High tensile strength of sputter-deposited ZrB_2 ceramic thin films measured up to 1016 K

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Abstract

We report the results of tensile experiments on 900 nm sputter-deposited films of ZrB_2 , performed at temperatures ranging from ambient to 1016 K. The ZrB_2 samples were tested using micromachined sample frames with integrated micro-heaters. Transmission electron microscopy shows that both as-deposited films and films heated above 1000 K consist of two distinct layers, an amorphous layer and a crystalline layer with a very fine columnar structure. The ZrB_2 films have a room-temperature tensile strength in excess of 1.2 GPa, far exceeding the tensile strength of bulk ZrB_2 , but their stiffness is lower and decreases significantly with increasing temperature. The reduction in stiffness is attributed to the presence of the amorphous phase and the high density of transverse grain boundaries in the crystalline region. The fracture toughness of the ZrB_2 films was measured by introducing pre-cracks in the tensile specimens with a focused ion beam, and was found to be $2.57 \pm 0.03 \text{ MPa}\sqrt{\text{m}}$, similar to values reported for bulk ZrB_2 .

Keywords: Zirconium diboride; thin film; in-situ tension test; high-temperature deformation; fracture toughness

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1. Introduction

Ultra-high-temperature ceramics (UHTC) are loosely defined as ceramics with melting points in excess of 2500°C and are usually based on the transition metal borides, nitrides, or carbides[1]. Among these ultra-high temperature ceramics, zirconium diboride (ZrB_2) stands out with a unique combination of properties, including a very high melting point (above 3000°C), high hardness, excellent oxidation resistance, as well as outstanding thermal and electrical conductivities[2]. This combination of properties makes ZrB_2 an attractive material for use in extreme environments. Examples include leading edges of hypersonic space vehicles, crucibles, high-temperature electrodes, and components for corrosive environments[2-7]. ZrB_2 is also of interest as a substrate material for hetero-epitaxial growth of GaN single crystals because of the small lattice mismatch between ZrB_2 and GaN, and their closely matched coefficients of thermal expansion[8-10].

Comprehensive studies have been performed to understand and improve the physical and mechanical properties of bulk ZrB_2 . These studies have shown that the behavior of bulk ZrB_2 depends sensitively on the degree of densification achieved during synthesis and on the ensuing microstructure[2, 11-14]. While there are many reports on the behavior of bulk ZrB_2 , the properties of ZrB_2 thin films are relatively less explored[15, 16]. Thin films are expected to behave differently from bulk ZrB_2 because of the much smaller grain size and flaws present in the films. A better understanding of the mechanical behavior of ZrB_2 with microstructures at the nano-scale may lead to new applications such as hard, oxidation-resistant coatings, conductive layers for ultra-high temperature electronics, or high-temperature solar selective absorbers[17].

In this paper, we report on the mechanical behavior of 900 nm sputtered ZrB_2 thin

films measured at temperatures up to 1016 K. ZrB_2 thin-film samples were prepared by magnetron sputtering onto micro-machined frames with integrated heating elements. The samples were deformed inside a scanning electron microscope (SEM) using a custom-built tensile tester [18, 19]. Details of the sample fabrication procedure and a method for measuring the fracture toughness of freestanding thin films are presented. Cross-sectional transmission electron microscopy (TEM) images reveal that the ZrB_2 films consist of an amorphous layer and a crystalline layer with a very fine columnar grain structure. Although ZrB_2 has relatively low tensile strength in bulk form, we report exceptionally high tensile strength, both at room temperature and at elevated temperatures. In contrast to the strength, the stiffness of the films is much lower than for bulk ZrB_2 .

2. Materials and methods

2.1. Specimen preparation and material characterization

The ZrB₂ tensile samples and supporting frames were fabricated using standard silicon micromachining techniques. As illustrated in Figure 1(a), the fabrication process starts with a (100) Si wafer coated on both sides with a 300 nm low-pressure chemical vapor deposited (LPCVD) Si₃N₄ film and an additional 200 nm plasma-enhanced chemical vapor deposited (PECVD) SiO₂ film. First, a positive photoresist (Shipley, S1831) is spin-coated on the front side of the wafer and exposed to UV for patterning. A 1.4 μm film of tungsten is sputter deposited on the front side and patterned by lift-off (Figure 1(b)) to fabricate the micro-heaters. The front side of the wafer is again coated with photoresist and patterned to define the shape of the tensile specimens. The film of interest – a 900 nm film of ZrB₂ in this study – is deposited and patterned using lift-off (Figure 1(c)). To make the tensile sample freestanding, the Si₃N₄ on the other side of the substrate is selectively removed and the Si substrate is etched using a 30% potassium hydroxide (KOH) solution at 85°C (Figure 1(d)). In the final step of the fabrication process, the Si₃N₄/SiO₂ layer, which acts as an etch stop during KOH etching, is removed by reactive ion etching with CF₄ (Figure 1(e)). The sample frames have two sets of supports to facilitate sample handling. Once the frame with the sample is mounted in the tensile tester, both supports are removed and the sample is ready for testing (figure 1(f)).

