Acta Materialia 111 (2016) 166–172

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Hard and elastic epitaxial ZrB_2 thin films on $Al_2O_3(0001)$ substrates deposited by magnetron sputtering from a ZrB_2 compound target

Lina Tengdelius [a, *], Esteban Broitman [a], Jun Lu [a], Fredrik Eriksson [a], Jens Birch [a], Tomas Nyberg [b], Lars Hultman [a], Hans Högberg [a]

[a] Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden
[b] Department of Solid State Electronics, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 12 February 2016
Received in revised form
18 March 2016
Accepted 23 March 2016

Keywords:
Borides
Epitaxial growth
Mechanical properties
Nanoindentation
Sputter deposition

ABSTRACT

Zirconium diboride (ZrB_2) exhibits high hardness and high melting point, which is beneficial for applications in for e.g. metal cutting. However, there is limited data on the mechanical properties of ZrB_2 films and no data on epitaxial films. In this study, $ZrB_2(0001)$ thin films, with thicknesses up to 1.2 μm, have been deposited on $Al_2O_3(0001)$ substrates by direct current magnetron sputtering from a compound target. X-ray diffraction and transmission electron microscopy show that the films grow epitaxially with two domain types exhibiting different in-plane epitaxial relationships to the substrate. The out-of-plane epitaxial relationship was determined to $ZrB_2(0001)\|Al_2O_3(0001)$ and the in-plane relationships of the two domains to $ZrB_2[10\bar{1}0]\|Al_2O_3[10\bar{1}0]$ and $ZrB_2[11\bar{2}0]\|Al_2O_3[10\bar{1}0]$. Mechanical properties of the films, evaluated by nanoindentation, showed that all films exhibit hardness values above 45 GPa, a reduced Young's modulus in the range 350–400 GPa, and a high elastic recovery of 70% at an applied load of 9000 μN.

1. Introduction

Early transition metal diborides are ceramic materials that, like early transition metal carbides and nitrides, demonstrate high melting points, high hardness values, chemical inertness, and good wear and corrosion resistance [1,2]. However, some properties of the diborides differ from those of the carbides and nitrides. The larger size of the B atom compared to C and N atoms is reflected in their crystal structures; the hexagonal AlB_2 type is seen for the diborides with the B atoms in trigonal prismatic interstitials, whereas the NaCl structure with filling of C/N in octahedral sites is typically found for the carbides and nitrides. In addition, B has a smaller number of valance electrons available for chemical bonding as well as a lower electronegativity value than C and N. Thus, the electronic properties of B combined with the symmetry of the AlB_2 structure affect the bonding in the diborides to give them more metallic character compared to carbides and nitrides, which is beneficial for development of hard but less brittle materials used in, e.g., metal cutting.

The literature shows that the mechanical properties of diboride bulk and thin films have been studied to a much lesser extent than the carbides and nitrides, used extensively in the metal cutting industry today. Among the diborides, titanium diboride (TiB_2) has attracted the most interest mainly due to its use in machining of aluminum, while e.g., zirconium diboride (ZrB_2) has attracted little interest. Studies on bulk materials reveal similar hardness values for TiB_2 and ZrB_2 with 24 GPa [3] and 23 GPa [1], respectively, suggesting that ZrB_2 is a suitable material to rival TiB_2 in metal cutting. For thin films, there is a large spread in hardness. TiB_2 range from 15 to 70 GPa [4–10] and ZrB_2 exhibits a spread in hardness values between 16 GPa and 5480 HV (~54 GPa) [11–13], determined from a small number of studies. The scarce data available in the literature for mechanical properties of ZrB_2 films, and the limited comparison to film microstructure as well as the lack of results from epitaxial films, warrants this study.

ZrB_2 thin films are typically synthesized by sputtering from a compound or composite target [12,14–21]. However, sputtering from compound targets introduces complexity to the process, owing to the different physical properties of the two elements, resulting in films that are usually non-stoichiometric [17,22] and/or

* Corresponding author.
E-mail addresses: lina.tengdelius@liu.se (L. Tengdelius), esteban.broitman@liu.se (E. Broitman), jun.lu@liu.se (J. Lu), fredrik.eriksson@liu.se (F. Eriksson), jens.birch@liu.se (J. Birch), tomas.nyberg@angstrom.uu.se (T. Nyberg), lars.hultman@liu.se (L. Hultman), hans.hogberg@liu.se (H. Högberg).

http://dx.doi.org/10.1016/j.actamat.2016.03.064
1359-6454/

have a high level of contaminants [14,17,18,22,23]. For direct current magnetron sputtering (DCMS) from ZrB_2 compound targets, we have previously presented a synthesis route for growth of stoichiometric films with a low level of contaminants [20], including epitaxial growth on Si(111) and 4H-SiC(0001) [21,24].

In this study, we used our previous development of DCMS of ZrB_2 thin films to investigate epitaxial growth of ZrB_2 thin films on Al_2O_3(0001) substrates. The mechanical properties of these films were then evaluated by nanoindentation. Al_2O_3 was chosen as the substrate material due to its suitable lattice match with ZrB_2 and because it has sufficient mechanical hardness to enable reliable measurements of the film's mechanical properties.

2. Experimental details

ZrB_2 thin films were deposited by a DCMS process described recently [21,24] onto Al_2O_3(0001) substrates. All films were deposited using a sputtering power of 400 W at a temperature of 900 °C and the substrate held at floating potential. The applied deposition times were 5 min and 15 min, yielding layer thicknesses of about 400 and 1200 nm, respectively. Prior to deposition, the substrates were degreased in 5 min sequential ultrasonic baths of trichloroethylene, acetone and isopropanol, and blown dry with pure nitrogen.

