Full Length Article

Enhanced quality of single crystal CrBₓ/TiBᵧ diboride superlattices by controlling boron stoichiometry during sputter deposition

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Abstract

Single-crystal CrB₂/TiB₂ diboride superlattices with well-defined layers are promising candidates for neutron optics. However, excess B in sputter-deposited TiB₂ using a single TiB₂ target deteriorates the structural quality of CrBₓ/TiBᵧ (0001) superlattices. We study the influence of co-sputtering of TiB₂ + Ti on the stoichiometry and crystalline quality of 300-nm-thick TiB₂ single layers and CrBₓ/TiBᵧ (0001) superlattices on Al₂O₃(0001) substrates grown by DC magnetron sputter epitaxy at growth-temperatures Ts ranging from 600 to 900 °C. By controlling the relative applied powers to the TiB₂ and Ti magnetrons, y could be reduced from 3.3 to 0.9. TiB₂, grown at 750 °C exhibited epitaxial domains about 10x larger than non-co-sputtered films. Close-to-stoichiometric CrB₁.₇/TiB₂, superlattices with modulation periods Λ = 6 nm grown at 750 °C showed the highest single crystal quality and best layer definition. TiB₂, layers display rough top interfaces indicating kinetically limited growth while CrB₁.₇ forms flat and abrupt top interfaces indicating epitaxial growth with high adatom mobility.

1. Introduction

Single crystal, hetero-epitaxially grown periodic multilayers, also known as superlattices (SLs), have great potential for highly efficient interference neutron mirrors at large-scale neutron facilities owing to the possibility of achieving extremely abrupt interfaces (±0.5 atomic layer). CrB₂ and TiB₂ exhibit a small lattice mismatch (1.92 % along the a-axis) and a large difference in neutron scattering cross section which make CrB₂/TiB₂ SLs a suitable candidate for neutron optics. Hence, for this application, it is crucial to obtain high-quality single crystal SLs with periodicities (Λ = DₓB₂ + DᵧTiB₂) in the range of 1–100 nm with as abrupt interfaces as possible.

We previously demonstrated the possibility of growing relatively high-crystalline-quality CrBₓ/TiBᵧ (0001) diboride SLs [xy ∈ 1.7–3.3] on Al₂O₃(0001) substrates by magnetron sputter epitaxy (MSE) [1]. However, over-stoichiometric TiB₂, and the formation of B-rich tissue phases, particularly for SLs with layer-thickness ratios Γ = \frac{DₓB₂}{DᵧTiB₂} > 0.5, was found to cause deterioration of the epitaxy and interface quality [1]. Hence, controlling the B stoichiometry is key to obtain high-quality epitaxial growth of CrBₓ/TiBᵧ SLs with flat and abrupt interfaces. Due to the differences between sputter-ejected target constituents, where sputtered B atoms are preferentially ejected along the target surface normal, while sputtered Ti atoms have a wider angular ejection distribution with a relatively higher off-normal flux [2], sputter-deposited TiB₂ are typically over-stoichiometric (B/Ti > 2) [3–6]. Some methods were proposed to control the compositions of over-stoichiometric monolithic TiB₂ thin films [7–9]. However, they merely focus on tuning the composition of polycrystalline and nanostructured single-phase thin films rather than the crystalline quality and are not suited for growing CrBₓ/TiBᵧ SL neutron mirrors engineered with sub-nm layer thickness precision. A method to control the TiB₂ stoichiometry should not negatively affect the epitaxial growth and composition of the CrBₓ layers, for which good growth conditions for the composition (x = B/Cr ratio = 1.7 for CrB₁.₇ single layers) and crystalline quality have already been established [1]. Recently, the interest in transition metal diboride SLs for hard-coating applications has also increased owing to a possible improvement in mechanical properties through the hindering of dislocation mobility at the interfaces [10]. Mechanical properties of TiB₂/
WB₂ and TiB₂/ZrB₂ polycrystalline SLs have been studied which showed over-stoichiometric TiB₂₀₀ [11], further underlining the importance of controlling the B stoichiometry for better crystalline quality metal diboride SLs. Hellgren et al. [12] showed that the B/Ti ratio of TiB₂ thin films co-sputtered from Ti and TiB₂ targets can be tuned from y = 2.8 to 1.2 by increasing the Ti-target power while maintaining the TiB₂-target power constant. However, the as-deposited layers were amorphous, and a high-temperature (1100 °C) vacuum-annealing process was essential to achieve polycrystalline thin films. In this work, we explore a strategy for achieving high crystal quality CrB₂/TiB₂ SLs, with emphasis on obtaining the highest possible layer definition, by employing co-sputtering from TiB₂ and Ti targets to control the B stoichiometry, y, in TiB₂ₙ at substrate temperatures between 600 and 900 °C.

