Thin Solid Films 649 (2018) 89–96

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Chemical bonding in epitaxial ZrB_2 studied by X-ray spectroscopy

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ARTICLE INFO

Keywords:
Zirconium boride
Thin films
Bond distances
Chemical bonding
X-ray spectroscopy
X-ray photoelectron spectroscopy
X-ray diffraction

ABSTRACT

The chemical bonding in an epitaxial ZrB_2 film is investigated by Zr *K*-edge (1*s*) X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies and compared to the ZrB_2 compound target from which the film was synthesized as well as a bulk α-Zr reference. Quantitative analysis of X-ray photoelectron spectroscopy spectra reveals at the surface: ~5% O in the epitaxial ZrB_2 film, ~19% O in the ZrB_2 compound target and ~22% O in the bulk α-Zr reference after completed sputter cleaning. For the ZrB_2 compound target, X-ray diffraction (XRD) shows weak but visible $\bar{1}11$, 111, and 220 peaks from monoclinic ZrO_2 together with peaks from ZrB_2 and where the intensity distribution for the ZrB_2 peaks show a randomly oriented target material. For the bulk α-Zr reference no peaks from any crystalline oxide were visible in the diffractogram recorded from the metal with preferred 0001-orientation. The Zr *K*-edge absorption from the two ZrB_2 samples demonstrate more pronounced oscillations for the epitaxial ZrB_2 film than in the bulk ZrB_2 attributed to the high atomic ordering within the columns of the film. The XANES exhibits no pre-peak due to lack of *p-d* hybridization in ZrB_2, but with a chemical shift towards higher energy of 4 eV in the film and 6 eV for the bulk compared to α-Zr (17.993 keV) from the charge-transfer from Zr to B. The 2 eV larger shift in bulk ZrB_2 material suggests higher oxygen content than in the epitaxial film, which is supported by XPS. In EXAFS, the modeled cell-edge in ZrB_2 is slightly smaller for the film (a = 3.165 Å, c = 3.520 Å) when compared to the bulk target material (a = 3.175 Å, c = 3.540 Å) and for the hexagonal closest-packed metal (α-phase, a = 3.254 Å, c = 5.147 Å). The modeled coordination numbers show that the EXAFS spectra of the epitaxial ZrB_2 film is highly anisotropic with strong in-plane contribution, while the bulk target material is more isotropic. The Zr-B distance in the film of 2.539 Å is in agreement with the calculated value from XRD data of 2.542 Å. This is slightly shorter compared to that in the ZrB_2 compound target 2.599 Å, supporting the XANES results of a higher atomic order within the columns of the film compared to bulk ZrB_2.

1. Introduction

Transition metal borides with an AlB_2 type structure (Strukturbericht notation C32) are an emerging class of thin film materials that are much less investigated compared to hard and refractory carbides and nitrides. Among these borides, ZrB_2, demonstrates properties favorable for metal cutting, aerospace or electronic applications. This is due to the materials property envelope including high melting point (3245 °C), high hardness (23 GPa), and good corrosion resistance in combination with the highest electrical conductivity of borides with a C32 structure seen from a value of $1.0 \times 10^7\,\mathrm{S\,m^{-1}}$ [1]. The crystal structure is the key to the properties exhibited by ZrB_2. The unit cell of ZrB_2 has Zr atoms at the basis (0,0,0) and boron atoms positioned in the trigonal prismatic interstitials at (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2). From translating the unit cell of ZrB_2, the symmetry in the boride becomes evident, where the B atoms form honeycombed, graphite-like sheets that are interleaved between hexagonal close packed Zr layers. Charge-transfer occurs from Zr to B to stabilize the B-B sheet, which results in an anisotropic electronic structure and chemical bonding. This is different from the hard and refractory transition metal carbides and nitrides with their NaCl type structure (Strukturbericht notation B1) that are isotropic materials and in contrast to borides, the C or N atoms are separated in the crystal structure.