The ZrB₂ films were deposited in a magnetron sputter deposition system (AJA International) with a base pressure of 1×10^{-7} Torr. The depositions were performed using a 50.8 mm diameter ZrB₂ target at a DC power of 200 W and an argon working pressure of 4 mTorr. Figure 1(g) shows the micro-fabricated frames with the freestanding ZrB₂ tensile samples.

Figure 1(h) is an SEM image of a typical sample, clearly showing the integrated heaters at either end. The samples had an average thickness of 907 ± 26 nm, gauge widths of 100, 150, and 200 μm , and gauge lengths of 1243 ± 12 and 2452 ± 32 μm . Film thicknesses were measured using a physical profilometer (Veeco Dektak 6M). Pre-cracks in the specimens for the fracture toughness measurements were fabricated using a 30 keV focused Ga^+ ion beam in a Zeiss NVision 40 Dual-Beam focused ion beam. The cracks were oriented perpendicular to the tensile axes of the specimens and extended through the thickness of the specimens. The lengths of the pre-cracks varied from 5 to 17 μm . Figure 2 shows an SEM image of a typical pre-crack. The crystallinity of the films was assessed by X-ray diffraction (XRD) in a Bruker D8 Discover system using $\text{CuK}\alpha$ radiation. The surface structure of the sample was characterized in a Zeiss Ultra55 field emission SEM. Cross-sectional TEM images were acquired using a JEOL 2010 system operating at 200 keV.

2.2. Mechanical testing at room temperature

Uniaxial tensile tests were performed inside a scanning electron microscope using a custom-designed tensile tester described in detail in reference[18]. All tests were performed at a nominal strain rate of $3 \times 10^{-5} \text{ s}^{-1}$. Displacement and load were measured with a resolution of 10 nm and 9.7 μN , respectively. The fracture toughness of the samples was measured by loading tensile samples with pre-cracks until failure. The fracture stress, σ_f , i.e., the maximum nominal stress in the stress-strain curves, was measured as a function of pre-crack length and the fracture toughness of the film was determined from a simple fracture mechanics analysis. According to linear elastic fracture mechanics[20], the stress intensity factor K for a crack in the center of a plate subject to a remote tensile stress σ perpendicular to the crack can be calculated from

$$K = \sigma \sqrt{\pi a} f\left(\frac{a}{W}\right), \quad (1)$$

where W is the width of the sample, a is half the crack length, and $f(a/W)$ is a function approximated by

$$f\left(\frac{a}{W}\right) = \sqrt{\frac{\pi a}{4W} \cdot \sec\left(\frac{\pi a}{2W}\right)} \left[1 - 0.025 \left(\frac{a}{W}\right)^2 + 0.06 \left(\frac{a}{W}\right)^4\right]. \quad (2)$$

The crack propagates when the stress intensity factor is equal to the fracture toughness, K_C , of the material. Thus, the fracture stress σ_f of a tensile specimen with a pre-crack can be written as

$$\sigma_f = \frac{K_C}{\sqrt{\pi} f\left(\frac{a}{W}\right)} \cdot a^{-1/2}, \quad (3)$$

i.e., the fracture toughness of the sample is readily determined from a graph of fracture stress versus $a^{-1/2}$.

2.3. Mechanical testing at elevated temperatures

To determine the temperature of the micro-heaters, the temperature coefficient of resistance (TCR) of the tungsten heating elements was measured by placing the sample frames on a hot plate and measuring the resistance of the heating elements as a function of temperature from 20 to 180°C. The TCR measured using this procedure was shown previously to accurately determine the temperature of the heating elements even above 1000 K [21]. During testing, the ZrB_2 specimens were heated inside the SEM chamber by passing a current through the micro-heaters. The precise temperature of the micro-heaters was monitored by measuring the resistance of the heating elements using a four-point measurement setup. Finite element modeling has demonstrated that, for this test setup, the temperature variation across the tensile specimens is less than 2% at temperatures up to 1020 K (Figure S1 in Supporting Information). A similar approach was used previously to measure the stress-strain curves of copper and gold thin films at temperatures up to 430°C [18, 19]. Further details on the tensile tester and the micro-heaters can be found in reference [18].