2. Material and methods

0001-oriented TiB₂ single layers and CrB₂/TiB₂ superlattices (SLs) were grown in a direct-current MSE system on Al₂O₃(0001) substrates. The deposition system is equipped with two type II 7.5-cm-diameter unbalanced magnetrons with a tilt angle of 25° and one 5-cm-diameter balanced magnetron with a tilt angle of 50° to the substrate normal, which are mounted in a confocal geometry at the top of the chamber. Stoichiometric 7.5-cm CrB₂ and TiB₂ compound targets, and a 5-cm Ti metal target (99.9 % purity) were used. The substrates were mounted on a substrate table below the magnetrons at a target-to-substrate distance of about 12 cm, rotating at a constant rate of 17 rpm in order to ensure good lateral thickness uniformity of the deposited layers. All three magnetrons were continuously running during the deposition, and fast computer-controlled shutters were used in front of each target to obtain the desired layer thicknesses. The base pressure for the deposition system was 3 × 10⁻⁷ Torr. Polished Al₂O₃(0001), 1.0 x 1.0 cm², substrates were chemically cleaned sequentially in trichloroethylene (3 min), acetone (5 min), and isopropanol (5 min) in an ultrasonic bath, and then blown dry with pure nitrogen before inserting the substrates through a load-lock into the deposition chamber.

All substrates were pre-heated in vacuum at 900 °C for about one hour before deposition to produce a clean well-ordered surface. A negative bias voltage of –30 V was applied to the substrate to attract ions from the plasma. To further enhance the ion flux a solenoid surrounding the substrate which dynamically coupled to the magnetic field of each of the type II magnetrons was utilized [13]. A series of 300-nm-thick single-layer thin films were synthesized by co-sputtering of Ti and TiB₂ at Tₛ = 600 °C and 750 °C, respectively. At the optimum applied power of P₁ = 120 W. Selected TiB₂ single layers were grown at Tₛ = 750 °C and 900 °C. A first series of CrB₂/TiB₂ SLs with a modulation period of Λ = 6 nm, thickness ratio Γ = B₂⁰₆/Ti = 0.7, and N = 50 bilayers was studied using co-sputtering for TiB₂ layers with P₁ = 20 and 25 W, at two different growth temperatures Tₛ = 600 °C and 750 °C. A second series of SLs with different thickness ratios Γ ≈ 0.3, 0.5, and 0.7 was deposited at a substrate temperature of Tₛ = 750 °C with Λ = 6 nm, N = 50, at the optimum applied power of P₁ = 100 W/20 W. For growing SLs, the applied power to the CrB₂ target was 80 W, yielding a CrB₂ deposition rate of 0.066 nm/s. For TiB₂, with P₁ = 20–25 W and a constant total power of P₂ = 120 W, the deposition rate was 0.055 ± 0.005 nm/s. Information about how to calculate the deposition rate in SL structures is described in [14].

X-ray diffraction (XRD) 0-2θ was performed using a Panalytical X’Pert Bragg-Brentano diffractometer with a Cu X-ray source, operating at 45 kV and 40 mA, generating Cu-Kα X-rays. On the primary side a Bragg-Brentano HD mirror was used with a ½° divergence slit and a ½° antiscatter slit, and on the secondary side a 5-mm antiscatter slit was used together with an X’celerator detector operating in scanning line mode. The elemental compositions of the films were determined using time-of-flight elastic recoil detection analysis (ToF-ERDA) and was carried out with a 36 MeV ¹²⁷I⁺⁺ probe beam incident at 67.5° with respect to the sample surface normal and the recoils were detected at an angle of 45° [15]. The Linköping double-corrected FEI Titan™ 60–300 microscope, operated at 300 kV was used for (scanning) transmission electron microscopy (STEM) studies. The microstructure and local composition were investigated by STEM high angle annular dark field (HAADF-STEM) imaging and electron energy loss spectroscopy (EELS). Cross-sectional TEM sample preparation was performed using mechanical polishing followed by Ar ion milling. Plan-view TEM samples were prepared by conventional cutting and cleaving followed by a gentle...
focused ion beam (FIB) milling [16]. X-ray reflectivity (XRR) was performed using a Panalytical Empyrean diffractometer with a Cu X-ray tube, operating at 45 kV and 40 mA. On the primary side, a parallel beam X-ray mirror was used in combination with a 1/32’ divergence slit and a parallel plate collimator was used in combination with a collimator slit at the reflected beam using a PiXcel-3D area detector in 0D mode. Neutron reflectivity (NR) was conducted at the Institut Laue-Langevin in Grenoble with the Swedish neutron reflectometer SuperADAM [17]. The measurement was performed using a monochromatic wavelength of 5.183 Å and a sample-to-detector distance of 250 cm. Footprint correction was applied using dedicated data reduction software at the beamline.

