Age hardening in superhard ZrB_2-rich Zr_{1-x}Ta_xB_y thin films

Babak Bakhit a,4, Justinas Palisaitis a, Zhengtao Wu b, Mauricio A. Sortica c, Daniel Primetzhofe c, Per O.A. Persson a, Johanna Rosen a, Lars Hultman a, Ivan Petrov a,d,e, J.E. Greene a,d,e, Grzegorz Greczynski a

a Thin Film Physics Division, Department of Physics (IFM), Linköping University, Linköping SE-58183, Sweden
b School of Electromechanical Engineering, Guangdong University of Technology, Guangzhou 510006, China
c Applied Nuclear Physics, Department of Physics and Astronomy, Uppsala University, Uppsala SE-75236, Sweden
d Materials Research Laboratory and Department of Materials Science, University of Illinois, Urbana, IL 61801, USA
e Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

ABSTRACT

We recently showed that sputter-deposited Zr_{1-x}Ta_xB_y thin films have hexagonal AlB_2-type columnar nanostructure in which column boundaries are B-rich for x < 0.2, while Ta-rich for x > 0.2. As-deposited layers with x ≥ 0.2 exhibit higher hardness and, simultaneously, enhanced toughness. Here, we study the mechanical properties of ZrB_{2.4}, Zr_{0.8}Ta_{0.2}B_{1.8}, and Zr_{0.7}Ta_{0.3}B_{1.5} films annealed in Ar atmosphere as a function of annealing temperature T_a up to 1200 °C. In-situ and ex-situ nanoindentation analyses reveal that all films undergo age hardening up to T_a = 800 °C, with the highest hardness achieved for Zr_{0.8}Ta_{0.2}B_{1.8} (45.5 ± 1.0 GPa). The age hardening, which occurs without any phase separation or decomposition, can be explained by point-defect recovery that enhances chemical bond density. Although hardness decreases at T_a > 800 °C due mainly to recrystallization, column coarsening, and planar defect annihilation, all layers show hardness values above 34 GPa over the entire T_a range.

Transition-metal (TM) diboride thin films have attracted attention as a new class of hard coatings with a high potential for replacing TM nitrides [1–5]. They typically crystallize in a hexagonal AlB_2-type crystal structure (P6/mmm, SG-191) in which B atoms form graphite-like honeycomb sheets between hexagonal-close-packed TM layers [6–8]. Strong combined covalent/ionic bonding between TM and B atoms together with covalent bonding within honeycomb B sheets [9] result in high melting temperature, hardness, and stiffness [7,10], while metallic bonding between TM atoms provides good conductivities [6]. Hence, this unique combination of ceramic and metallic properties makes TM diboride films promising candidates for many applications such as cutting tools [11–16], aerospace engine components [17,18], nuclear fusion devices [19,20], semiconductor metallic contacts [21], and microelectronic components [22,23].

Although TM diborides are categorized as hard materials [24], this alone is not enough to prevent failure. Hardness is usually accompanied by brittleness causing crack formation and propagation at the presence of high stresses [25]. To avoid brittle cracking, diborides require to be both hard and relatively ductile. We recently showed that alloying ZrB_2 films with Ta causes an ~20% increase in hardness with a simultaneous increase of ~30% in toughness [26]. Zr_{1-x}Ta_xB_y alloys with x ≥ 0.2 exhibited a self-organized columnar core/shell nanostructure in which crystalline Zr-rich cores provide high hardness, while disordered Ta-rich, B-deficient, metallic-glass-like shells give enhanced ductility [26,27].

In addition to increasing mechanical properties, the stability of nanostructure and mechanical properties at high temperatures are also essential. Here, thermal stability of ZrB_{2.4}, Zr_{0.8}Ta_{0.2}B_{1.8}, and Zr_{0.7}Ta_{0.3}B_{1.5} thin films are studied at annealing temperatures T_a ranging from 600 to 1200 °C in Ar atmosphere. We demonstrate that crystal structure does not change up to 1200 °C. Hardness increases for all films up to 800 °C due to retaining planar defects and chemical-bond recovery, followed by a decrease at T_a > 800 °C during recrystallization.