3. Experimental Results

3.1. Microstructure of the ZrB₂ samples

Figure 3 shows typical X-ray diffraction results for an as-deposited ZrB₂ sample, along with TEM and SEM images of the film. The TEM cross-sections reveal that the sputtered ZrB₂ film consists of an amorphous layer (Figure 3(b,d)), followed by a layer with a fine columnar structure (Figure 3(b,c)). The diffraction results confirm that the top layer is crystalline and has a preferred (0001) crystallographic orientation [22, 23]. The average width of the grains in the crystalline layer is 12.7 ± 3 nm; no voids are observed at the grain boundaries. The SEM image in Fig. 3(e) shows that the surface of the film in the as-deposited state is smooth. Figure 3 also shows SEM and TEM images of a sample annealed at 1060 K for 3 minutes. The microstructure of the annealed sample (figure 3(f, g)) is unchanged from the as-deposited sample (figure 3(c, d)), but its surface roughness has increased significantly (figure 3(e, h)), indicative of at least some surface diffusion during the annealing process.

Both amorphous and nano-crystalline structures are reported for films of refractory materials that are sputter-deposited at room temperature [24-26]. Amorphous structures are attributed to rapid quenching of the atoms as they arrive on the substrate [27-29], while nano-columnar structures [30-32] occur if there is some mobility. We believe that the amorphous-to-nano-crystalline transition in these sputter-deposited films is the result of an increase in the substrate temperature during the sputter deposition process.

3.2. Stress-strain curves

Figure 4 shows the stress-strain curves of 900 nm sputtered ZrB_2 films obtained at several different temperatures. The curves are linear up to final rupture, indicating elastic deformation without any plastic deformation. Films tested at room temperature show an exceptionally high fracture stress of 1300 ± 79 MPa (Table I) compared with previously reported flexural strengths of 350 - 723 MPa for bulk ZrB_2 [2, 12, 13, 23, 33]. Uniaxial tensile testing is not a common method for evaluating the mechanical behavior of brittle ceramics such as ZrB_2 , because the strength of a brittle material when loaded in tension is greatly reduced by the presence of flaws in the material. Even so, sputter-deposited ZrB_2 thin films show a significantly higher fracture stress in tension than bulk material. This observation suggests that these samples have much smaller flaws than bulk ZrB_2 because of the unique sample synthesis. Table I lists the strength of the samples as a function of temperature – the strength initially increases with temperature and is still 950 MPa at 1016 K. The stiffness of the films, on the other hand, is much lower than for bulk materials and decreases significantly with increasing temperature.

3.3. Room-temperature fracture toughness of sputtered ZrB₂ films

Typical stress-strain curves of tensile specimens with pre-cracks are presented in figure 5(a). Figure 5(b) shows the fracture stress σ_f corrected for the effect of the finite sample width as a function of crack length. As expected from equation (3), the fracture stress is inversely proportional to the square root of the crack length. SEM images of the samples (e.g., figure 6) show that all samples failed at the pre-crack. The fracture toughness K_{IC} of the coatings can then be calculated using equation (3) (Table II). The experimental value of the fracture toughness is $2.57 \pm 0.03 \text{ MPa}\sqrt{\text{m}}$, similar to values reported for bulk ZrB₂ ceramics [7, 12, 33, 35, 36]. Strictly speaking, this value is an upper bound for the fracture toughness of the coatings because of the finite radius (Figure 2 (b)) of the crack tip. Because the crack tip radius is very small ($\sim 100 \text{ nm}$), we expect this effect to be small.

4. Discussion

4.1 Elastic moduli

The elastic modulus of the sputter-deposited ZrB₂ coatings is much lower than for bulk ZrB₂[2, 12, 13]. While low elastic moduli are commonly reported in studies on thin films or nano-crystalline materials[37-39], the stiffness of a material is not intrinsically length-scale dependent; a reduced elastic modulus is typically caused by a strong crystallographic texture or imperfections in the coating. Here, we consider the following four possibilities: 1) crystallographic texture, 2) film porosity, 3) microcracking and 4) the effects of the amorphous/nano-crystalline structure.