X-ray diffraction (XRD) θ/2θ scans were performed to determine the structural properties of the ZrB_2 films, using a Philips PW1820 diffractometer equipped with a Cu Kα source operated at 40 kV and 40 mA. XRD pole figures and reciprocal space maps (RSM, as described in Refs. [25,26]) were measured with a PANalytical EMPYREAN diffractometer at 45 kV and 40 mA. RSM of the symmetrical 0002 and the asymmetrical $10\bar{1}3$ ZrB_2 peaks were used to determine the lattice parameters of the films. The maps were recorded as consecutive coupled θ/2θ scans, each separated by an ω offset. The strain was assessed by using the following formulas:

$$\text{In}-\text{plane strain}: \ \varepsilon_a = \frac{a_{meas} - a_0}{a_0} \tag{1}$$

$$\text{Out}-\text{of}-\text{plane strain}: \ \varepsilon_c = \frac{c_{meas} - c_0}{c_0}, \tag{2}$$

where a_0, c_0 are the literature values of the *a* and *c* axes, i.e. 3.1687 Å and 3.5300 Å respectively, and a_{meas} and c_{meas} are the corresponding measured axis values, extracted from the RSM.

Transmission electron microscopy (TEM) imaging, of cross-sections of the films, was carried out by using a FEI Tecnai G2 TF20 UT HRTEM with a field emission gun operated at 200 kV. The cross-sectional TEM specimens were prepared by gluing two pieces of samples face to face together, polishing from both sides of the specimen down to 60 μm in thickness, and finally ion milling to electron transparency. Scanning transmission electron microscopy (STEM) imaging of the film surface and electron energy loss spectroscopy (EELS) was performed using a double corrected Cs FEI Titan^3 microscope operated at 300 kV. The plan view specimens for STEM were manufactured by polishing the substrate from the back side down to 50 μm and ion milling from the substrate side until the sample was electron transparent.

The hardness (H) and reduced Young's modulus (E_r) as well as the elastic recovery (W_e) were investigated using a Hysitron Triboindenter TI950 instrument. The nanoindentations were conducted using a Berkovich diamond probe at applied loads in the range 500–10000 μN. In the indentation experiments, the penetration depth of the indenter was kept lower than 10% of the film thickness to avoid influence from the substrate. H and E_r were calculated by the method of Oliver and Pharr using the unloading elastic part of the load–displacement curve [27]. W_e was calculated as:

$$W_e = 100 \times \frac{\left(h_m - h_f\right)}{h_m}, \tag{3}$$

where h_m is the maximum penetration depth (produced at the maximum indentation load) and h_f corresponds to the final displacement after complete unloading. W_e is calculated taking into account both elastic and plastic deformations, and results are closely related to the work of indentation [28]. To be able to relate Vickers hardness values reported by others to our values given in GPa, an approximate conversion of the Vickers hardness values to GPa were made by multiplying the Vickers hardness values by 0.009807, i.e. converting kg/mm^2 to Pa. The exact conversion from a Vickers hardness into the nanoindentation hardness values needs a geometrical factor correction which is ~0.927 for a perfect Berkovich diamond. Scanning probe microscopy (SPM) images were obtained using the nanoindenter Berkovich diamond probe raster scanned at 0.5 Hz on areas of 5 × 5 μm size across the surface of the sample.

The electrical resistivity values of the films were calculated from measured sheet resistivity data determined from four point probe measurements with a CMT-SR200N instrument from Advanced Instrument Technology and using the film thicknesses from TEM images.

3. Results and discussion

3.1. Characterization of fundamental film properties

Fig. 1 shows a θ/2θ diffractogram obtained from a ZrB_2 film deposited on Al_2O_3(0001) for 15 min, yielding a film thickness of ~1200 nm. The diffractogram shows peaks of high intensities at 2θ angles of 25.2°, 51.8°, 81.7°, and 121.5°. These are the 0001, 0002, 0003, and 0004 peaks of the ZrB_2 phase. Other peaks visible in the diffractogram are 0006 and 00012 of the Al_2O_3 substrate at 2θ angles 41.7° and 90.6° as well as a weak ZrB_2 $10\bar{1}0$ peak at $2\theta \approx 32.7°$. This type of diffraction pattern with high intensities of the ZrB_2 000ℓ peaks indicates a large vertical coherence length in the film, i.e. the film is well-ordered from the substrate to the

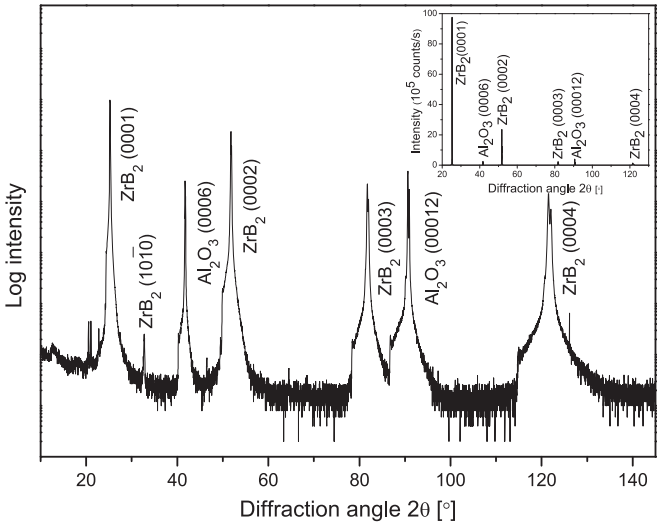

Fig. 1. X-ray θ/2θ scan of a ZrB_2 film. The inset displays the same θ/2θ scan using a linear intensity scale.