The films are grown on Al_2O_3 (0001) in a CC800/9 CemeCon system equipped with rectangular (8.8 × 50 cm^2) ZrB_2 and Ta targets. The base pressure is 3.8 × 10^{-6} Torr (0.5 mPa). The deposition temperature is 475 °C. ZrB_{2.4} films are deposited by DC-magnetron sputtering (DCMS) at a 5000-W power and a negative
100-V DC-substrate bias. The alloys are deposited in a hybrid scheme [28] in which the ZrB2 target is continuously sputtered by 5000-W DCMS, while the Ta magnetron is operated in high-power-impulse-magnetron-sputtering (HIPIMS) mode with 50-μs pulses. The average powers (and pulse frequencies) applied to the Ta target for growing Zr0.8Ta0.2B1.8 and Zr0.7Ta0.3B1.5 are 1200 W (200 Hz) and 1800 W (300 Hz), respectively. A negative 100-V bias is applied synchronously to substrates with a 30-μs offset and 100-μs pulse width. Deposition times are adjusted such that all films are ∼1.6-μm thick.

θ-2θ X-ray diffraction (XRD) scans are carried out using a PANalytical Empyrean X-ray diffractometer with a Cu Kα source (λ = 1.5406 Å) to determine the crystal structure and orientations of the layers. Substrate curvatures are determined from XRD rocking-curve measurements to obtain films’ residual stresses, based on modified Stoney equation [26,29,30]. To obtain film compositions, time-of-flight elastic recoil detection analyses carried out in a tandem accelerator with a 36 MeV 127I+ probe beam. Chemical bonding in the layers is evaluated by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra DLD instrument employing monochromatic Al Kα radiation (hv = 1486.6 eV). For XPS experimental details see reference 26.

Plan-view transmission-electron-microscopy (TEM) analyses are carried out on a monochromated and double-corrected FEI Titan3 60-300 electron microscope operated at 300 kV. Imaging is performed using scanning TEM (STEM) high-angle annular dark-field (HAADF-STEM), annular bright-field (ABF) imaging and conventional TEM modes. Energy-dispersive X-ray (EDX) and electron energy-loss spectroscopy (EELS) elemental maps are obtained using SuperX and GIF Quantum ERS spectrometers embedded in the FEI instrument. TEM specimens are prepared by focused ion beam method using Carl Zeiss Cross-Beam 1540 EsB system.

The films are annealed in a furnace with a continuous Ar flow. The annealing peak temperature Tα is varied from 600 °C to 1200 °C in 100 °C increments. After reaching Tα, with heating rate of 10 °C/min, temperature is held constant for 30 min. Then, samples are cooled down to room temperature, while the furnace is turned off.

Nanoindentation analyses are performed in an Ultra-Micro Indentation System at room temperature (ex-situ measurements) and Anton-Paar-TrTech UNHT3 ultra-nanoindentation system at high temperature (in-situ measurements) with sharp Berkovich diamond tips calibrated using a fused-silica standard. The in-situ measurements are performed in Ar atmosphere up to 800 °C, in which the tip is heated with infrared heating. For hardness H and elastic modulus E measurements, the films are indented 35 times using a fixed load of 12 mN, while indentation depths are maintained below 10% of film thickness. The results are analyzed using Oliver and Pharrr method [31]. E are calculated from reduced elastic moduli using the diamond indenter’s elastic modulus (1141 GPa) and Poisson’s ratio ν = 0.07. The ν values of Zr0.8Ta0.2B and that of TaB2 (0.21 [33,34]).

XRD patterns of as-deposited and annealed films reveal that all peaks detected in the 2θ range from 20° to 100° originate from the hexagonal AlB2-type structure. All reflections are preserved throughout the entire Tα range, and no new peaks are observed. Hence, only (0001) reflections of as-deposited, 800 °C- and 1200 °C-annealed films are shown in Fig. 1. The (0001) reflection also shifts toward higher 2θ values from 25.1° for x = 0, to 25.6° for x = 0.2, to 25.7° for x = 0.3 exhibiting a decrease in out-of-plane c-lattice parameters from 3.54 Å to 3.48 Å to 3.46 Å, respectively, due to replacing Zr by Ta atoms which have a smaller covalent radius [35]. The (0001)-reflection intensities of all annealed films increase with increasing Tα, in good agreement with results of sputter-deposited Ti0.7Al0.29B1.08 annealed at 1000°C [36]. Over the entire Tα range, XRD does not provide evidence for phase separation in the annealed films such as secondary phase precipitation or spinodal decomposition, which are classical cases of age hardening in metastable TM nitride alloys [37-41].