Unlike growth of hard and refractory carbide and nitride films there is no reactive sputtering process for borides such as ZrB_2. Consequently, sputtering of ZrB_2 films are conducted from ZrB_2 compound targets or from Zr-B composite targets. Recently, we advanced sputtering of ZrB_2 films by demonstrating epitaxial growth on Si(111) [2], 4H-SiC(0001) [2,3], and Al_2O_3(0001) substrates [4], using a substrate temperature of 900 °C. On investigated substrate materials, the ZrB_2 films grow as epitaxial columns a few to some tens of nm wide parallel to the substrate that extend all the way to the film-vacuum interface orthogonal to the substrate. The deposition of ZrB_2 films is typically troubled by

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https://doi.org/10.1016/j.tsf.2018.01.021
Received 3 November 2017; Received in revised form 19 December 2017; Accepted 13 January 2018
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growth of amorphous films and fine-grained films with composition that deviates from stoichiometry as well as growth of films with a high level of contaminants then foremost oxygen, see *e.g.* [5–12]. In order to advance the synthesis and control properties of this interesting boride, the chemical bonding needs deeper understanding. Comparison between epitaxial films and bulk polycrystalline samples has been lacking in the literature.

X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) are ideal techniques for determining the electronic structure properties of ZrB_2 including thin films. Both techniques have the advantage of being element specific, with signals like fingerprints, in terms of coordination chemistry around the Zr atoms. For ZrB_2, mainly bulk materials have been studied and with one study on thin films. Chu *et al.* [13] reported on EXAFS on polycrystalline ZrB_2 samples synthesized from Zr and B powders by floating zone method. The temperature-dependence showed little difference between the in-plane and out-of-plane vibrations of the Zr-Zr bonds [14]. On the other hand, Bösenberg *et al.* [15] investigated the chemical states of ZrB_2 and Zr powders by both XANES and EXAFS. The Zr edge energy of the ZrB_2 was found to be 10 eV above that of the Zr foil reference. For e-beam co-evaporated ZrB_2 thin films, EXAFS and XANES have been applied to investigate the atomic distances and the local chemical bonding structure [16]. The oxygen content in these films resulted in the formation of crystalline tetragonal ZrO_2, which yielded longer atomic bond distances as determined by EXAFS, while XANES showed high-energy shifted unoccupied Zr 4*d* electronic states.

In this work, we investigate the properties of a ~1100 nm thick epitaxial ZrB_2 film deposited on $Al_2O_3(0001)$ substrate by direct current magnetron sputtering (DCMS), using a combination of Zr *K*-edge (*1s*) XANES and EXAFS spectroscopies. The local chemical bonding structure and atomic distances in the epitaxial film is compared to these properties determined for the ZrB_2 compound target from which the film was deposited as well as to a bulk α-Zr reference. The XANES and EXAFS measurements are supported by X-ray photoelectron spectroscopy (XPS) for composition and chemical bonding structure and X-ray diffraction (XRD) for structural properties and atomic distances.

2. Experimental details

2.1. Thin film deposition and fundamental characterization

The investigated epitaxial ZrB_2 film was deposited on a $Al_2O_3(0001)$ substrate by DCMS from a ZrB_2 compound target 99.5% purity from Kurt J. Lesker Company, Clairton, PA, USA using a laboratory scale ultrahigh-vacuum deposition system. The film was grown to a thickness of ~1100 nm at a substrate temperature of 900 °C with a sputtering power of 400 W on the three-inch circular sputtering source and in an argon plasma (99.9997%) held at a 0.53 Pa. For further details of the process conditions, the reader is referred to Ref. [2] and for the properties of the films to Ref. [4]. The investigated α-Zr bulk reference was a commercial zirconium target with a purity of 99.9% from Kurt J. Lesker Company, Clairton, PA, USA. The thickness of the target materials was 3175 μm (1/8 in.).

