Nanostructure and Bonding of Zirconium Diboride Thin Films Studied by X-ray Spectroscopy

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Abstract

Zirconium diboride (ZrB_2) is an important ceramic due to its extremely high melting temperature of 3245°C and metallic electrical conductivity, properties that make it an ideal candidate thin film electrode material for high temperature electronics. In this report, thin films of varying B:Zr ratio ranging from 3–0.67 have been grown by e-beam evaporation from elemental sources. X-ray absorption spectra at the Zr K-edge were measured before and after annealing in ultra-high vacuum for 9 hours at 1000°C . Films with compositions near ZrB_2 stoichiometry show x-ray absorption fine structure that can be well modeled by crystalline ZrB_2 with a small portion of a coexisting tetragonal zirconia (t-ZrO_2) phase. Films far from stoichiometry show substantial disorder beyond the nearest-neighbor distances, and after vacuum annealing exhibit high levels of oxidation. Contributions to the x-ray absorption fine structure from a pure Zr phase are very small compared to ZrB_2 and t-ZrO_2 phases. The fact that nearly stoichiometric ($3 < \text{B} : \text{Zr} < 1.6$) as-deposited amorphous films form the same crystalline ZrB_2 nanostructure after annealing is particularly encouraging for high temperature thin film electronics applications, because it would allow the production of highly stable electrodes with e-beam evaporation without the need of any high temperature heating during film growth.

Keywords: zirconium diboride, thin film, high temperature, XANES, EXAFS, nanostructure

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1. Introduction

In the last decade, considerable effort has been directed at studying compounds of bulk zirconium diboride (ZrB_2) for structural aerospace applications,[1–4] owing to the extremely high melting temperature (3245°C) and large energy barriers for defect formation.[5, 6] ZrB_2 , like other transition metal borides, is also an excellent electrical conductor, exhibiting metallic-like conductivity that is higher than in nitride and carbide materials.[5, 7] Combined with remarkable high temperature stability, these properties make ZrB_2 an attractive material for thin film based electronic devices that must withstand harsh, high temperature environments.[7, 8]

For several decades it has been known that agglomeration limits the morphological stability of metallic thin films at elevated temperatures,[9, 10] where the dewetting process is driven by atomic diffusion that minimizes the total surface and interfacial energy of the system.[11] Some success has been achieved in avoiding agglomeration in Pt films by using adhesion layers and combining Pt with nanostructured oxide phases.[12–14] The strong bonding within ZrB_2 is expected to inhibit diffusion and limit grain growth and agglomeration, and so ZrB_2 -based thin films could replace Pt-based ones at high temperatures.

The bulk phase diagram for the Zr-B system is well understood,[15] with a few stable compositions such as ZrB_{12} , ZrB_2 , and ZrB having been observed experimentally.[16–18] ZrB_2 is by far the most stable stoichiometry, and the melting temperature decreases significantly as the composition deviates from the ideal ZrB_2 structure. Furthermore, the energy for defect formation in ZrB_2 is quite large, and thus two phase mixtures are expected when excess Zr or B is present.[6, 15] The lower melting temperature and increased reactivity of the second phase could be highly detrimental to the stability of the material at high temperatures.

Recently, the means to produce highly stoichiometric thin films of ZrB_2 have been reported.[19–21] These films are typically deposited using Ar sputtering from compound ZrB_2 targets, and the resulting films are highly textured and nanocrystalline, with conductivities $\sim 10^5$ S/m. For thin film electronics, electrodes are often patterned using photo-resist and a lift-off process in order to avoid chemical etching. Sputter deposition tends to coat the side-walls of the photo-resist, causing poor pattern definition, and thus the lift-off process benefits from the line-of-sight directionality of electron beam (e-beam) deposition.

