *et al.* [25], and thus the mechanical properties are not expected to be the same. In this study, a CVD HfB₂ film grown on Si(100) at 200°C is tested and compared to two films alloyed with nitrogen.

A HfBN film is deposited by growing HfB₂ on a substrate heated to 400°C with a 0.275 mTorr partial pressure of ammonia. At substrate temperatures above 350°C, ammonia decomposes on the growth surface and adds nitrogen to the film [25]. A HfBN/HfB₂ multilayer film is synthesized by introducing ammonia at regular intervals during the HfB₂ growth. The samples studied here consists of 4 bilayers – each HfB₂ layer is approximately 100 nm-thick and is separated by a ~20 nm-thick layer of HfBN. The terminal surface of the multilayer film is HfBN. Film deposition parameters are recorded in Table 1.

2.2. X-ray diffraction (XRD) studies

XRD analysis was performed utilising PANalytical / Philips X'pert MRD with Cu K_α radiation, (wavelength $\lambda = 1.5418 \text{ \AA}$). Scans were performed at 40 kV and 30 mA power, using 1° divergence and scatter slit with a receiving slit of 0.3 mm, scanning with 0.02° pitch at a speed of 0.1 °/min.

2.3. Morphology of the films (SEM)

The morphology and thickness of the films were measured using a JEOL 6060 SEM at an operating voltage of 10 keV. The samples were cleaned and sputtered-coated before imaging.

2.4. Roughness of the films (AFM)

A Digital Instruments Dimension 3100 Atomic Force Microscope (AFM) was utilized to measure the surface roughness. The root-mean-square (rms) roughness was determined from

ten measurements obtained from different areas of each film.

2.5. XPS and AES

XPS analysis was conducted on a Perkin Elmer PHI 5400 spectrometer equipped with a hemispherical electron analyzer and a non-monochromatic Mg K α X-ray source (1253.6 eV). All reported photoelectron binding energies were referenced to the C1s feature of adventitious carbon at 285 eV (internal standard) to take into account charging effects. The survey spectra were acquired at a pass energy of 178.95 eV. A certain region of the spectrum was scanned a number of times to obtain a good signal-to-noise ratio (the detailed scan was performed at a pass energy of 35.75 eV). AES spectra were recorded with a Physical Electronics PHI 660 scanning Auger microprobe. The background pressure and operating pressure were maintained at 5×10^{-9} and 2×10^{-8} Pa, respectively. The samples were excited with a LaB₆ Filament Electron Gun, operated using 3 kV voltage. To remove the surface oxide, the sample surfaces were etched by a 1 keV argon ion beam.

2.6. Nanoindentation

The nanoindentation measurements were restricted to a depth less than 20% of the film thickness and calibrated against a reference Fused-Quartz sample. The nanoindentation was performed using a TI-950 TriboIndenterTM equipped with a standard transducer. This transducer has a maximum load limit of ~12 mN and maximum displacement of ~4.5 μ m. The Berkovich tip is a three-sided pyramid with semi-vertical angle of 70.3°. The most important criterion for indentation measurements is the calibration of the tip, known as area function. The Oliver–Pharr [26] method is utilized for measuring the area function. The contact depth (h_c) is information obtained from the indentation measurements. The tip area function correlates the contact area to the contact depth. This relation needs to be determined

for the Berkovich tip during measurements. For a perfect tip the area function is the geometrical function given by

$$A_c(h_c) = 24.5h_c^2$$

However due to tip imperfections, for the Berkovich tip, the area function usually takes the following form

$$A_c(h_c) = C_0h_c^2 + C_1h_c + C_2h_c^{1/4} + C_3h_c^{1/8} + C_4h_c^{1/16} + C_5h_c^{1/32}$$

where coefficients $C_1 - C_5$ are obtained from experimental data with the fused quartz standard.

2.7. Nano-scratch and shear strength measurements

The nanoscratch technique was utilized to measure the friction and wear. To eliminate the directional effects of tip geometry, a conospherical tip (870 nm radius) was used for the nanoscratch experiments. The scratch measurements were performed under constant normal loads of 100, 200, 350 and 500 μN and a sliding speed of 0.33 $\mu\text{m/s}$. The scratch or wear length was 10 μm . At the end of each scratch, wear depths were rescanned using the same tip to measure the post (plastic or residual) wear depth. This also allows for an estimation of the elastic recovery of the coatings.

