

Abstract

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The aim of this dissertation thesis is to investigate the effect of boron understoichiometry on structure and mechanical properties of transition metal diboride (TMB₂) films. This group of materials is currently widely studied due to excellent physical properties, including high hardness, wear resistance and high temperature stability, making them promising candidates for applications as hard protective coatings in extreme conditions. Current research focuses on improvement of toughness and oxidation resistance, which are the main drawbacks of TMB₂ films. Studies indicate, that a promising way to enhance these properties is to lower the boron concentration and aim for synthesis of understoichiometric films with B/TM ratio below 2. Since the trends in the functional properties are closely related to the changes in the microstructure, it is important to gain understanding of how the boron deficiency is accommodated in the diboride systems.

One of the ways to reduce the B/TM ratio in magnetron sputtered films is using co-deposition from a TMB₂ and a metallic target. In this work, this approach is utilized to grow ternary V_{1-x}Mo_xB_{2-Δ} and V_{1-x}W_xB_{2-Δ} films, which are subsequently annealed in vacuum to study the effect of temperature on structural evolution. Analysis by high-resolution transmission electron microscopy reveals that slight understoichiometry leads to heterostructural decomposition into V-rich regions with higher B content and hexagonal *P6/mmm* structure, while orthorhombic *Cmcm* phase is formed in W(Mo)-rich areas with lower B concentration. The separation is accompanied by formation of anti-phase boundary defects APB-2i, which enable coherent incorporation of the orthorhombic areas into the hexagonal lattice. The results are supported by density functional theory (DFT) calculations, indicating that the observed decomposition is energetically favorable due to different affinity of the respective binary systems towards formation of B vacancies. The findings show that boron concentration plays a key role in determining the structural stability of ternary diboride systems.

Boron understoichiometry can be also achieved by deposition from a single TMB_2 target containing a high-mass metal due to re-sputtering of B from the growing film. In the next part of the thesis we grow highly understoichiometric $\text{TaB}_{1.2}$ films by sputtering of a TaB_2 target, where significant level of B deficiency results in formation of disordered structure. Exposure to elevated temperatures then leads to crystallization into orthorhombic $Cmcm$ structure with a high density of planar defects, including twinning. Using DFT calculations we show that twinning occurs naturally as a result of competition between the $Cmcm$ and another orthorhombic $Pnma$ phase, which have very similar formation energy. Calculations on supercells with different stacking faults arrangements reveal that in TaB_{1+x} with Ta vacancies, twinning leads to reduction of the formation energy of the system and there is a dependence on the twin lamellae thickness. Annealing of the TaB_x films results in an increase in hardness which according to the calculations might be related to strengthening in the twinned structure.

However, formation of the crystal phase due to vacuum annealing causes undesirable increase in the surface roughness. Therefore, it is interesting to explore ways to synthesize crystalline monoboride films directly during deposition. One promising approach which avoids using very high deposition temperatures might be utilizing high-power impulse magnetron sputtering (HiPIMS). The last part of this thesis deals with $\text{Ti}_{1-y}\text{W}_y\text{B}_x$ films grown by hybrid TiB_2 -Ti-DCMS/ W_2B_5 -HiPIMS co-deposition without external substrate heating. Synchronized bias is used to provide $\text{W}^{+/2+}$ ion irradiation of the growing films, effectively replacing the thermally induced adatom mobility by generation of low energy recoils due to the large mass difference between W and other film constituents. We demonstrate that this approach can be used to obtain dense crystalline $\text{Ti}_{1-y}\text{W}_y\text{B}_x$ films in a wide range of the B/TM ratio with excellent mechanical properties, with the benefit of reduced energy consumption.

Keywords: transition metal diborides, monoborides, thin films, magnetron sputtering, HiPIMS, understoichiometry, B deficiency, chemical decomposition, planar defects, anti-phase boundaries, twinning, ion irradiation, low-temperature growth, mechanical properties, density functional theory