Synthesis and characterization of CrB₂ thin films grown by DC magnetron sputtering

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CrBx thin films with 1.90 ≤ x ≤ 2.08 have been deposited by direct-current magnetron sputtering (DCMS) from a stoichiometric CrB₂ target at 5 and 20 mTorr (0.67 and 2.67 Pa) Ar pressure onto sapphire (0001) substrates. All films, irrespective of deposition conditions, exhibit a (0001) texture. Attesting to the achievement of close-to-stoichiometric composition, epitaxial film growth is observed at 900°C, while film growth at 500 °C yields (0001) fiber texture. Film composition does not depend on substrate temperature but exhibits slightly reduced B content with increasing pressure for samples deposited at 900°C. Excess B in the overstoichiometric epitaxial CrB₂:tx films segregates to form B-rich inclusions. Understoichiometry in CrB₂:tx films is accommodated by Cr-rich stacking faults on [1100] prismatic planes.

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Transition metal diborides have attracted extensive attention over the last decades owing to their unique properties, including high melting point and thermal conductivity, chemical inertness, and excellent mechanical properties [1]. Among these, TiB₂ is arguably the most studied [2]. Off-stoichiometric TiB₂ thin films have proven to be superhard, with values exceeding 40 GPa reported for both over- [3] and under-stoichiometric [4] conditions. The high hardness can be explained by disruptions in the hexagonal microstructure, induced by the unbalanced stoichiometry, which hampers dislocation propagation through the effective nanostructure [3,5].

Chromium diboride, CrB₂, is comparatively less studied than thin films. In bulk form, it has a melting point of 2200°C, high bulk modulus (211 GPa), oxidation resistance (up to 1000°C), high thermal conductivity (31.8 Wm⁻¹K⁻¹), low thermal expansion coefficient (6-10 × 10⁻⁶ K⁻¹ from room temperature to 1400°C), as well as good wear resistance, and chemical inertness [6]. It is noted that CrB₂ has superior corrosion resistance compared to TiB₂ [7]. Such excellent properties make CrB₂ a candidate for high temperature structural applications and hard coatings for cutting tools and dies [8].

CrBx thin films have to date been prepared by conversion treatment [9], thermal evaporation [10], chemical vapor deposition [11], pulsed laser deposition [12], pulsed- [13-17] and radio frequency magnetron sputtering (RFMS) [18,19], direct current magnetron sputtering (DCMS) [16,18,20-22], as well as inductively coupled plasma assisted DCMS [7].

Reports on the effects of growth parameters are limited. Dahm et al. [22] grew films by DCMS at room temperature, with varying pressure (pAr = 2 or 5 mTorr, 0.27 or 0.67 Pa). The films showed (0001) or (1011) texture. Zhang et al. [20] explored pAr = 0.28 Pa (2.1 mTorr) and substrate temperature (Ts) varied between 100 and 400°C, and found that with increasing temperature, the microstructure evolved from under-dense amorphous to dense nanocolumnar structure with a strong (0001) texture. This was explained by increased surface mobility during growth. Nedfors et al. [21] sputter-deposited nanocrystalline coatings from a CrB₅ target and obtained coatings with a slightly reduced B content (B/Cr = 1.4) and a (1011) preferred texture. Zhou et al. [18,19] em-

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ployed RFS of a CrB target to deposit CrBx films at \( p_A = 0.3 \) Pa (2.2 mTorr) and temperatures between 150 and 450°C. The latter films were highly understoichiometric, with B/Cr \( \approx 1.1 \) for all temperatures, which was explained by a higher sputtering yield of Cr from the target. While this might be true at the initial stage of the deposition, at steady state the total sputtered flux from the target must equal the bulk target composition, unless the angular distribution of sputtered species is nons isotropic. Nevertheless, their observation was similar to that made by Nedfors et al. [21], i.e., that the film B/Cr ratio is lower than that of the target. This was also observed by Audronis et al. [13-17] who performed several studies of pulsed magnetron sputtering from loosely packed powder targets. The use of a stoichiometric CrB target resulted in CrB0.92 [15], i.e., close to the results by Zhou et al. [19]. It is, however, unclear if the results from an under-dense powder target can be directly compared to a solid sintered target. Independent of choice of technique or process conditions in previous reports, no epitaxial growth of stoichiometric or close to stoichiometric films have been reported.