Crystallographic texture

Several studies have reported experimental or calculated elastic constants for ZrB₂ single crystals [10, 34, 40]. The elastic modulus of a hexagonal crystal such as ZrB₂ can be calculated from the single-crystal elastic constants using,[41]

$$1/E = s_{11} \cdot \sin^4\theta + s_{33} \cdot \cos^4\theta + (s_{44} + 2s_{13})\sin^2\theta \cdot \cos^2\theta, \quad (4)$$

where θ is the angle between the tensile direction and the c -axis of the crystal, and s_{ij} represents the compliance constants. The elastic modulus of single-crystal ZrB₂ ranges from 388 GPa for the c -axis orientation to 533 GPa in the basal plane of the crystal. From Table I, it is evident that the elastic moduli of the polycrystalline ZrB₂ films are well outside this range. Since hexagonal crystals are elastically isotropic in the basal plane, a film with a perfect (0001) texture would have an in-plane modulus of 533 GPa. Bounds for the elastic modulus of a random polycrystalline solid can be calculated from the single-crystal constants using Reuss[42] and Voigt[43] averages, yielding a possible range of 524 to 538 GPa. Thus, if the reduced stiffness were due to the crystallographic texture of the coatings, the experimental

modulus would lie between the moduli of polycrystalline samples with an arbitrary and a perfect (0001) fiber texture, which is clearly not the case.

Film porosity

The presence of porosity in the film is another possible cause for a reduced elastic modulus. The effect of porosity on the stiffness can be estimated using a simple empirical relation [13, 44]:

$$E = E_0(1 - bp) \quad (5)$$

where E is the elastic modulus of the porous material, E_0 the elastic modulus of the fully dense material, p is the volume fraction of pores and b a numerical constant that accounts for pore geometry. While several empirical relations have been introduced in the literature to fit modulus-porosity data for ceramic materials, a simple linear dependence seems to represent the data very well [13, 44-46]. If we take a b -value of 2.52, as reported for ZrB_2 -based materials [46], a decrease of the elastic modulus to 295 GPa would require a porosity of approximately 18 % according to equation (5). This is a very high level of porosity and inconsistent with the SEM surface and TEM cross-sectional images of the sputtered films (figure 3).

Micro-cracking

Micro-cracking along grain boundaries is another possible cause for the reduction in stiffness. The effects of micro-crack geometry and density on the effective modulus have been analyzed by several researchers for different types of cracks [47, 48] and micro-cracking has been suggested as the main mechanism for the reduced elastic modulus observed for evaporated films [39]. Huang et al [39] reported an average decrease of 20% in the elastic modulus of Al, Ag, Cu and Ag/Cu multilayer thin films. Micro-cracks arise along

grain boundaries because of limited diffusion during deposition of the film. This effect is especially important for refractory materials and can lead to a fibrous structure with poor cohesion between the grains. TEM images of the sputtered ZrB₂ films do not, however, reveal any micro-cracking (Figure 3), ruling out this potential cause.

Effects of the amorphous/nano-crystalline structure

TEM cross-sections (Figure 3 (d) and (f)) show that the lower half of the ZrB₂ film is amorphous. The thickness of this amorphous layer is approximately 400 nm. While there is little or no information on the elastic modulus of amorphous ZrB₂, a few groups have compared the stiffness of other amorphous materials with their crystalline counterparts, including Ni-P [49, 50], Pd-Si [51, 52], Si₃N₄ [53, 54] and have reported 30 to 40% lower values for the elastic modulus or shear modulus of amorphous materials.

The upper half of the film has a nano-crystalline structure with an average grain width of 12.7 ± 3 nm. Several groups [55-57] have reported that the elastic moduli of nano-crystalline materials can be significantly reduced because of the large fraction of grain boundaries in the materials: grain boundaries are less dense than the crystalline material and have a lower stiffness than the grain interior. Molecular dynamics simulations [55, 57] have suggested that the elastic stiffness of a grain boundary can be as low as 25% of the stiffness of the grain interior, leading to significant reductions in the elastic moduli for materials with grain sizes below 20 nm. Assuming a simple array of hexagonal columnar grains, the effective stiffness of a material E_{eff} can be estimated from [39]

$$\frac{3d/4}{E_{eff}} = \frac{3d/4 - 2\delta/\sqrt{3}}{E_{eff}^*} + \frac{2\delta/\sqrt{3}}{E'} \quad (6)$$

In this expression,

$$E_{eff}^* = \frac{\delta E' + (d\sqrt{3}/2 - \delta)E}{d\sqrt{3}/2}, \quad (7)$$

while E and E' represent the elastic moduli of the grain interior and the grain boundary, respectively, δ is the grain boundary thickness, and d is the grain diameter. Assuming that $\delta = 0.5$ nm (estimated from grain boundary diffusion measurements and HRTEM studies[58-61]) and taking $E' = 0.25 E$ yields an effective modulus of approximately 400 GPa for a crystalline film with a 12.7 nm grain size.