3. Results and discussion

3.1. Structure of the films

The XRD patterns for the as-deposited films revealed their amorphous nature. The XRD patterns of the annealed samples also show that the films are amorphous, following vacuum annealing at 700°C. Previous studies showed that the HfB_2 films are turning into crystalline

following annealing process at 600°C [25]. Though, in that particular study, it had been found that the XRD peaks were broad and diffuse, demonstrating the nanocrystalline nature of the films. In the case of Hf-B(N) films it has been reported that the presence of additional phases (due to the presence of nitrogen) retarded the crystallization process, giving rise to poorly crystalline films [25]. In the present study, the deposition conditions applied led to a rather amorphous or very small crystallites embedded into the amorphous matrix escaping the XRD detection. The films are expected to crystallize upon annealing to 700°C, however the resulting grain diameter is only ~5nm, as revealed by lattice imaging high resolution TEM (HRTEM) [25]. The lack of grain coarsening reflects the low homologous temperature; since bulk Hafnium-Borides melt at ≥ 3500 K, whereas annealing at 700°C corresponds to a low value of $T/T_{\text{melt}} = 0.28$. These films are essentially stoichiometric (based on AES studies) and impurity-free, smooth on the nm scale (based on AFM studies). By adjusting the growth parameters, good conformal coverage, on features with aspect ratio $\leq 5:1$, can be obtained at growth rates up to 20 nm/min.

Fig. 1 presents a cross section SEM image, a cross section TEM image and an XRD measurement of the multilayered HfB₂/HfBN. The total film thickness is 679 nm (Fig. 1a) and each film layer is approximately 100 nm (Fig. 1b). These thickness values are in agreement with the AES depth profile results (Sec. 3.3). The film compositions exhibit a rather dense columnar and dense smooth texture, based on SEM images, respectively.

3.2. Film roughness (AFM)

The AFM images are shown in Fig. 2 and the rms roughness values extracted are given in the Table 2. As-deposited HfB₂ films exhibit the lowest rms roughness in the 2.18-2.56 nm range, compared to HfBN and HfB₂/HfBN films (4.70-7.63 nm). Annealed HfB₂ and HfB₂/HfBN compositions exhibited lower rms roughness compared to the as-deposited films, which can

be due to island coalescence phenomenon (that reduces the top to valley distance (asperities) in the films). This is in agreement with previous roughness results reported on CVD-synthesized HfB₂ films [18].

3.3. XPS and AES Studies

Fig. 3 presents the B1s and N1s core level spectra obtained over the as-deposited and annealed HfB₂ and HfBN films. In these spectra, B-Hf bonding contributions at 187.5-188.7 eV range can be clearly seen [28]. Despite the fact that short term sputtering was performed (to avoid the preferential erosion of the light elements such as B, N) for cleaning the oxide top surface layer, contributions from B-O bonding at 191.5 eV can still be observed. In the case of HfBN films, the B-N bonding at a binding energy of 190.5 eV was observed. Another important finding is the shift of the binding energy with the applied annealing conditions (700°C). This shift can be correlated with the anticipated change in the grain size following the annealing process. In particular, it is known that the holes created during the photoemission process, participate into relaxation processes by recombining with electrons. Thus, the kinetic energy of the outgoing electron is influenced by the screening effect of the hole. It has been reported that in the case of a cluster size of about ~12 nm, the relaxation leads to significant increase in binding energy compared to bigger clusters [8,29,30]. The effect is dominant in the case of nm-sized crystals, where a lower number of electrons participate in the screening of the holes formed in the photoemission process. This condition is most likely applied in the current films, since based on the XRD studies the films were found to be amorphous or amorphous-like.

AES depth profiling spectra for the HfB₂ and HfB₂/HfBN films are presented in Fig. 4. For the case of HfB₂ films, the stoichiometry was very close to the nominal one (1:2), whereas the thickness of the film (~100 nm) was also verified using these profiles (substrate-film

interface). The successful incorporation of nitrogen into the film was also verified (Fig. 4b). The hafnium content in both cases (presence or absence of nitrogen) proved to be constant.