In previous work,[22] e-beam co-evaporation of elemental Zr and B sources was used to grow films with different Zr-B compositions at low substrate temperatures (~ 50 or 600°C), and the

films were characterized before and after annealing up to 1000°C in ultra-high vacuum (UHV). However, many films were amorphous and were largely unaffected by annealing for only 1 hour, thus characterization of the film structure was difficult. In this paper, the x-ray absorption near
35 edge spectra (XANES) and extended x-ray absorption fine structure (EXAFS) are reported for Zr-B films that are amorphous as deposited, as well as films with excess Zr content. X-ray absorption spectroscopy permits the investigation of both crystalline and amorphous phases in these films before and after much longer vacuum annealing times (9 hours) at 1000°C.

2. Experimental

40 2.1. Film Growth and Characterization

Thin films with different Zr-B compositions were grown using e-beam co-evaporation from elemental Zr and B sources (99.5% purity), as described previously.[22] As before, film composition was measured using x-ray photoelectron spectroscopy (XPS) analysis of the newly grown film surface before exposure to air. In this study, films grown with B:Zr ratios measured to be 3, 1.6, and
45 0.67 were selected, covering a range from B-rich ZrB₂ to about half way between ZrB₂ and pure Zr. The XPS results showed low levels of contamination in the films, with 5–10 at% C (increasing at higher B:Zr ratios) and typically 3–14 at% O (increasing at lower B:Zr ratios.)

Films were deposited onto polished r-cut sapphire substrates, either at ambient temperature or while the substrate was heated to 600°C, in a UHV chamber with base pressure $< 10^{-7}$ Pa. The rate
50 of film growth was limited by a minimum measurable B evaporation rate of 0.1 Å/s, which forced the total growth rate to vary between 0.37 Å/s for films near ZrB₂ stoichiometry up to 0.64 Å/s for films at a B:Zr ratio of 0.67. Following deposition, films were annealed in vacuum ($< 10^{-4}$ Pa) at 1000°C for a cumulative 9 hours. During annealing, outgassing primarily released H₂O, CO, and CO₂ into the chamber, as determined by a residual gas analyzer. After 1 hour at 1000°C, films were
55 removed from vacuum and examined for grain growth with x-ray diffraction (XRD), then reinserted for a further 8 hours of annealing, after which XRD was performed again. For XRD measurements a Bragg-Brentano geometry was used with a 7° sample tilt to remove diffraction from the sapphire substrates.

X-ray absorption spectra (XAS) at the Zr K-edge were recorded using fluorescence measure-
60 ments at the MRCAT beamline 10-BM at Argonne National Laboratory.[23] Magic angle spinning at grazing incidence was employed to remove strong Bragg diffraction of the beam from the sap-

phire substrate and minimize the effects of crystallographic texture in the films themselves. The sample area was 8 mm $\times$ 8 mm, with a film thickness of $\sim$ 200 nm, and a beam spot size of 0.5 mm $\times$ 20 mm. A ZrB₂ powder standard (99.5% purity, 44 micron particle size, tape mounted) was also scanned in transmission mode. A pair of Si(111) monochromators were used, and initial energy calibration was performed with a Zr foil in the incident beam (after I₀). Thereafter, Zr reference foils were kept after the sample in the transmitted beam (after I_t) for scan-to-scan energy alignment.

2.2. XAS Data Analysis

XAS data processing was performed using the Demeter software package.[24] The absorption edge was determined by the first and second derivative, and the spectra were background subtracted by fitting pre-edge and post-edge polynomials and normalized by the difference between these polynomials at the absorption edge. The EXAFS was isolated by fitting a smooth, cubic spline polynomial above the edge and subtracting it from the data. This spline was fit up to $k = 15 \text{ \AA}^{-1}$ where possible, but in two cases aberrant oscillations prevented fitting beyond $k = 12 \text{ \AA}^{-1}$. The EXAFS were then weighted by k^2 and Fourier transformed from 2–12 $\text{\AA}^{-1}$.

