A TEM study of the structure of magnetron sputtered chromium diboride coatings

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Abstract. Chromium diboride thin films possess desirable combinations of properties, which are attractive for a wide range of potential industrial applications. However, these properties are strongly dependent on the deposition process and parameters. In this paper, CrB$_2$ coatings deposited by DC and pulsed-DC magnetron sputtering of loosely packed blended powder targets are characterised by transmission electron microscopy techniques (electron diffraction and bright-field/dark-field imaging). Coatings with an extremely fine, nanocolumnar structure were observed. DC sputter deposited coatings exhibit a dense, short range ordered structure, while the pulsed-DC deposited coatings are defect-free, crystalline and show strong preferred orientation. A small amount of contamination of the interfacial sub-layers of the coatings by oxygen (from the target material) was found to affect the structure by suppressing growth of nanocolumns and promoting equiaxial grains of about 4-8 nanometres size, in the first ~70 nanometres of coating, close to the substrate interface. The majority of the coating however remains nanocolumnar.

1. Introduction

CrB$_2$ thin films possess attractive combinations of properties (high hardness, wear resistance, chemical inertness, high thermal and electrical conductivity), with a wide range of potential industrial applications. However, these properties are strongly dependent on the deposition process and parameters [1-10]. To understand the relationships between these deposition parameters and the resulting properties requires detailed structural analysis of the films. This understanding may then point to directions for improvement and give important information about the characteristics of the deposition process, which in this particular case is a recently-developed method involving magnetron sputtering of loosely packed powder (LPP) targets [1-4]. The combination of a pulsed magnetron sputtering (PMS) process [5] with the use of LPP targets is a new, highly flexible deposition tool, suitable for the development of novel coating systems and the optimization of film properties.

In this paper, CrB$_2$ coatings deposited in an earlier study [1] by DC and pulsed-DC magnetron sputtering of loosely packed blended powder targets are characterized by transmission electron microscopy (TEM) techniques (electron diffraction and bright-field/dark-field imaging). PMS deposited coatings analyzed in this paper exhibit the stoichiometric CrB$_2$ compositions and hardness values of the order of 39GPa. The structures of the coatings are investigated and compared.
2. Experimental Details
CrB₂ coatings were deposited in a magnetron sputter deposition rig, which had a closed field unbalanced magnetron (CFUBM) configuration, described in detail elsewhere [1-4]. The rig contained a 180 mm diameter unbalanced magnetron, installed in the ‘sputter-up’ configuration. The substrate holder, mounted 100 mm above the target, was water-cooled to ensure constant substrate temperature during each run. Substrate temperature was in the range of 110-150 °C during all runs. This range of temperature would correspond to a homologous temperature [6, 7] \( T_s/T_m \) of ~ 0.2 (melting point of CrB₂ is 2123 K), where \( T_s \) is the substrate temperature and \( T_m \) is the melting point of coating material.

For coating deposition, the target consisted of Cr (99.9% purity) and amorphous B powders (average particle size was ~ 5 µm) blended at an atomic ratio of 1:2. No further compaction was performed after mixing the blend. Additional pieces of solid boron (~1 cm³ each) were also placed at regular intervals around the ‘racetrack’ region to achieve the required film stoichiometry.

The coatings analyzed in the current study were deposited onto polished silicon wafer [(100) orientated]. The details of the coating process were reported previously [1]; however, they are also summarized briefly in table 1.

| Coating No. | Deposition mode | Target Power | Target – Substrate Distance | Deposition Pressure | Run Time | Substrate voltage |
|-------------|-----------------|--------------|-----------------------------|---------------------|----------|-------------------|
| 1           | DC              | 500 W        | 10 cm                       | 0.2 Pa              | 240 min  | -30 V             |
| 2           | Pulsed DC°      | 500 W        | 10 cm                       | 0.1 Pa              | 240 min  | -30 V             |

°Target Pulsing conditions: 100 kHz, 80% duty cycle.

TEM studies of the films were performed using a Philips EM430 microscope, operated at 300kV. Cross-section specimens of the coatings were prepared using the ‘sandwich’ technique. They were thinned mechanically to approximately 30 – 40 µm, followed by ion milling (Gatan PIPS 691—Precision Ion Polishing System) to electron transparency.

3. Results and Discussion
The lower magnification BF XTEM image in figure 1a) shows a through-thickness cross-section of the DC-deposited CrB₂ coating, with corresponding selected area electron diffraction (SAED) pattern. According to the widely accepted structure zone model and film growth descriptions [5, 6], the morphology of the film can be ascribed to ‘zone T’.

As is typical for a ‘zone T’ morphology (V-shaped columns), the macrostructure of the DC-deposited CrB₂ coating is columnar [6, 7]. Many defects are observed at the column boundaries (fig.1a), however the columns themselves are quite densely packed (probably as a result of beneficial surface bombardment conditions created by the CFUBM sputter configuration [8, 9]). The fibrous nanostructure obtained can clearly be seen in cross-sectional and plan-view BF TEM image (fig. 1b, 1d). The brighter areas visible in these images can be ascribed to low density amorphous (possibly partially voided) regions surrounding high density parallel fibers.