3.4. Hardness and reduced modulus

The area function was determined using multiple indentations on the fused quartz standard: Specifically sixteen (16) indentations, starting from 100 μN to 1700 μN , were performed. Multiple indentations, with constant step load of 50 μN , starting from 50 μN up to 500 μN , were employed and the depth of penetration was kept below 20% of the total film thickness to avoid substrate effects. From Fig. 5, for the case of annealed films, it can be seen that the HfB_2 films possessed the highest hardness value (21.6 GPa) and reduced modulus of elasticity (219.5 GPa) in comparison to the HfBN ($H = 14.6$ GPa, $E_r = 173.8$ GPa) and the multilayered HfB_2/HfBN films ($H = 12.9$ GPa, $E_r = 147.68$ GPa). Note that these values are in general lower than earlier reported values [18,25], which could be due to differences in the film structure (percentage of amorphous versus nanocrystalline phases). It was found that the annealed films exhibited higher hardness and modulus values, compared to the as-deposited films. This finding is in good agreement with research work published elsewhere, e.g., Pang et al. [31] studied chromium films and reported increase of both elastic modulus and hardness values after annealing. The lower hardness values of the HfBN films is in agreement with the studies performed by Jayaraman et al. [25] due to the somewhat softer BN phase formation and poorer crystallinity. Based on these results, it can be stated that annealing improves the hardness of the films, which is be due to a profound effect of annealing on the film adhesion and the phase transformation of amorphous to “amorphous-like” films, where in the latter, nanocrystallites are embedded in the amorphous matrix.

3.5. Nanoscratch

3.5.1. Load-dependence of friction and wear recovery

The friction behavior was studied at different constant loads, namely at 100, 200 and 350 μN and at a constant sliding velocity of 0.3 $\mu\text{m/s}$. With increasing load, the coefficient of friction (COF) increases slightly, as seen in Fig. 6a. Typical surface morphologies of the residual scratches, obtained by AFM, are shown in Fig. 6b. The COF increases to about 0.1 with increasing load from 100 to 350 μN , with the annealed samples exhibiting a lower COF than the as-deposited films. This can be attributed to the fact that in the steady state phase, the COF of the films depends mainly on their microstructure: Namely, the denser the microstructure, the smaller grain size and thus harder films result in a lower COF [32]. After the annealing process, due to residual stress annihilation and interdiffusion effects, a denser structure is anticipated, and the adhesion is expected to improve. These factors are expected to lead to less delamination and improved wear performance [33]. The HfBN possessed the lowest COF among the three compositions investigated in the present study.

To measure the wear and elastic recovery of the films, the constant load function with retrace was implemented. Fig. 7 depicts the *in-situ* and residual wear values with the percentage of elastic recovery, for the cases of 200 μN and 350 μN applied loads. The as-deposited films exhibited elastic recovery in the range of 31-39 %, whereas for the case of the annealed films the % recovery is highly dependent on the film composition/structure. HfBN and HfB₂/HfBN films showed excellent elastic recovery (52-86%), whereas annealed HfB₂ films showed poor elastic recovery. This difference in the elastic recovery between the as-deposited and annealed samples suggests a different wear mechanism for the as-deposited and annealed films. Note that the multilayered annealed HfB₂/HfBN film exhibited minimal wear at both normal loads, and coupled with its low friction characteristics, makes it the best performing tribological coating investigated in this study.

3.5.2. Shear strength

To obtain the shear strength of the films, ramp-loading scratch testing procedure involving the moving of a sharp diamond tip along the coating surface in order to initiate delamination of the coating was performed. The delamination event is prompted by the combination of tip movement in the vertical and horizontal directions along the surface. The critical load is defined as the load that is required to initiate failure of the film. The failure is recognized by a sudden displacement jump in the normal direction as depicted in Fig. 8a. There is a large discontinuity in the plot, which corresponds to the onset of detachment. The location of failure is verified with optical microscopy images (Fig. 8b). A typical scratch experiment, showing the optical image after the experiment, and *in-situ* normal displacement, normal force and COF for the as-deposited HfB₂ is shown in Fig. 8a. Fig. 8a and Fig. 8d show the point where detachment of the HfB₂ coating is initiated during the scratch test. It is believed that delamination is the main mode of detachment at the beginning of the tip penetration into the coating layer.