The EXAFS data were modeled using several single scattering paths (and one double scattering path) from crystalline ZrB₂ and tetragonal zirconia (t-ZrO₂) structures, and fit over a range of 1.15–4.7 $\text{\AA}$ in R . An example spectrum and fit of a film at a B:Zr ratio of 3 after annealing is shown in Fig. 1, with corresponding fitting parameters shown in Table 1. This model constrains all paths to the same amplitude reduction factor and offset in the absorption edge position. Three Debye-Waller factors (σ) were used: one for the first O and B shells, a second for the first and second Zr shells, and a third for the third Zr shell and the double scattering path. Because of the high symmetry of the ZrB₂ lattice, the half-path lengths for those paths were fitted with two hexagonal lattice parameters, a and c , while a single fitted parameter was subtracted from the two t-ZrO₂ paths. Finally, a parameter approximately representing the percentage composition of each phase in the film was multiplied by the amplitude.

3. Results & Discussion

XRD analysis (not shown) indicated that, for all compositions, films deposited with no substrate heating were amorphous, while films deposited with heating showed a fine degree of nanogained structure and preferred crystallographic texture. Films with B:Zr > 2 were preferentially oriented in the $\langle 10\bar{1}0 \rangle$ direction, though other orientations were found as well. Films with B:Zr < 2 were

oriented in the $\langle 0001 \rangle$ direction. Specifically, one B-rich film deposited at 600°C (B:Zr ratio 3, denoted as film 1 in subsequent discussion), exhibited exceptionally strong ZrB_2 (0001) peak crystallinity, that remained unchanged after annealing at 1000°C for 9 hours. In Zr-rich films deposited with heating, XRD patterns revealed the growth of ZrB_2 crystallites, as well as the formation of sparse, randomly oriented t- ZrO_2 grains after annealing. However, in films deposited at ambient temperature and subsequently annealed, both ZrB_2 and t- ZrO_2 grain growth was suppressed. The formation of t- ZrO_2 (instead of monoclinic ZrO_2) is consistent with other reports of preferential growth of the tetragonal phase due to confinement during oxidation of nanolaminate films,[14, 25, 26] and may be induced by compressive stresses during oxidation of ZrB_2 . [27]

3.1. XANES of Zr-B Thin Films

Fig. 2 shows the XANES from Zr-B films with B:Zr ratios of 3, 1.6, and 0.67, as deposited and after annealing at 1000°C for 9 hours in vacuum. The first derivatives of these spectra are provided as an aid for the reader, to better illustrate the shifts in edge position and shape. XANES from a Zr foil standard and a ZrB_2 powder reference are also displayed in Fig. 2 for comparison. The data are offset for clarity, beginning with B-rich films at the bottom, and moving upward with increasing Zr concentration. The Zr K-edge energy for ZrB_2 is found to be shifted up by 1 eV relative to the Zr foil, and the Zr foil exhibits a two step edge characteristic of elemental Zr,[28] which is not present in the ZrB_2 powder.

Three trends emerge from the data in Fig. 2a. The first is a smooth decrease in the edge energy with increasing Zr concentration for as-deposited films. As the B:Zr ratio reaches 0.67, the edge energy becomes aligned with that of the Zr foil. The second trend is the increased prominence of a pre-edge feature as the Zr concentration increases. This feature is associated with transitions into hybridized p-d states in elemental Zr.[28, 29] Since there is no hybridization of the Zr p and d states in ZrB_2 , [30] this feature is suppressed at compositions around ZrB_2 stoichiometry. Finally, the features above the edge change from a large dip in absorption seen in the ZrB_2 standard, to a more level absorption plateau with two peaks near the edge as seen in the Zr foil.

After vacuum annealing at 1000°C (Fig. 2b), these trends with composition are no longer present. Prior to annealing, films 3 and 4 show less ZrB_2 character in their XANES than films 1 and 2, but after annealing all four films exhibit almost identical XANES features. Film 1 (B:Zr ratio 3, deposited with heating) was unchanged by annealing, which agrees with XRD results that indicate a much higher degree of ZrB_2 crystallinity. The edge energy of all films is shifted higher

after vacuum annealing, indicating a degree of oxidation in all films. On average, the edge energy of films 1–4 shifted up to 3.6 eV above that of the Zr standard.