3. Results and discussion

To explore if co-sputtering of TiB$_2$ and Ti can dilute the amount of B in the over-stoichiometric TiB$_2$ layers without causing any amorphization, a series of TiB$_2$ single layers were grown with different relative applied power to the Ti and TiB$_2$ targets at $T_s = 600 ^\circ$C, and evaluated with respect to composition and quality as presented in Supplementary Materials (SM). The y value in TiB$_y$ was gradually decreased from 3.3 to 0.9 by increasing the relative applied power to the Ti vs. TiB$_2$ target. TiB$_{2.3}$ gave optimal crystalline quality and stoichiometry (Fig. S1 in SM). The crystalline quality of TiB$_{2.3}$ further improved by increasing $T_s$ up to 750 °C, as discussed and shown in Fig. S2 in SM.

Fig. 1(a-f) compare plan-view HAADF-STEM micrographs and color-coded Ti-L$_\alpha$ (red), B-K (green), and O-K (blue) EELS elemental maps from the non-co-sputtered TiB$_{3.3}$ grown at $T_s = 600 ^\circ$C and co-sputtered TiB$_{2.3}$ grown at $T_s = 750 ^\circ$C. Low-magnification and lattice-resolved plan-view micrographs of TiB$_{3.3}$ in Fig. 1(a) and 1(b) show bright contrast crystalline domains embedded in a matrix of low-density. The corresponding EELS map in Fig. 1(c) indicate that the excess B in this single layer segregates to the column boundaries, forming an amorphous B-rich phase. This is a typical nanostructure of TiB$_2$ thin films grown by magnetron sputtering [18,19].

Fig. 1(a) and 1(d) show that crystalline domains in TiB$_{2.3}$ are approximately ten times larger across, than those in the highly over-stoichiometric TiB$_{3.3}$. The lattice-resolved images in Fig. 1(b) and 1(e) reveal that the larger domains in TiB$_{2.3}$ are single crystalline in nature, exhibiting clear lattice fringes in all domains, showing a higher degree of crystalline order than in TiB$_{3.3}$. Fig. 1(f) shows EELS elemental map from a junction between multiple domain boundaries in TiB$_{2.3}$. The map indicates that the boundaries are B rich, while the junctions are O rich, proving the formation of large porosities along boundary junctions where atmospheric oxygen can enter the porous TiB$_{2.3}$, possibly deteriorating the film properties [20]. This is supported by ToF-ERDA that shows 9 at. % O in the TiB$_{2.3}$ single layer grown at $T_s = 750 ^\circ$C, as compared to 1.6 at. % O in the TiB$_{3.3}$ layer.

Fig. 1(g) shows the corresponding XRD 0-20 scans of TiB$_{3.3}$ and TiB$_{2.3}$ single layers. Comparatively higher intensity of the 000 peaks in TiB$_{2.3}$ and absence of 1011-oriented crystallites indicate higher crystalline quality than for the TiB$_{3.3}$ owing to the reduced amount of B in the film.