Analysis by XPS was conducted in a Kratos AXIS UltraDLD, Manchester, U.K. system with monochromatic Al-K_α (1486.6 eV) radiation to determine the composition and chemical bonding structure of the epitaxial ZrB_2 film, the ZrB_2 compound target, and the bulk α-Zr reference. The samples were analyzed both in the as-deposited state and after sputter-cleaning with 4 keV Ar^+ ions incident at an angle of 70° with respect to the surface normal, to remove adsorbed contaminants following air exposure. The sputtered area was $3 \times 3\ mm^2$ and the analyzed area was $0.3 \times 0.7\ mm^2$. The epitaxial film was analyzed after sputter-cleaning for 60, 120, and 180 s, while the target and the reference were analyzed after 120, 240, 360, 480, 600, and 720 s sputter-cleaning. The binding energy scale was calibrated against the Fermi level cut-off using the procedure described in detail elsewhere [17]. In this way, the uncertainties associated with using the C 1*s* peak of adventitious carbon for calibration of the binding energy scale [18] are avoided. Quantification of the elements in the samples was performed using Casa XPS software (version 2.3.16), based upon peak areas from narrow energy range scans and elemental sensitivity factors supplied by Kratos Analytical Ltd. [19]. The quantification accuracy of XPS is typically around ± 5%. The structural properties of the films were assessed by XRD performing θ/2θ scans in a Philips PW 1820 Bragg-Brentano diffractometer using Cu *Kα* radiation at settings of 40 kV and 40 mA. XRD pole figures were recorded in a PANalytical EMPYREAN diffractometer at 45 kV and 40 mA to determine the epitaxial growth relationships of the ZrB_2 film to the $Al_2O_3(0001)$ substrate.

2.2. XANES and EXAFS measurements

The XANES and EXAFS spectra were measured at the undulator beamline I811 on the MAX II ring of the MAX IV Laboratory, Lund, Sweden [20]. The energy resolution at the Zr *1s* edge of the beamline monochromator was 0.5 eV. The X-ray absorption spectra were recorded in reflection mode by detecting the fluorescence yield [21], using a passivated implanted planar silicon (PIPS) detector from 150 eV below to 1200 eV above the Zr *1s* absorption edge energy (E_0 = 17.993 keV) with 0.5 eV energy steps. To minimize self-absorption effects in the sample and Bragg scattering from the substrate, the incidence angle on the sample was normal to the sample surface and varied in 0.25° steps in a maximum range of ± 3° using a stepper motor. For the thick and concentrated bulk reference samples, the extracted values of the coordination numbers represent a lower limit due to self-absorption effects, while their bond lengths are not affected. Out-of-plane measurements were not included in this study, as in the grazing incidence geometry there are major self-absorption effects resulting in reduced amplitudes and significantly lower signal-to-noise ratio.

Based on the fitting results, the Zr-B, and Zr-Zr scattering paths obtained from the Effective Scattering Amplitudes (FEFF) [22,23] were included in the EXAFS fitting procedure using the *Visual Processing in EXAFS Researches* (VIPER) software package [24]. The threshold energy E_0, is defined through the point of inflection of the absorption edge. In the fitting procedure, E_0 is used as an adjustable parameter that partly compensate for errors in the phase shifts. The edge reference energy E_0 was set to the pre-peak of each Zr *1s* X-ray absorption spectrum as determined from the first peak of the derivative of each spectrum relative to the pure hexagonal Zr reference sample E_0 was set to 17.99273 keV (α-Zr, $x = 0$).

The k^2-weighted χ EXAFS oscillations were extracted from the raw absorption data after removing known monochromator-induced glitches and peaks originating from substrate diffraction, subsequent atomic background subtraction, and averaging of 15 absorption spectra. The bond distances (R), number of neighbors (N), Debye-Waller factors (σ^2, representing the amount of disorder) and the reduced χ_r^2 as the squared area of the residual, were determined by fitting the back-Fourier-transform signal between $k = 3$–$12\ Å^{-1}$ originally obtained from the forward Fourier-transform within $R = 2$–3.5 Å of the first coordination shell using a Hanning window function [22,23] and a global electron reduction factor of $S_0^2 = 0.8$. The disorder and high-frequency thermal vibration of the atoms was accounted for by a Debye-Waller term that is proportional to the difference of the mean square atomic displacements.

3. Results and discussion

Prior to analysis by EXAFS and XANES, we determined the chemical bonding structure, composition, and structural properties of the three samples investigated. From the peaks of high intensities in the high-resolution O *1s* spectra (in the left side of Fig. 1) and peaks attributed to Zr-O bonding in the high-resolution Zr *3d* XPS spectra (in the right side of Fig. 1 and spectra at the bottom), it is evident that all samples exhibit

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