The Cr-B system with prevailing understoichiometry from vapor deposition is in contrast to related diborides of transition metals, for example TiB2 [3,23] and ZrB2 [24], where overstoichiometry is the norm. So, the quest becomes to develop synthesis processes that provide stoichiometric films of either sort. Here, we demonstrate how close-to-stoichiometric and epitaxial CrB2 films can be prepared applying DCMS by varying the deposition parameters of pressure (\( p_A = 5 \) and 20 mTorr; 0.67 and 2.67 Pa) and substrate temperature (\( T_s = 500 \) and 900°C) from a CrB2 compound target.

The CrBx thin films are deposited by DCMS in an Ar (99.9999% purity) discharge from a 76-mm-diameter and 6-mm-thick CrB2 target prepared by powder metallurgy (Plansee, 99.9% purity, actual composition CrB2.03 as determined by indistinguishably coupled plasma-optical emission spectrometer, ICP-OES, impurities of C, Fe, N, H, and O) positioned at a distance of 6.5 cm from the substrate, in a deposition system with a base pressure of 2.6 \( \times 10^{-7} \) Torr (~3.5 \( \times 10^{-5} \) Pa). All films are grown on 10 \( \times 10 \) mm2 α-Al2O3 (0001) substrates cleaned by ultrasonication for 5 min in trichloroethylene, acetone, and isopropanol, in sequence, followed by blow drying in N2 prior to being transferred into the deposition system via a load-lock. The substrates are preheated to the deposition temperatures of 500 or 900°C. The targets are pre-sputtered for 5 min before each deposition at the same Ar pressure and target power as used for the materials synthesis. During deposition, a -60 V bias is applied to the substrate, which is rotated at 10 rpm. The CrBx thin films are grown at \( p_A = 5 \) or 20 mTorr (-0.67 or -2.67 Pa) with an Ar flow of 10.3 and 47.3 sccm, respectively. The target power is kept at 200 W, corresponding to a target voltage and current of ~645 V and ~0.31 A at 5 mTorr and ~585 V and ~0.34 A at 20 mTorr, respectively. The deposition rate is ~35 nm/min, with no significant dependence on \( p_A \) or \( T_s \). All films are deposited for 10 min which results in final thicknesses for all films around 370 nm.

X-ray diffraction (XRD) \( \theta-2\theta \) scans, X-ray reflectivity (XRR), and XRD pole figures are performed using a PANalytical EMPYREAN powder diffractometer equipped with a Cu Kα radiation (\( \lambda = 1.54 \) Å) source operates at 45 kV and 40 mA. The optics utilized for \( \theta-2\theta \) scans are a graded mirror with 1/2° divergent slit for the incident beam side, and a parallel plate collimator with beta-filter nickel for the diffracted beam side. The incident beam optics for XRR and XRD pole figures are a hybrid mirror and an X-ray lens, respectively, and a parallel plate collimator with a nickel foil Cu Kα2-filter for the diffracted beams.

Film morphology and structure are studied by scanning electron microscopy (SEM), LEO 1550 Gemini operating with an acceleration voltage of 10 keV.

Film compositions are determined by Rutherford backscattering spectroscopy (RBS). The probe beam consisted of 2 MeV He\(^+\) ions incident at an angle of 22.5° relative to the sample surface normal with the detector set at a 150° scattering angle. Backscattered spectra are quantified using the SIMNRA software [25].