After achieving high crystalline quality TiB$_{2.3}$ by co-sputtering at $T_s = 750 ^\circ$C, we investigated its impact on improving epitaxial growth of 0001-oriented CrB$_x$/TiB$_y$ SLs on c-plane sapphire. Without employing Ti co-deposition, CrB$_x$/TiB$_y$ SLs with highly non-stoichiometric individual layers were obtained at an optimum temperature of $T_s = 600 ^\circ$C [1]. The established, considerably higher, optimum growth temperature for TiB$_{2.1}$ by Ti co-sputtering, implies that a higher $T_s$ may be expected also for SLs. In addition to $y = 2.3$, the lower B/Ti ratio $y = 2.1$, established for TiB$_{2.1}$ single layers, would be of interest for SLs for achieving a closer-to-stoichiometry composition. Thus, a series of CrB$_x$/TiB$_y$ SLs were grown using TiB$_{2.3}$ + Ti co-sputtering with the optimal deposition parameters for TiB$_{2.3}$ and TiB$_{2.1}$, at two different growth temperatures $T_s = 600$ and 750 °C with the modulation period $\Lambda = 6$ nm and thickness ratio of $\Gamma = \frac{D_{TiB_2}}{D_{TiB_y}} \approx 0.7$. For comparison, a SL with the same $\Lambda$ and $\Gamma$ was grown without Ti co-sputtering at $T_s = 600 ^\circ$C (the same growth conditions as in [1]). The large relative thickness of TiB$_{2.1}$ $\Gamma \approx 0.7$ was chosen to give a large impact on reducing excess B leading to an improved nanostructure by co-sputtering. Fig. 2 shows the XRD 0-20 data of CrB$_x$/TiB$_y$ SLs for $y = 3.3, 2.3$, and 2.1, corresponding to TiB$_{2.3}$ single layers. The intensities of the 0001 and 0002 SLs average peaks (marked by * in the figure) and the intensities and number of visible satellite peaks, indicate that the SL grown at $T_s = 750 ^\circ$C with TiB$_{2.3}$ has the highest crystalline quality.

Compositional analyses show that the average B/transition metal (TM) ratio for the co-sputtered SLs is about 2.1, and for the non-co-sputtered SL is 2.7. In addition, there is a considerable decrease in the oxygen concentration (see in Fig. 2) from 4.6 at. % to 0.3 at. % when increasing $T_s$ from 600 °C to 750 °C in SLs with TiB$_{2.3}$. A slightly higher oxygen concentration with a similar decreasing effect (from 6.1 at. % to 1.3 at. %) upon increasing $T_s$ is observed for SLs grown with optimum deposition parameters for TiB$_{2.1}$ layers. The reduced oxygen content is attributed to a higher crystalline quality of SLs grown at 750 °C (for both $y = 2.3$ and 2.1) compared to those grown at 600 °C. This is in qualitative agreement with the observations of reduced oxygen content with improved crystal quality upon increased growth temperature as observed in ZrB$_2$ epilayers [21].

The SL grown from a single TiB$_2$ target exhibits an oxygen concentration of 0.9 at. % which is much lower than SLs synthesized at the same temperature $T_s = 600 ^\circ$C using co-sputtering. This may be explained by the elimination of O-rich free volume by segregation of excess B from the TiB$_{3.3}$ layers to triple points and domain boundaries which is known to occur in CrB$_x$/TiB$_y$ SLs grown under these conditions [1]. A higher layer definition in SLs synthesized using single TiB$_2$ target compared to the SLs co-sputtered at $T_s = 600 ^\circ$C is supported by the observation of more intense and higher order satellite peaks around the 000l average crystal peaks. However, this SL exhibits a poor crystalline quality as evidenced by low intensities of the average SL crystal peaks, the emergence of an additional peak indicating partial 1011 orientation, and with a B/TM ratio of 2.7. Hence, it is unfavourable compared to the close-to-stoichiometric SL grown at $T_s = 750 ^\circ$C which, based on the XRD, exhibits superior crystal quality and SL layer definition. Therefore, SLs

![Fig. 2. XRD 0-20 scans for superlattices with different y values corresponding to TiB$_y$ single layers, grown at $T_s = 600$ and 750 °C. Modulation period $\Lambda = 6$ nm, thickness ratio $\Gamma = 0.7$, and number of bilayers $N = 50$ were kept constant. The average 0001 superlattice peaks are marked by *](image_url)
with high structural quality and close-to-stoichiometry composition can be achieved by applying the optimized Ti and TiB2 growth conditions for synthesizing TiB2 single layers with $y = 2.3$ at $T = 750 \, ^\circC$. The oxygen concentration in this SL (0.3 at. %) is significantly less than that in single layer TiB2 (9.0 at. %), which is due to a change from porous columnar epitaxial growth to a dense 2D epitaxial growth, by the periodic introduction of CrB2 layers which are grown with a relatively higher adatom mobility, as discussed below.