125 Films 5 and 6 (B:Zr ratio 0.67, deposited with and without substrate heating, respectively), which originally had similar features to the Zr foil, lack the pre-edge step after annealing, as well as the post-edge plateau and pair of peaks. The K-edge energy is shifted upwards to 4.1 eV above the Zr foil (an energy which is consistent with a large amount of ZrO₂ phase) despite receiving the same level of exposure to atmosphere after deposition as the other films.

130 The XPS from films 5 and 6 exhibited a second, chemically shifted ZrO₂ doublet between the B 1s and Zr 3d_{3/2} peaks. This region was fit with Doniach-Sunjic-like line shapes for the B 1s and Zr 3d doublet against a Tougaard-like background, with two additional Voigt-like line shapes for the ZrO₂ doublet.[22] As seen in Fig. 2a, this disordered oxide phase had little effect on the overall electronic structure of the films based on the as-deposited XANES. After annealing the upward
135 shift in edge energy and changes in the pre- and post-edge features in the XANES of films 5 and 6 imply significant rearrangement of the oxide phase, the coexistence of ZrB₂ and oxide phases, and the absence of any elemental Zr phase.

3.2. EXAFS of Near-Stoichiometric Films

The model used to fit the data (described in Sec. 2.2) is based on the structural information
140 deduced from the XRD data. No crystalline phases other than ZrB₂ and t-ZrO₂ were observed in these Zr-B thin films. Therefore, the model assumes that the EXAFS is a linear combination of scattering paths from these two phases. A fitting parameter corresponding to the fraction of ZrB₂ phase, balanced by a t-ZrO₂ phase, was included as a multiplicative factor on the amplitude of the paths. Films 1–4 were all fitted in this way, and the correlations between the ZrB₂ fraction and the
145 amplitude was found to be less than 0.4 in each fit. The ZrB₂ fraction varied from 0.97 to 0.83 between films, with an average uncertainty of 0.051 in each fit. Thus, these four films contained nearly the same composition of ZrB₂ and t-ZrO₂ phases after annealing.

Figs. 3a and b show the magnitude of the Fourier transform of the EXAFS data for films 1–4 before annealing. Films deposited with substrate heating (1 and 3) show much longer range order
150 than films deposited at ambient temperature (2 and 4), with visible peaks out to almost 4.5 Å. Films 2 and 4 show only a small degree of nearest-neighbor order. The broad peak around 2 Å corresponds to first shell B and O atoms, which have very similar bond lengths, as seen in Fig. 1. Peaks at 3 Å and 4.3 Å correspond to the first three Zr shells in the system, and the absence of these

peaks in films 2 and 4 implies very low order in the Zr–Zr bond distances at low film deposition
155 temperature. This is not surprising for amorphous films, however, and can be explained by a lower
rate of atomic diffusion during deposition.

Surprisingly, after annealing at 1000°C for 9 hours, all four films have very similar EXAFS
features. Figs. 3c and d show the magnitude of the Fourier transform of the films after annealing,
as well as the best fit of the data to the two phase (ZrB₂ and t-ZrO₂) model. Generally, the fits are
160 quite good, though in all four samples there is intensity in the B peak that is unaccounted for, and
the shoulder produced by the O path is greater than the data. Since the path degeneracy (interpreted
as the coordination number in single scattering paths) was not varied from that of pure ZrB₂ and
t-ZrO₂ phases, this disagreement with the model may indicate that, on average, there are fewer than
eight O nearest-neighbors at each Zr site. Additionally, the deviation of B intensity from that of
165 crystalline ZrB₂ implies the coexistence of B and Zr within the unordered, amorphous phase in the
films, which has only short-range order.