XPS is employed to probe changes in chemical bonding and composition of layers as a function of Tα. As previously determined for the as-deposited films [26], the B 1s peak shifts slightly toward higher binding energy from 188.1 eV for ZrB2.4 to 188.4 eV for both Zr0.8Ta0.2B1.8 and Zr0.7Ta0.3B1.5 due to higher electronegativity of Ta compared to Zr, while no visible shift is observed for Zr 3d signals. In the present experiment, no detectable change in B 1s, Zr 3d, and Ta 4f core-level spectra is observed as a function of Tα, indicating that annealing has no effect on bonding states. This is in accordance with XRD results shown in Fig. 1 exhibiting no phase separation by annealing. In addition, there is no significant change in the films’ compositions up to Tα = 1200 °C, which reveals no B evaporation or oxidation.

Fig. 2 compares plan-view HAADF-STEM images and corresponding EDX maps of ZrB2.4 and Zr0.8Ta0.2B1.8 before and after annealing at Tα = 800 °C and 1200 °C. Dark regions in the HAADF-STEM image of as-deposited ZrB2.4 correspond to low-Z column boundaries. Fig. 2(a). The Zr EDX map in Fig. 2(d) indicates that these dark regions are Zr deficient, while the corresponding B EELS map in the inset of Fig. 2(d) confirms that the column boundaries are B rich compared to the columns. Contrary to as-deposited ZrB2.4, the HAADF-STEM image of as-deposited Zr0.8Ta0.2B1.8 film reveals column boundaries with lighter contrast, indicating an enrichment with heavier elements. Fig. 2(g). Complementary Zr and Ta EDX map in Fig. 2(j) shows that the column boundaries contain more Ta than the columns, in agreement with APT and XPS results published in reference 26. The B EELS map in the inset of Fig. 2(j) exhibits that the Ta-rich column boundaries are B deficient compared to the Zr-rich columns.

Annealing at Tα = 800 °C does not have a significant effect on ZrB2.4 nanostructure, Figs. 2(b) and 2(e). However, Fig. 2(c) shows...
the nanostructure of ZrB₂₄ annealed at 1200 °C comprises columns with thick, dark boundaries and small dark regions distributed inside the columns. The corresponding Zr EDX map in Fig. 2(f) reveals that these regions are Zr deficient, while the B EELS map, inset in Fig. 2(f), affirms the dark areas in Fig. 2(c) are B rich. The plan-view HAADF-STEM image, Fig. 2(h), and the corresponding Zr and Ta EDX map, Fig. 2(k), of Zr₀₈Ta₀₂B₁₈ annealed at 800 °C do not show a considerable change in the nanostructure, while annealing at 1200 °C results in more Ta segregation to the column boundaries, Figs. 2(j) and 2(l). The B EELS maps of the Zr₀₈Ta₀₂B₁₈ films annealed at 800 °C and 1200 °C, shown in the insets of Fig. 2(k) and 2(l), reveal that the column boundaries contain less B than the columns, similar to the as-deposited alloys.

Fig. 2. Plan-view HAADF-STEM images with corresponding EDX elemental maps of as-deposited (a and d) ZrB₂₄ and (g and j) Zr₀₈Ta₀₂B₁₈ films, 800 °C annealed (b and e) ZrB₂₄ and (h and k) Zr₀₈Ta₀₂B₁₈ films, and 1200 °C annealed (c and f) ZrB₂₄ and (l and l) Zr₀₈Ta₀₂B₁₈ films. B EELS maps are shown as insets.