The critical load is obtained from the normal force curve at the corresponding time determined from the normal displacement curve. In the case of the as-deposited films the critical load (P_c) values obtained from the experiments were in the range of 48-53 mN, whereas in the case of the annealed films the critical load was increased to 74-121 mN (Table 1). In terms of shear strength values, it was found that the annealed films exhibited values of 2-3 GPa higher compared to the as-deposited films. Among the three film compositions studied herein, the annealed HfBN film possessed the highest shear strength (τ_c).

4. Conclusions

Single-layered and multi-layered Hf-B(N) films were deposited using low temperature CVD technique. The films were amorphous both in the as-deposited and annealed states. The annealed Hf-B(N) showed higher hardness (H) and reduced elastic modulus (E_r), compared to the as-deposited films. Among the three different compositions: HfB₂, HfB₂/HfBN and HfBN studied herein, the HfBN possessed the lowest COF, implying the beneficial effect of N-addition in terms of tribological property improvement. N-incorporation into the films led to lower values of hardness most likely due to the new nanocrystalline phases formed. In the case of wear performance and elastic recovery both annealed HfBN and HfB₂/HfBN films showed excellent wear recovery (32-76%) under different loads studied, compared to the HfB₂ films (9.5-39%). In terms of the shear strength, the HfBN films exhibited the highest shear strength (5.96 GPa) among the compositions investigated, followed by the HfB₂ annealed film (5.4 GPa). The as-deposited films in all compositions studied exhibited comparatively low shear strength (2.66-3.24 GPa). Clearly, examining the hardness alone is inadequate to evaluate the tribological performance of thin protective films, as in this case the lower hardness films (annealed HfBN, and annealed HfB₂/HfBN) exhibited superior shear strength, friction, and wear performance, compared to the hardest annealed HfB₂ films.

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Fig. 2. 5μm×5μm AFM images of HfB(N) films.

Fig. 3. XPS of the Hf-B(N) films: (a) B1s spectra of as-deposited and annealed HfB₂, (b) B1s spectra of HfB₂/HfBN films, (c) N1s spectra of HfBN.

Fig. 4. AES depth profiles of (a) HfB₂ and (b) HfB₂/Hf-B-N films.

Fig. 5. Nanomechanical properties of the Hf-B(N) films: (a) hardness, (b) reduced modulus.

Fig. 6. (a) Coefficient of friction values, (b) AFM residual scratches at different loads as obtained from nanoscratch studies of the Hf-B(N) films.

Fig. 7. *In-situ* and residual wear depths, showing % elastic recovery: (a) load 200 μN, (b) load 350μN.

Fig. 8. Ramp-loading nanoscratch experiments to measure shear strength values: (a) *in-situ* normal displacement, (b) microscopic image of scratch trace, (c) *in-situ* COF, and (d) *in-situ* normal force.

Tables

Table 1: Deposition parameters, film thickness, critical load and shear strength values of tHf-B(N) films.

	T_{sub} (°C)	$P_{\text{precursor}}$ (mTorr)	t (nm)	P_c (mN)	τ_c (GPa)
HfBN, as-deposited	400	0.05	102	49	3.24
HfBN, annealed	400	0.05	102	121	5.96
HfB ₂ /HfBN, as-deposited	400	0.05	640	53	2.78
HfB ₂ /HfBN, annealed	400	0.05	640	91	4.80
HfB ₂ , as-deposited	200	1.5×10^3	100	48	2.66
HfB ₂ , annealed	200	1.5×10^3	100	74	5.41

Table 2: 5 μm x 5 μm rms roughness of annealed and as-deposited Hf-B(N) films

rms roughness (nm)		
	As-deposited	Annealed
HfBN	5.4	7.6
HfB ₂ /HfBN	5.7	4.7
HfB ₂	2.6	2.2

Fig. 1. Microstructure of the HfB₂/HfBN films (a) SEM, (b) TEM, (c) XRD.

Fig. 2. $5\mu\text{m}\times 5\mu\text{m}$ AFM images of HfB(N) films.

Fig. 3. XPS of the Hf-B(N) films: (a) B 1s spectra of as-deposited and annealed HfB₂, (b) B 1s spectra of HfB₂/HfBN films, (c) N 1s spectra of HfBN.

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