Based on the discussions above, we submit that the combined amorphous/nano-crystalline structure of the ZrB_2 coatings is likely the main cause of the reduced stiffness. Given this structure, we would expect an elastic modulus in the 350 to 375 GPa range. This is still larger than the experimental value, but this gap can be readily accounted for by a low level of porosity or small deviations in the stoichiometry of the coatings.

4.2. Temperature dependence of mechanical behavior

The ZrB₂ coatings have a room-temperature tensile strength above 1.2 GPa, far exceeding the flexural strength of typical bulk ZrB₂ (Figure 7 (a)). Initially the strength increases with temperature and then decreases to 950 MPa at 1016 K. The size of the largest flaws in the ZrB₂ samples can be estimated from the measured fracture toughness and the room-temperature fracture strength of the un-notched samples using equation (3). This estimate yields a maximum flaw size of approximately 1.25 μm , i.e., on the order of the film thickness. Since the flaw size is independent of temperature, one would expect the fracture toughness to have a similar temperature-dependence as the fracture strength. Thus, the initial increase in fracture strength with rising temperature can be attributed to an increase in the fracture toughness of the coatings.

As the temperature increases, the elastic modulus decreases from 295 GPa at room temperature to 170 GPa at 1016 K. This reduction cannot be explained by the effect of temperature on the intrinsic elastic behavior of the coatings, since the elastic modulus estimated from the single-crystal elastic constants [10, 34] decreases by at most 6% over the same temperature range (Table I). The reduction in modulus is, however, consistent with experiments on bulk ZrB₂ [23, 36, 62] (Figure 7(b)): the stiffness decreases gradually at first and then drops more rapidly at elevated temperature. Similar behavior has been reported in other ceramics including alumina, silicon nitride, magnesia, etc. [63-65]. This behavior is attributed to a softening of the grain boundaries and the activation of grain boundary sliding. Similar behavior is also observed in amorphous solids, where the stiffness drops precipitously near the glass transition temperature [66]. It should be noted that the reduction in stiffness occurs at significantly lower temperatures in the ZrB₂ coatings than for bulk samples. While

a deeper study is required to further elucidate the reason for this difference, we suggest that the amorphous and nano-crystalline nature of the ZrB_2 coatings facilitates limited inelastic deformation at higher temperatures, making the temperature effect more pronounced for the coatings.

4.3. ZrB₂ as a structural material for high-temperature MEMS

The resistivity of the ZrB₂ films was measured to be $258 \mu\Omega \cdot cm$, larger than the reported bulk value ($7 - 22 \mu\Omega \cdot cm$ [7, 68, 69]), but comparable to the resistivity of sputtered ZrB₂ thin films in other studies ($95 - 440 \mu\Omega \cdot cm$ [15, 24, 70, 71]). We attribute the larger resistivity to the effect of the grain boundaries, as commonly observed in thin films or nanocrystalline metals, and to the amorphous structure. Amorphous metals are reported to exhibit much higher electrical resistivity than their crystalline counterparts because of their intrinsically disordered nature [72-75]. While the resistivity of the films is indeed larger than the bulk value, the films still exhibit metal-like electrical conductivity.

The combination of excellent electrical conductivity, thermal conductivity, and high tensile strength makes sputtered ZrB₂ a promising structural material for microelectromechanical systems (MEMS). To date, silicon has been widely used as a structural MEMS material in room temperature applications. However, the need for MEMS materials that can be used in extreme environments calls for the development of other materials that can be fabricated at the micro/nano scale. Electrodeposited nickel has gained interest as a structural material for MEMS applications because of its high mechanical strength at room temperature, excellent electrical, and thermal conductivity [76, 77]. However, the use of Ni in high-temperature applications is severely limited due to creep and microstructural instabilities that lead to loss of mechanical strength at elevated temperatures [78]. As a result, research on high-temperature MEMS materials recently shifted towards Ni-based superalloys, which offer good high-temperature strength [79]. Still, Ni-based superalloys face problems related to their large coefficient of thermal expansion (CTE). Materials with good mechanical strength at elevated temperature and lower CTE