Fig. 3 shows plan-view high-resolution HAADF-STEM, ABF-STEM, and TEM images acquired from a B-rich region of ZrB₂₄ annealed at 1200 °C. The HAADF-STEM image in Fig. 3(a) exhibits that the dark B-rich area is surrounded by crystalline columns, while the ABF-STEM image reveals that this B-rich region is not crystalline, Fig. 3(b). The high-resolution TEM image, which is acquired from another area, shows that the B-rich regions, indicated by dashed lines, have amorphous nanostructure, Fig. 3(c).

All as-deposited films have compressive residual stresses (-0.5±0.1 GPa for ZrB₂₄, -1.5±0.3 GPa for Zr₀₈Ta₀₂B₁₈, and -1.8±0.3 GPa for Zr₀₇Ta₀₃B₁₅). Annealing at 800 °C results in a decrease in stress to -0.3±0.2 GPa for ZrB₂₄, -1.2±0.2 GPa for Zr₀₈Ta₀₂B₁₈, and -1.4±0.3 GPa for Zr₀₇Ta₀₃B₁₅. The decrease in the residual
stress is interpreted as lattice point-defect annihilation. The stress after 1200°C annealing is +1.1±0.3 GPa for ZrB$_{2.4}$, -1.6±0.2 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and -1.9±0.3 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$. The observed increase in the alloys’ compressive stress results mainly from more Ta segregation into the column boundaries.

The ex-situ nanindentation hardness H and elastic modulus E of as-deposited and annealed films are shown in Fig. 4. The as-deposited alloys, Fig. 4(a), show higher H values than ZrB$_{2.4}$ (35.0±0.8 GPa for ZrB$_{2.4}$, 42.3±0.9 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and 40.5±0.5 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$). The higher H values of as-deposited alloys are primarily attributed to solid-solution hardening [44] and their narrow columns (Hall–Petch effect [45,46]). H increases for all films as a function of $T_a$ up to 800°C: 38.5±0.7 GPa for ZrB$_{2.4}$, 45.5±1.0 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and 42.7±1.0 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$. These results are confirmed by the in-situ nanindentation measurements, which reveal a similar increase in H for all layers up to 800°C: from 33.0±2.1 to 37.1±2.3 GPa for ZrB$_{2.4}$, 42.7±2.6 to 46.8±2.4 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and from 41.6±1.7 to 45.1±2.5 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$.

Fig. 4(b) shows a continuous increase in the ex-situ nanindentation E of all layers as a function of $T_a$ up to the highest annealing temperature $T_a = 1200°C$, from 480±8 to 519±9 GPa for ZrB$_{2.4}$, from 503±9 to 562±13 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and from 489±7 to 565±11 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$. The same trend is observed in the in-situ nanindentation E of the films up to 800°C: from 486±20 to 505±16 GPa for ZrB$_{2.4}$, from 495±18 to 543±22 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and from 494±17 to 538±20 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$.

The combination of XRD, XPS, STEM, EDS, and EELS results reveals that no secondary phase precipitation or spinodal decomposition takes place in the Zr$_{1-x}$Ta$_x$B$_y$ films annealed up to 800°C. This can be mainly attributed to their high melting points (3245°C for ZrB$_2$ and 3000°C for TaB$_2$ [47]). Bulk diffusion which results in recrystallization typically occurs at a homologous temperature $T_h$ (annealing temperature to melting-point temperature ratio) above
Fig. 5. Plan-view HAADF-STEM images of (a) as-deposited, (b) 800 °C, and (c) 1200 °C annealed Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$ thin films. Arrows indicate stacking faults and microtwins. Semicoharent column boundaries can also be seen. The images are trimmed much to offer lattice resolution because the main purpose here is comparing planar defects at different temperatures. Yet, inspection of larger sets of images from wider areas of the samples confirm that the microstructure with defect density is the same between (a) and (b).

-0.5 [48]. Hence, diffusion is significantly limited in the Zr$_{1-x}$Ta$_x$B$_y$ films up to 800 °C as their $T_B$ is -0.2 at 800 °C.