Values for the Zr–B bond length and ZrB₂ lattice parameters derived from these fits are pre-
sented in Table 2 for films 2 and 4, as well as for the ZrB₂ powder standard and results reported
for bulk ZrB₂. [31] There is good agreement between the values in Ref. [31] and the data here for
170 the ZrB₂ powder, and the Zr–B bond lengths for all four measurements are in agreement as well.
The *a* and *c* lattice parameters are generally not in agreement, however. The B-rich films have a
longer *a* axis than in bulk, but the *c* axis is similar. Just above ZrB₂ stoichiometry, the *a* axis is
longer still, and the *c* axis is below the bulk values by more than twice the uncertainty in the fitted
parameter. Zr-rich films were found by XRD to be preferentially oriented in the $\langle 10\bar{1}0 \rangle$ direction,
175 so compression of the *c* axis is not unreasonable.

3.3. EXAFS of Films Far from ZrB₂

Fig. 4a shows the EXAFS from as-deposited Zr-rich films (B:Zr ratio 0.67). Both films exhibit
weaker EXAFS signals than films 1–4, indicating a higher degree of disorder even in the nearest
neighbor regions. Film 5 (deposited with substrate heating) shows a small peak just below 3 Å,
180 corresponding to scattering from Zr sites. This peak appears at smaller lengths than in films near
ZrB₂ stoichiometry, which is consistent with increased scattering from nearest neighbor Zr sites in
elemental Zr. Both films 5 and 6 also exhibit broad peaks between 1–2.5 Å, similar to those seen
in nearly stoichiometric films.

Fig. 4b shows the results of vacuum annealing films 5 and 6 at 1000°C. The EXAFS signal

185 from these films did strengthen after annealing, but not as much as for the nearly stoichiometric films. It is clear from the strong peaks at 1.5 Å, corresponding to O scattering, that the level of oxidation is much greater in films 5 and 6 compared to nearly stoichiometric films, and that film 5 is more oxidized than film 6. There is also an observed splitting in the Zr scattering peak in film 5, due to the scattering from first shell Zr in the t-ZrO₂ phase. The EXAFS of film 6 shows a smaller
190 shoulder on the high side of the Zr scattering peak, due to a smaller amount of t-ZrO₂ phase, which is consistent with the XANES analysis from Sec. 3.1.

When attempting to apply the two phase model previously discussed to the data in Fig. 4, it was found that the fit considerably underestimated the intensity at the lower edge of the Zr scattering peak. The nearest neighbor Zr scattering path in elemental Zr provides strong intensity at the lower
195 edge of the 3 Å peak. Thus, the fitting model was modified to include contributions from elemental Zr paths, as shown in Fig. 4c, and used to fit the data in Fig. 4b. Due to the number of paths that contribute to the same region, the *a* and *c* axis lengths for the ZrB₂ paths were constrained to the average values found in fitting the near-stoichiometric films, leaving the elemental Zr and t-ZrO₂ path lengths to vary independently. An additional parameter representing the fraction of elemental
200 Zr was used to allow the modeling of a three phase mixture, but the values for these parameters can only be discussed qualitatively due to increased correlations with other parameters in the fit.

Fitting the data from films 5 and 6 indicates that the intensity contributions from an elemental Zr phase were less than a quarter of the contributions from ZrB₂ and t-ZrO₂ phases. In fact, overwhelmingly the strongest peaks in the Fourier transform are from the t-ZrO₂ paths. XRD spectra
205 from these films showed only diffraction from these same two phases, with no evidence of a pure Zr crystalline phase. The lack of XRD peaks from a metallic Zr phase could be due to the fact that the majority of highly reactive Zr atoms not already in a ZrB₂-like environment become preferentially oxidized and form the t-ZrO₂ phase seen in the EXAFS. Furthermore, it was estimated from XPS that, as deposited, around than 40% of the Zr atoms in films 5 and 6 were in an oxide phase, and
210 so despite the 24000 Langmuirs of exposure to background gases during vacuum annealing, very little additional oxidation of the zirconium was actually observed.