are needed. Among silicon-based material systems, silicon carbide (SiC) and silico-carbonitride (Si-C-N) offer the advantage of high specific strength and thermal stability, making both materials promising candidates for high-temperature MEMS [80-84]. Here we suggest that ZrB_2 should also be considered as a potential MEMS material for use under extreme conditions. Okamoto et al [10] reported CTE values of bulk ZrB_2 along the a - and c -axis directions as 6.66×10^{-6} and $6.93 \times 10^{-6} \text{ K}^{-1}$, respectively, when averaged over the temperature range from room temperature to 1073 K. These values are considerably smaller than the CTE values reported for most metals and comparable to the CTE of many ceramics [85]. With high strength up to 1000 K, excellent electrical conductivity, thermal conductivity and low CTE, sputtered ZrB_2 is indeed a promising MEMS material.

5. Conclusions

We have fabricated tensile specimens of sputter deposited ZrB_2 thin films with integrated micro-heaters using standard photolithography and silicon micromachining techniques. The ZrB_2 coatings consisted of two distinct layers, an amorphous layer and a crystalline layer with a very fine columnar microstructure. Tensile tests were performed at temperatures ranging from room temperature to 1016 K. Samples deformed at room temperature had a fracture strength of 1300 ± 79 MPa, which is much higher than the flexural strength of 350 - 723 MPa for bulk ZrB_2 . The strength of the coatings initially increased with increasing temperature and then decreased to approximately 950 MPa at 1016 K. The elastic modulus of the samples was significantly lower than for bulk materials, most likely as a result of the amorphous/nano-crystalline structure of the coatings. The fracture toughness of the ZrB_2 films was measured at room temperature by introducing pre-cracks in the tensile specimens using a focused ion beam and was determined to be $2.57 \pm 0.03 \text{ MPa}\sqrt{\text{m}}$, which is comparable to the fracture toughness of bulk ZrB_2 .

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Table I. Summary of experiment results at different temperatures

Temperature (K)	Tensile strength (MPa)	Elastic modulus (GPa)	Elastic modulus calculated from single-crystal elastic constants for a perfect (001) texture (GPa) [10, 34]
293	1300 ± 79	295 ± 9	533
791	1480 ± 42	249 ± 9	512
1016	950 ± 27	170 ± 15	502

Table II. Summary of of fracture toughness measurements

Crack length 2a (μm)	Measured fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
5.65 ± 0.12	2.57 ± 0.03
10.26 ± 0.26	2.56 ± 0.03
16.76 ± 0.49	2.59 ± 0.03

Figure 1. Schematic of the steps used to micro-fabricate a sample frame with micro-heaters and a freestanding ZrB_2 tensile specimen (a-f); optical image of sample frames (g); SEM image showing tungsten heaters and a freestanding tensile specimen (h).

Figure 2. SEM image of a freestanding ZrB₂ thin film with a pre-crack at the center of the sample (a), and a magnified view of a typical pre-crack (b).

Figure 3. (a) XRD result of a 900 nm sputtered ZrB₂ film in the as-deposited state; (b) low-magnification TEM cross-section of an as-deposited film; high-magnification TEM cross-sections of the (c) crystalline and (d) amorphous layers in an as-deposited film; high-magnification TEM cross-sections of the (f) crystalline and (g) amorphous layers in an annealed film - figure insets shows corresponding diffraction patterns; (e) SEM image of the surface of an as-deposited film and an (h) annealed film.

Figure 4. Stress-strain curve of the sputtered ZrB₂ thin film tested at various temperatures.

Figure 5. (a) Typical stress-strain curves of ZrB₂ thin films tested at room temperature with different crack lengths. (b) Fracture stress as a function of pre-crack size.

Figure 6. (a) Low-magnification SEM image of the sample after fracture toughness testing; (b) magnified image of the region near the pre-crack indicating crack initiation from the crack tip.

Figure 7. Comparison of the elevated-temperature (a) strength and (b) elastic modulus of sputter-deposited ZrB_2 thin films with literature values for bulk ZrB_2 . Bulk results are flexural strengths reported by Rhodes [67], Zhu [36], Neuman [62] and Melendez-Martinez [33].