The thin films are investigated at the atomic scale using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging, selective area electron diffraction (SAED) and electron energy loss spectroscopy (EELS) techniques. Characterization is performed using the Linköping double Cs corrected FEI Titan3™ 60-300 operated at 300 kV. HAADF-STEM images are performed by using a 21.5 mrad convergence semi-angle with -90 pA beam current. The HAADF-STEM images are recorded using an angular detection range of 46-200 mrad. EELS analyses were performed using a Catan GIF Quantum ER3 post-column imaging filter. Plan-view TEM samples are prepared by a combined approach, which includes mechanical cutting, cleaving, and polishing to a few hundred μm thickness from the substrate side. The samples are fixed to the Cu grid and final milling is performed by FIB to achieve electron transparency.

**Fig. 1** shows the B/Cr ratio of CrBx films deposited at \( p_A = 5 \) and 20 mTorr (0.67 and 2.67 Pa), as a function of substrate temperature. All films have compositions close to the target composition (CrB2.03), where the B/Cr ratio is confined to the range 1.90 to 2.08. These values can be compared to the boron-to-metal ratio in TiB2 deposited in the same deposition system under similar conditions, which varies over a much wider range, between ~1.9 to ~3 [26]. The B/Cr ratio has no significant dependence on \( p_A \) or \( T_s \), within the ranges investigated. Only a slight pressure dependence is found for samples deposited at 900°C, with a reduced B content with increasing pressure. This is consistent with trends of TiB2, though less pronounced [26].

**Fig. 2** shows \( \theta-2\theta \) X-ray diffractograms from CrBx films deposited at different pressures and temperatures. Apart from the Al2O3(0006) substrate peak, all films show diffraction from the (0001) and (0002) reflections of CrB2 in the P6/mmm hexagonal AlB2 structure. The peaks have relatively low intensity for the films grown at \( T_s = 500°C \). At \( T_s = 900°C \), however, the films have higher crystalline quality with a preferred (0001) orientation. The films grown at 500°C have peaks shifted roughly 0.1° to higher angles relative to the ICDD-PDF positions and are broader. On the contrary, films grown at 900°C do not display any significant peak shift. This suggests that all CrBx films deposited at 500°C have a shorter c axis with corresponding in-plane expansion compared to films deposited at 900°C. Accounting for the thermal contraction upon cooling, we find that the films deposited at 500 °C grow in a state of mild compression of ~0.5 GPa. The tensile strain in the latter films, measured at room temperature is almost entirely due to the difference in the thermal expansion coefficient between film
and substrate, $1.05 \times 10^{-5}$ K$^{-1}$ and $7.5 \times 10^{-6}$ K$^{-1}$, respectively \[27,28\]. The films at the growth temperature of 900 °C are under a compressive stress of −0.9 GPa, due to incomplete relaxation of the 8% lattice mismatch. This growth stress is almost completely compensated upon cooling by virtue of the difference in the thermal expansion coefficients.

Fig. 3 shows pole figures of 0006 and 1014 from the α-Al$_2$O$_3$ substrate, as well as 0001 and 1011 poles from the four CrB$_x$ films. The single peak at the center of the 0001 pole plots confirms that the films have a strong texture in this direction, in agreement with the θ-2θ scans shown above. The exception is the film grown at 500 °C and 20 mTorr (Fig. 3c), i.e., the condition with the least thermal and ballistic energy input to the growth surface, where crystallites are oriented with the 0001 planes in multiple directions. The 1011 pole plots from both films grown at 900 °C (Fig. 3d and e) show six distinct points at $\psi \approx 50^\circ$, and separated by 60° in $\phi$. They are rotated by 30° relative to the 1014 poles of the substrate which confirms these films have in fact grown epitaxially onto the c-axis-oriented α-Al$_2$O$_3$, with the epitaxial relationship CrB$_2$ [0001] $\langle 10\bar{1}0\rangle$ // Al$_2$O$_3$ [0001] $\langle 1\bar{1}2\bar{0}\rangle$. The CrB$_2$ films are grown with 30 degree in-plane rotation relative to the substrate. This is in agreement with reported ZrB$_2$ epitaxial growth \[24,30\].