Fig. 5 compares the plan-view high-resolution HAADF-STEM images of as-deposited, 800-°C and 1200-°C annealed Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$. The nanostructure of as-deposited films, Fig. 5(a), consists of crystalline columns (cores) surrounded by narrow disordered boundaries (shells) [27]. Planar defects, most notably stacking faults, can be observed inside the columns. In addition, there are some contrast changes in the columns, which result from local residual strain in the lattice caused by compositional inhomogeneities at a length scale shorter than that required for spinodal decomposition. Annealing the alloys at 800 °C does not significantly change the nanostructure; the columns retain the planar defects, indicated by arrows in Fig. 5(a) and 5(b). This confirms that no considerable atomic rearrangement (e.g. recrystallization) occurs in Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$ nanostructure by annealing up to 800 °C. However, the plan-view high-resolution HAADF-STEM image of the alloy annealed at 1200 °C in Fig. 5(c) reveals a significant planar defect annihilation inside the columns, while the column boundaries still appear disordered.

Excluding the two classical mechanisms of age hardening (secondary phase precipitation and spinodal decomposition) and establishing no considerable residual-stress effect on hardening (compressive stresses decrease during annealing up to 800 °C), we instead consider the role of point defects. Sputter-deposited films typically have significant fractions of vacancies, interstitials, and anti-site substitutions of atoms [49] that require lower activation energies for annihilation at $T_B < -0.5$ than recrystallization [50]. Hence, the increase in thehardness of the Zr$_{1-x}$Ta$_x$B$_y$ films by annealing up to 800 °C can be mainly due to point-defect recovery. Correspondingly, the elastic moduli of layers increase during the recovery of strong chemical bonds, Fig. 4(b). In addition, stacking faults that serve as barriers against dislocation glide are preserved up to 800 °C and contribute to maintain hardness high.

However, the ex-situ nanoindentation hardness decreases to 36.5±0.8 GPa for Zr$_{2.4}$, 41.5±0.8 GPa for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and 40.2±0.5 GPa for Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$ at 1200 °C, Fig. 4(a). This softening can be attributed to recrystallization and column coarsening. For these layers, $T_B$ is -0.4 at 1200 °C that is sufficiently high for diffusion and activating recrystallization. This atomic rearrangement is also demonstrated in Fig. 5(c) indicating stacking fault annihilation inside the columns, which contributes to a decrease in hardness. The films’ elastic moduli continue increasing at $T_B > 800 °C$, Fig. 4(b), due to recrystallization, which reduces the volume of the disordered metallic-glass-like boundary regions [51]. In general, all layers have high hardness values (H > 34 GPa) over the entire $T_B$ range.

To conclude, we study thermal stability and mechanical properties of Zr$_{2.4}$, Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$, and Zr$_{0.7}$Ta$_{0.3}$B$_{1.5}$ thin films as a function of annealing temperature. All films become harder during annealing up to 800 °C, with the highest hardness achieved for Zr$_{0.8}$Ta$_{0.2}$B$_{1.8}$ (45.5±1.0 GPa). This age hardening is attributed to point-defect recovery that results in enhanced chemical-bond density, in combination with retaining stacking faults. Eventually, hardness decreases at $T_B > 800 °C$ due to recrystallization, column coarsening, and stacking fault annihilation.

Declaration of Competing Interest

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

Acknowledgments

We acknowledge support from the Knut and Alice Wallenberg (KAW) foundation for Project funding (KAW 2015.0043), a Fellowship/Scholar Grant, and support of the electron microscopy laboratory in Linköping. Financial support from the Swedish Research Council VR Grant 2014-5790, 2018-03957, and 642-2013-8020, the VINNOVA Grant 2019-04882, and Carl Tryggers Stiftelse contracts CTS 15:219, CTS 17:166, and CTS 14:431 are also gratefully acknowledged. Furthermore, the authors acknowledge financial support from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University.
(Faculty Grant SFO Mat LIU No. 2009 00971). Supports from the Swedish research council VR-RI (2017-00646-9) for the Accelerator based ion-technological center and from the Swedish Foundation for Strategic Research (contract RIF14-0053; for the tandem accelerator laboratory in Upplands University, and contract RIF14-0074; for the electron microscopy laboratory) are acknowledged.

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