Fig. 3(a) shows XRD 0-2θ patterns of CrB1.7/TiB2.3 SLs with different thickness ratios $\Gamma \approx 0.7, 0.5, 0.3$. Period $\Lambda = 6 \, \text{nm}$ and number of layers $N = 50$ were kept constant. The average 0002 superlattice peaks are marked by (*) and the order of satellites are shown by ± integers. (b, c, d) cross-sectional HAADF-STEM micrographs of CrB1.7/TiB2.3 superlattices (corresponding to (a)) with $\Gamma \approx 0.3, 0.5,$ and 0.7.

The asymmetric interface widths and their evolution during SL growth observed by TEM and revealed by XRR and NR, indicate significantly different conditions for nucleation and growth of TiB2.3 and CrB1.7. The CrB1.7 exhibits 2D growth which provides flat surfaces for TiB2.3 nucleation forming abrupt interfaces. Each TiB2.3 layer is observed to develop a rough surface, which is most pronounced for thicker TiB2.3 layers, which then are smoothened by subsequent 2D...
growth of CrB$_{1.7}$. We submit that such a growth scenario is possible by noting a large difference in homologous temperature ($T_h$) between CrB$_2$ and TiB$_2$ at $T_3 = 750$ °C ($T_{h\text{CrB}_2} = 0.4$ and $T_{h\text{TiB}_2} = 0.3$), where $T_h = (T_f/T_m)$ and $T_m$ = absolute melting temperature, that would lead to a kinetically limited growth of TiB$_{2.3}$, while the CrB$_{1.7}$ growth is characterized by a high adatom mobility. That would place the CrB$_{1.7}$ close to the sweet spot for ion-assisted epitaxial growth in the Thornton structure zone diagram [23] modified by Anders [24], while the high $T_3$ for TiB$_{2.3}$ places it in the region characterized by columnar grain growth. This model may also explain how high-quality epitaxial growth of CrB$_{1.7}$/TiB$_{2.3}$ SLs are obtained while growth of TiB$_{2.3}$ single layer occurs in a porous columnar epitaxial fashion under the same conditions.

4. Conclusions

Co-sputtering from Ti and TiB$_2$ targets provides significant control over the B content in TiB$_{x}$ (0.9 ≤ y ≤ 3.3), enabling the growth of high crystal quality CrB$_{x}$/TiB$_y$ (0001) diboride superlattices (SLs). Close-to-stoichiometry single layer TiB$_{2.3}$ grown at 750 °C represents the optimum growth conditions producing a columnar epitaxial film with a high (9 at. %) oxygen content due to porous column boundaries. The same growth conditions yield single crystal growth of CrB$_{1.7}$/TiB$_{2.3}$ (0001)/Al$_2$O$_3$(0001) SLs with an oxygen content of only 0.4 at. % which is attributed to a transition from a 3D columnar growth mode for single layer TiB$_{2.3}$ to a dense epitaxial 2D growth when introducing nm-thin CrB$_{1.7}$ layers, featuring a relatively high adatom mobility, to form SLs. Within the SLs, TiB$_{2.3}$ layers display rough top interfaces indicating a kinetically limited growth, while CrB$_{1.7}$ forms layers with flat and abrupt top interfaces with a smoothing effect, indicating epitaxial growth with high adatom mobility. The rough top surfaces of the TiB$_{2.3}$ layers result in locally abrupt interfaces with an accumulating roughness evolution. The structural analyses show that SLs grown at 750 °C exhibit the highest crystalline quality and the highest layer definition.

CRediT authorship contribution statement

Samira Dorri: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Naureen Ghafoor: Writing – review & editing, Writing, Data curation.

Justinas Palisaitis: Writing – review & editing, Investigation, Data curation.

Sjoerd Stendahl: Data curation, Investigation, Writing – review & editing.

Anton Devishvili: Formal analysis, Investigation, Writing – review & editing.

Alexei Vorobiev: Data curation, Formal analysis, Writing – review & editing.

Fredrik Eriksson: Writing – review & editing, Data curation.

Per O.Å. Persson: Writing – review & editing, Funding acquisition, Data curation.

Jens Birch: Writing – review & editing, Supervision, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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