For the film grown at 500 °C and 5 mTorr (Fig. 3b and c), the 1011 pole forms a continuous circle at $\psi \approx 50^\circ$, showing that this film has no in-plane orientational relationship to the substrate. Instead, it has a fiber texture in the 0001 direction, in agreement with the θ-2θ XRD results in Fig. 2. Finally, the 1011 pole plot of the film grown at 500 °C and 20 mTorr (Fig. 3c), shows intensity also at other angles, because of more randomly oriented grains.

Fig. 4 shows cross-sectional SEM images of the four CrB$_x$ films grown with $p_{Ar} = 5$ and 20 mTorr (0.67 and 2.67 Pa) and $T_s = 500$ and 900 °C. The samples deposited at 500 °C display a columnar microstructure, which is typical for sputtered ceramic thin films like metal diborides \[3,4,23\], while films grown at 900 °C are more homogenous, corresponding to their epitaxial nature, see XRD pole figures in Fig. 3d and e.

Fig. 5 compares plan-view HAADF-STEM images and SAED of a slightly overstoichiometric CrB$_{2.08}$ film grown at $T_s = 900^\circ$C and $p_{Ar} = 5$ mTorr (a and c), and an understoichiometric CrB$_{1.90}$ film grown at $T_s = 900^\circ$C and $p_{Ar} = 20$ mTorr (b and d). The SAED patterns from these samples in Fig. 5a and b, reveal discrete diffraction spots that indicate high-crystalline quality, in line with our XRD results. Fig. 5a, the HAADF-STEM image of the overstoichiometric CrB$_{2.08}$ film shows dark contrast, low-atomic number, regions - up to 20 nanometers in diameter - indicating B-rich inclusions. EELS analysis confirmed that these regions are B-rich and Cr-deficient.

For the understoichiometric CrB$_{1.90}$ case, Fig. 5b, exhibits higher contrast Cr-rich planar defects (confirmed by EELS analysis) - up to 30 nanometers long - and situated on [1100] planes. These defects appear as metal-rich stacking faults of the type reported for understoichiometric TiB$_2$ films, (1.4 $< x < 2$) \[4,5\]. In ref. [5], using analytical HRSTEM, density functional theory, and image simulations, the unpaired Ti was pinpointed to inclusion of Ti-based stacking faults within a few atomic layers, which terminates the (1100) prismatic planes of the crystal structure and attributed to
the absence of B between Ti planes. Stacking faults are present in the overstoichiometric CrB₄ thin film’s crystal structure, Fig. 5, though they do not host excess B (confirmed by EELS analysis, not shown). High-resolution HAADF-STEM images in Fig. 5c and d further accentuate the high-crystalline quality of both films grown at Tₛ = 900°C.

In summary, close-to-stoichiometric CrB₄ films, 1.90 ≤ x ≤ 2.08, can be grown using DCMs from a CrB₂ target at pressures of 5 and 20 mTorr and substrate temperatures of 500 and 900°C. The film composition does not depend on substrate temperature, and has a weak dependence on pressure only for the samples deposited at higher temperature, where increasing pressure results in lower B content. At lower temperature, the films exhibit an (0001) fiber texture when grown at 5 mTorr, and more randomly oriented grains at 20 mTorr. At 900°C, the CrB₄ films grow epitaxially on Al₂O₃(0001) substrates with high-crystalline quality. Excess B in the overstoichiometric CrB₂.₀₃ films segregates into B-rich inclusions. Understoichiometric CrB₁.₅₀ films displayed B-deficiency is accommodated as planar defects comprised of Cr-rich stacking faults residing on the [1100] prismatic planes of the CrB₂ crystal structure, identical to the ones reported for understoichiometric TiB₂ epitaxial layers.

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.

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