The diffuse SAED pattern indicates that the film possesses short range crystallographic order and can generally be described as amorphous. However, since the (101) CrB₂ diffraction ring may still be resolved, the DF image using this ring can be constructed (fig. 1c). This picture shows a discontinuous arrangement of crystalline nanofiber regions. The size of the features, i.e. the width and diameter of the fibers and size of crystallites as measured from XTEM and plan-view images is in the range of 2-3 nm. The thickness of the secondary phase surrounding the nanofibers appears to be ~1-2 nm.

The structure of PVD thin films is generally dependant on diffusion of atoms at the growing surface and in the bulk. In the case of sputtering, besides the homologous temperature, the energetic particle bombardment is an important factor in this respect. The CFUBM sputter configuration increases the ion-to-atom ratio incident at the substrate [8, 9]. Pulsed magnetron sputtering (PMS) is known to cause even greater energy fluxes to be delivered to the substrate [5] and thus a shift in structure to ‘high temperature’ forms at relatively low \( T_s/T_m \) values [10].
Fig. 2 is a plan-view TEM and XTEM images of a PMS deposited CrB$_2$ coating. A through-thickness cross-section of the coating is shown in Fig. 2a. It reveals fine, dense and almost perfectly perpendicular to the coating-substrate interface columnar morphology. No defects were detected at this or higher magnifications and the surface of the coating is very smooth. Also it is evident from the SAED pattern (zone axis - [0 1 0]) that the coating has a strong (0 0 1) texture. This kind of structure (achieved at a $T/T_m$ value of only ~ 0.2) can be ascribed to the ‘high temperature’ (likely ‘zone II/III’) zone and demonstrates clearly the significant impact of PMS on coating growth behavior.

At higher magnification the nanostructure of the PMS deposited CrB$_2$ coating is revealed. BF XTEM (fig. 2b) shows nanocolumns, which extend throughout the thickness of the coating and have a diameter of ~ 4-6 nm, which is also evident from the DF XTEM (fig. 2e) and plan-view BF image (fig. 2d). The SAED pattern taken from a plan-view specimen (fig. 2b) is a series of rings, indicative of a randomly-oriented polycrystalline structure. Considering SAED patterns obtained from cross-section and plan-view samples it is apparent that the (0 0 1) textured nanocolumns are strongly oriented along the $c$ axis and therefore a single-crystal type SAED pattern is formed (fig. 2a), but each nanocolumn is
differently rotated about this axis as well, resulting in a ring-type SAED pattern obtained from a plan-view specimen (fig. 2b).

The brighter intercolumnar areas are visible in plan-view (fig. 2d) as well as in cross-section (fig. 2b) TEM images of the coating. However, in contrast to coating No.1, which has a lower density phase surrounding the dense nanofibers (fig.1d), the secondary (amorphous) phase in coating No.2 is rather rod-like (with diameter/thickness of ~0.5-1 nm) and is inter-disposed between the crystalline CrB₂ nanocolumns. The nanostructure is most likely to be responsible for the near super-hardness of the PMS deposited CrB₂ film (~39GPa) through the restriction of dislocation formation and/or their motion.

The peculiarity of the method that we have used to deposit CrB₂ coatings resulted in some contamination of the coating at the beginning of the deposition process [1, 2 and 4]. XTEM revealed that this small amount of contamination of the interfacial sub-layers of the coatings by oxygen affects significantly the coating structure by inhibiting nanocolumnar growth and promoting equiaxial grains of about 4-8 nanometres size (fig. 2c), in the first ~70 nanometres of coating, close to the substrate interface. The secondary phase surrounding the grains is seen clearly in this region. In the next ~30 nanometres the structure gradually changes and the majority of the coating thereafter remains nanocolumnar. The process of formation of this nanocomposite-like structure in the contaminated regions has been explained by Barna and Adamik [7].

4. Conclusions
DC magnetron sputtered PVD CrB₂ coatings typically exhibit a ‘zone T’ morphology and a dense, fibrous nanocolumnar structure consisting of dense parallel fibres of 2-3 nm diameter surrounded by a less dense amorphous (possibly partially voided) 1-2 nm thick secondary phase.

The application of pulsed magnetron sputtering allowed the deposition of dense, smooth and defect free CrB₂ coatings, with a ‘high temperature’ (likely ‘zone II/III’) structure, at a relatively low homologous temperature (T/Tₘ) of ~ 0.2.

PMS deposited coatings exhibit complex, composite nanostructures composed of 4-6 nm highly crystalline and (001) preferentially-oriented columns, with a rod-like secondary phase inter-dispersed between them. This nanostructure is most likely to be responsible for the near super-hardness of the PMS deposited CrB₂ films (~39GPa) through the restriction of dislocation formation and/or motion.

A small amount of contamination of the interfacial sub-layers of the coatings by oxygen was found to affect the structure by suppressing growth of nanocolumns and promoting equiaxial grains of about 4-8 nm size, in the first ~70 nanometres of the coating, close to the coating/substrate interface. The majority of the coating however remains nanocolumnar.

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