4. Conclusions

The fabrication of highly stoichiometric ZrB₂ thin films is an important step in the development of high temperature thin film electronics. Thin films with different Zr-B compositions were grown

215 by e-beam co-evaporation from elemental Zr and B sources onto sapphire substrates with and without heating. The XANES of as-deposited films show a smooth transition in Zr K-edge energy and absorption features from B-rich ZrB_2 films towards elemental Zr. The pre-edge feature characteristic of transitions from s to p-d hybridized orbitals in Zr is suppressed around ZrB_2 stoichiometry, which is expected due to the low degree of p-d hybridization in ZrB_2 .

220 EXAFS analysis of as-deposited films indicates a higher degree of disorder with higher Zr concentrations, which remains true after annealing in vacuum at 1000°C for 9 hours. After annealing, films near ZrB_2 stoichiometry all showed a highly ordered, ZrB_2 nanostructure, with lattice parameters extracted from the EXAFS that agree well with those of bulk crystalline ZrB_2 . A small amount of t- ZrO_2 phase (~ 10 mol%) was observed in films near stoichiometry, despite deposition and annealing under UHV conditions, and the inclusion of this phase aided the EXAFS fitting. EXAFS from films with a B:Zr ratio of 0.67 indicate a much larger percentage of O nearest-neighbors than in films near ZrB_2 stoichiometry, and very small contributions from metallic Zr. The amount of ZrO_2 phase is not observed to change appreciably after vacuum annealing in any of the films.

230 The high propensity for oxidation during deposition in Zr-rich films is the primary reason that the stoichiometry of Zr-B thin films is important to their high temperature stability. Rather than observing a mixture of ZrB_2 and pure Zr at high Zr concentrations (as predicted by the bulk phase diagram), only small contributions from pure Zr are found, and instead, coexisting ZrB_2 and t- ZrO_2 phases account for the majority of the EXAFS signal. For films with B:Zr ratios between 3 and 1.6, very similar nanostructure and bonding associated with a ZrB_2 crystalline phase is observed after annealing. The fact that even amorphous films deposited with no substrate heating form the same ZrB_2 nanostructure after annealing with very little grain growth is particularly encouraging for high temperature thin film electronics, because highly stable electrodes will be able to be produced by e-beam evaporation without the need for any high temperature heating during film growth.

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Table 1: Table of fitting parameters used in modeling the EXAFS spectra in Fig. 1. The ZrB₂ paths were constrained to the hexagonal lattice parameters a and c , while the t-ZrO₂ paths were fitted with a constant offset.

Half-Path Length			
Path	Function	Value (Å)	$\sigma (\times 10^{-3})$
B ₁	$\sqrt{\frac{a^2}{3} + \frac{c^2}{4}}$	2.546	3.99(1.80)
Zr ₁	a	3.182(8)	3.35(1.00)
Zr ₂	c	3.526(15)	3.35(1.00)
Zr ₃	$\sqrt{a^2 + c^2}$	4.749	4.26(1.11)
B ₁ -Zr ₃	$B_1 + \frac{1}{2}Zr_3$	4.921	5.84
O ₁	$0.2220 - \Delta$	2.207(39)	3.99(1.80)
Zr ₁	$0.3625 - \Delta$	3.612(39)	3.35(1.00)

Table 2: Fitted values for the ZrB_2 lattice parameters and Zr-B bond distance in films 2 and 4 after annealing, compared with the ZrB_2 powder standard, and Ref. [31].

Sample	Distance	Value (Å)	$\sigma (\times 10^{-3})$
Ref [31]	Zr-B	2.54(6)	4.2(6)
	<i>a</i>	3.18(0)	2.6(5)
	<i>c</i>	3.54(2)	2.9(8)
ZrB_2 powder	Zr-B	2.542	4.62(1.86)
	<i>a</i>	3.175(5)	2.60(97)
	<i>c</i>	3.532(20)	2.60(97)
Film 2	Zr-B	2.550	4.17(1.56)
	<i>a</i>	3.192(7)	3.73(81)
	<i>c</i>	3.527(13)	3.73(81)
Film 4	Zr-B	2.549	6.15(2.17)
	<i>a</i>	3.208(8)	4.20(88)
	<i>c</i>	3.504(13)	4.20(88)

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Figure 1

Figure 2

Figure 3

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